FRONTIERS OF CHEMICAL SCIENCES

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Navanila Maruthi Publication

Pollachi

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Dr. R. Muthukumaran
Principal
Nallamuthu Gounder Mahalingam College, Pollachi

A Nation's growth is in proportion to education and intelligence spread the masses. Having this idealistic vision the founders established NGM College in 1957 to impart holistic education with an objective to cater the higher educational needs of those who wish to aspire for excellence in knowledge and values. We feel proved of celebrating the centenary year of Padma Bushan Arutchelvar N. Mahalingam, who is a versatile leader, visionary legend, foreseeing industrialist with patriotic outlook and Gandhian ideology.

The College has achieved greater academic distinction with blossomed in to a premier post Graduate and Research Institution, which has been ranked 72nd among Colleges in India by MHRD-NIRF

Post Graduate Research Department of Chemistry crammed with new innovations and promotes quality education in a very short span of period. The department imparts quality education with industrial connectivity, with skill enhancement programme and gives progressive research with environmental concern to meet the demands of various research institutions and industries.

Chemical Sciences have been playing a vital role in the field of energy, water, agriculture, and health have contributed a substantial part to society's overall evolution. Green chemistry concepts should be embraced by industries in order to fulfill the aims of environmental protection and sustainable development.

I congratulate the editors for assembling original research and review papers from various institutions and universities to publish this collection. Each study was written in a scientific manner using the most up-to-date information.

I wish the Faculty members of the Post Graduate and Research Department of Chemistry under the stewardship of Dr. K. Poonkodi all success and the efforts will be continued in the future to reach greater heights of this reputed institution.

With Best Wishes

Dr. R. Muthukumaran

FORWARD

We owe this to the Almighty to provide us the grace of finishing this edited book on "Frontiers of Chemical Sciences." The book highlights recent advances in chemical sciences and engineering, with a focus on new and multidisciplinary domains, as well as international research and development trends. Several important directions are required to abate pollution, impart green and sustainable environment, drug design and discovery, recycling of materials, efficient industrial production and management of fertilizers, pesticides, polymers, nanomaterials are the need of the hour etc. The young researchers should focus on these problems and tackle it in an economically and environmentally feasible way.The overall aim of this endeavour is to compile the latest research and development, up-to-date issues in the field of education with the contribution of Science and Technology.

This book covers key areas in Chemical sciences, which includes catalysis, corrosion, Phytochemistry, clean energy, functional materials, food technology, biomaterials and biotechnology, particle technology, sustainable technologies and green processing.It could be conceived as a science of techniques, methods and media by which educational goals could be realized.

We would like to express our gratitude to the Management, Principal, Dean (Academics) and Dean (Research) for their encouragement and support to bring out this book.

We thank all the authors and all those who directly and indirectly helped to make this book.

We would like to extend our sincere thanks to the publishers for publishing the book in a very short time.

We are very happy to place this edited book in the hands of our esteemed readers.

EDITORS

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CONTENTS

Synthesis and utility of 2-hydroxymethylene-1-oxo-3, 8-dihydro cyclopent [b] indoles

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Abstract — *There has been a great deal of interest in synthesizing annulated heterocycles for designing novel structures due to the capability of performing multiple functions. This work describes a strategic approach for the synthesis of efficient precursor 2-hyroxymethylene-1-oxo-3,8-dihydrocyclopent[b]indoles which can be synthesized from the corresponding 1-oxo-1,2,3,8-tetrahydrocyclopent[b]indoles. The latter was refluxed with hydrazine hydrate and hydroxylamine hydrochloride in glacial acetic acid under proper condition gave an the respective 3,4-dihydro-2H-pyrazino[3',4':5,4]cyclopent[b]indole and 3,4-dihydroisoxazolo[3',4':5,4]cyclopent[b]indole.*

Keywords — *Cyclopent[b]indoles, pyrazino carbazole, isoxazolo carbazole, hydrazine hydrate, hydroxylamine hydrochloride*

I. INTRODUCTION

Indole derivatives are fused with different heterocycles which are active compounds in pharmaceuticals, alkaloids and potential therapeutic agents[1]. A large number of naturally occurring biologically active molecules contain indole nucleus, which create attention to the synthesis of indole fused heterocyclic molecules[2]. A large number of alkaloids such as paxilline, paspaline, lolitrems, janthitrems and yuehchukene[3] contain cyclopent[*b*]indole units which were found to exhibit potential antimicrobial, anti-inflammatory, antioxidant, anti-implantation and tremorgenic activities[4]. Amino carbazoles and indole derivatives have shown potential activities to both Alzheimer's disease and cancer[5,6]. The significant ability of heterocyclic nuclei to serve both as biomimetics and reactive pharmacophores in the pharmaceutical industry. Many of the indole and carbazole containing heterocyclic compounds has an most important class of compounds based on their structures and biological activities such as antitumour[7,8], anti-inflammatory[9], antibacterial[10,11] and antifungal[10,11].

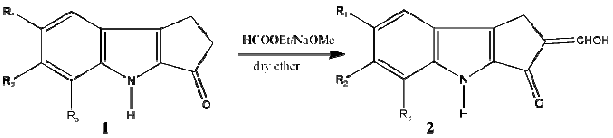
In recent years researches on alkaloids containing carbazole moiety exhibit significant and diverse biological activities especially in the treatment of cancer therapy and Alizemer disease. Whereas the major drawback of using these compounds as drugs is their solubility in water and this makes it very difficult to administer the drug in intravenous form. Since the incorporation of amino group in pyrazole, isoxazole and substituted pyrimidine[12] heterocyclic moieties will enhance the water solubility and they possess a wide spectrum of biological activities such as antiviral, bactericidal, ulcer inhibitor etc. Hence the incorporation of an amino group into this system will enhance the water solubility. A multitude reports of these compounds having some pharmacological and chemotherapeutic properties[13] and hence, based on the above facts we decided to synthesize some novel compounds containing amino groups.

II. RESULTS AND DISCUSSION

A. *Synthesis of 2-hyroxymethylene-1-oxo-3,8-dihydrocyclopent[b]indoles (2)*

2-hyroxymethylene-1-oxo-3,8-dihydrocyclopent[*b*]indoles (**2**) were synthesized from the corresponding 1-oxo-1,2,3,8-tetrahydrocyclopent[*b*]indoles[14] (**1**) as follows. In a typical experiment, 5-methyl-1-oxo-3,8-dihydrocyclopent[*b*] indole (**1a**) on treatment with ethyl formate in presence of sodium methoxide yielded 2-hydroxymethylene-5-methyl-1-oxo-3,8-

dihydrocyclopent[*b*]indole (**2a**). The structure of **2a** was well established on the basis of its elemental analysis and spectral data. The IR spectrum of **2a** exhibited sharp and strong bands at 3294 cm^{-1} and 1658 cm^{-1} for the presence of hydroxyl group and carbonyl group respectively. The disappearance of C_2-methylene protons and appearance of –CH and –OH protons as singlets at δ 8.65 and δ 9.87, in its ^1H NMR spectrum suggested the structure of **2a** to be a hydroxymethylene compound. The protons attached to C_3 resonated as a singlet at δ 3.40. While that of methyl group attached to C_5 and indole –NH appeared as singlets δ 2.39 and δ 8.90 respectively. In addition, the two doublets at δ 7.41 - 7.43 (*J = 6.9 Hz*) and δ 7.29 -7.31 (*J = 6.9 Hz*) were assigned for C_7-H and C_6-H respectively. A proton attached to C_4 resonated as a singlet at δ 7.14. The elemental analysis data obtained for the compound **2a** was also in good agreement with the molecular formula $C_{13}H_{11}NO_2$. A series of similar compounds **2b** and **2c** were synthesized by using **1b** and **1c** respectively. (**Scheme 1**)

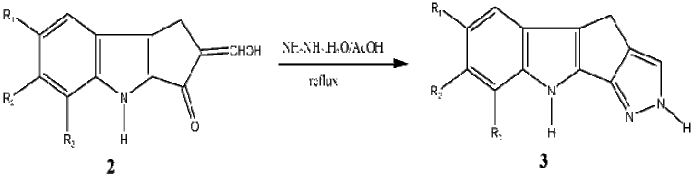


1,2 a : $R_1 = CH_3$, $R_2 = R_3 = H$
b: R_1 = Br, $R_2 = R_3 = H$
c: $R_1 = R_2 = R_3 = H$

Scheme 1

B. Reaction of 2-hydroxymethylene-1-oxo-3,8-dihydrocyclopent[b]indoles (2a-2c) with hydrazine hydrate

When 2-hydroxymethylene-5-methyl-1-oxo-3,8-dihydrocyclopent[*b*]indole (**2a**) was treated with hydrazine hydrate in glacial acetic acid at 110°C for 1 h, it afforded the expected 6-methyl-3,4-dihydro-2*H*-pyrazino[3',4':5,4]cyclopent[*b*]indole (**3a**) in 75% yield.IR spectrum of **3a** revealed the presence of >C=N group at 1544 cm^{-1} and absence of carbonyl absorption. $^{\text{the 1H NMR}}$ spectrum of **3a** showed a two singlet at δ 12.45 and δ 11.41 for pyrazino –NH proton and indole –NH proton respectively. A one proton doublet at δ 6.86–6.88 (*J = 8.0 Hz*) ascribed to C_8-H and a two protons multiplet at δ 7.25-7.28 corresponding to C_5-H and C_7-H. The C_3-H, C_6-CH_3 and C_4-H_2 protons provided the signal as a singlet at δ 7.50, δ 2.37 and δ 2.50 respectively. The molecular ion peak in its mass spectrum at m/z 209 and the elemental analysis agreed well with the molecular formula $C_{13}H_{11}N_3$. Similar reaction conducted with **2b-2c** yielded the corresponding pyrazino cyclopent[*b*]indoles (**3b-3c**) **(Scheme 2)**

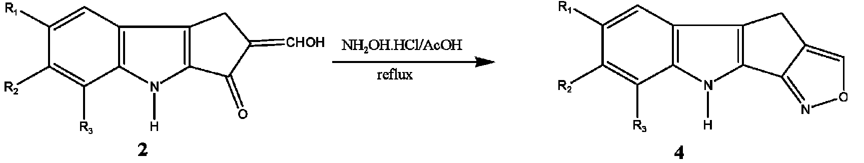


2,3 a : $R_1 = CH_3$, $R_2 = R_3 = H$
b: R_1 = Br, $R_2 = R_3 = H$
c: $R_1 = R_2 = R_3 = H$

Scheme 2

C. Reaction of 2-hydroxymethylene-1-oxo-3,8-dihydrocyclopent[b]indoles (2a-2c) with hydroxylamine hydrochloride

In another reaction 2-hydroxymethylene-5-methyl-1-oxo-3,8-dihydrocyclopent[*b*] indole (**2a**) was treated with hydroxylamine hydrochloride in glacial acetic acid at 110°C for 1 h. After workup, the reaction mixture gave a single product, which was characterised as 6-methyl-3,4-dihydroisoxazolo[3',4':5,4]cyclopent[*b*]indole (**4a)** on the basis of the following spectra features. The IR spectrum of **4a** showed absorption bands at 1562 cm^{-1} for >C=N accompanied by the fading of carbonyl group (>C=O) and signal at 3205 cm^{-1} for indole –NH which is broad. It was enhanced through the ^{1}H NMR spectrum since the singlet at δ 11.61 for indole –NH. Three singlets at δ 2.50, δ 3.35 and δ 7.73 for C_4-H_2, C_6-CH_3 and C_3-H respectively. A multiplet for three protons resonates in the aromatic region at the range δ 7.16 - 7.52 for C_5-H, C_7-H and C_8-H. Mass spectra have given the m/z ratio 210 for **4a**. Elemental analysis provided the carbon, hydrogen and nitrogen composition which agreed with the calculated value. Thus the molecular formula of a **4a** is $C_{13}H_{10}N_2O$. As in **Scheme 3** with hydroxylamine hydrochloride **2b** and **2c** compounds react and gave the respective products **4b** and **4c**.



2,4 a : $R_1 = CH_3$, $R_2 = R_3 = H$
b: $R_1 = Br$, $R_2 = R_3 = H$
c: $R_1 = R_2 = R_3 = H$

Scheme 3

III. EXPERIMENTAL SECTION

A. General procedure for the preparation of 2-hydroxymethylene-1-oxo-3,8-dihydro cyclopent[b]indoles (2) :

An appropriate 1-oxo-3,8-dihydrocyclopent[*b*]indole (**1,** 0.001 mol) was treated with ethyl formate (0.002 mol) in the presence of sodium methoxide (5 mL). The mixture was allowed to stir for 2 h. After complete stirring the reaction mixture was poured into ice and neutralized with dilute HCl which gave yellow solid mass. The precipitate obtained was filtered off and washed with water. The product was purified by column chromatography over silica gel using petroleum ether-ethylacetate (95:5) as an eluent to give the corresponding product as yellow crystals.

i) 2-Hydroxymethylene-5-methyl-1-oxo-3,8-dihydrocyclopent[*b*]indole (2a)

Yellow solid, Yield : 0.182 g (85.44%); m.p. : 182-184°C; IR (KBr cm^{-1}) ν max : 3294, 1658, 1589, 1489, 1303, 1251, 1141, 910, 686; ^{1}H NMR ($CDC1_3$) [δ ppm] : 2.39 (s, 3H, C_5-CH_3), 3.40 (s, 2H, C_3-H_2), 7.14 (s, 1H, C_4-H), 7.29-7.31 (d,1H,C_6-H, *J = 6.9 Hz*), 7.41-7.43 (d, 1H, C_7-H, *J = 6.9 Hz*), 8.65 (s,1H, C_2-H), 8.90 (s,1H, indole –NH), 9.87 (s,1H,-OH) ; Anal.calcd for $C_{13}H_{11}NO_2$: C, 73.23%; H, 5.20%; N, 6.57%; Found: C**,** 72.87%; H, 5.02%; N, 6.11%.

ii) 5-Bromo-2-hydroxymethylene-1-oxo-3,8-dihydrocyclopent[*b*]indole (2b)

Yellow solid, Yield : 0.201 g (73%); m.p. : 187-189°C; IR (KBr cm^{-1}) ν max : 3385, 3213, 1618, 1543, 1440, 1303, 1092, 994, 794; ^{1}H NMR ($CDC1_3$) [δ ppm] : 2.55 (s, 2H, C_3-H_2), 7.13-7.43 (m, 3H, C_4-H, C_6-H, C_7-H), 8.35 (s, 1H, C_2-H), 9.20 (s, 1H, indole –NH), 11.42 (s, 1H, -OH). Anal.calcd for $C_{12}H_8BrNO_2$: C, 51.83%; H, 2.90%; N, 5.04%; Found: C**,** 51.03%; H, 2.12%; N, 4.87%.

iii) 2-Hydroxymethylene-1-oxo-3,8-dihydrocyclopent[*b*]indole (2c)

Yellow solid, Yield : 0.150 g (73%); m.p. : 180-182°C; IR (KBr cm^{-1}) ν max : 3301, 3463, 1655, 1521, 1323, 1123, 894, 667; ^{1}H NMR ($CDC1_3$)[δ ppm] : 2.50 (s, 2H, C_3-H_2), 7.08-7.31 (m, 2H, C_5-H, C_6-H), 7.40-7.43 (d,1H, C_4-H, *J=8.0 Hz*), 7.29-7.31 (d, 1H, C_7-H, *J = 8.0 Hz*), 7.48 (s, 1H, C_2-H), 10.56 (s, 1H, indole –NH), 11.67 (s, 1H, -OH).

Anal.calcd for $C_{12}H_9NO_2$: C, 72.35%; H, 4.55%; N, 7.03%; Found: C**,** 72.10%; H, 4.21%; N, 6.85%.

B. General procedure for the preparation of 3,4-dihydro-2H-pyrazino[3',4':5,4] cyclopent[b]indoles (3) :

A mixture of an appropriate 2-hydroxymethylene-1-oxo-3,8-dihydrocyclopent[*b*]indole (**2**, 0.001 mol) and hydrazine hydrate (0.001 mol) was refluxed in glacial acetic acid at 110°C for 1 h. After completion of the heating the reaction mixture was then poured into a crushed ice. The solid thus separated was filtered, dried and purified by column chromatography over silica gel using petroleum ether-ethyl acetate mixture (80:20) as an eluent to give the respective pyrazino compound as white solid.

i) 6-Methyl-3,4-dihydro-2*H*-pyrazino[3',4':5,4]cyclopent[*b*]indole (3a)

White solid, Yield : 0.176 g (84.21%); m.p. : 210-212°C; IR (KBr cm^{-1}) ν max : 3383, 3237, 2916, 1622, 1544, 1438; ^{1}H NMR ($CDC1_3$) [δ ppm] : 2.37(s, 3H, C_6-CH_3), 2.50 (s, 2H, C_4-H_2), 6.86-6.88 (d, 1H, C_8-H, *J =8.0 Hz*), 7.25-7.28 (m, 2H,C_5-H, C_7-H), 7.50 (s, 1H, C_3-H), 11.41 (s, 1H, indole –NH), 12.45 (s, 1H, pyrazino –NH). Anal.calcd for $C_{13}H_{11}N_3$: C, 74.62%; H, 5.30%; N, 20.08%; Found: C**,** 73.87%; H, 5.02%; N, 19.76%.

ii) 6-Bromo-3,4-dihydro-2*H*-pyrazino[3',4':5,4]cyclopent[*b*]indole (3b)

White solid, Yield : 0.200 g (73%); m.p. : 215-217°C; IR (KBr cm^{-1}) ν max : 3362, 3253, 2926, 1698, 1583, 1486; ^{1}H NMR ($CDC1_3$) [δ ppm] : 2.50 (s, 2H, C_4-H_2), 7.14-7.16 (d, 1H, C_7-H, *J =7.20 Hz*), 7.33-7.35 (d, 1H, C_8-H, *J =8.0 Hz*), 7.63 (s, 1H,C_5-H), 7.69 (s, 1H, C_3-H), 11.83 (s, 1H, indole –NH), 12.56 (s, 1H, pyrazino –NH). Anal.calcd for $C_{12}H_8BrN_3$: C, 52.58%; H, 2.94%; N, 15.30%; Found: C**,** 52.13%; H, 2.09%; N, 14.98%.

ii)3,4-Dihydro-2*H*-pyrazino[3',4':5,4]cyclopent[*b*]indole (3c)

White solid, Yield : 0.150g (73%); m.p. : 210-211°C; IR (KBr cm^{-1}) ν max : 3359, 2959, 1672, 1521, 1486; ^{1}H NMR($CDC1_3$) [δ ppm] : 2.50 (s, 2H,C_4-H_2), 7.13-7.43 (m, 4H, C_5-H, C_6-H, C_7-H, C_8-H,), 7.71 (s, 1H, C_3-H), 9.50 (s, 1H, indole –NH), 11.42 (s, 1H, pyrazino –NH). Anal.calcd for $C_{12}H_9N_3$: C, 73.83%; H, 4.65%; N, 21.52%; Found: C**,** 73.15%; H, 4.01%; N, 20.89%.

C. General procedure for the preparation of 3,4-dihydroisoxazolo[3',4':5,4] cyclopent [b] indoles (4) :

Where the respective 2-hydroxymethylene-1-oxo-3,8-dihydrocyclopent[*b*]indole (**2**,0.001mol) was refluxed with hydroxylamine hydrochloride (0.002 mol) in glacial acetic acid (5 mL) at 110°C for 1 h. The completion of the reaction was checked by TLC. Then the reaction mixture was poured into a crushed ice with constant stirring. The precipitate obtained was filtered, dried and purified by column, eluting with petroleum ether and ethyl acetate mixture (80:20) to yield the respective 3,4-dihydroisoxazolo[3',4':5,4]cyclopent[*b*] indole (**4**)

i) 6-Methyl-3,4-dihydroisoxazolo[3',4':5,4]cyclopent[*b*]indole (4a)

White solid, Yield : 0.176 g (83.80%); m.p. : 220-222°C; IR (KBr cm^{-1}) νmax : 3205, 2358, 1562, 1493,1379,1260,912; ^1H NMR ($CDC1_3$) [δ ppm] : 2.50 (s, 2H, C_4-H_2), 3.35(s, 3H, C_6-CH_3), 7.16-7.52 (m, 3H, C_5-H, C_7-H, C_8-H), 7.73 (s, 1H, C_3-H), 11.61 (s, 1H, indole –NH). Anal.calcd for $C_{13}H_{10}N_2O$: C, 74.27%; H, 4.79%; N, 13.33%; Found: C**,** 73.87%; H, 4.15%; N, 12.87%.

ii) 6-Bromo-3,4-dihydroisoxazolo[3',4':5,4]cyclopent[*b*]indole (4b)

Dirty white solid, Yield : 0.204 g (83.80%); m.p. : 225-227°C; IR (KBr cm^{-1})ν max : 3207, 2353, 1532, 1492, 1227; ^1H NMR ($CDC1_3$) [δ ppm] : 2.50 (s, 2H, C_4-H_2), 7.39-8.00 (m, 3H, C_5-H, C_7-H, C_8-H), 7.80 (s, 1H, C_3-H), 11.97 (s, 1H, indole –NH). Anal.calcd for $C_{12}H_7BrN_2O$: C, 52.39%; H, 2.56%; N, 10.18%; Found: C**,** 51.89%; H, 2.07%; N , 9.78%.

iii) 3,4-Dihydroisoxazolo[3',4':5,4] cyclopent[*b*]indole (4c)

White solid, Yield : 0.145 g (73.97%); m.p. : 240-242°C; IR (KBr cm^{-1})ν max : 3262, 2936, 1648, 1553, 1482, 1320, 1260, 1076; ^1H NMR ($CDC1_3$) [δ ppm] : 3.30 (s, 2H, C_4-H_2), 7.10-7.14 (m, 1H, C_6-H), 7.32-7.36 (m, 1H, C_7-H), 7.73-7.71 (d, 1H, C_5-H, *J =7.6 Hz*), 7.42-7.44 (d, 1H, C_8-H, *J =8.0 Hz*), 7.60 (s, 1H, C_3-H), 11.64 (s, 1H, indole –NH).

Anal.calcd for $C_{12}H_8N_2O$: C, 73.46%; H, 4.11%; N, 14.28%; Found: C**,** 73.03%; H, 3.97%; N, 13.87%.

D.Biological study of cyclopent[b]indole and cyclohept[b]indole derivatives:

In vitro antibacterial and antifungal activity of synthesized compounds are observed against certain micro-organisms. The microbial activities are observed from the inhibition zones, which are measured with respect to the concentration that are entered. Streptomycin and Nystatin are used as reference against bacterial and fungal strains respectively. Using this standard drug to compare the resistivity pattern of the synthesized compounds can be expressed accordingly with the obtained result. Certain series of concentration of synthesized compounds were prepared and screened for the antimicrobial activity against bacterial and fungal strains such as *Pseudomonas aeruginosa*, *Aeromonas hydrophila*, *Thiobacillus thidurance*, *Serratiamarcescens*, *Acinetobater baumanii*; *Aspergillus niger* and *Candida tropicali* in separate culture.

The antimicrobial activity of pyrazino cylopent[*b*]indoles (**3a-3c**); the compound **3a** having no activity against *Pseudomonas aeruginosa*, *Thiobacillus thidurance*, *Serratiamarcescens*, *Acinetobater baumanii* and *Aspergillus niger* even in a high concentrations. Whereas in a high concentration the compound **3a** has moderate activity against *Aeromonas hydrophila* bacteria and *Candida tropicali* fungi. All the bacterial strains and fungal strains were highly resisted by the compound **3b** and **3c** except *Thiobacillus thidurance* and *Serratiamarcescens*. On the whole, the series of pyrazino cyclpent[*b*]derivatives bromo compounds having the potency to act against both bacteria and fungi. For isoxazolo cyclopent[*b*]indoles (**4a-4c**) the resistivity of all the three compounds in this series towards *Pseudomonas aeruginosa*, *Aeromonas hydrophila*, *Serratiamarcescens* and *Candida tropicali* is moderate and the zone of inhibition does not attained the level of 10 mm in diameter; bacterial strains *Thiobacillus thidurance* and *Acinetobater baumanii* were encountered by **4b** and **4c**; Similarly the fungal strains *Aspergillus niger* and *Candida tropicali* were destroyed by 4**c** at higher concentration. **4b** has strength against *Aspergillus niger*. Finally we conclude that from **Table 2** isoxazolo compounds are having activity in moderate level.

Table 1. Antimicrobial activity of 3,4-dihydro-2*H*-pyrazino-[3',4':5,4]cyclopent[*b*]indoles (**3a-3b**)

Compounds	**Concentration (µg/mL)**	**Zone of the inhibition (mm)**						
		Bacteria					**Fungi**	
		Pseudomonas aeruginosa	Aeromonas hydrophila	Thiobacillus thidurance	Serratiamarcescens	Acinetobater baumanii	Aspergillus niger	Candida tropicali
3a	**20**	3	4	4	4	5	5	5
	40	4	6	6	7	5	6	7
	60	6	9	7	8	6	7	9
	80	9	**10**	7	8	9	8	**10**
3b	**20**	7	7	8	8	9	6	7
	40	9	8	9	7	9	8	8
	60	9	9	9	8	8	9	9
	80	**12**	**10**	9	9	**12**	**11**	**10**
3c	**20**	4	5	5	6	7	6	6
	40	7	6	6	7	7	7	8
	60	8	8	9	8	8	9	9
	80	**11**	**10**	9	9	**10**	**11**	**12**
Streptomycin	**100**	21	19	18	19	22	-	-
Nystatin	**100**	-	-	-	-	-	21	21

Table 2 Antimicrobial activity of 3,4-dihydroisoxazolo[3',4':5,4]cyclopent[*b*]indoles (4a-4c)

Compounds	**Concentration (µg/mL)**	**Zone of the inhibition (mm)**						
		Bacteria					**Fungi**	
		Pseudomonas aeruginosa	Aeromonas hydrophila	Thiobacillus. thidurance	Serratiam arcescens	Acinetobater baumanii	Aspergillus niger	Candida. tropicali
4a	**20**	2	3	5	4	5	5	3
	40	3	5	6	5	5	6	7
	60	5	7	8	7	6	9	8
	80	7	9	**11**	8	**10**	**10**	8
4b	**20**	4	5	7	6	4	7	7
	40	6	6	9	7	5	9	8
	60	8	7	**10**	8	9	9	9
	80	9	8	**11**	9	**12**	**11**	9
4c	**20**	4	5	5	6	7	6	6
	40	7	6	6	7	7	7	8
	60	8	8	9	8	8	9	9
	80	9	9	**12**	9	**10**	**11**	**10**
Streptomycin	**100**	20	21	18	20	22	-	-
Nystatin	**100**	-	-	-	-	-	19	21

IV. CONCLUSION

The synthesis of an efficient precursors 2-hydroxymethylene-1-oxo-3,8-dihydro cyclopent[*b*]indoles (**2**) from the reaction of the corresponding 1-oxo-1,2,3,8-tetrahydrocyclopent[*b*]indoles(**1**) with ethyl formate. The effectiveness of 2-hydroxymethylene-1-oxo-3,8-dihydrocyclopent[*b*]indoles(**2**) in the construction of a wide range of cyclopent[*b*]indole derivatives was assessed in the following reactions. Accordingly, pyrazino compounds 3,4-

dihydro-2*H*-pyrazino[3',4':5,4]cyclopent[*b*]indoles (**3**), isoxazolo compounds 3,4-dihydroisoxazolo [3',4':5,4] cyclopent [*b*] indoles(**4**), have been prepared using suitable reagents. An *in vitro* study on the antibacterial and antifungal activity of all the synthesized compounds showed moderate activity against the growth of micro-organisms and showed better activity in some micro-organisms on increment of concentration.

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Chemical Profile and *In vitro* Radical Scavenging Activity of Essential Oil from *Hyptis Suaveolens* (L.) Poit

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Abstract -- *In a biological system, an antioxidant is defined as any substance that when present at low concentrations compared with those of an oxidizable substrate significantly delays or prevents oxidation of that substrate. The antioxidant activity of plant extracts is attributed to phenolics and flavonoids, many essential oils have been reported to possess antioxidant activity. The present study highlights the chemical composition and antioxidant potential of the essential oil of Hyptis Suaveolens. The volatile oil composition was analyzed by GC/MS analysis. A Total of 26 components were identified. The major compounds present in the oil were Eucalyptol (15.2 %), beta.-Phellandrene (13.3 %), Caryophyllene (9.9%), Alpha Phellandrene (7.0 %), Phenanthrene (6.9 %), Beta - Pinene (3.6 %), α-humulene (3.5 %). The radical scavenging activity of essential oil from Hyprtis Suaveolens was performed by DPPH and ABTS scavenging radical activity assay's showed the* IC_{50} *values of 112µg/mL and 156µg/mL respectively. Ascorbic acid was used as a standard with* IC_{50} *values of 13.8µg/mL and 14.4µg/mL. The obtained results in the present study indicates that the essential oil of Hyptis Suaveolens scavenge free radicals and could serve as a mild source of natural antioxidant.*

Key words*: Hyptis Suaveolens, GC/MS, in vitro, DPPH, ABTS, Antioxidant*

I. INTRODUCTION

Natural products have long been implemented as alternative health care treatment and in discovery of modern drugs [1]. Plants and plant-derived medicinal products have been used to help humankind to continue its healthiness from the dawn of medicine. Over the past century, the phytochemicals in plants play an important role in pharmaceutical discovery [2]. Essential oils have been used for thousands of years in various cultures for medicinal and health purposes. Essential oil uses range from aromatherapy, household cleaning products, personal beauty care and natural medicine treatments [3]. The plant *Hyptis suaveolens* (L.) Poit commonly known as *Wilayati tulsi* belongs to the family and it is one of the underexplored valuable medicinal plant used to treat various ailments in traditional system of medicine. The leaves of the plant are the source of pharmacologically important secondary metabolites having antispasmodic, anti-colic, anti-rheumatic, and anti-fertility properties [4,5]. The plant has various pharmacological activities like antifungal, antibacterial, antioxidant and mosquito repellant activity [6-10]. Therefore, this present study aimed to evaluate the chemical composition and *in-vitro* antioxidant activity of this plant.

II. MATERIALS AND METHODS

A. Plant Material

Fresh leaves of *H. suaveolens* were collected from near Pollachi, Tamil Nadu, South India. The plant sample was identified and authenticated by Dr.P.Sathishkumar, Assistant Professor, Department of Botany, Nallamuthu Gounder Mahalingam College, Pollachi and the voucher specimen was preserved in the chemistry department.

B. Isolation of essential oil from H. suaveolens

About 500g of fresh leaves were taken in a round bottom flask and subjected to hydrodistillation using Clevenger type apparatus for 4h. The essential oil was dried over anhydrous sodium sulphate (Merck) until the last traces of water were removed and then stored in a container at 4˚C prior to GC-MS analysis.

C. GC-MS Analysis

GC-MS analysis of the phytoconstituents of *H. suaveolens* was carried out using thermo GC –trace ultra-version: 5.0 coupled with thermo MS DSQ II instrument. Compounds were separated on DB-35, MS capillary standard non – polar column (30m × 0.25 mm), film thickness 0.25µm. Helium was used as the carrier gas and the temperature programming was set with initial oven temperature at 700C and held for 2 minutes and the temperature of the oven was raised to 2600C for 10min and raised 60C/MIN and final temperature was 3500C for 10 min. The sample of 100mL was dissolved in 1mL of acetone and injected with split less mode. Mass spectra were recorded over 50-500 amu range with electron impact ionization energy 70 eV, while injector and MS transfer line temperature were set at 2800C respectively.

D. Identification of phytoconstituents

The components were identified by comparison of their mass spectra with those of National Institute of Science and technology (NIST) mass spectral library version 2.0d, as well as on their comparison of their retention time either with those of authentic compounds or with their literature values.

E. Determination of in vitro antioxidant activity

DPPH radical scavenging activity

Different volumes of essential oil with ethanol were made up to 40µL with DMSO and 2.96mL DPPH (0.1mM) solution was added. The reaction mixture was incubated in dark condition at room temperature for 20 min. After 20 min, the absorbance of the mixture was read at 517 nm by UV-Vis Spectrophotometer 3ml of DPPH was taken as control. To measure emulsifying capacity, an amount of surimi powder was added to 25 mL of distilled water and 25mL of corn oil to give a final concentration of about 0, 0.5, 1, 1.5 and 2%. The mixture was blended (Waring Commercial blender, Stamford, CT, USA) for 1 min and transformed to a 50 Ml calibrated centrifuged tube and centrifuged (Hettich Universal 30 RF) at 7500g for 5 min.

Emulsifying stability was determined by the same procedure except that before the sample was centrifuged, the emulsion was

$$\% \text{ RSA} = \frac{\text{Abs control} - \text{Abs sample}}{\text{Abs control}} \times 100$$

Where, RSA is the Radical Scavenging Activity; Abs control is the absorbance of DPPH radical + ethanol; Abs sample is the absorbance of DPPH radical + sample essential oil.

ABTS·+ Decolorization Assay

The working solution of ABTS·+ radical was made by reacting ABTS (9.5 mL, 7mM) with potassium persulfate (245 µL, 100 mM), and raising the volume to 10 mL with distilled water. The solution was kept in the dark at room temperature for 18 h, and then diluted with potassium phosphate buffer (0.1M, pH 7.4) to an absorbance of 0.70 (±0.02) at 734 nm. Samples were prepared in methanol with dilutions 50-1250 µg/mL. A sample (10 µL) was placed in a test tube and mixed thoroughly with 2.99 mL ABTS radical working solution. Absorbance of the resulting clear mixture was recorded at 734 nm.

The percent antioxidant activity of the sample was determined using the following formula:

$$\% \text{ Antioxidant activity} = [(Ac-As)/Ac] \times 100$$

Where Ac and As are the absorbance's of the control and sample, respectively, the control was prepared by adding 10 µL of methanol in place of the sample.

III. RESULTS AND DISCUSSION

The chemical composition of essential oil of fresh leaves of *H. suaveolens* was analyzed by GC/MS method. The GC/MS chromatogram was shown in fig. 1. A total of 26 compounds were identified (Table 1). The major compounds present in the oil were Eucalyptol (15.2 %), beta.-Phellandrene (13.3 %), Caryophyllene (9.9%), Alpha Phellandrene (7.0 %), Phenanthrene (6.9 %), Beta - Pinene (3.6 %), α-humulene (3.5 %) and minor components were Copaene (2.3%), Fenchyl acetate (2.1%), Spathulanol (1.6%), Androst-5-en-4-one (1.5%), alpha.-Farnesene (1.3%), Eicosane (1.3%), L-Fenchone (1.0%).

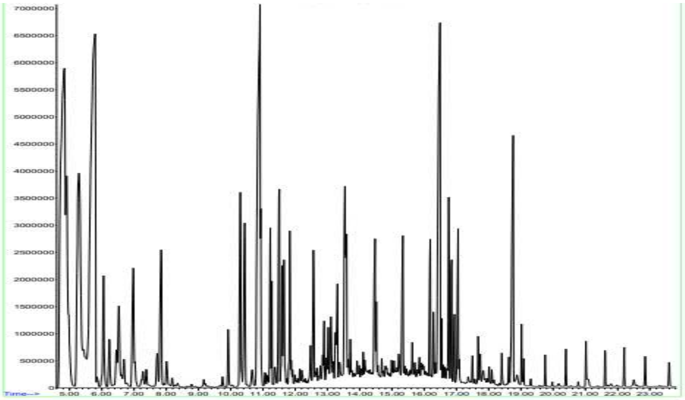

Fig.1. GC/MS chromatogram of essential oil from *H. suaveolens*

Table 1: Components in essential oil from *H. suaveolens*

S. No	*Compound Name*	*R.T*	*Percentage %*
1	beta.-Phellandrene	4.842	13.3
2	Beta - Pinene	4.909	3.6
3	Alpha Phellandrene	5.287	7.0
4	Eucalyptol	5.796	15.2
5	Beta Terpineol	6.231	0.6
6	L-Fenchone	6.531	1.0
7	alpha.-Pinene	6.687	0.3
8	Fenchyl acetate	6.975	2.1
9	Borneol	7.720	0.5
10	Alpha cubebene	9.919	0.5
11	Copaene	10.297	2.3
12	Caryophyllene	10.908	9.9
13	aromadendrene	11.275	0.6
14	Alpha Cadinol	12.475	0.4
15	alpha.-Farnesene	12.564	1.3
16	tau.-Muurolol	13.252	0.4
17	Globulol	13.308	0.8
18	Eicosane	16.185	1.3
19	Phenanthrene	16.496	6.9
20	Spathulanol	16.763	1.6
21	Androst-5-en-4-one	17.052	1.5
22	Heptadecane	17.674	0.3
23	α-humulene	18.763	3.5
24	abietatriene	19.018	0.4
25	Heptacosane	21.018	0.5
26	Nonacosane	22.207	0.3

The antioxidant efficiency of essential oil of *H. suaveolens* were performed by DPPH and ABTS scavenging radical activity assay's with IC_{50} values of 112 µg/mL and 156 µg/mL respectively. Ascorbic acid was used as a standard with IC_{50} values of 13.8 µg/mL and 14.4 µg/mL. It showed a concentration dependent antiradical activity given in the table 1 and table 2 respectively. The percentage inhibitions of the essential oil of *H. suaveolens* were shown in fig 1 and fig 2. From the results the essential oil of *H. suaveolens* showed significant antioxidant potential which may due the presence of various complex terpenes in it.

Table 2: In vitro antioxidant activity of essential oil of *H. suaveolens* -DPPH Assay

Concentration (µg/mL)	**DPPH % inhibition**	**Standard % inhibition**
25	12.2	64.5
50	23.0	87.5
75	34.6	90.1
100	45.1	95.2
150	66.0	125.3
IC50 (µg/mL)	**112 µg/mL**	**13.8µg/mL**

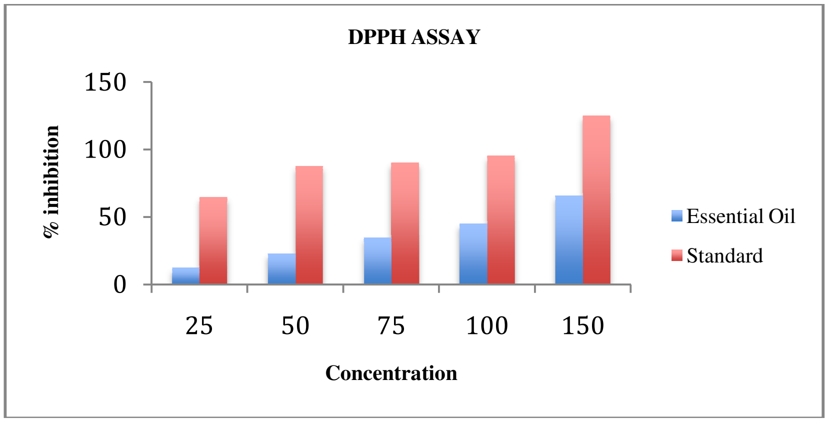

Fig 2: % Inhibition of essential oil of *H.suaveolens*-DPPH Assay

Table 3: In vitro antioxidant activity of essential oil of H. suaveolens - ABTS Assay

Concentration (µg/mL)	**ABTS·+ % inhibition**	**Standard % inhibition**
25	9.8	69.5
50	17.4	90.5
75	25.9	97.1
100	32.0	105.2
150	48.5	125.3
IC50 (µg/mL)	**156 µg/mL**	**14.4µg/mL**

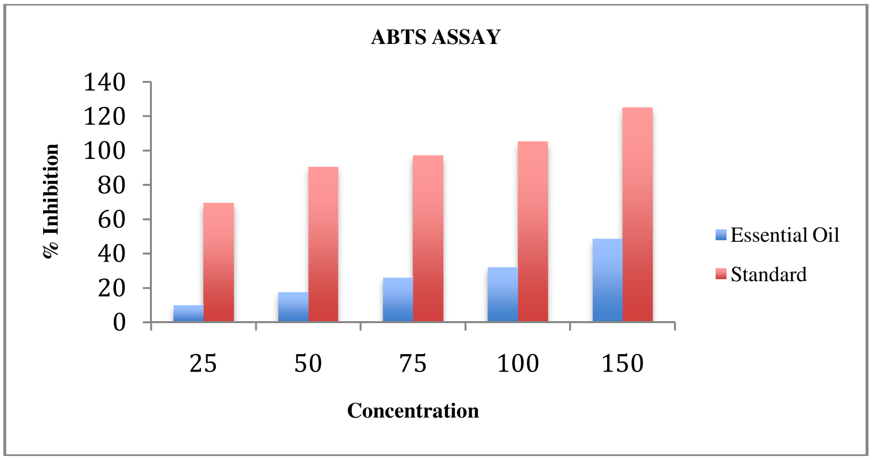

Fig 3: % Inhibition of essential oil of *H. suavelones*-ABTS Assay

IV. CONCLUSION

The chemical composition of essential oil from *H.suaveolens* was analyzed by GC/MS method. A total of 26 components was identified The *in vitro* antioxitant activity of essential oil from *H. suavelones* was tested. The essential oil showed a concentration dependent activity with IC_{50} value of 112 µg/mL for DPPH assay and 156 µg/mL for ABTS assay. From the results of the DPPH assay and ABTS assay of essential oil showed mild *in vitro* antioxidant property.

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Synthesis, Characterization and antimicrobial activity of hippurato and glycino hippurato (mixed ligand) complexes of Cobalt (II) and Nickel (II)

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Abstract - *The Hippurates of Co(II) and Ni(II) and mixed ligand glycino hippurato complexes of Co(II) and Ni(II) were synthesized. The mode of coordination was characterized by various physicochemical methods such as IR, UV, NMR, thermal analysis and molecular weight determination by Rast method. The complexes were screened for antimicrobial activity against Gram positive microorganisms such as Bacillus cereus (MTCC 430), Staphylococcus aureus (MTCC 3160), Gram negative microorganisms such as Escherichia coli (MTCC 1698) and Klebsiella pneumoniae (MTCC 10309) by agar well diffusion method. The results revealed that all the synthesized compounds showed significant antimicrobial activities compared to standard employed Tetracycline.*

Key words *: Hippurates of Co(II) and Ni(II), mixed ligand glycino hippurato complexes of Co(II) and Ni(II) Hippuric acid, antimicrobial activity, TG, FT-IR and NMR.*

I. INTRODUCTION

Organometallic chemistry finds wide application in our day to day life. The role of amino acids in synthetic organic and organometallic chemistry is very important. Amino acids find wide application not only in organometallic chemistry but also in pharmaceutical chemistry. The multifarious role of transition metals in chemistry suggests that considerable potential exists for the development of new organometallic chemistry.

Hippuric acid and its derivative belong to the group of biologically relevant ligands [1]. Hippuric acid is biosynthesized from glycine, benzoic acid and CoA by enzymes located in the mitochondrial matrix of liver and kidney cells and is a physiological component of human urine, filtered in the glomerula and secreted by proximal tubular cells [2,3]. The literature reveals that the hippuric acid is potentially capable of forming coordinate bonds with many metal ions through a carboxylic oxygen atom as a monodentate or bound through the carboxylic oxygen atoms as a bidentate [1, 4-14]. Glycine has an amino and a carboxyl group and is the simplest amino acid in the body. It is the only protein amino acid that does not have optical isomers. There is substantial experimental evidence that free glycine may have a role in protecting tissue, against insults such as ischemia hypoxia and reperfusion [15]. Glycine is a necessary building block for all protein in the body, glycine plays a major role in calcium absorption,building muscle protein, recovering from surgery or sports injuries and the body's production of hormones, enzymes and antibodies [15].

Antimicrobial resistance is becoming a global concern with rapid increase in multidrug resistant bacteria and fungi. This has mandated continued search for new antimicrobial compounds, including coordination complexes of biologically important molecules [16, 17]. Excellent antimicrobial activities of some amino acids chelates including those of histidine glycine, arginine and glutamic acid [19]have been reported [17-19]. However, there is a dearth of information for antimicrobial activities of mixed ligand complexes. It has been reported that the polarity of the metal ion is reduced by chelation by partial sharing of its positive charge with the donor group of ligands [20, 21]. It was therefore suggested, based on the chelate theory [21, 22], that increasing the number of chelate rings may improve the antimicrobial activities of these complexes. Hence the objective of this work was to synthesize, characterize, screen and compare the antimicrobial activities of mono ligand and mixed ligand metal (II) complexes of amino acids.

II. EXPERIMENTAL

A. Synthesis of hippurates of Co(II) and Ni(II)

The metal complexes of Co (II) (1A) / Ni (II) (1B) are prepared by dissolving the chloride salt of Co (II) 2.37g (0.01mole) / Ni (II) 3.74g (0.01mole) in ethanol were added to the stirred hot ethanolic solution of ligand hippuric acid in 1:2 ratio. The stirring is continued for 8 hours and allowed to stand overnight. The precipitated complex is removed by filtration and washed with ether & ethanol, dried in air and recrystallized from hot ethanol.

B. Synthesis of Mixed ligand (hippuric acid + glycine) complexes of Co (II) and Ni (II)

The mixed ligand metal complexes of Co (II) (2A) / Ni (II) (2B) are prepared by dissolving the chloride salt of Co(II) 2.37g (0.01mole) / Ni(II) 3.74g (0.01mole) in ethanol were added to the stirred hot ethanolic solution of ligand hippuric acid and glycine in 1:1:1 ratio. The stirring is continued for 8 hours and allowed to stand overnight. The precipitated complex is removed by filtration and washed with ether & ethanol, dried in air and recrystallized from hot ethanol.

C. Molecular weight determination by Rast Method

A known amount of solvent naphthalene (3g) was powdered well and taken in a freezing point apparatus. A thermometer and a stirrer were introduced through the holes in the cork. It was then immersed in a water bath and heated. The solvent melting point was noted. The content was heated to about 5^0C above the melting point. The apparatus was taken out and cooled by stirring. The temperature at which the first crystal appeared was noted. This gives the freezing point of the solvent. Then 0.3 g of the powdered solute is added and the freezing point of the mixture was noted by following the same procedure. The molecular weight is confirmed by repeating the experiment with different percentage of solute and solvent. The difference in the freezing point gives ΔT_f of the solution. The molecular weight of each complex was determined by the equation,

$$M_2 = \frac{K_f \times W_2 \times 1000}{W_1 \times \Delta T_f} g.mol^{-1}$$

Where,

M_2 - Molecular weight of the complex , K_f - Molar depression constant
W_2 - Weight of solute (0.3g), W_1 - Weight of solvent (3g)
ΔT_f - Depression in freezing point of the solution

D. Determination of antimicrobial activity by agar well diffusion method

The samples 1A, 1B, 2A and 2B were tested for antimicrobial activity. Liquid nutrient agar media and the Petri plates were sterilized by autoclaving at 121°C for about 30 minutes at 15 lbs pressure. Under aseptic conditions in the laminar airflow chamber, about 20ml of the agar medium was dispensed into each Petri plate to yield a uniform depth of 4mm. After solidification of the media, 24 hrs culture of Gram positive microorganisms such as *Bacillus cereus (MTCC 430), Staphylococcus aureus* (MTCC 3160), Gram negative microorganisms such as *Escherichia coli (MTCC 1698)* and *Klebsiella pneumoniae (MTCC 10309)* obtained from MTCC, Chandigarh were swabbed on the surface of the agar plates. Well was prepared by using cork borer followed with loading of 100 µl of samples Viz., 1A, 1B, 2A and 2B dissolved in Dimethyl sulfoxide (DMSO) to the distinct well with DMSO as negative control and Tetracycline as positive control. The sample loaded plates were then incubated at 37° C for 24 hours to observe the zone of inhibition.

III. RESULTS AND DISCUSSION

A. Melting point determination

Melting point was recorded on an electro thermal analyser working in the temperature range of (20°C and 370°C). The melting point of the prepared complexes are given below

1A - 230°C 1B - 270°C
2A - 210°C 2B - 190°C

B. IR spectral Analysis

IR spectra of synthesized complexes show strong bands in the region of 1572-1519 cm^{-1} due to asymmetrical vibration of carboxylate anion ν_{as} (COO). The corresponding symmetric vibration ν_s (COO) is observed in the region 1423-1401 cm^{-1}. The shift of bands of ν_{as} (COO) to lower frequency indicates that the carboxylate anion in the complexes behave as chelating ligands. The bands at 1759 cm^{-1} and 1743 cm^{-1} arising due to free carboxylic acid group in hippuric acid, 1770 cm^{-1} and 1737 cm^{-1} arising due to free carboxylic acid group in glycine disappear in the synthesized complexes. This shows that the hydrogen atom in hippuric acid and glycine is replaced by metal ions. The coordination of the metal ions via oxygen of carboxylate is confirmed by observing M-O bond stretching frequencies, ν(M-O) at 584 cm^{-1} and 457 cm^{-1} for Complex 1A, 595 cm^{-1}, 459 cm^{-1} and 495 cm^{-1} for Complex 1B, 547 cm^{-1}, 452 cm^{-1} and 481 cm^{-1} for Complex 2A, 544 $cm^{-1}$and 495 cm^{-1} for Complex 2B.These bands are not observed in the spectrum of hippuric acid and glycine. A new broadband is also observed in the complexes in the region 3400-3700cm^{-1} due to vibration of water ν (OH) in hydrated complexes. The IR spectra of the prepared complexes at 3381-3070cm^{-1} and 1649-1602cm^{-1} is due to N-H vibrations. The assignment of these bands agrees quite well with those of related complexes containing hippurate and mixed hippurate glycinate ligands.

C. Electronic spectra

The absorption spectra of the prepared complexes are compared with the absorption maxima of hippuric acid, the results showing that there is increasing absorbance (i.e., hyperchromic effect). From this data it was evident that the prepared hippurates have complexation behavior of hippuric acid towards metal (III) ions.

D. 1H-NMR spectra

The disappearance of the proton signal of carboxylic acid in the prepared complexes showed the coordination via the carboxylic acid group. The peak for water molecules was observed in the region of (δ 3.3 and δ 3.4). The aromatic signals nearly do not shift and revealed that the magnetic environment of the aromatic ring has not changed significantly with coordination.

TABLE 1: Characteristic ^{1}H-NMR peak of ligands and prepared complexes.

Complexes	-COOH	-NH	AROMATIC RING	$-CH_3$	$-H_2O$	$-CH_2$
Hippuric acid	δ12.5	δ8.8	δ7.4, δ7.5	-	-	δ3.9, δ4.1
Glycine	δ12.6	δ8.8	-	δ1.39	-	-
1A	-	δ8.3	δ7.4, δ7.5	-	δ3.3	δ3.9
1B	-	δ8.3	δ7.4, δ7.5	-	δ3.4	δ3.9, δ4.2
2A	-	δ8.7	δ7.4, δ7.5	-	δ3.4	δ3.9
2B	-	δ8.7	δ7.4, δ7.5	-	δ3.4	δ3.9, δ4.2

E. TG-DTA Analysis

Complex 1A showed weight loss in the temperature range of 40-100℃ may due loss of two molecules of water (7.0% loss in weight). The further loss in weight at the temperature range of 220-300°C may be due to decomposition of amino acid moiety. Above 400°C a constant plateau is observed indicates the complete decomposition of the complex into its oxide (CoO) (79.0% loss in weight).1B complex showed weight loss in the temperature range of 140-200°C may due loss of two molecules of water (8.0% loss in weight) which may involve in H-bonding. The further loss in weight at the temperature range of 220-300°C may be due to decomposition of amino acid moiety. Above 400℃ a constant plateau is observed indicates the complete decomposition of the complex into its oxide (NiO) (78.0% loss in weight).Complex 2A showed weight loss in the temperature range of 140-200℃ may due loss of two molecules of water (9.0% loss in weight). The further loss in weight at the temperature range of 220-300℃ may be due to decomposition of amino acid moiety. Above 400°C a constant plateau is observed which shows the complete decomposition of the complex into its oxide form (76.0% loss in weight).Complex 2B showed weight loss in the temperature range of 140-200°C may due loss of two molecules of water (7.9% loss in weight). The further loss in weight at the temperature range of 220-300°C may be due to decomposition of amino acid moiety. Above 400℃ a constant plateau is observed which shows the complete decomposition of the complex into its oxide form (79.7% loss in weight).

Table. 2: Thermo gravimetric analysis of prepared complexes

Complex	*DTA peak (℃)*	*TG temp. Range(^{0}c)*		*% Mass loss*		*Decomposed Product*
		Initial	*Final*	*Observed*	*Theoretical*	
1A- $C_{18}H_{20}N_2O_8$.Co	60.83-endo 284.86-endo	40	730	7.0 79.0	7.9 80.0	Elimination of $2H_2O$ Cobalt oxide
1B- $C_{18}H_{20}N_2O_8$.Ni	191.98-endo 289.68-endo	40	730	8.0 78.0	7.9 78.7	Elimination of $2H_2O$ Nickel Oxide
2A- $C_{11}H_{16}N_2O_7$.Co	187.96-endo 293.15-endo	40	730	9.0 76.0	10.08 76.6	Elimination of $2H_2O$ Cobalt oxide
2B- $C_{11}H_{16}N_2O_7$.Ni	168.98-endo 288.153-endo	40	739	7.9 79.7	8.2 79.6	Elimination of $2H_2O$ Nickel oxide

F. Molecular weight determination by Rast Method

The molecular weight of the complexes determined by Rast method is tabulated below:

Table. 3: Molecular weight of prepared complexes

Complexes	ΔT_f	M_2
1A	1.5	456.67g
1B	1.5	456.67g
2A	2.0	350.00g
2B	1.9	368.42g

G. In vitro Antimicrobial activity of complexes

In Vitro antibacterial activities as synthesized complexes were evaluated against *Bacillus cereus, Staphylococcus aureus, Escherichia coli* and *Klebsiella pneumonia,* tetracycline was employed as standard. The results are given in table.4.

Table. 4: **Antimicrobial activity of complexes**

S.No	*Microorganisms*	*Zone of inhibition (mm)*				*Standard*
		1A	**1B**	**2A**	**2B**	*Tetracycline*
1	*Bacillus cereus*	20	23	29	30	23
2	*Staphylococcus aureus*	21	22	28	26	21
3	*Escherichia coli*	22	25	30	32	22
4	*Klebsiella pneumonia*	19	20	29	28	19

The activity was found to be higher for mixed ligand complexes (2A, 2B) compared to hippurates (1A, 1B) and all the four samples exhibited the best action against *Escherichia coli.*

IV. CONCUSION

The Hippurates of Co(II) and Ni(II) and mixed ligand glycino hippurato complexes of Co(II) and Ni(II) were synthesized and characterized by various spectral analysis for confirmation of the formation of expected complexes. The efficacy of the pharmacological properties of the complexes were tested for its *In- Vitro* antimicrobial activities using agar well diffusion method and zone of inhibition was significant compared to the standard. These findings suggest that these complexes may be used for the alternative for available antibiotics.

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Removal of Vat Red Dye From Aqueous Solution Using *Eichhornia Crassipes* Leaves as Adsorbent

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Abstract - *Adsorption efficiency of prepared biomass of Eichhornia crassipes leaves powder (REC) as low-cost adsorbent material for efficient removal of vat red dye was carried out. The effects of pH, contact time, dye concentration and adsorbent dosage were studied using batch mode studies. The removal mechanism of vat red dye was calculated by fitting experimental data into Langmuir and Freundlich equations. Experimental results suggest that REC, an agricultural weed, is resourceful adsorbent for removal of vat red dye from aqueous solutions.*

Keywords *: Eichhornia crassipes leaves, vat red dye, adsorption, isotherm.*

Introduction

Water contamination is one of the serious issues worldwide and most significant reasons for passings and ailments. The textile industry has been sentenced to be the world's dreadful water polluters.Textile waste water is heavily loaded with unconsumed dyes and metal traces.These releases cause a major destruction to the earth. So everywhere analysts are searching for proper managements to dispose these toxins safely [1].To lessen the perilous effects of dye wastewater, many methods such as microbial degradation, coagulation, incineration, adsorption on activated carbon, bio-sorption, sedimentation and filtration etc., have been devoted [2-4].

Adsorption has emerged to be a successful method with its effectiveness, capability and applicability on a huge scale to evacuate dyes and also having the potential for recovery, regeneration and reusing of adsorbents. Activated carbon is found to be ideal for adsorption of most important classes of dyes such as basic, acidic, direct and vat dyes. A very efficient technique for treatment of textile waste water is proved to be adsorption on activated carbon. However, in view of enormous expenditure and problems associated with regeneration, there is a continuoushunt for alternate inexpensive adsorbents [5].

Agricultural waste materials are extensively used as adsorbents for dye removal either as in its raw form or in its modified form by converting it into carbon and activated carbon. *Eichhorniacrassipes* (Water hyacinth) is an aquatic weed plant, which belongs to the family of pontederiaceae. The extensive growth of this weed plant creates enormous problems like eutrophication, depletion of oxygen etc. A proper method of disposal is yet to be found [6].

Considering the utilization and applications of water hyacinth, its most important task in effluent treatment is recently undergoing superior attention to find an alternative for the presently available wastewater treatment techniques [7]. It has been noticed that in almost all cases the focus is done on various cationic and anionic dyes and very few on non ionic dyes. Vat dyes possess complex chemical structure and hence are very difficult to be removed. Removal of vat dyes by adsorption using agricultural waste is an area still to be explored.

In the present study leaves of water hyacinth is used as adsorbent for the removal of Vat red dye from aqueous solution.

II. MATERIAL AND METHODS

A. Preparation of Adsorbent (Leaves of Eichhornia crassipes)

The leaves of *Eichhornia crassipes* were washed extensively in running tap water to remove dirt and other particulate matter.They were air-dried, powdered in a grinder and then dried at 110 °C in a hot air oven. The powdered leaves (REC) were then stored in an air-tight container and used for further experiments.

B. Preparation of Stock Solution

The dye stock solution (1000 ppm) was prepared by dissolving 1 g of pure dye in one liter of double distilled water. By adding either 0.1 M HCl or 0.1 M NaOH, the initial pH of the solution was adjusted. The chemicals used all through this study were of analytical-grade reagents. The experiments were performed at room temperature (27 ± 2 °C). The original stock solution was diluted in appropriate volume to obtain different concentrations of the working solution.

C. Characterization of the Adsorbent

Functional group analysis was done with FTIR [Shimadzu] Spectrometer. Crystallinity and crystal phases were identified with X-Ray Diffraction [Perkin–Elmer] spectrometer Elemental analysis was done with the Energy Dispersive X-Ray [RONTEC'S EDX system] spectrometer. Scanning electron microscopy (SEM) analysis was carried out on the REC, to study its surface texture before and after Vat red dye adsorption.

D. Batch Mode Adsorption Studies

The adsorption experiments were performed in a batch process in order to investigate the effect of various parameters such as initial pH, adsorbent dosage, dye concentration, and contact time of vat red dye onto REC.

The dye solutions of different concentrations and pH were agitated with the adsorbent (about 0.2 g) in a mechanical shaker at room temperature. The agitation was maintained constant at a speed of 120 rpm and the final concentration was measured. The following equation is used to calculate the adsorption percentage.

Percentage of adsorption = $\frac{C_i-C_f}{C_i}\times 100\frac{C_i-C_f}{C_i}\times 100$ ………….. (1)

where C_i represents initial concentration of the dye and C_f indicates concentration of the dye after adsorption.

III. RESULTS AND DISCUSSION

A. Fourier Transform Infrared Spectroscopic Analysis (FTIR Spectroscopy)

The FTIR spectra of powdered raw leaves of *Eichhornia crassipes* (REC) is given in Figure 1. The peaks identified at 3738 cm^{-1}and 3616 cm^{-1}in REC may be attributed to that of O-H stretching of alcohols. The band witnessed at 2956 cm^{-1}in REC corresponds for C-H vibration of alkenes [8]. The peak at 2358 cm^{-1}is because of KBr and the peak at 1651 cm^{-1}in is because of aromatic C=C stretching. The peaks obtained at 1428 cm^{-1}in REC may be attributed to C-H bending [9]. The peak at 1325cm^{-1}in REC corresponds to O-H bending of alkanes and phenols. The observed peaks at 1243 cm^{-1}, 1153 cm^{-1}, 1060 cm^{-1}, 1047 cm^{-1}, 767 cm^{-1}and 696 cm^{-1}corresponds to that of C-O stretching and O-H bending of primary, secondary and tertiary alcohols, esters and ethers.

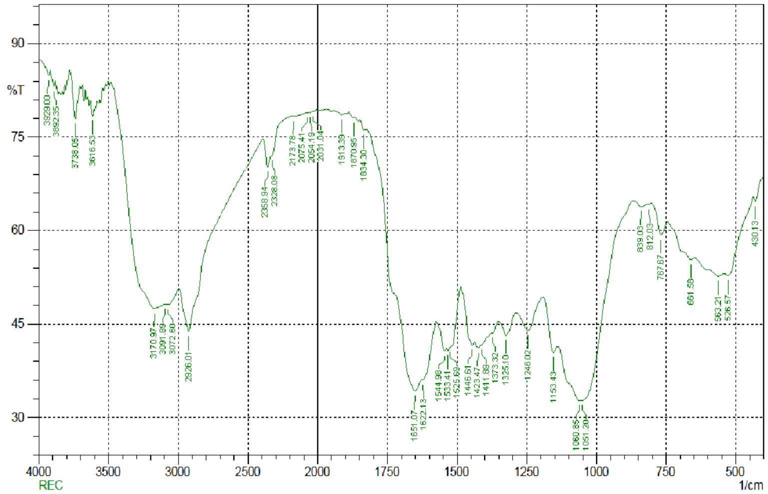

Fig.1: FTIR spectrum of REC

B. Scanning Electron Microscope Analysis (SEM)

The surface morphology and the pore size of the samples were studied using Scanning electron microscopy. Samples of REC were subjected to SEM studies before and after adsorption and the SEM micrographs are shown in fig 2. It is clear that the adsorbent exhibit uneven and rough surface morphology and possess a significant number of heterogeneous pores and hence there is a good chance for dye to be wrapped up and adsorbed. The particles appeared evidently varied. Visibly, there were particle fragments and rough structure on the surface. Such cracks and irregularities are advantageous for the dye to diffuse to the internal adsorption sites located in the adsorbent. Similar trends were reported in adsorption of direct blue -106 onto pomegranate peel [10], adsorption of methylene blue onto pumpkin seed hull [11] and adsorption of methylene blue onto spent tea leaves [12].

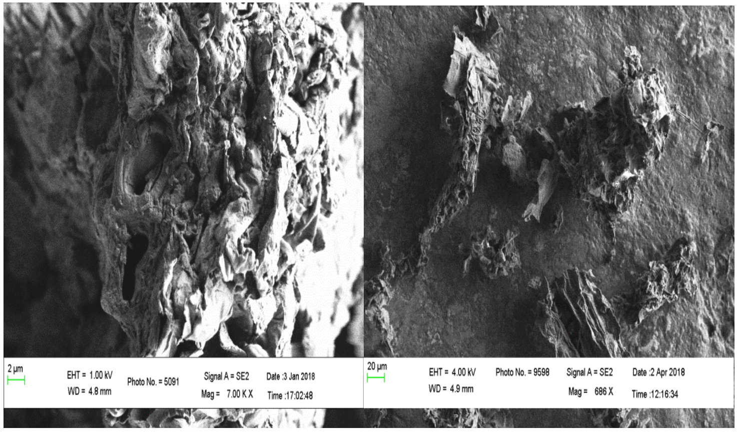

Fig.2: SEM Analysis of REC before and after adsorption

C. Energy-Dispersive X-Ray Spectroscopy (EDS OR EDX)

Energy-dispersive X-ray spectra of the adsorbent before and after adsorption are illustrated in fig. 3. From the images it is observed that a little difference is seen in the spectrum of REC after adsorption which may be attributed to the fact that there is adsorption.

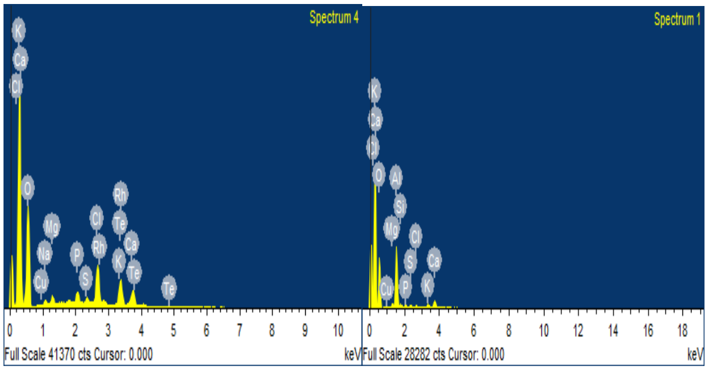

Fig.3: EDAX of REC before and after adsorption

D. X-Ray Refractory Diffraction (XRD)

The X-ray diffraction patterns of REC before and after adsorption of vat red dye are shown in fig. 4. From the results it is evident that the adsorbents exhibited broad peaks at around 2θ = 21, 26 which resembles that of the peak obtained for graphite as given by International Centre for Diffraction Data. The appearance of broad peaks and absence of sharp peaks exposed an amorphous structure for the adsorbent.

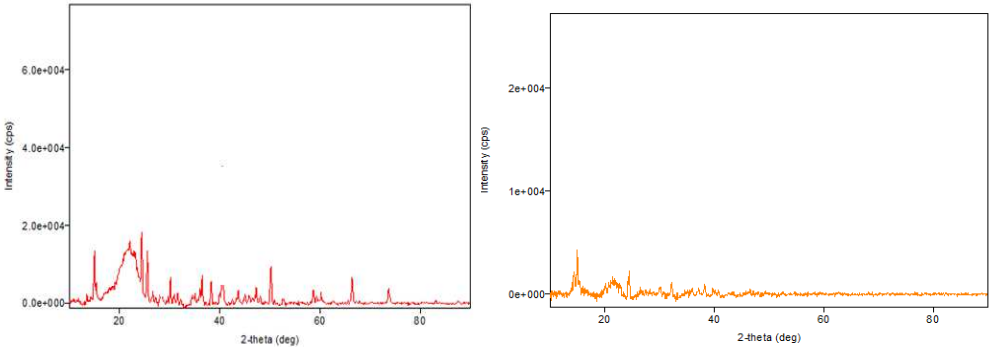

Fig.4: XRD of REC before and after adsorption

E. Effect of PH on the Vat Red Dye Adsorption

The pH of the aqueous solution is a significant factor affecting the adsorption process. The influence of pH is studied to know the adsorbing capacity of REC on vat red dye. The experiments were performed with different initial solution pH values, ranging from 3 to 10. The effect of pH of solution is very significant when the adsorbing molecules are able to ionize in response to the current pH [13].

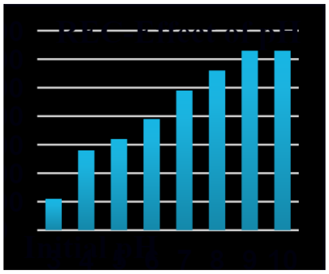

Fig.5: Effect of pH on vat red dye adsorption onto REC

F. Effect of Contact Time

Effects of agitation time on the elimination of vat red dye by the adsorbent showed that as the agitation time increased the amount of dyes adsorbed (mg/g) also increased and it attained equilibrium after 90 minutes. This may be attributed to the fact that more surface area is available at the beginning for the adsorption of vat red dye and as time goes on the rate of adsorption decreases due to less availability of active sites.

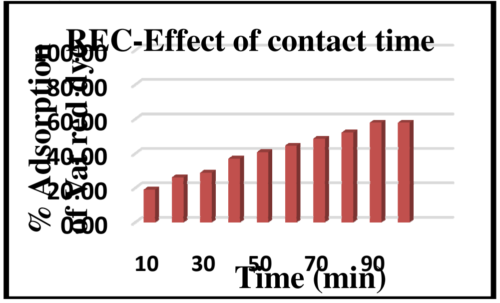

Fig.6: Effect of contact time on vat red dye adsorption onto REC

G. Effect of Dye Concentration on the Vat Red Dye adsorption

The effect of concentration of vat red dye on the rate of adsorption onto the adsorbent was studied by conducting adsorption experiments. By fixing the adsorbent dose as 0.2 g, the experiments were performed with different dye concentrations at different intervals of time.

The maximum adsorption capacity of the adsorbent with regard to the dye concentration of the adsorbent is illustrated in Figure 7. The percentage of adsorption of vat red dye decreased with increase in dye concentration. This may be due to the fact that as concentration of dye increases the active sites and surface area on the surface of the adsorbents may get saturated.

Fig. 7: Effect of dye concentration on vat red dye adsorption onto REC

H. Effect of Adsorbent Dose on the Vat Red Dye Adsorption

The effect of adsorbent dose on adsorption of vat red dye demonstrated that as the adsorbent dose increases, the percentage of adsorption increases. This is primarily because of the fact that as the adsorbent dose increases, the surface area and number of adsorbent sites available for adsorption increases and hence results in increased percentage of adsorption [14].

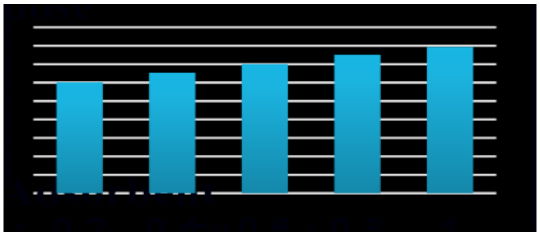

Fig.8: Effect of adsorbent dose on vat red dye adsorption onto REC

I. Adsorption Isotherm

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface[15]. The isotherm results were analyzed using the Langmuir, and Freundlich isotherms. The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface. A basic assumption is that sorption takes place at specific homogeneous sites within the adsorbent. The linear plot of specific adsorption (Ce/qe) against the equilibrium concentration (Ce) (fig.7) shows that the adsorption obeys the Langmuir model. The Langmuir constants were determined from the slope and intercept of the plot.

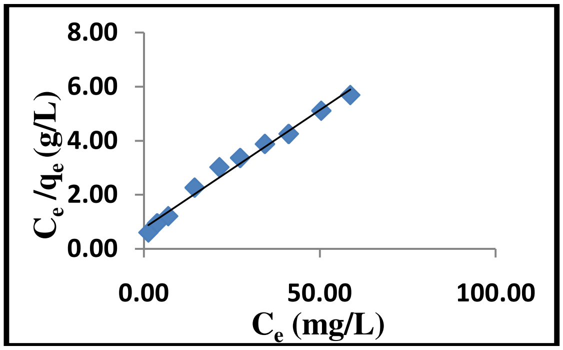

Fig.9: Langmuir adsorption isotherm plot for vat red dye adsorption onto REC

The Freundlich isotherm model is the earliest known empirical equation that can be applied for non-ideal adsorption on heterogeneous surfaces as well as multilayer sorption The Freundlich isotherm can be obtained by assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites and is commonly given by the following non-linear equation:

$$q_e = K_F C_e^{1/n}$$

A plot of log q_e versus log C_e (Figure 8) facilitates to find out the constant K_f and 1/n.

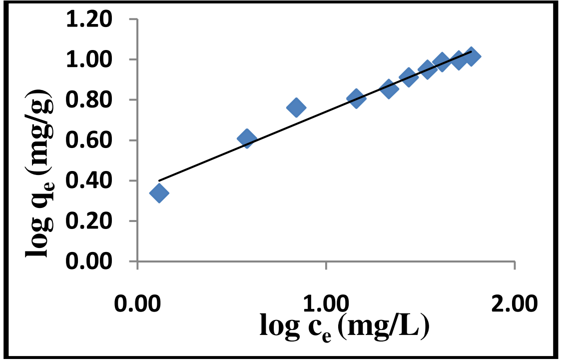

Fig.10: Freundlich adsorption isotherm plot for vat red dye adsorption onto REC

As shown in fig. 9, it was observed that experimental processes are more fitted to Langmuir Model compared to Freundlich. The experimental data of adsorption gives linear regression coefficient values with R^2 = **0.984** for Langmuir model and R^2 = **0.9695** for Freundlich model.

IV. CONCLUSION

The removal of vat red dye by Raw *Eichhornia Crassipe*s Leaves, an agricultural waste, had been carried out using different parameters such as pH, contact time, dye concentration and adsorbent dose. Equilibrium data fitted very well in the Langmuir isotherm equation, confirming the monolayer adsorption of vat red dye onto REC. Since REC used in this work is freely, abundantly and locally available aquatic weed, it can be expected as an economically viable and promising adsorbent for the removal of vat red dye from aqueous solutions and also finds a prolific way for disposal of *Eichhornia Crassipe*s, the weed plant.

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The Effect of Immersion Time on the Corrosion Behavior of Expired Glycomet (500mg) Tablet on Mild Steel Sample

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Abstract — *Recently drugs have now been used as corrosion inhibitors. The use of drugs as corrosion inhibitors for metals corrosion possess some merits over using some inorganic/ organic inhibitors because of their little or insignificant impact on the environment, so it is suggested replacing the traditional toxic corrosion inhibitors. Many of the researchers in this field generally agree that drugs are corrosion inhibitors that can compete favorably with discovered green corrosion inhibitors and the most of these drugs can be synthesized from natural products. So in this research work we are concentrated on the effect of immersion time on the inhibition efficiency of Glycomet 500mg tablet in 20% citric acid medium.*

Keywords — *Corrosion, Green inhibitor, Glycomet, Citric acid, immersion time.*

I. INTRODUCTION

Corrosion is the deterioration of the useful properties of materials caused by the environment. Both direct and indirect losses due to corrosion are huge and will further increase with industrialization. A Substantial portion of the government and industrial funds are being spent all over the world for combating corrosion losses. The corrosion problem needs to be brought forcibly to the attention of engineers of all disciplinary and in all fields of Endeavour. The corrosion of metals is a matter as much of economic and technical concern. It affects economy, safety, product reliability, and people-oriented activities.

A. Citric acid as corrosion medium

Thermal power equipment is chemically cleaned with citric acid solutions ($C_6H_8O_7$) before the launch (pre-operational chemical cleaning) to remove rust, scaling and other sediments and in the process of operation (operational cleanings) to remove iron oxide and carbonate (crust) formations [1-3]. These solutions demonstrate low aggressiveness towards steel equipment and remove roll scale, magnetite sediments and crust formations well, including through their complexing properties. Treatment with citrate solutions is quite frequently carried out at temperatures (t) close to 100^0 C. The solutions of other organic acids (adipic, maleic, oxalic, succinic) are less effective in thermal power equipment cleaning than citric acid solutions. Mixtures containing pyridine toxic derivatives – Catapin K and the inhibitor I-1-A [1], benzotriazol [4], cinnamic aldehyde [5] and various vegetal extracts [6-8] are recommended as additives to inhibit the corrosion of steels in citric acid solutions.

II. MATERIALS AND METHODS

A. Preparation of stock solution of citric acid

About 125gm of citric acid is dissolved in small amount of distilled water. Then it was making up into 250ml SMF using distilled water to get 50% corrosion medium. Each 40ml of this stock solution in 100ml distilled water would make 20% corrosion medium.

B. Preparation of stock solution of Glycomet tablet

One gram Glycomet tablet is crushed, powdered and dissolved in small amount of distilled (DD) water. Then it is make up into 100ml SMF using DD water to get 10,000ppm.

Fig. 1. Molecular formula:$C_4H_{11}N_5$

C. Preparation of Specimen

Mild steel specimens of size 1.0 cm ×4.0 cm ×0.2 cm and chemical composition 0.026 % sulphur,0.06 % phosphorous, 0.4 % manganese, 0.1% carbon and the rest iron were polished to a mirror finish and degreased with acetone.

D. Weight – loss method

Mild steel specimens were immersed in 100 ml of the aqueous medium containing 60 ppm Cl^- ions in various Concentration of the inhibitor in the absence and presence of Zn^{2+} for one day. The Inhibition efficiency (IE %) was calculated using the equation.

Inhibition Efficiency (IE %) = $(1-W_1/W_2) \times 100$

Surface coverage (Θ) = $(1-W_1/W_2)$

Where W_1 and W_2 are the weight loss for mild steel in the presence and absence of inhibitor.

E. Determination of corrosion Rate

The corrosion rate (CR) is directly proportional to the weight loss cm^2 in a specified time and was calculated by the formula.

$CR = (87.6 \times W)$ DAT

Where, W = weight loss in mg

D = density of mild steel (7.86 g cm^2 for mild steel)

A = Area in cm^2

T = Exposure time in hours

Trends of CR and IE are graphically evaluated.

III. RESULT AND DISCUSSION

A. Influence of Immersion period on the inhibition efficiency % (IE)of inhibitor Glycomet 500mg tablet in 20% citric acid medium

When characterizing the ability of a corrosion inhibitor, the well-known standard factor is immersion period. The immersion periods taken in these studies were varied from 1 to 5days. The results are shown in Fig.1, which indicated the effect of immersion time on IE and CR of Glycomet 500mg tablet in 20% citric acid medium. The maximum corrosion inhibition efficiency of 71% was attained at the first day . This was due to the quick adsorption of the inhibitor on to mild steel surface because there were maximum numbers of available active inhibitor molecules to inhibit mild steel from corroding[9]. After, that on the upcoming days, the IE was observed to decrease. The decrease in IE was recognized to desorption of the corrosion inhibitors from MS surface. Moreover, the corrosion rate (CR) also increased rapidly with a longer period of immersion. These happened because when the inhibitor was being desorbed from MS surface, a bare metal was exposed to corrosive media thereby increasing metal-solution contact that led to more metals being dissolved. Moreover, the increase in CR after long period of immersion can also be attributed to a less concentration or limited number of available inhibitor to stop or reduce metal dissolution. It is evident that after the Glycomet inhibitor had been desorbed from the metal surface they become inactive and therefore did not take part in the inhibition process. Owing to the biodegradability, it would bring no or major thread to the environment after its disposal.

The influence of immersion period on IE of Glycomet 500mg tablet in 20% citric acid medium is given in Table 1. The data in Table.1 and curves of Fig.1, revealed that, as the period of immersion time increases, while IE decreases, CR increases. This is due to the fact that as the immersion period increases the protective film is ruptured by the corrosive citrate ions present in the system [10,11].

Table I. Influence of duration of immersion on the IE of inhibitor Glycomet 500mg tablet in 20% citric acid medium

Immersion period (Day)	*System*	*Weight loss(g)*	*CR mmpy*	*Surface coverage (θ)*	*IE (%)*
1	**Blank:** 20% Citric acid	0.3010	139.78	0.7149	71
	Inhibitor medium: 20% Citric acid +250 ppm Glycomet inhibitor	0.0858	39.84		
2	**Blank:** 20% Citric acid	0.3020	70.12	0.7043	70
	Inhibitor medium: 20% Citric acid +250 ppm Glycomet inhibitor	0.0900	20.90		
3	**Blank:** 20% Citric acid	0.3060	47.37	0.6732	67
	Inhibitor medium: 20% Citric acid +250 ppm Glycomet inhibitor	0.100	15.48		
4	**Blank:** 20% Citric acid	0.6050	70.24	0.5758	57
	Inhibitor medium: 20% Citric acid +250 ppm Glycomet inhibitor	0.2990	34.71		
5	**Blank:** 20% Citric acid	1.027	90.38	0.1889	19
	Inhibitor medium: 20% Citric acid +250 ppm Glycomet inhibitor	0.833	77.36		

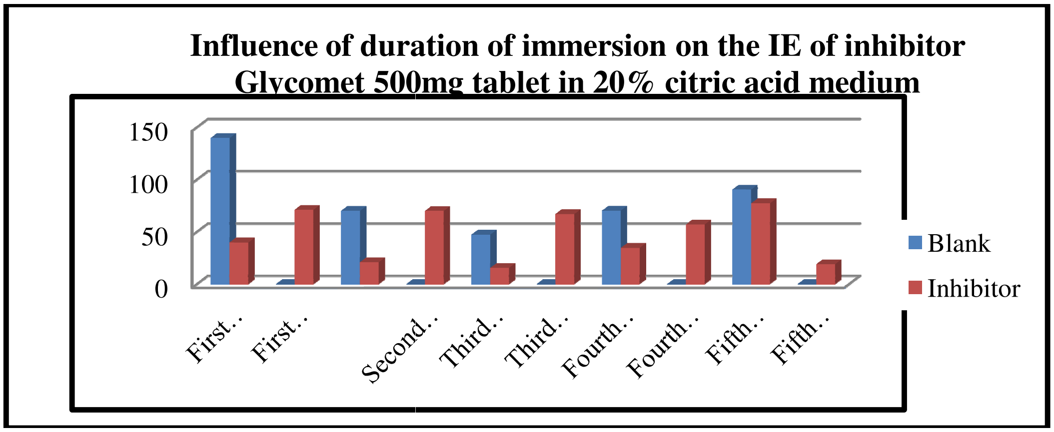

Fig1. Influence of duration of immersion on the IE of inhibitor Glycomet 500mg tablet in 20% citric acid medium

IV. CONCLUSION

The most effective corrosion inhibitors are those compounds containing hetero atoms like nitrogen, oxygen, sulfur and phosphorus as well as aromatic rings. The reactive centers like O, N and/or S atoms containing lone pairs of electrons and aromatic rings with delocalize π electron systems which can aid their adsorption onto metal surfaces. Furthermore, the high molecular weights of inhibitors are likely to effectively cover more surface area (due to adsorption) of the metal thus preventing corrosion from taking place. Corrosion scientists are attempting to integrate environmental considerations directly into corrosion inhibitor selection processes, in order to respond to an increased awareness of the need to protect the environment. It is evident that the support for the choice of some drugs as corrosion inhibitors is mostly due to their environmentally friendly nature. Since drugs come in a wide variety of molecular weights, structure, polarities, activities and salt forms, they can be hydrophilic or lipophilic, biodegradable or persistent, polar or non-polar. Thus in this work it is found that the immersion period effect of environment friendly green corrosion inhibitor of Glycomet 500mg tablet in 20% citric acid medium for seven days. It is concluded that this drug is effective for one day immersion, and after that due to the easy biodegradation nature of this drug it is easily cleaved away from the mild steel surface.

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Phytochemical Studies on Specific Plants of *Cyperaceae* Family: A Review

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Abstract — *Reviewing the available Literature in a particular field is a primary need for conducting specific and elaborative research. It empowers the research scholar to become knowledgeable in his/her research work. Literature Review gives the summary of the literature available in the specific area of research. Plants are the gift of nature. They are used as basic elements for producing natural chemical compounds. Some of them are used as herbal medicines. The herbal nature of the plants depends on the bioactive compounds such as flavonoids, tannins, alkaloids, and phenolic compounds which are present in the plants. Most of the medicinal plants are useful for human beings and animals for their well-being. Phytochemicals are the chemicals which are produced by plants through primary or secondary metabolism. The most important bioactive compounds of plants include flavonoids, tannins, alkaloids, saponins, glycosides and phenolic compounds. Phytochemical research or analysis is used to detect the presence of natural chemical compounds in the plants with some specific quantitative methods. The Cyperaceae family consists of grass-like monocotyledonous plants. They are known as sedges. It is one among the top 10 families of flowering plants. There are about 5,500 species in Cyperaceae family. In this Review, the research on the phytochemical screening and Chemical composition of oil of some of the Cyperaceae family of plants are presented.*

Keywords — *Review, Cyperaceae family, Phytochemical Research, Chemical Composition*

I.Introduction

The use of medicinal plants has been considered for the treatment of human diseases since ancient times. Medicinal herb is a plant that is able to change the physiological and pathological processes and can be used to prevent diseases [1]. The family Cyperaceae is of the largest and most intricate groups of angiosperms. The members of the family are commonly called as sedges. It is represented by about 80-104 genera and over 5000 species distributed throughout the world. In India it has 28 genera and about 500 species. In peninsular India alone it is represented by 16 genera and about 400 taxa (320) species. It was raised by Linnaeus C. The genus is large with over 600 species in the world, well represented by 84 taxa in India. Some treat Cyperus in a broad sense, merging about 9-10 smaller genera including Kyllinga in it. Recent taxonomists treat Cyperus in a narrow generic sense & all other 9-10 smaller genera considered distinct generically. It is the second largest family among monocotyledons and stands next to the grass family [2]. Some of the important species of Cyperaceae family are *Cyperus aggregatus, Cyperus congestus, Cyperus conglomeratus, Cyperus cyperoides, Cyperus difformis, Cyperus eragrostis, Cyperus esculentus, Cyperus exaltatus, Cyperus imbricatus, Cyperus involucratus, Cyperus longus, Cyperus reflexus, Cyperus rotundus, Cyperus virens* [3] *Cyperus brevifolioides, Cyperus diffusus, Cyperus helferi, Cyperus surinamensis, Cyperus distans, Cyperus acuminatus, Cyperus michelianus , Cyperus prolixus, Cyperus strigosus, Cyperus erythrorhizos, Cyperus lucidus, Cyperus andinus, Cyperus schomburgkianus , Cyperus compactus, Cyperus alternifolius [4]*. The grasses that yield therapeutically important products are among the least studied in the Cyperaceae family. Herb-based medicine from ancient times have played a vital role in ailments of various disease and nowadays it has been a particular area of interest in medicine. Phytochemicals are inherent compounds derived from plants that are biologically active, non-nutritive chemicals that act as a defensive or prophylactic medicine in humans. Their extracts have proven to show inhibition properties against different microbes. Despite the prevalence of *Cyperus* species and their traditional use in medicine, the chemical components responsible for their attributes remain largely unknown [5].

II. Scientific classification of Cyperaceae

Kingdom - Plantae
Order - Poales (Cyperales)
Family - Cyperaceae
Genus - Cyperus [6]

III. Vernacular name

Hindi - Motha, Nagagmotha
Gujrati - Nagarmothaya
English - Nutgrass, purple nutsedge
Kanada - Koranari-gadde
Assamese - Keyabon
Malayalam - Korakizanna,
Marathi - Barik motha, Bimbal
Sanksrit - Muthakasu, Musta, Varida [6]

IV. Phytochemical Researches on Cyperaceae Plants

Udari, Lata Maishaya [7] analyzed and compared ten species of sedges such as *Cyperus rotundus*, *Cyperus esculentus*, *Cyperus diffusus*, *Cyperus involucratus*, *Cyperus helferi*, *Cyperus prolixus*, *Cyperus papyrus*, *Cyperus surinamensis*, *Cyperus hortensis*, *and Cyperus squarrosus* with respect to their phytochemical constituents by examining their chemical profiles using HPLC. Methanol-based leaf and root extracts between species were shown to have significantly unique phytochemical profiles, with many extracts containing phytochemicals that support mammalian health (e.g. asiatic acid). In addition, comparing fresh plant extracts with dried samples (historical specimens) revealed that some of the phytochemical components appeared to be reasonably stable over decades. This study also examined antimicrobial properties of extracts from these plants, although results were inconclusive due to solvent incompatibility with either the phytochemicals or microbial species. Overall, this research revealed the unique phytochemical profiles of *Cyperus* species, and underscored the importance of considering each species and tissue type individually when investigating the medicinal properties of this genus.

Baig Zeba Rafat and Kareppa [8] studied annual & perennial habits found in Cyperaceae often with adventitious root systems. The underground parts in perennial show remarkable variability. Both the microscopic and macroscopic morphological features are highly variable in Cyperaceae. The sedges are distributed in every farming area (except epiphytes). They form a major component of wetland flora (with very few exceptions). Many species are indeed more or less grass-like but often with a characteristic yellowish or brownish tinge or often partly or wholly reddish or purplish colored but few species have white color that is why Cyperceous plants are easily recognizable among the grasses and other flora.

Jagdamba Singh and Shiv Kumar, [9] observed the phytochemical investigation of Cyperus scariosus. They isolated and identified the compound 2,3-diacetoxy-19-hydroxy-urs-12-ene- 24-O-β-D-xylopyranoside 1 based on chemical and spectroscopic studies. Cyperus scariosus (Cyperaceae) commonly known as Nagarmotha. The plant is generally distributed in damp places in Bengal, Sundarbans, Uttar Pradesh and eastern and southern parts of India. It is also grown in Australia. This plant has been reported to have many medicinal properties.

Srivastava et. al., [10] gave a review on Chemical Constituents and Biological Activities of Promising Aromatic Plant Nagarmotha (Cyperus scariosus R.Br. Nagarmotha is a pestiferous perennial, delicate slender sedge found wildly in various parts of the country, especially in damp or marshy areas and collected wildly for extraction of its essential oil using steam distillation. The Rhizomes of C. scariosus possess pleasant aromatic odor, the essential oil is used as anti-inflammatory, antimicrobial and anti-fungal agent and it is also used as one of the ingredients in several formulations for the Ayurvedic systems of medicine. Phytochemical studies have shown that the major chemical components of this herb are polyphenol, flavonol, glycoside, alkaloid, saponins, sesquiterpenoids and essential oil. Rhizome of the plant is used in fever, arthritis, diuretic, nervine tonic, treatment of diarrhea and dysentery, leprosy, bronchitis, amenorrhea and blood disorders. The fruits of the plant are used as carminative, diuretic tonic and have stomachic.

Lydia and Sundarsanam [11] conducted a study titled as "Phytoconstituent of C*yperus rotundus* l. That is attributed to its medicinal value and antioxidant property". They followed the experimental part as follows. The dried and powdered whole plant parts (which includes roots, rhizomes, flowers and leaves) of *C. rotundus* L. (500g) were incubated in Hexane, (1:3 ratio)for 48 hours in a shaker. The extract was collected. They found the following phytochemicals present in the methanolic extract of C. *rotundus.*

Table 1: Phytochemical Analysis [11]

Carbohydrate test	Present
Tannins test	Strongly present
Saponin test	Strongly present
Flavonoid test	Strongly present
Alkaloid test	Strongly present
Anthocyanin and Betacyanin test	Presence of β cyanins
Quinones	Strongly present
Glycosides test	Absent
Cardiac glycosides test	Absent
Terpenoids test	Strongly present
Triterpenoids	Absent
Phenols	Strongly present
Coumarins	Present
Acids	Absent
Proteins	Present
Steroids and Phytosteroids	Presence of Steroids
Phlobatannins	Absent
Anthraquinones	Absent

Ghannadi *et al* [12] carried out Phytochemical investigations of tuber extracts and evaluation of the hydro-distilled essential oil, obtained from *Cyperus rotundus* L. (Cyperaceae Family) growing wild in Isfahan Province (Iran) were studied. Phytochemical surveys revealed the presence of flavonoids, tannins, alkaloids and essential oils. Chemical composition of dried tubers essential oil was also analyzed by GC/MS. Sixty natural compounds consisting 95.8% of the total components were identified from the essential oil obtained with a yield of 0.2% (w/w). Sesquiterpene compounds have been found to occur in largest amount in the oil. Among the oil constituents, cyperene (16.9%), caryophyllene oxide (8.9%), α-longipinane (8.4%) and β-selinene (6.6%) were the major components. Cyperus eragrostis seed extracts have also demonstrated vasodilatory properties and ability to inhibit the mammalian arginase enzyme in both an ex vivo experiment on rat aortic rings and an in vitro assay with purified bovine liver arginase [13].

Oladipupo A. Lawal and Adebola O. Oyedeji [14] conducted a first time study on the volatile oil of *C. distans* growing wild in KwaZulu-Natal, South Africa. The essential oil composition is given in Table 2, where compounds are listed in order of their elution from the DB-5 column. The oil yield was 0.02% (w/w) based on the fresh weight of the plant. Eight constituents were identified, representing 99.6% of the total oil. It is of interest to note that this oil had a relatively high concentration of sesquiterpene hydrocarbons (51.6%), while the oxygenated sesquiterpene content was 8.6%. Monoterpenes constituted 39.5% of the oil, of which the hydrocarbon fraction was relatively higher (24.9%) than the oxygenated fraction (14.5%). The sesquiterpene composition of the oil was dominated.

Table 2: Chemical composition of the essential oil of Cyperus distans. [14]

Compound	RRI	%
α-Pinene	938	18.8
β-Pinene	975	4.5
Limonene	1028	1.6
1,8-Cineole	1032	14.5
Cyperene	1396	47.6
β-Cadinene	1471	4.0
Caryophyllene oxide	1583	7.3
Humulene epoxide II	1596	1.3
Monoterpene hydrocarbons		24.9
Oxygenated monoterpenes		14.5
Sesquiterpene hydrocarbons		51.6
Oxygenated sesquiterpenes		8.6
Total identified		99.6

***RRI = Retention Relative Indices**

Sudeshna Datta, Tapan Seal, BK Sinha, Soumen Bhattacharjee [15] conducted a study on RP-HPLC based on evidence of rich sources of Phenolics and water-soluble vitamins in an annual sedge *Cyperus compressus.* They evaluated the content of water-soluble vitamins like ascorbic acid (C), thiamine (B1), riboflavin (B2), niacin (B3), pantothenic acid (B5), pyridoxine (B6) and folic acid (B9) by HPLC of *Cyperus compressus*. The in vitro antioxidant activity was carried out in different solvent systems of varying polarity. The 70% ethanol appeared to be the most potent solvent for extraction of antioxidant compounds. The total phenolic and flavonoid content were found 72.544 ± 0.144 mg/g dm and 12.930 ± 0.144 mg/g dm respectively in the plant. Simultaneous HPLC fingerprinting of some standard phenolic acids and flavonoids in the 70 % aqueous ethanol extract was also carried out. B vitamins ranged between 0.028 to 0.431 mg/100g dm. The results confirm that this annual seed is an excellent source of antioxidant- based phyto-nutrients, which could be used for the good of human beings at the same time it can be used as a vitamin supplement to our diet. The study also provides the scientific basis of traditional significance of *Cyperus compressu*s.

V. Essential Oil Composition of Cyperaceae Plants

Abdulkhader Hisham, Koranappallil B Rameshkumar, Neelam Sherwani, Salim Al-Saidi, Salma [16] conducted a study on the essential oil compositions of the rhizomes of Cyperus conglomeratus (Cyperaceae) collected from Oman. The Collected plants were studied by GC, GC-MS and 13C NMR spectroscopy. Twenty-six compounds, representing 84.4% of the oil, were identified in C. conglomeratus, where eugenol (31.3%), alpha-cyperone (10.5%) and cyperotundone (8.4%) were the major compounds. Twelve compounds, constituting 100%, were identified in D. lawii oil, of which benzyl benzoate (58.7%), beta-caryophyllene (23.2%), limonene (4.9%) and alpha-humulene (4.0%) were the major constituents. Thirty-two compounds, comprising 98.0%, were identified in C. zeylanicus oil, of which beta-caryophyllene (21.6%), alpha-pinene (20.4%) and E-beta-ocimene (11.8%) were the major components.

VI. Conclusion

The genus *Cyperus* L. i.e family Cyperaceae comprises about 600 species of annual or perennial plants, mostly aquatic and widely distributed in tropical, subtropical and temperate regions. *Cyperus* species have been found to possess significant pharmacological and biological properties. Some of the phytochemical studies of *Cyperus species* have reported the isolation of flavonoids, tannins, saponins and essential oils. In this report, a comprehensive review on the phytochemical studies and anti-diarrheal research on the Cyperaceae family of plants are given. From this review, it is found that, the *Cyperus species* consists of various significant chemical compounds.

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Analysis of Water Quality (Physico–Chemical) Parameters of Ground Water Samples from Athoor, Dindigul District, Tamilnadu, India

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Abstract — *Water quality alludes to the synthetic, physical and natural attributes of water in light of the guidelines of its utilization. It is most often utilized by reference to a bunch of guidelines against which consistency, by and large accomplished through treatment of the water, can be evaluated. The most well-known principles used to screen and survey water quality convey the soundness of biological systems, wellbeing of human contact, reach out of water contamination and state of drinking water. Water quality fundamentally affects water supply and periodically decides supply choices. Because ofhuge development of populace, industrialization, agrarian exercises and urbanization, huge amounts of sewage and modern wastewater are released into water bodies has essentially added to the contamination of the surface and groundwater. Helpless state of water bodies is the indicator of ecological corruption, it is likewise a danger to the biological system. The target of the current review was to survey the water nature of different groundwater hotspots for the purpose of drinking in Athoor, Dindigul district. The water tests gathered from five inspecting destinations and broke down for 13 physico - compound boundaries according to standard system. This investigation additionally uncovers that the ground water of this region needs a few levels of treatment before utilization and it likewise should be shielded from additional pollution.*

Keywords - *Physico-chemical parameters, EC, TDS, TH, pH*

I. INTRODUCTION

Water quality is estimated by a few variables, for example, the convergence of disintegrated oxygen, microorganisms' levels, how much salt (or saltiness), or how much material suspended in the water (turbidity). In certain waterways, the grouping of tiny green growth and amounts of pesticides, herbicides, weighty metals, and different toxins may likewise be estimated to decide water quality. There are things to forestall debasement to safe-haven waters, for example, supporting and taking part in cutting edge wastewater treatment programs that eliminate undesirable supplements and destructive microbes, utilizing "siphon out" stations for vessel's sterilization gadget, utilizing as quite a large number "green" items as conceivable at home, and diminishing or killing the utilization of manures, herbicides, and pesticides.

Water quality is impacted by a wide scope of regular and human impacts. The most significant of the regular impacts are topographical, hydrological and climatic, since these influence the amount and the nature of water accessible. Their impact is for the most part most prominent when accessible water amounts are low and greatest utilize should be made of the restricted asset; for instance, high saltiness is a successive issue in parched and beach front regions. In the event that the monetary and specialized assets are accessible, seawater or saline groundwater can be desalinated however, as a rule, this is not possible. Consequently, in spite of the fact that water might be accessible in sufficient amounts, inadmissible quality restricts the utilizations that can be made of it. Albeit the regular environment is in concordance with normal water quality, any huge changes to water quality will for the most part be troublesome to the biological system. Significance of hydrochemistry of groundwater has prompted various nitty gritty examinations on groundwater quality crumbling and geochemical advancement of groundwater in many pieces of the globe (Anku et al. 2009; Prasanna et al. 2011; Srinivasamoorthy et al. 2009; Sarala Thambavani 2014, Sarala Thambavani 2015, Uma Mageswari et al. 2019).

II. MATERIALS AND METHOD

A. Study Area and Sample Collection

Athoor taluk is situated a way off of 15 km from Dindigul. Athoor is a town in the Dindigul locale of Tamilnadu among Dindigul and Bathalagundua around 3 km west of Sempatti. It is one of the authoritative congregations of Tamil Nadu. Rice development is the significant occupation. The Kamaraj Reservoir in Athoor is the fundamental wellspring of drinking water for individuals of Dindigul. The scope for Athoor, Tamil Nadu 624701, India is: 10.288646 and the longitude is: 77. 853165. As per Census 2011 data the area code or town code of Athoor town is 635424. The complete geological area of the town is 1399.73 hectares. Athoor has a complete populace of 6,279 people. There are around 1,669 houses in Athoor town. The guide of the review region as displayed in Fig.1. The groundwater tests gathered from various examining locales (Table 1) and investigated according to the standard system portrayed by Trivedy and Goel (1984) as displayed in Table 2.

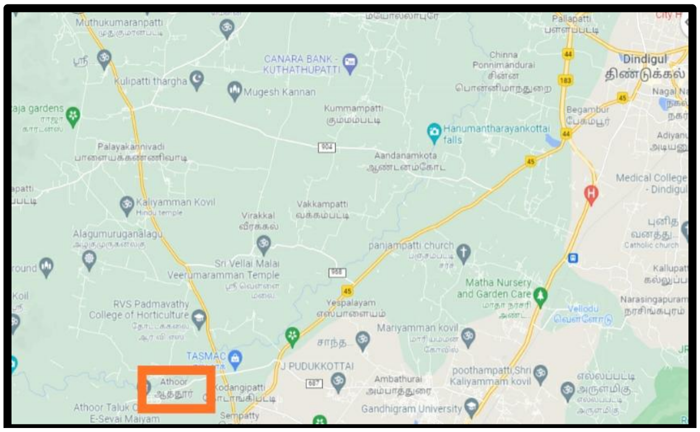

Fig.1 Map of the Study Area

TABLE 1. SAMPLING SITES OF THE STUDY AREA

S. No	Sample No	Sample Sites
1	S1	Kadai Veethi
2	S2	Alampatty
3	S3	Malaipatty
4	S4	Chettiyar Street
5	S5	South Street

TABLE 2. METHOD OF ANALYSIS OF VARIOUS PHYSICO-CHEMICAL PARAMETERS

Parameters	Descriptions	Instruments or Methods
Temperature	Temperature exerts a major influence on the biological activities and growth.	Thermometer
Turbidity	Turbidity in water is the reduction of transparency.	Turbidity meter
Electrical Conductivity	Measurement of electrical conductivity of water	Digital conductivity meter
TDS	The number of particulate solids that are in the water	TDS meter
Total Hardness	Measurement of calcium and magnesium in water.	Titrimetric method
pH	The major of acidity in the water.	pH meter
Calcium	Measurement of Calcium amount in water	Titrimetric method
Magnesium	Measurement of Magnesium amount in water	Titrimetric method

Sodium	Measurement of sodium amount in water	Flame photometric method
Potassium	Measurement of Potassium amount in water	Flame photometric method
Chloride	Measurement of Chloride amount in water	Titration method
Sulphate	Measurement of Sulphate in water	Spectrophotometric method
Phosphate	Measurement of Phosphate amount in water	Spectrophotometric method
Fluoride	Measurement of Fluoride amount in water	Spectrophotometric method

III. RESULTS AND DISCUSSION

B. Temperature

Water temperature is basic since it is a significant quality in natural boundaries. It is essential to quantify water temperature. An ascent in temperature of the water prompts the accelerating of the compound responses in water, diminishes the dissolvability of gases and intensifies the taste and smell. In our current examination ground water temperature shifted somewhere in the range of 24^0C and 29^0C, which falls inside as far as possible.

C. Turbidity

Turbidity is brought about by particles suspended or disintegrated in water that disperse light causing the water to seem shady or dim. Particulate matter can incorporate residue - particularly earth and sediment, fine natural and inorganic matter, dissolvable shaded natural mixtures, green growth, and other minute life forms. The nephelometric technique analyzes how light is dissipated in a water test against how much light dispersed in a reference arrangement. 40% of the examples in the review region, for example, S2 and S4 surpassing the beneficial furthest reaches of 5NTU endorsed by BIS. Sarala etal (2013) detailed that high turbidity was because of the release of waste and algal development.

D. Electrical Conductivity (EC)

Electrical conductivity is the limit of electrical momentum that goes through the water. It is straightforwardly connected with grouping of ionized substances in water and may likewise be connected with issues of inordinate hardness. Salts or different synthetics that disintegrate in water can separate into decidedly and contrarily charged particles. These free particles in the water lead power, so the water electrical conductivity relies upon the centralization of particles. As per BIS (1999) the advantageous furthest reaches of Conductivity is 300 µS/cm. The examining locales, for example, S2, S3 and S4 surpassing as far as possible. It could be because of the long home time and factors of lithology of water bodies.

E. Total Dissolved Solids (TDS)

Total dissolved solids (TDS) are a proportion of the disintegrated consolidated substance of all inorganic and natural substances present in a fluid in sub-atomic, ionized, or miniature granular suspended structure. TDS fixations are frequently revealed in parts per million (ppm). Water TDS fixations can be resolved utilizing an advanced meter. As far as possible for TDS for drinking water is 500 mg/L. The scope of TDS levels in the review region is 445-562 mg/L. High convergences of TDS in groundwater influence people who are experiencing kidney and heart illnesses. (Umamageswari etal, 2019).

F. Total Hardness (TH)

Total hardness is an estimation of the mineral substance in a water test that is irreversible by bubbling. All the more explicitly, all out not entirely settled by the convergence of multivalent cations in water. These cations have a positive charge that is greater than 1+. Regularly, cations have a charge of 2+. The most widely recognized cations present in hard water are Mg2+ and Ca+. Hard water is not truly unsafe to human wellbeing. Nonetheless, water with a significant degree of hardness could lead to major issues in modern settings, where water hardness is commonly observed to forestall exorbitant disappointments in parts like cooling pinnacles, boilers and other gear that contain or handle water. Total hardness is because of the presence of bicarbonates, sulfates and chlorides of calcium and magnesium. As far as possible is 300 mg/L, and the greatest allowable breaking point for drinking water is 600 mg/L according to Indian norms. The samples such as S2, S3 and S4 are exceeds the desirable limit as mentioned in the Table 3. Hujare (2008) reported total hardness was high during summer than rainy and winter season.

G. pH

pH is a proportion of acidic/essential water. The reach goes from 0 to 14, with 7 being unbiased. pHs of under 7 demonstrate corrosiveness, while a pH of more noteworthy than 7 shows a base. The pH of water is a crucial assessment concerning water quality. pH is one of the main factors that fill in as a list of contamination. In the current examination pH values for all the five inspecting locales were found inside the scope of BIS (6.5-8.5) principles.

H. Calcium and Magnesium

Higher concentration of calcium and magnesium in the sampling sites S2, S3 and S4 also reflected the concentration of total hardness in the same sampling sites.

I. Sodium and Potassium

Sodium content adversely affects the soil nutrients up taking capacity. Water containing in excess of 200 mg/L sodium ought not be utilized for drinking. In our present study except S1 and S5, all other sampling sites S2, S3, and S4 were found to be more than 200 mg/L. According to BIS the prescribed limit of potassium is 200 mg/L. The values of potassium for all sampling sites were found to be within the limits of BIS standard.

J. Chloride

The greatest source of chloride in fresh water is disposal of sewage and industrial wastes. Chloride concentration was observed as high for all sampling sites except S1. Sarala Thambavani *et al* 2014 reported that soil porosity and permeability have a key role in increasing the concentration of chloride.

K. Sulphate

The sulphate concentration in the study area varied between 66 and 112 mg/L due to the discharge of effluent and fertilizers. Elevated level of sulfate causes gastrointestinal irritation when magnesium and sodium are present.

L. Phosphate

The presence of phosphates in groundwater may be attributed to natural minerals or through contamination by use of compost, sewage and modern waste (Alemu et al. 2015). The concentration of phosphate for the collected sampling sites is in the range of 0.07–1.2 mg/L which falls within the prescribed limit of BIS standards.

M. Fluoride

Low concentration of fluoride below 0.5 mg/L causes dental caries and higher concentration beyond 1.5 mg/L causes dental and skeletal fluorosis. The convergence of fluoride at all the examining locales saw inside as far as possible. The results of analyzed physico - chemical parameters were depicted in Table 3.

TABLE 3. ANALYTICAL VALUES OF PHYSICO-CHEMICAL PARAMETERS OF SAMPLES

Physicochemical Parameters	BIS (1999)	Sample (S1)	Sample (S2)	Sample (S3)	Sample (S4)	Sample (S5)	% Of sample	
							Within the Desirable limit	Exceeding the Desirable limit
Temperature	±40°C	26	24	29	28	27	100	-
Turbidity	5 NTU	5	5.4	4.8	5.35	4.95	60	40
Electrical Conductivity	300µs/cm	292	324	346	337	292	40	60
TDS	500mg/l	487	521	545	563	435	40	60
Total Hardness	300mg/l	294	345	327	351	299	40	60
pH	6.8 – 7.5	5.7	6.3	6.2	7.1	5.7	100	-
Calcium	<75mg/l	52	84	78	81	49	40	60
Magnesium	<30mg/l	24	34	37	42	29	40	60
Sodium	200mg/l	124	208	264	279	168	40	60
Potassium	200mg/l	192	176	174	116	186	100	-
Chloride	<250mg/l	244	251	264	257	265	20	80
Sulphate	<200mg/l	72	111	105	94	68	100	-
Phosphate	5mg/l	0.08	0.07	1.04	1.15	1.24	100	-
Fluoride	1-1.5mg/l	0.04	0.05	0.07	0.08	0.04	100	-

IV. CONCLUSION

The most major human necessities of water are for drinking, cooking, washing and individual cleanliness. To address these issues, the nature of the water utilized should fix no gamble to human wellbeing. The nature of the water in nature likewise affects the state of biological systems that all living life forms rely upon. Simultaneously, people use water bodies as helpful sinks for the removal of homegrown, modern and horticultural squanders. Clashes among different clients of water are progressively over issues including water quality along with water amount. Regular water bodies can serve many utilizations, including the vehicle and absorption of waterborne squanders. In any case, as normal water bodies absorb these squanders, their quality changes especially. Assuming the quality drops to the degree that other advantageous uses are unfavorably impacted, the assimilative limits of those water bodies have been surpassed concerning those impacted employments. Water quality administration measures are activities taken to guarantee that the all-out toxin loads released into getting water bodies don't surpass the capacity of those water bodies to acclimatize those heaps while keeping up with the degrees of value determined by quality guidelines. Water assets the executives include the checking and the board of water quality as much as the observing and the board of water amount. The groundwater is the main wellspring of water supply for drinking, water system and modern purposes. The water quality at all the inspecting locales obviously showed that the situation with the water body was debased and inadmissible for drinking reasons. It has been inferred that releasing of homegrown and other anthropogenic exercises was the fundamental variables for sullying the review region. In this way, consequently we must improve the nature of groundwater and limit the tainting of ground water by legitimate release of modern as well as homegrown wastages and outlets.

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Sea contamination and warming seas: toward sea arrangements and normal marine bioremediation

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Abstract - *Marine ecosystems are aquatic environments with high levels of dissolved salt. These include the open ocean, the deep-sea ocean, and coastal marine ecosystems, each of which have different physical and biological characteristics.The worldwide sea is in danger, so is the marine biodiversity occupying this interesting domain. Since the beginning of the anthropocene, a heap of anthropogenic effects have been attacking the natural nature of the seas and the wealth of marine living assets. While in excess of 10,000 synthetics, a large number of which are polluting the seas, are exchanged the world, the sped up pace of a dangerous atmospheric deviation has surpassed pre industrial levels by 1°C because of total CO2 discharges, causing sea warming and fermentation. Unavoidable contamination by plastic (e.g., microplastics) is currently constant and broadly spread, influencing numerous species in the sea. The environmental impression of these stressors is uncovered in the communication of sea contamination and environmental change, modifying the biogeochemical processes supporting marine biological systems and pushing marine biodiversity to tipping focuses; be that as it may, the sea is the best natural partner for people to defy and alleviate these effects. While the seas and blue carbon environments fill in as sinks to catch and store* CO_2*, normal marine bioremediation with the related depuration framework performed by marine species can assist with neutralizing compound contamination to reestablish marine and beach front biological systems.*

Key words *: Environment, Marine diversity, contamination, bioremediators*

I. INTRODUCTION

Marine contamination and anthropogenic environmental change have been affecting and reshaping the science of the worldwide sea at various scales since the beginning of the anthropocene, that is to say, the age arising around the last part of the 1700s and mid 1800s when people and social orders turned into a worldwide topographical and biological driving constraining. Expanding human populations and our related requests for food, industrialization, and worldwide vehicles with attendant discharges of compound foreign substances are fundamentally influencing the powers of nature. Worldwide temperatures keep on expanding, as of now at 1^0C comparative with pre industrial levels because of expanding CO2 discharges. Since the last century, heritage and rising toxins are neutralizing the strength of the worldwide sea and the endurance of marine species. Besides, the bioaccumulation and impacts of environmental anthropogenic toxins in blend with environmental change are being intensified and exacerbated in marine food networks and biological systems [1].

A. Sea contamination

Sea contamination by substance toxins has arisen since the 1500s (sixteenth century) dueto arrivals of anthropogenic mercury from mining, and constant natural contaminations (POPs) and anthropogenic radionuclides before the mid-1900s (e.g., B193045). Albeit a few POPs, including polychlorinated biphenyls (PCBs) and dichloro-diphenyl-trichloroethane (DDTs), were restricted in created and industrialized nations during the 1970s, some organochlorine pesticides (OCPs) are as yet utilized in emerging nations to control jungle fever vectors and yield bothers (i.e., DDT) and later arising POPs, including polybrominated diphenyl ethers (PBDE) fire retardants and perfluorinated synthetics, are sullying food networks. However our blue planet is as yet defiled with the tradition of that time of uncontrolled and abused farming pesticides and modern synthetic substances. Inheritance and arising toxins, including POPs, current-use pesticides, weighty metals, marine garbage and microplastics, individual consideration items and drugs (PCPPs), polycyclic sweet-smelling hydrocarbons (PAHs), and radionuclides, are universal in the worldwide sea. For instance, the bio accumulative and harmful nature of POPs and natural mercury is a specific stressor influencing organic entities at the highest point of marine food networks (i.e., seabirds, marine vertebrates, enormous pelagic fish, and people) due to the intrinsic poisonousness furthermore, wellbeing impacts of these synthetic substances [2].

Marine contamination and warming seas are among the major anthropogenic factors influencing marine biodiversity and fisheries in the worldwide sea, setting off the challenge to seek after new arrangement of situated research for ecotoxicologists, sea life researcher, oceanographers, sea engineers, and ecological researchers. Subsequently, ecotoxicological exploration and science-based data are pivotal to help the gamble evaluation and the board of anthropogenic poisons notwithstanding worldwide ecological change. The interaction of environmental change (i.e., sea warming and sea fermentation) and marine contamination with related impacts on marine organic entities and food networks addresses a new approaching danger to be evaluated and tended to as of now. This part offers an examination of the heaviness of proof of marine contamination and environmental change associations and the inquiry for sea contamination arrangements zeroing in on regular marine bioremediation to hamper the openness to, bioaccumulation of, and chance of poisons to marine fauna, shellfishes, andpeople in our evolving seas [3].

B. Sea contaminations and environmental change

The creation, use, emanations, and removal of 100,000 synthetic substances have direct ramifications for the soundness of the world's seas. The worldwide sea is the extreme "sink" for anthropogenic poisons and a repository taking-up around 28% of the climatic CO_2 outflows, causing sea fermentation. The communication of environmental change and sea contamination is promptly influencing and projected to affect the science and nature of our seas, compromising the endurance of numerous marine species, fisheries, and prosperity for people. The collaboration of environmental change-hotter temperatures, sea fermentation and contaminations is additionally anticipated to expand the degree of openness and poisonous impacts of numerous natural toxins because of changes in the examples, transport, also, destiny of synthetic compounds, as displayed. Of specific consideration are the combined impacts of these anthropogenic stressors in marine environments and food networks since environmental change can influence toxin bioaccumulation by intensifying POPs (i.e., PCBs) and methylmercury (CH3Hg) in marine food networks [4], as represented. This cooperation may then influence the practicality of waterfront assets, vocation and culture, and food security. The effects might be especially high for weak networks, for example, seaside native individuals who depend intensely on living marine assets as a wellspring of conventional food and culture [4].

C. Polychlorinated biphenyls (PCBs)

Thinking about marine warm blooded animals as sentinels of sea contamination (i.e., canaries in the coal mine), various toxicological impacts have been ascribed to PCBs in this utilitarian gathering of species. The heaviness of proof in light of field and semi captive examinations, lab examination, and demonstrating work features the wellbeing impacts of PCBs at the hereditary, cell, living being, and populace levels, including immunotoxicity, multiplication debilitations, and endocrine disturbance harmful impacts. As of now, late model projections by Desforges for instance, demonstrate that PCB-interceded consequences for propagation and invulnerable capacity might compromise the drawn out reasonability and lead to the breakdown of half of the executioner whale (*Orcinus orca*) populaces inside the following 3050 years at the worldwide level. The effect of environmental change on PCB bioaccumulation in executioner whales and their fundamental prey may additionally fuel the PCB wellbeing poisonous impacts in imperiled populaces [5].

Roundabout impacts in life forms and food networks by POPs are the most uncomprehended impacts from both field and observational exploration studies and displaying work. Both immunotoxicity and endocrine interruption impacts by POPs are probably going to be the most malicious debilitations in creatures with likely circuitous outcomes at the populace level. A split the difference resistant and endocrine framework influences the capacity of creatures to battle infection and to effectively replicate, which is particularly applicable during times of healthful pressure and different kinds of stressors affected by environmental change and in profoundly factor conditions (e.g., El Nin˜o occasions or ENSOs) when mass mortality happens and populaces regularly approach the basic tipping point of elimination. Openness to immunotoxic toxins might have huge populace level outcomes as a contributing variable to expanding anthropogenic pressure in natural life and working with the rise of irresistible sickness episodes. Potential feminization causing profoundly slanted sex proportions (i.e.females versus,guys) by estrogenic synthetics, for example, DDTs [6] can have suggestions at the populace level, predominantly in little populaces of undermined and imperiled species confronting bottleneck or Allee impact processes inside their populace elements.

D. Methyl mercury

Extra worldwide contaminations affecting the sea climate in close mix with sea warming and fermentation are metals, including mercury and its methylated structure, methylmercury (i.e., CH3Hg), as displayed. Anthropogenic wellsprings of metals incorporate mines, metal processing plants/smelters, petroleum product burning, squander cremation, pesticides and wood additives, and delivery from homegrown and modern waste. While environmental change can change the normal pattern of different metals like zinc (Zn) and cadmium (Cd) modifying openness and aversion to these metals in Arctic biota, the Arctic is probably going to turn into a more compelling snare for these metals since precipitation is thought to increment in this polar locale [7]. Methylmercury is exceptionally neurotoxic and bioaccumulates all through the food web primarily by means of dietary take-up, coming to the most noteworthy fixations in fish and creatures at the highest point of the food web notwithstanding, inside the environmental change setting and given the worldwide course and intricacy of mercury cycling in the sea, this is a metal of dire worry that warrants unique consideration in various seas bowls.

An expansion in openness to mercury focuses in biota, including dominant hunters due to contrasts in taking care of inclinations has been related with changes in essential creation also, species arrangement of amphibian networks in Arctic sans ice waters all through both base up and hierarchical cycles. Changing seas and contracting of polar ice (i.e., Arctic and Antarctic) is influencing natural surroundings and food networks with significant outcomes of mercury openness to essential makers and top hunters. For example, mercury openness and biomagnification has been connected to natural surroundings determination, diet pliancy, and taking care of conduct of beluga whales. These climatic-prompted changes in conduct can influence the aggregation of mercury in a few other top hunters of the Arctic, for example, seals, polar bears, and executioner whales, and Inuit individuals. For example, the ramifications of a changing Arctic environment on mercury destiny in beluga food networks and the ramifications for the wellbeing of beluga whales stay squeezing research needs. Expanding chance of mercury harmfulness because of bioaccumulation exacerbated by environmental change has been anticipated for the food web and fisheries of the Faroe Islands, where fishing networks depend emphatically on Atlantic cod (Gadusmorhua) and pilot whales (Globicephalamelas) [8]. The effect of expanding sea surface temperature and fermentation on mercury and methylmercury bioavailability and bioaccumulation in food networks is a continuous exploration front raising red banners. Diverging from our present comprehension on environmental change communications with POPs and mercury in marine environment and food networks, questions remain concerning the effect of expanding ocean surface temperature and sea fermentation on the bioavailability and food web bioaccumulation of microplastics, PCPPs, PAHs, antifouling paints, and radionuclides.

E. Plastic contamination

The seas and marine life overall are extraordinarily affected and undermined by marine trash, especially enormous plastics and microplastics. All seas are contaminated by marine flotsam and jetsam, from which around 73% is plastic, and in excess of 1300 species are impacted through snare and ingestion [9]. The volume of plastic that entered the seas in 2010 from 192 seaside nations (93% of the worldwide populace) went from 4.8 to 12.7 million metric tons [10]. Notwithstanding pernicious snares and ingestion, marine flotsam and jetsam and plastics fill in as vectors for natural poisons [e.g., PAHs, phthalates, furthermore, nonylphenols, as well as POPs like PCBs and dichlorodiphenyldichloroethylene (DDE), which is a result of DDT and obtrusive species, and filter poisonous synthetic substances A new report assessed that at least 5.25 trillion particles gauging 268,940 tons are drifting on the planet's sea.,which are characterized as particles ,5 mm and can be purposely made (plastic pitch pellets and powder) or produced as breakdown side-effects of bigger trash and macroplastic (e.g., clothing, ropes, sacks, bottles). Both the beginning and last destiny of most plastics is gotten from land-based sources, including family and modern water, hydroponics, delivery, and the travel industry. Microplastics can likewise carry on their surfaces epiplastic networks, including pathogenic microscopic organisms like Vibrio, Aeromonas, Enterobacter, Halomonas, Mycobacterium, Photobacterium, Pseudomonas, Rhodococcus, and Shigella [11]. Taking into account the sped up pace of inescapable sea contamination by plastics and microplastics, coordinated administration activities and proactive arrangements are expected to hamper and take out plastics contamination.

Macroplastics and microplastics contamination are perplexing and involve a few fronts of arrangement situated activities to battle the existence pattern of plastics and reestablishing marine furthermore, seaside conditions from the neighborhood level to worldwide sea administration To diminish the worldwide natural impression by plastic contamination, logical aptitude, local area investment, and market-based procedures are required. While there are effective guidelines to restrict microbeads from the seas, more undertakings to encourage arrangements to get rid of the creation and modify the market of plastics and microplastics are required. A key strategy is to look for escape clauses in the horrible financial pattern of plastics to decrease also, turn away the utilization and creation of plastic, as people and related plastic requests are the reasons for plastic creation and contamination. Despite the fact that reusing is as yet a essential thought and work to limit plastic contamination, this squander the executives methodology isn't adequate as just 5% of plastic pressing material is held toward the finish of the reusing process for resulting use, that is to say, 95% of plastic bundling material worth is lost to the economy following a short first use or one use cycle [12]. The arrangement of plastic waste as "dangerous" was proposed as a strategy approach for nations to making due plastic flotsam and jetsam and to move to a shut circle arrangement of plastic use and reuse (i.e., all plastics are reused and reused) with the mean to reestablish impacted environments and forestall morehazardous trash from gathering in the marine climate.

F. Sea arrangements and regular marine bioremediation

Marine environments, bioremediation can be an effective and attractive biotechnology to decrease the level of pollution. Bioremediation is a waste management technique that involves treatment using naturally occurring organisms to break down hazardous substances into less toxic or nontoxic substances.The Microorganisms transform organic contaminants in oceans, soils, groundwater, sludge and solids, into an energy source.In bioremediation, microorganisms with biological activity, including algae, bacteria, fungi, and yeast, can be used in their naturally occurring forms.Some examples of bioremediation related technologies are phytoremediation, bioventing, bioattenuation, biosparging, composting (biopiles and windrows), and landfarming. Other remediation techniques include, thermal desorption, vitrification, air stripping, bioleaching, rhizofiltration, and soil washing.A good example of bioremediation of marine ecosystem is the natural cleanup of oil spills. In many cases the oil is cleaned up over time by the natural processes taking place in marine ecosystems. In case of larger oil spills, human intervention and knowledge about the processes that make natural oil processing possible is necessary. In this case residual oil can be further broken down by an artificial method called biostimulation.

G. Biostimulation

Biostimulation refers to the addition of specific nutrients, air, organic substrates or other electron donors/acceptors, nutrients, and other compounds that affect and normally limit treatment in their absence. This way the microorganisms will clean the waste source more efficiently and faster than in normal circumstances

Biostimulation is a good technique when all the bacteria needed for the cleaning of a certain waste type naturally occur in the treated environment. Examples of biostimulation are grease accumulation in sewers and grease traps. Grease is a biodegradable substance that can be found in the environment, sewers house a large bacteria population. The substances needed for an efficient cleanup are present: nitrogen and phosphor. In other words, the grease present in sewers should disappear naturally. Paradoxically, grease accumulates in the sewer system. With this in mind, biostimulation won’t work when you want to clean the sewer system. The solution for this problem is bioaugmentation.

H. Bioaugmentation

Bioaugmentation is a treatment where you want to achieve a controlled, predictable and programmed biodegradation. In other words bioaugmentation is the controlled addition of specially formulated microbial cultures that assist those found naturally in the soil. It is done in conjunction and monitoring of an ideal growth environment in which these selected bacteria can live and work.

Ecotoxicological risk evaluations, ecological observing and logical information give leaders in public states with essential synthetic, physical, and toxicological data on the side of public guidelines to carry out order and control and traditional decrease strategies to address water contamination like wastewater treatment plants - WWTP(e.g., tertiary wastewater treatment plants) and remediation draws near for natural toxin and metal-defiled silt (i.e., dregs covering, dry unearthing, digging and sea removal, geotextiles mats, human-made bioremediation, also, bioaugmentation innovations) to recuperate and remediate marine conditions from substance tainting. Similarly, a doable and traditional case to diminish both anthropogenic synthetic substances (e.g., mercury) and ozone depleting substances is the mechanical Sea contamination and warming seas 501 decrease of environmental outflows from non-renewable energy source/coal ignition and electric power creating businesses. While reduction is a receptive measure (i.e., order and control way to deal with) balance discharges "toward the finish of the line" before substance discharges, more proactive and prudent activities are completely expected to target decrease objectives of compound outflows. For the instance of POPs and mercury, cutting and forestalling outflows locally and/ or on the other hand provincially has clearly differing levels of adequacy for nearby fixations, contingent upon the circumstance, when contrasted with the worldwide endeavors by countries to encourage what's more, set up global instruments (i.e., Stockholm Convention on POPs and Minamata Convention on Mercury, individually) to abridge discharges at the worldwide level.

I. Climate change sea arrangements

An exceptional arrangement of sea arrangements and activities to moderate and adjust to the effect of environmental change on the marine biological system and the acknowledgment of the vulnerabilities and limits of at present accessible environment and sea the executives choices have been surveyed as of late. An amazing illustration of these sea arrangements is the normal take-up of CO_2 discharges (i.e., blue carbon: carbon put away in waterfront or marine biological systems) performed by marine vegetation and beach front arrangement networks, for example, mangrove woodlands, seagrass beds, and salt bogs [91,9396]. In spite of marine vegetation territories covering,2% of the beach front sea, these territories have entombment rates multiple times higher than tropical rainforests and record for over half of the carbon covered in marine residue. Especially mangrove woods biological systems have been distinguished as productive regular carbon sinks be that as it may, mangroves can convey back put away carbon by means of methane (CH_4) outflows, to some degree counterbalancing blue carbon entombment.

J. Marine bioremediation

Differentiating the significant number of human-moved activities and choices for arrangements to conquer marine contamination and the effect of environmental change in the seas, very little exertion and an absence of arrangements situated research exist to settle marine contamination and decrease foreign substances by promoting the utilization of normal bioremediation performed by the inherent environmental administrations of marine biological systems and the particular working job of marine species, or at least, regular phytoremediation and zooremediation.

While the seas offer natural and actual types of assistance for the planetary framework, counting nourishment for marine life and individuals, assimilation of hotness and energy from the environment framework and barometrical warming, take-up of anthropogenic CO_2 from the environment, and the capacity and worldwide circulation of abundance water from dissolving ice pack what's more, ice sheets, the seas likewise harbor huge number of species with a huge hereditary variety pool that can serve not just for supporting the capacity of marine environments, for food and for medication and biomedical exploration purposes, however to normally bioremediate and environmentally reestablish marine biological systems and waterfront regions from contamination. Also, among the marine estuarine microbial world, there are microorganisms that could assume a part in the destiny of plastics, including plastic-deteriorating and biodegrading microorganisms (e.g., Pseudomonas spp.), hydrocarbon-debasing microbes (hydrocarbonoclastic microorganisms), and growths. The dependence on the marine and estuarine microbiome to characteristically biodegrade pollutants is promising and endeavors can be contributed to monitor what's more, advance the normal utilization of these microorganisms.

Notwithstanding their capacity as a plausible environmental change variation measure for fish security and to conquer ocean level ascent, these customary bivalve frameworks can likewise possibly fill in as regular "self-filtration treatment and bioreactor frameworks" that can be proactively oversaw by seaside networks to sift through contaminations and remediate beach front conditions in distant regions. Subsequently the normal improvement of bivalve biotreatment frameworks and old shellfish gardens as biological administrations presented by bivalves (e.g., mussel and shellfish reefs) ought to be additionally encouraged and applied as solid methodologies for marine zooremediation.

At last, the job of top hunters like marine well evolved creatures, including enormous whales (i.e., sperm whales, *Physetermacrocephalus*; and blue whales, *Balaenopteramusculus*) in the sea is of vital significance to control and assist with moderating environmental change by taking up CO_2 through iron preparation set free from whale feces (e.g., the sperm whale populaces in the Southern Ocean alone go about as a carbon sink by eliminating 23105 tons of carbon from the climate), driving the sea natural siphon and usefulness. Additionally, a few different types of baleen whales, toothed cetaceans, and seals play out a significant errand by adding to the nitrogen reusing in waterfront waters and improving essential creation. Seabirds are additionally basic for improving coral reef efficiency and working, featuring the requirement for reestablishing seabird-inferred supplement appropriations from huge areas of sea.

Comprehensive and coordinated ecological administration approaches working together with regular bioremediation in the seas ought to secure and upgrade not just low trophic level marine biota and people, yet in addition upper trophic level marine fauna, particularly dominant hunters as signs of sea wellbeing. This is of basic significance for top hunters previously confronting what's more, attempting to adjust to environmental change as they assume a critical part to control hierarchical cycles over food networks, and safeguard and keep up with carbon stocks and sinks in blue carbon environments.

K. Conversation

Since fisheries, marine untamed life, and biological systems give life support, food, natural administrations and capacities as well as financial open doors through collecting, marine fisheries gets, and ecotourism in many created and non-industrial nations, the wellbeing of the sea can't be seen independently from human wellbeing. Waterfront waters that are debased with diligent synthetics and exacerbated by environmental change effects can lead to human sickness and unfavorable wellbeing, diminished fisheries quality and amount, and effects on the wellbeing of marine untamed life. This has clear friendly and financial outcomes.

Risk the board and correspondence processes that balance the dangers and advantages of an eating regimen of conventional food have been fruitful through input from an assorted gathering of local specialists and networks expecting to join numerous sociocultural and monetary variables to show up at a gamble the executive’s choice that will be the most advantageous. Coastalmarine conditions and networks encouraging upgrade of regular bioremediation, moderation, and transformation procedures as proactive answers for face environment change and safeguard from synthetic poisons can accommodate an overflow of clean fisheries items and solid marine fauna for the travel industry, fundamental starting points for the prosperity of marine biodiversity, human occupants, and the ecotourism area. An equilibrium needs to be struck between general wellbeing and environment wellbeing gambles versus the utilization and arrival of substance toxins possibly exacerbated by environmental change. While the toxicological worldview 'the portion makes the toxin' gives a hypothetical establishment to a methodology that limits environmental harm by synthetics while upgrading human medical advantages (e.g., DDT use to control the Malaria mosquito, Anopheles, in non-industrial nations), the obsolete contamination rule 'the answer for contamination is weakening' has shown to be mistaken since the 1950s, in view of the diligent, bioaccumulative and harmful nature of numerous poisons (e.g., PCBs, dioxins, DDTs, OCPs, CH3Hg) released into the seas. [13]

Moreover, environmental change strategy and global administrative instruments ought to be pointed at limiting and adjusting the financial and natural difficulties by taking a gander at the versatility and inborn remediation limit of regular marine biological systems even with sea warming and fermentation in the seas. All the while, government plans carrying out efficient power energy choices, carbon expenses and market-based instruments to progressively eliminate contamination, and restricting substance discharges from coal-terminated power age furthermore, oil ventures, would assist with decreasing the adverse consequences by both anthropogenic stressors.

At long last, when environmental change arrangements and contamination the board activities are not adequate to defeat effects and arrive at decrease focuses in a sensible time, social preparation is a significant partner to connect with and propel the general population and partners to execute environment also, contamination arrangements through friendly learning, social change, and local area based protection activities.

II. CONCLUSION

The evaluation of disposal and management options needs to be based on the fullest practical consideration of the relevant risk factors as well as on technological feasibility and economic viability.

Similar inattention to risk is evident in the permitting processes for sediment disposal. Currently, different types of permits must be secured for the placement of sediments in navigation channels or ocean waters as part of the construction of land or containment facilities (under the RHA), the dumping of sediment in the ocean (under the MPRSA), sediment disposal in inland waters or wetlands (under CWA), and the containment of contaminated sediments on land (under the RCRA). The regulations also distinguish between sediments removed during navigation dredging (CWA or MPRSA) and sediments excavated for environmental remediation (Superfund). In other words, the regulatory framework does not differentiate between the placement of contaminated sediments in an ecologically sensitive and commercially valuable shellfish bed and the deposition of contaminated sediments within the confining walls of an offshore containment dike or in the depths of an anoxic, deep ocean pit.

The committee can see little technical justification for the inconsistent regulation of contaminated sediments, given that neither the location of an aquatic disposal site (freshwater versus saltwater) nor the reason for the dredging (navigation versus environmental remediation) necessarily affects the risks posed by the in-place contamination. In the committee's view, the regulatory regime payslittle or no attention to the question of risk, focusing instead on the types of activities to be carried out—removal, placement, or treatment. The problem has been eased in some cases by objectives-based interpretation of regulations, as demonstrated by the carefully considered solution in the Port of Tacoma case history.

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Adsorptive Removal of Crystal Violet and Methyl Orange Dye Banyan Leaf (*Ficus Citrifolia*) Derived Carbon

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Abstract — *As a sequel to the removal of waste using wastes based technologies we present here our results of the study utilizing banyan leaf, an agricultural waste, as an interesting carbon precursor for Crystal Violet (CV) and Methyl Orange (MO) dye removal. Waste banyan leaf is activated to form an activated carbon and it is tested for its efficiency by the adsorption studies. Dye solution of CV was prepared and tested for its removal efficiency with this activated carbon. The Batch mode of experiments has been carried out for adsorption studies of the Ficus citrifolia (Banyan) Leaf Carbon (FLC). Effect of parameters like pH, adsorbent dose, contact time, temperature and initial metal ion concentration were also determined. The optimum conditions obtained were 60 min contact time, 1.0g adsorbent dose, 40 ^{0}C, 100mg/L CV and pH 12 for CV/MO removal. The results revealed that CV & MO is considerably adsorbed on banyan leaf derived carbon and it could be an economic method for the removal of MB and MG from aqueous solutions. Moreover this study gives a value added utilization of biomass to remove CV and MO from waste water. The results revealed that FLC adsorbent is potentially low cost adsorbent for the removal of dyes.*

Keywords — *Adsorption, Bioadsorbent, Biomass Carbon, crystal violet dye, methyl orange dye, banyan Leaf*

I. INTRODUCTION

One of the environmental issues worldwide is the contamination of water resources by industrial effluents. Among various industries, the textile industry waste water is considered to be an intensive water consuming area of activity besides utilizing a wide variety of chemicals and dyes. The effluent discharged from the textile industries leads to grave concern for the environment and health if it is to be mixed with sewage systems or neighboring water-receiving bodies. Effluent is a complex solution of chemicals having intense color value besides salt in terms of high TDS. Although the textile dyes contribute only a small portion of the total volume of discharged wastewater after the dyeing process, they are deeply coloured [1]. Color removal is generally considered more important than the removal of the soluble colorless chemical contaminants since it is an aesthetic problem and also detrimental to microbial life. The coloured wastewater interferes with the photosynthetic activity of plants impeding solar radiation penetration and thereby affects the ecosystem. Conventional wastewater treatment processes do not remove the dyes and colors as they are fairly stable to light, heat and resist biodegradation because of their complex molecular structures.

In recent years a number of processes such as physical, chemical and biological (e.g., Adsorption, coagulation/flocculation, biodegradation, ion-exchange, chemical oxidation, ozonation, reverse osmosis, membrane filtration and electrochemical methods) have been subjected to remove dye molecules from effluents [2,3]. However, it is evident from the literature that the ambiguity of applicability and shake the flask status of biological processes, limits of chemical coagulation / flocculation to produce good quality effluent besides sludge handling problems. Moreover, economical non-feasibility and possible detrimental effects of chemical oxidation along with technical and economic constraints of reverse osmosis due to the short membrane life make adsorption a more attractive alternative method for the wastewater treatment. Adsorption using activated carbon has been conventionally practiced for the treatment of coloured wastewaters. However, the prohibitive cost of activated carbon has restricted its use and hence it is desired to replace it by low cost effective and easily available alternatives.

Activated carbon in granular and powdered form is the most widely used material as an adsorbent. However, it has the disadvantage of being quite expensive depending on the quality. Both chemical and thermal regeneration of spent carbon is expensive, impractical on a large-scale and produces additional effluent and results in considerable loss of the adsorbent. This has led many workers to search for the use of cheap and efficient alternative materials [4].

Performance of non-conventional adsorbents for wastewater treatment has been used by various workers as has been referred to [5]. Chemically treated *Psidium guava* leaves and Neem saw dust have been used to the adsorbate like methylene blue, malachite green, crystal violet and Rhodamine–B. Chitin, cellulose derivatives and chitosan have been used for treatment of dyestuffs, acid dyes and basic dyes. Activated alumina, clay, waste Fe(III) / Cr(III) hydroxides, carbonized wool, silica, chemically treated modified peat have been extensively used for the treatment of dyes. Fly ash and boiler bottom ash is treated as an adsorbent for methylene blue and malachite green and also victoria blue. Paddy straw is also used for congo red. Palm fruit bunch is used as an adsorbent for basic red and basic yellow. Rice husk carbons for safranine methylene blue and perlite for methylene blue are some of the adsorbents used for treatment purposes. Eucalyptus bark is also used for treatment of reactive dyes. Bentonites are used for treatment of acid yellow-23, direct red, basic violet-10 and basic oxygen furnace slag for acid black-1. Ashes of cow dung, saphada, rice husk, bagasse and bottom ash are the adsorbent for the reactive yellow-85, reactive red-31, acid violet-49 and reactive blue-5. Although these adsorbents have been used considering their cost effectiveness and availability, wide variations in the quality and localized availability resulting in higher transportation cost naturally restricts their prospect for industrial utilization [5].

Now turning to the global tendency with regard to the use of plant wastes and agro-industrial wastes, conversion of these into carbon may add economic value to a large quantity of wastes that are generally discarded. In India, annual production of biomass waste is estimated to be 135 thousand metric tons mostly from agriculture residues, industrial, domestic and yard wastes [6]. With the view of utilizing waste, we have chosen the biomass viz., banyan tree leaf and it is important to look how these wastes are really taken and how it could be transformed/utilized in a better way with a concern on society.

Thus it is clear that these waste biomass materials might have only little or no economic value and may often present disposal problems by and large. But there is a wise possibility left to us in converting these low-cost biomass materials into activated carbon, which would add economic value, help reduce the cost of wastes disposal and most importantly provide a potentially inexpensive alternative to the existing high-cost commercial activated carbon powders. It is a freely and abundantly available local resource and it can be used for the preparation of an effective activated carbon and for its application in the textile wastewater treatment.

Thus, the present work would represent an essential and innovative attempt to produce carbon powders from biomass waste by thermal treatment that may have industrial applications as adsorption or removal of synthetic dyes. The adsorption study of dyes from wastewater was done by varying pH, initial concentration of dyes, adsorbent dosage, temperature and contact time and the results are presented in a systematic way.

II. MATERIALS AND METHODS

A. Preparation of *Ficus citrifolia* (banyan) leaf Carbon (FLC)

The biomass precursors were washed with distilled water, dried in shade and thermally treated in a furnace at 350^0 C for 2 hours the furnace cooled to give a black mass. The black mass from the furnace was collected, and washed with dilute HCl and deionized water until the pH of the decant solution was approximately 7. The char was dried at 80^0C in the oven, ground using mortar and pestle and finally sieved to uniform size for 250 micron particles. The above obtained powder is called *Ficus citrifolia* (banyan) leaf Carbon (FLC) and used for further studies.

B. Stock Solution Preparation

Stock solution of crystal violet/methyl orange dye was prepared by dissolving 100mg/L of crystal violet/methyl orange dye in 1 liter of water. Hydrochloric acid and sodium hydroxide were used to adjust the solution pH. Distilled water was used throughout the experimental studies. The adsorption studies were done in 250 ml Erlenmeyer flasks with 100 ml volume of CV solution. It was shaken on a rotary shaker set at 120 rpm speed and at room temperature. The supernatant liquid was collected and analyzed for remaining dye concentration using a UV spectrophotometer and the % removal of dye was calculated.

The amount of dye adsorbed per gram of the biomass was calculated using the equation:

$$q_e = (C_i - C_e)V/M$$

where q_e is the amount of dye adsorbed per gram of the biomass in mg/g, C_i is the initial concentration of the metal ion in mg/L, C_e is the equilibrium concentration of the dye in mg/L, M is the mass of the biomass in grams and V is the volume of the metal ion in liters. The experiment was done in triplicate and the mean value was taken for each parameter.

III. RESULTS AND DISCUSSION

A. Effect of Contact Time on Dye Adsorption

The effect of contact time on the adsorption of crystal violet and methyl orange dyes using FLC were studied and the results are tabulated in Table 1. All parameters such as dose of adsorbent, temperature, initial dye concentration and pH of solution were kept constant.

Table 1 Effect of contact time on crystal violet/methyl orange dye adsorption
[CV/MO dye]-100mg/L, pH-7, Wt of biomass carbon – 0.5g, Temp -30 ^{0}C

Time (min)	% removal of crystal violet dye	% removal of methyl orange dye
10	30.6	28.4
20	41.7	41.8
30	50.3	48.3
40	60.7	56.4
50	65.5	76.8
60	92.2	84.8
70	92.2	90.1
80	92.2	90.1

From the results, it is noted that % of dye removal increases with increase in contact time before equilibrium was reached, after which there was no significant increase in dye adsorption uptake. This is because the strong chemical binding of the adsorbate with adsorbent requires longer contact time for the attainment of equilibrium. Available adsorbent studies in the literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are difficult to occupy due to repulsive forces between the solute molecules on the solid and bulk phases.

From table 1, it can be seen that the rate of adsorption is very rapid at the initial period of contact time. Thereafter, it decreases gradually with time until adsorption is reached at the equilibrium point. This trend of adsorption kinetics is due to the adsorption of dye on the exterior surface of adsorbent at the initial period of contact time. When the adsorption on the exterior surface reaches the saturation point, the dye diffuses into the pores of the adsorbent and is absorbed by the interior surface of the adsorbent. The curves of contact time are single, smooth and continuous leading to saturation. These curves indicate the possible monolayer coverage of dye on the surface of FLC [7-10]. The equilibrium time for FLC -CV and FLC -MO systems are 60 min and 70 min respectively, thereafter, no further adsorption occurred with prolonged time.

B. Effect of pH on Dye Adsorption

The effect of pH on the adsorption of CV/MO using FLC was studied and the results are tabulated in Table 2.

Table 2 Effect of pH on dye adsorption
[CV/MO]-100mg/L, Time-60/70min, Wt of biomass carbon-0.5g, Temp- 30 ^{0}C

pH	% removal of CV	% removal of MO
2	89.7	84.6
4	90.8	88.0
6	92.9	91.3
8	97.0	94.6
10	97.5	96.9
12	97.8	96.8

The value of pH is known as one of the most important factors in considering the removal of dye molecules from aqueous solutions. To determine the optimum pH conditions for the adsorption of cationic dyes onto FLC, the effect of pH is studied over a wide pH range of 2-12. The results infer the effect of pH on the adsorption quantity of various cationic dyes namely MB and MG. It can be seen that dye adsorption is unfavorable at pH < 4. The decrease in the adsorption with a decrease in pH may be attributed to two reasons. As the pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favor the adsorption of positively charged dye cations due to electrostatic repulsion [11] while, the lower adsorption of dyes at acidic pH is due to the presence of the excess H^+ ions competing with dye cations for the adsorption sites of mesoporous carbon. It is known that pH can affect the structural stability of dyes and consequently its color intensity [12]. It may be due to the structural changes of dye molecules at high pH. On the contrary, the surface of the FLC acquires a negative charge at a high pH, OH^- on the surface of the adsorbent favors the adsorption of cationic dye molecules. The electrostatic attraction between the negatively charged surface of the FLC and cationic dye molecule could result in an increase in the adsorption capacity of various dyes. Several investigations reported that the adsorption quantity of cationic dyes usually increased as the pH increased [13-14]. Therefore, from the results of the experiment and the point of view of application, pH above 7 is chosen as the appropriate value of the initial solution. Differences in % removal ranged from 91.7 to 97.8 % and 84.6 to 96.8 % and increased with the pH for FLC-CV and FLC-MO systems.

C. Effect of Adsorbent Dose on Dye Adsorption

The effect of adsorbent dose on the adsorption of dye using FLC for a given initial concentration of the adsorbate was studied and the results are tabulated in Table 3. The parameters namely, pH, contact time, and temperature are kept constant.

Table 3 Effect of adsorbent dose on dye adsorption
[CV/MO]-100mg/L, Time – 60/70min, pH – 7, Temp – 30 ^{0}C

Wt of biomass carbon(g)	% removal of CV	%removal of MO
0.2	60.3	61.7
0.4	77.0	82.3
0.6	91.6	91.1
0.8	92.0	94.2
1.0	92.1	97.0
1.2	92.1	97.1

It clearly indicates that the dye removal increased with increase in adsorbent dosage and it is evident that the removal of dyes increased from 60.3 to 92.1 % and 61.7 to 97.0 % with respect to CV and MO system. As the adsorbent dosage increased from 0.2 to 1.2 g with respect to the fixed dye concentration, 100 mg/L. This is because of fixed initial dye concentration, increase in the total adsorbent dosage provides a greater surface area or active sites thus it increases the adsorption potential. However, it is observed that after the higher % removal of dyes, there is no significant change in the percentage removal of dyes. It may be due to overlapping of active sites at higher adsorbent doses. So, there is no appreciable increase in the adsorptions because of saturation of the effective surface area and the results a conglomeration of exchange particles [15]

The optimum dosage of adsorbent is 0.8 g and 1.0 g for FLC-CV and FLC-MO systems respectively. Similar trends are reported with methylene blue onto beer brewery waste [16], Cationic dye adsorption on peanut hull [17], Basic dye onto banana stalk waste [18] Kapok hull onto Malachite green [19].

D. Effect of Temperature on Dye Adsorption

The effect of temperature on removal of dyes using FLC were studied within the range of 25 to 50 ^{o}C and the results are tabulated in Table 4. Other parameters such as dose of adsorbent, pH, metal ion concentration, contact time and pH of solution were kept constant.

Table 4 Effect of temperature on dye adsorption
Wt of biomass carbon – 0.5g, Time – 50min, pH – 7, [CV/MO]-100mg/L

Temperature (^{0}C)	% removal of CV	% removal of MO
25	87.2	84.8
30	90.8	88.4
35	94.6	90.3
40	96.3	94.8
45	90.8	89.6
50	86.5	84.7

The temperature dependence of the adsorption process is related with several thermodynamic parameters. The temperature showed the positive and then negative effect on adsorption of dye using FLC. With increase in temperature the removal of dyes was increased from 87.2 to 96.3% for CV and from 84.8 to 94.8 % for MO after that increase in temperature leads to desorption of dyes.

From the results it is clear that the low temperature is in favor of dye removal. This may be due to a tendency for the dye to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The result shows that the adsorption mechanism related with removal of dye is physical in nature. The adsorption process takes place from the electrostatic interaction, which is in general related to low adsorption heat. This implies that the adsorption process was exothermic in nature. Similar findings are also reported by other researchers [20].

E. Effect of Initial Metal Ion Concentration on Dye Adsorption

The effect of initial dye concentration on the adsorption rate was studied in the range of 100 mg/L to 300 mg/L (variation of 50 mg/L) at pH 7, temperature 30 ^{0}C, 0.5g of adsorbent and 60/70 min contact time. The results obtained are tabulated in Table 5.

Table 5 Effect of initial dye concentration on adsorption
Wt of biomass carbon – 0.5g, Time-60/70min, pH-7, Temp-30 ^{0}C

[CV/MO](mg/L)	% removal of CV	% removal of MO
50	92.1	90.3
100	90.3	88.7
150	88.1	79.7
200	77.5	67.2
250	64.3	63.7
300	45.2	55.1

It is evident from the result that, as the concentration of dyes are increased, there is a decrease in % removal. It is because the initial dye concentration provides the necessary driving force to overcome the resistances to the mass transfer of dye molecules between the aqueous phase and the solid phase resulting in higher probability of collision between adsorbent and the active sites [21]. The increase in initial dye concentration also enhances the interaction between dye molecules and FLC i.e. adsorbent. Therefore, an increase in the initial concentration of dye enhances the adsorption uptake of dye and results in higher adsorption, while the adsorption is carried out for a fixed number of active sites, there is a decrease in the % removal of dye. This may originate from the microporous structure of the fabricated activated carbon. It is important to note that micropores are often the major contribution to the adsorption capacity, but the adsorbate molecule should be small enough to penetrate into the micropores [22]. Hence a higher initial dye concentration of will enhances the adsorption process. The dye removal decreased from 92.1 to 45.2% and 90.3 to 55.1% for FLC-CV and AHC-MO systems as the dye concentration is increased from 50 to 300 mg/L. Similar results have been reported in the literature on the extent of removal of dyes [23-24].

IV. CONCLUSION

The agricultural waste products are predominant in the commercial agricultural practices of countries like India, where the effluent holding the toxic pollutant from wastewater is a threatening factor. The low cost effective adsorbents from the agricultural waste for the quantitative removal of cationic dyes from aqueous solution are imperative. This study envisaged the equilibrium and the dynamics of the adsorption of various cationic dyes namely, crystal violet and methylene blue onto this carbon prepared by Banyan leaf.

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A Review on Biomass Based Activated Carbon Materials in Pollution Abatement

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Abstract—*Wastewater discharged from various industries is complex in nature contaminated by metals, pigments, organic and inorganic by-products, and domestic wastes. These compounds pollute the environment and become hazardous to flora and fauna. Therefore, it is very important to treat the wastewater discharged from various industries. The appropriate process of adsorption developed as an interesting and highly effective field offering the best prospect in this regard. The adsorption of pollutants from the wastewater can be achieved using activated carbon as adsorbent. However, the prohibitive cost of activated carbon has restricted its use and hence it is desired to replace it by cheaper and easily available alternatives. The low-cost adsorbents required for the treatment of industrial wastewater can be prepared from agricultural wastes such as coir pith, coconut husk, rice hulls etc. which are freely available. Different types of carbon were prepared from these wastes by various carbonization techniques such as acid, alkali followed by chemical treatment. Their characteristics such as surface area, bulk density, moisture, volatile, ash, sodium, potassium content etc., are determined to assess the suitability of these adsorbents for the treatment of wastewater. From the results of rate of adsorption, adsorption kinetics and isotherm studies it is revealed that the prepared activated carbon from agricultural wastes shows good response for the removal of pollutants from wastewater.*

Keywords— *Wastewater, Pollutants, Activated carbon, Adsorbent.*

I. INTRODUCTION

Water is a basic requirement of our planet, which plays a vital role in the ecosystem. In recent days it is challenging to preserve clean potable water in the world. The growth of population, domestic and agricultural activities, mushrooming industrialization, contemporary technocratic civilization, and other environmental, ecological and worldwide changes, cause water pollution [1, 2]. The various complex impurities found in wastewater even in low concentrations can create significant effects in the environment by causing various health hazards [3, 4]. Unclean water is one of the challenging issues because it involves huge risk to human health and the very existence of an interdependent relationship between environment and human is dubious. In view of the water contamination caused by the high concentration of harmful impurities, there is an urgent need for developing a healthy, economically viable and ecologically friendly treatment to abate the impurities from water to safeguard the human well-being and reinstate the environmental interaction [5, 6]. The discharge limitations of these impurities should be properly monitored and regulated. It is very essential to purify the wastewater discharged from various sources and keep our environment healthy, which requires an innovative technique for the removal of hazardous impurities. Several wastewater treatment methodologies have been developed over the years for the removal of diverse pollutants [7]. The various waste water treatment methods identified are filtration, dialysis, solvent extraction, coagulation, oxidation, evaporation, anaerobic and aerobic treatment, activated sludge flocculation, microbial reduction, ion exchange, magnetic separation and adsorption [8]. Comparing these methods, adsorption is a conversant separation method known to be an effective and manageable method for the elimination of an extensive range of hazardous pollutants one pot from industrial wastewater [9]. It has been found to be a more suitable method than other treatments of wastewater in terms of simplicity, cost effective, ease of operation, and sensitivity to dangerous pollutants [10]. To achieve the removal of toxic pollutants from wastewater by adsorption, activated carbon is employed as a suitable adsorbent material since these carbon rich materials have high porous, good surface area, and presence of a variety of functional groups present on the surface [11]. It is an adaptable material which has various applications. It has been globally accepted as the oldest, extensively used and supreme prevalent adsorbent in the treatment of wastewater discharged from various sources. It is extensively used as an adsorbent in the removal of disagreeable odour, colour taste and other organic and inorganic contaminants from wastewater of industries [12]. They are employed in the pharmaceutical industry for colour removal and removal of toxins from the human body. It is also used in the recovery of metal from effluents, as catalyst supports and catalysts. Activated carbon is also well-known for the applications in the gas mask filter manufacturing industry, automobile pollution control devices, chemical industries, and food processing industries [13, 14]. Even though it has enormous applications, there is a barrier observed in the usage of this material as adsorbent that are vague methods associated with production, regeneration processes and cost of manufacture. In the earlier days of the growth of activated carbons, coal was an affluent source of carbon, and it was considered as the best material for the manufacture of activated carbon with adequate surface area. Coal mines are inadequate and conventional. So the researchers are interested in searching for various non-conventional sources for the manufacture of carbon and found that biomass materials are suitable for the preparation of carbon. Since it can be developed through agricultural activities and formed in a short period, it is considered as a renewable resource. Most of the agricultural waste biomasses contain high amounts of carbon content, which make them the right precursor for activated carbon production process. It is a prudent approach for the production of activated carbon from biomass since it is helped in some ways like agricultural waste management, low cost raw material for the production and causes no pollution during its operation. These agricultural waste materials contain a lesser amount of carbon than coal, so the yield is expected to be lower. However, the activated carbon from agricultural sources gives significant impact despite its yield. The synthesis of activated carbon from low-cost agricultural by-products has proven to be a potential method. The process of production contains various steps such as pre-treatment process, carbonization, activation with suitable chemicals and post-treatment. In the pre-treatment process the biomass material is allowed to dehydrate to increase the yield. Carbonisation is a process in which the biomass material is converted into carbon by removing the hydrocarbon and volatile compounds. Once the charcoal is formed at low temperature it is heated in the range between 450^0 and 850^0 to complete the process. The obtained material is chemically activated by adding chemicals such as potassium hydroxide, sodium hydroxide, phosphoric acid and sulphuric acid etc., The prepared activated carbon material is analysed using XRD, SEM, TEM and it is used in the removal of pollutants in wastewater [15]. This review discusses the research on preparation and potential applications of activated carbons prepared from biomass as an adsorbent for the removal of various inorganic and organic pollutants.

II. MATERIALS AND METHODS

The agricultural wastes which are derived after harvesting the crop can be used as pioneer material for the preparation of activated carbon. The process is diagrammatically shown in figure 1. The materials abundantly available in the farming territories viz., coir pith, coconut husk, rice hulls, tobacco stem, Almond shell, Palm oil shell, sugar cane bagasse are collected and transferred to laboratories for further process. Initially the agricultural waste materials are subjected to pre-treatment process by removing unwanted things like dust, soil content, etc., The cleaned samples then allowed to carbonisation process. It is achieved by physical or chemical process. In physical process the samples are heated in pyrolysis chamber at inert atmosphere. The inert atmosphere created using nitrogen gas, it is ideal gas for creating inert atmosphere because of its virtues like easy handling, cost effective and cleanliness. In the Chemical activation method, the samples are impregnated in dehydrating chemical agents. Different chemicals such as phosphoric acid, sulphuric acid, nitric acid, zinc chloride, potassium hydroxide are used as an activating agent. Chemically soaked samples were subjected to heat treatment under an inert condition to get the porous-structure with large surface area. The chemicals used could enable to develop the pores in the materials. The chemically treated biomass heated at different temperatures to monitor its yield, surface area, and pores formed in the activated carbon. The chemical interaction between samples and activating agents compensate this temperature gap. The prepared activated carbon materials are subjected to characterisations like FTIR, SEM, TEM, XRD. Analytical characterisation reports could shows the influence on chemical compounds, surface properties, grainsize crystalline nature etc., These samples are employed as adsorbent for the removal of impurities present in the waste water discharged from industries. The adsorption efficiency can be studied using adsorption isotherms.

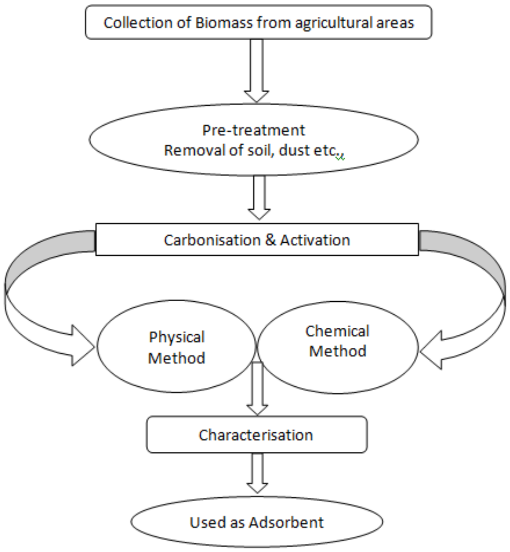

Figure 1. Flow process of preparation of activated carbon.

III. RESULTS AND DISCUSSION

Coir pith collected as a raw material, could be processed in proper methodology and used as an adsorbent in the removal of various pollutants. The maximum percentage of hexavalent chromium can be removed at 30^0, pH 2 and a duration of about 22 hours. The coir pith grafted with 2 M acrylic acid exhibited excellent hexavalent chromium adsorption capacity [16]. Cationic dyes such as rhodamine B and methylene blue and anionic dyes such as acid violet and acid brilliant blue can be removed using coir pith as an adsorbent material. The extent of adsorption increases with increase in the amount of adsorbent and concentration of the gas. But varies non-linearly with pH [17- 19]. The removal of uranium also achieved using coir pith under suitable conditions [20]. The ion exchange mechanism of adsorption removes the cadmium and lead metals by using this material as adsorbent [21-22].

The basic dyes can be removed by using coconut husk as an adsorbent. The reports show that the ideal condition are of contact time 1-30 hours, temperature $30\text{-}50^0$ and dye concentration 50 -500 ppm [23]. The coconut husk activated with alkali is used as potential adsorbent in the removal of elemental mercury [24]. It is reported as a suitable adsorbent in treatment of waste water containing mixed metals with the removal efficiency percentage of 95, 98, 91, 99, 88 and 90 for cadmium, chromium, copper, iron and lead respectively. The removal percentage increase with increase in pH [25].

The rice hull samples collected from rice mill waste product rice hull samples which are rich in cellulose and lignin content converted in to activated carbon possesses sufficient porosity and surface area. The yield of activated carbon from rice hull is comparatively better than other materials. The properties such as moisture, ash and volatile content are found to be 4.86%, 30% and 15.76% respectively. The adsorption efficiency is around 55 % in the treatment of car battery waste water [26]. It shows good results in the removal of hazardous heavy metals in industrial waste water. In the pH range between 5 and 8 it shows excellent adsorption efficiency in the removal of copper and cadmium. The removal of dye in textile industry waste water can also be achieved by using this material as an adsorbent. The adsorption capacity was authenticated by plotting adsorption isotherms [27].

The carbon prepared from tobacco stem waste, activated by alkali materials exhibits ideal properties such as high surface area, amorphous and porous nature of an adsorbent. The adsorption efficiency of this material reveals that it could be a capable alternative adsorbent for the elimination of cationic dye content in textile industry waste water [28]. Further to increase the surface area it is activated with potassium carbonate. The adsorption of cadmium, copper and lead is extensively achieved by using this as an adsorbent. The activated carbon produced at 700^0 shows good results on the remediation of lead. The carbon produces in the temperature 400^0 reveals better adsorption efficiency on copper [29].

The almond shell is a low-cost, comparatively abundant agricultural by-product. It is rich in lignocellulose and 75% weight of the fruit. The carbonised form of this material used in the treatment of industrial waste water as adsorbent produced excellent results in the removal of nickel and copper. The percentage of removal increased in acidic pH [30]. Phosphoric acid activated carbon of almond shell shows effective results in the dye removal [31].

The adsorption properties of palm oil shell activated by phosphoric acid shows better results in the removal of methylene blue [32]. Further studies state that it is one among the effective tools in the treatment of contaminated water close to mining site or pollution that may occur due to industrial effluents. The removal of the metals such as lead and cadmium has been achieved 87% and 88 % respectively [33].

Sugarcane bagasse is fibrous in nature and obtained as a residue of sugar cane juice. It made up of cellulose, hemicelluloses, lignin etc. It can competently remove a variety of target impurities from waste water including dyes, toxic heavy metals, phenolic compounds etc., The presence of a variety of bonding sites in both the raw and chemically activated sugarcane bagasse is proficient in the removal of pollutants [34].

IV. CONCLUSION

Biomass from agricultural practices as a raw material for the preparation of activated carbons has been reviewed based on some suitable work published. Activated carbons from these sources are effectual adsorbents that can remove variety of pollutants. Many low-cost adsorbents from agricultural waste products have been prepared and characterized in recent past years. The prepared carbonised material shows better performances in treating contaminations in the effluents. The cost of production of activated carbons from the agricultural waste is lower than the activated carbons from coal-based material since the raw materials are freely available and abundant. It is an excellent low cost replacement for the existing coal-based activated carbons and is used in the various field like drinking water filter bed, municipal wastewater treatment plant, manufacturing of gas mask filter, treatment of industrial water containing dyes and metals. In addition to that it would help the agriculturalist by resolving the waste management problem. Even it has numerous application it is suggested that some of the things to be considered in further research on this field. Cost of production for the activated carbon and surface area for large scale production should be taken in to an account. The adsorbed pollutants such as metals are recovered by suitable low cost process and can be recycled for further usage. This review article summarized the adsorption capacities of few of activated carbons from the agricultural waste products. Though the industrial effluents contain complex mixture of pollutants further research should concentrate on simultaneous removal of all the impurities present in the waste water. Generally, activated carbon from biomass can be a cost effective, better ability in the removal of pollutants and a suitable replacement for the commercially available activated carbon.

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Vitamins and Microencapsulation

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Abstract - *The continuous increase in the world's population made a drastic change in the annual food production. Bringing up technology and innovations out of the labs helps to tackle the above food challenge. This food challenge includes providing nutritious food without any loss. When coming to talkabout nutritious supplement of food, Vitamins is one of the important nutrients required for human growth and development. Vitamins are essential for human health, growth, development, reproduction and maintenance in human body. Basic introduction on vitamins, thirteen essential vitamins its functions, deficiencies and the method of preventing loss of vitamins have been discussed here.*

Keywords*:* *Vitamins, microencapsulation, vitamin C, Spray drying.*

I. INTRODUCTION

The Polish biochemist Casimir Funk coined the term 'vitamin' from 'vitamine' in 1912.The name vitamin comes from "Vita" means 'life' and 'amin' because it was believed that all types of vitamins contain the chemical amine structure. Vitamins are defined as organic compound distinct from fat, carbohydrate and proteins . Vitamins are categorized under micro nutrients because they are needed in only very small quantity. Each vitamin has chemical names, but they are usually referred by letters.

A. Classification of Vitamins

Vitamins are categorized into two types

- Water soluble vitamins
- Fat soluble vitamins

Water Soluble Vitamins

Water soluble vitamins are soluble in water. They are absorbed in tissues since they are not stored in body. The excess number of water-soluble vitamins in the body are excreted as urine. All B vitamins (Thiamine, Riboflavin, Niacin, Pantothenic acid, Pyridoxine, Biotin, Folic acid, Cobalamin, Ascorbic acid) and vitamin C are categorized under water soluble vitamins.

Fat Soluble Vitamins

Fat soluble vitamins are those that are soluble in lipids(Fats). These are absorbed by lactase in small intestine through chylomicrons since they cannot be absorbed directly by the blood stream they are stored in the body's tissue and in the liver. Fat soluble vitamins includes A,D,E&K.

13 ESSENTIAL VITAMINS

VITAMIN	*CHEMICAL NAME*	*FOOD SOURCES*	*DEFICIENCY*	*SYMPTOMS*
Vitamin A	Retinol	Carrot, spinach, egg and milk	Night blindness	Loss of vision in darkness, sometimes complete loss of vision
Vitamin B1	Thiamine	Fish, peas, beans, peanuts and meats	Beriberi	Weak muscles and very little energy to work
Vitamin B2	Riboflavin	Milk cheese, leafy green vegetables, animal liver, soya beans, yeast	Ariboflavinosis	Red and sore tongue, photophobia and scaly skin
Vitamin B3	Niacin	Bets, beef liver, beef kidney, pork, turkey chicken, salmon sword fish, peanuts	Pellagra	Dermatitis, diarrhea, loss of memory
Vitamin B5	Pantothenic acid	Fortified cereals, beef, chicken breast, mushroom, avocado, nuts, seeds, dairy milk.	Fatigue	Depression, vomiting, stomach pains, burning feet, upper respiratory infection
Vitamin B6	Pyridoxine	Meat, vegetables, tree nut, banana	Paresthesia	Hyper irritability, nausea, vomiting and fits
Vitamin B8	Biotin	Chocolate, leguminous vegetables, nuts, spinach, yeast.	Nausea, hair loss skin inflammation, hypersensitivity	-
Vitamin B9	Folate	Beans, whole grains, peanuts, fresh fruits, seafood, liver.	Anemia and heart disease	Tiredness, weakness,
Vitamin B12	Cyanocobalamin	Meat, fish, egg, milk	Anemia	Lean and week and less appetite
Vitamin C	Ascorbic acid	Citrus fruits such as lemon, orange, grapes	Scurvy and swelling of gums	Bleeding gums, wounds take longer time to heal
Vitamin D	Calciferol	Produced in human body when exposure to sunlight	Rickets and osteoporosis	Bones become soft and bent
Vitamin E	Tocopherol	Vegetable oil, nuts, fortified serials and multi grains	Loss of fertility	Sterility
Vitamin K	Phytonadione	Spinach, mustard greens, turnip greens, soya beans, cotton seeds	Hemorrhage,Clotting of blood	Excessive bleeding due to injury

OTHER VITAMINS

VITAMIN	*CHEMICAL NAME*	*FOOD SOURCE*	*DEFICIENCY*	*SYMPTOMS*
Vitamin B17	amygdalin	Almond,celeryberries,carrots,beans,legumes	Cancer	Fever,sickness, headaches, liver damage, eyelids
Vitamin H	biotin	Yolk,nuts, legumes,whole grains,banana	Dry eyes, insomnia and depression	Hair loss, dry scaly skin, dry eyes,insomnia, fatigue,depression
Vitamin P	flavonoids	Citrus fruits,red and blue fruits,black tea	Rickets	Bruising,increased tendency to bleed, greater to hemorrhage.
Vitamin U	S-methyl methionine	Cabbage,broccoli,Brussel sprouts	Leads to ulcers or other stomach problem	Lead to ulcers, stomach acidity

B. Vitamin Loss During Processing And Cooking

The process of cooking, conditions of fruits and vegetables causes discrete loss of vitamins. Most vitamins are sensitive to heat and water treatment. The loss of vitamin may vary widely according to the cooking methods and type of food. The denaturation of vitamins is based on several parameters such as temperature,pH,presence of oxygen,light,moisture and time exposure to the heat treatment. Water soluble vitamins such as vitamin B, B leach out into water during cooking.Similarly fat-soluble vitamins A,D, and Eleach out during cooking.Among the 13 essential vitamins, vitamin C is considered more likely to get lost during cooking. Only two vitamins,vitamin K and B3 or niacin can hold up and stable well during cooking.Hence to overcome the denaturation of vitamins during food processing and cooking microencapsulation technology of vitamins have been developed. Microencapsulation technology which aims to protect sensitive compounds which are prone to environmental conditions.This method is widely used in pharmaceutical and cosmetic industries but it has been introduced in food production too.

C. Microencapsulation

Microencapsulation can be defined as a process in which the tiny particles or droplets are enclosed into a barrier made of polymeric materials to control the release of ingredients. It is a formation of a barrier to avoid chemical reactions, or to be in control release of ingredients. It is a mass transfer behavior between the core (the ingredient) and the shell(capsule).It is simply defined as the process of surrounding or enveloping one substance within another substance. Microencapsulated particles possess diameter of about 1-1000µm.Microencapsulation is done to protect the inner core materials.

The process of microencapsulation possesses two phases:

1. Core material
2. Coating material

1. Core material:

The specific material to be coated is called the core material. The material which is the ingredient that needs to be protected from dispersing.

2. Coating material:

Inert substance which coats on the core particles should be stable during producing thin layers. The selection of coating material must be suitable to the inner core material.

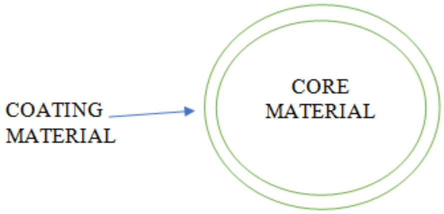

Figure 1 : Microencapsulation of materials

D. Techniques to Manufacture Microcapsules

A) Spray drying
B) Spray chilling / cooling
C) Coacervation
D) Liposome treatment
E) Extrusion

A) **Spray drying**

This is the most common method which is employed in encapsulating oils, flavors etc., using gum acacia and in encapsulation of number of liquid and solids material. It involves homogenization of core materials and wall materials, to create an emulsion by the process of atomization.

B) **Spray chilling/cooling**

In this method a homogenous mixture of core and molten liquid coating materials are atomized by cooled air through a sprayer below the melting point of the lipid.This method is similar to spray drying and the air temperature is cooler than that of spray drying. This method utilizes molten fat or wax as wall material for coating vitamin D.

This method is used to create microcapsules with hydrophobic cores and hydrophobic wall molten lipid. This method is used for Vitamin D by utilizing fat as wall material. It is a cheaper alternative to complex coacervation and processed at a temperature of 80-90^0 for animal feed products

This same method is also applied on vitamin D3 and found limited protection of core at 25^0 double layered microencapsulation core is coated first with ahydrophilic coat using spray drying and then again coated with hydrophobic coat by spray cooling.

C) Coacervation

Coacervation is defined as the separation of a colloidal solution into two liquid phases. Two types of coacervation processes includes simple and complex.

In simple coacervation it uses a single polymer to form coacervates through the addition of salt or dissolving agent. Alcohol or acetones are the dissolving agents. In food simple coacervation is relatively less. To encapsulate tannins kafirin and sorghum prolamin storage protein has been used.

In complex coacervation two or more polymer solutions with opposite charges electrostatically interact with each other in water resulting into immiscible liquid phases. The polymer rich dense phase and polymer-pour continuous phase are immiscible liquid phase.The polymer rich dense phase and polymer-pour continuous phase are immiscible liquid phases. Complex coacervation technique be applied for many water-insoluble compounds like fatty acids,flavor and fat-soluble vitamins.

D) Extrusion

In extrusion method, a molten carbohydrate mass a core material is incorporated and then the mixture is forced through a series of dyes and collected in bath of dehydrating solution. Glucose, sucrose, glucose syrup, glycerol, maltodextrin was common coating material. The protection of the core compounds from oxygen as they are isolated completely from air by wall material is the primary advantage of this method.

E) Liposome Treatment

Liposome are the vesicles made of bilayer mostly composed of phospholipids, it is formed as a result of dispersion of phospholipids into aqueous solution and exposed to high shear rates through micro fluidization. Polar end binds to water soluble particles and the non-polar end binds to oil-soluble particles. This method allows the core material to maintain high water activity which is the advantage of the liposome entrapment.

E. Release Mechanism

Appropriate place and time are the two important factors that decides the release of core material. The release rate of microcapsules depends upon the interaction between the core and wall material. The release rate also depends on the ratio of wall to core material, size of the capsule, viscosity of the medium in which the capsule to be added.

The release of core material takes place by one of the following methods: Diffusion, dissolution, osmosis or erosion.

A) Diffusion

When the microcapsule is introduced into the dissolution medium, the dissolution fluid penetrates the shell and dissolves the inner core material.

B) Dissolution

When the coating gradually dissolves, the core is released. The dissolution rate depends upon the thickness of the coating and its solubility in the dissolution fluid.

C) Osmosis

The core material is released by means of osmotic pressure which is created between the inner and outer wall material. Here the polymer coat (coating material) acts as a semi permeable membrane and induces osmotic pressure.

D) Erosion

The release of core material takes place by means of erosion of outer shell due to attaining desired pH and enzymatic hydrolysis.

F. Microencapsulation of Vitamin C with Gum Arabic

Among the 13 essential amino acids vitamins, vitamin C is a water-soluble vitamin with good antioxidant property. But it cannot be produced by humans and it needs to be supplemented in the human diet in appropriate levels. Vitamin C helps in manufacture of collagen protein, wound healing, healthy immune and nervous system and as an antioxidant preventing diseases however, environmental factors such as pH, temperature, oxygen, metal ion, UV and x-ray affect the stability of ascorbic acid purity processing, it changes the color from white to yellow. It may also react with other substances and produce an undesirable change in taste and color a food material. Therefore, for preventing drastic changed lesser microcapsules action of vitamin C has been introduced. It could be used to protect vitamin when added to different food products.

G. Microencapsulation of Vitamin C

A) Materials

Core material [L-ascorbic acid] for coating -gum Arabic, -and whey protein were used as coating material

B) Preparation

20% of gum Arabic and whey were blend and dispersed in water using ultra Truax mixer which is operated at11,200-20,000 rpm for 15 min. The dispersion was kept for complete rehydration for 12 hours at refrigerated temperature at (8-10^0) vitamin C was added to the wall at weight ratios of wall material (GA+WPI)/Vitamin C. The mixtures were directly sprayed using spray dryer at several operating conditions (feed rate 5m/minutes, aspirator of 96%) atomic pressure 0.3 bar, inlet temperature 160^0 outlet temperature 70^0) the collecting powder was stored, kept in freezer at -18^0 until use.

C) Evaluation of stability of microencapsulated VitaminC

The stability of microencapsulated vitamin C was evaluated under two different storage conditions 25^0 and 87^0. Samples microencapsulated were taken at time interval of 0,2,4,8,12 weeks.From microcapsule the ascorbic acid was released by dispersion in 25ml of 3.5% phosphoric acid, under ionic action for 5 minutes, and then centrifugated at 3500rpm for 3 minutes. It is then viewed under scanning electron microscopy.

D) Result Analysis

The stability of vitamin has greatly improved by micro encapsulation. Same results were found in encapsulation produce by using other different methods. The study concluded that the process of encapsulation of vitamins improves the shelf life of food materials which would usually degrade under normal environmental conditions and other factors involved while cooking.

H. Other Vitamins

The most common vitamin found in human beings is vitamin C which is water soluble. Hence most researchers make use of this vitamin for analysis. Fat soluble vitamin A (derived from b-carotene) is an important vitamin that merit lots of research. Vitamin A is found naturally in foods such as liver, fish ,oils, dairy product. B-carotene is used in dietary supplement tablets, if it leaks from a tablet & become exposed on the surface the result would be oxidation & loss of content.

Thus, microencapsulation is effective. The effects of colloid mixing ratio, hardening agent, concentration of core solution & drying method was investigated. Gelatin-acacia microcapsules were used which entrapped micro droplets of vitamin A palmitate in corn oil. Vitamin C&E can be used synergistically as an antioxidant. Vitamin E acts as the primary antioxidant reacting with & repairing free radicals & it is itself then regenerated itself by the vitamin C. Liposome entrapment can be used to protect these vitamins. The stability of vitamins especially vitamin C is greatly improved by microencapsulation. Difference techniques of encapsulation produce the same results. Process can be optimized by choosing the optimal wall material, core to wall ratios. Microencapsulated vitamins are used for nutritional properties to fortify foods as antioxidants. The increased stability in food makes them ideal for use in breads, infant formula cereal bars & dairy product.

II .CONCLUSION

Vitamins are organic compounds required in very small amount in diet so that vitamins are called as micro nutrients. Vitamins are essential to our body because it prevents deficiency diseases, maintain health and also help to process carbohydrates and release energy in the body. During processing and cooking vitamin losses takes place.To prevent those losses “MICROENCAPSULATION” can be introduced, which is defined as the process of surrounding or enveloping one substance within another substances.

ACKNOWLEDGEMENT

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Green Chemistry - An Introduction and Principles

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Abstract — *Over the course of the past decade, green chemistry has demonstrated how fundamental scientific methodologies can protect human health and the environment in an economically beneficial manner. Green chemistry has a framework of a cohesive set of Twelve Principles, this chapter covers the concept of design and the scientific philosophy of Green chemistry with an increased awareness of environmental impact. There are several activities within the green chemistry community that highlight the potential for chemistry to solve many of the global environmental challenges we face now. The origins and basis of green chemistry chart a course for achieving environmental and economic prosperity inherent in a sustainable world.*

Keywords — *Green chemistry,12 principles, Renewable feedstocks, Biocatalysis, Alternative solvents, Biomass*

I. INTRODUCTION

Green chemistry is defined as the "design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances [1,2]. The definition and concept of Green Chemistry were first formulated at the beginning of the 1990's nearly 30 years ago [3].In the years since, there has been international adoption that resulted in the creation of literally hundreds of programmes and governmental initiatives on Green Chemistry around the world with initial leading programmes located in the U.S., United Kingdom, and Italy [4].These have played a significant role in informing sustainable design[5].

The most important aspect of Green chemistry is the concept of design. Design of a statement of human intention and one cannot design an accident. It includes novelty, planning and systematic conception. The Twelve Principles of Green chemistry are "design rules" to help chemists achieve the international goal of sustainability [6]. Green Chemistry is characterized by careful planning of chemical synthesis and molecular design to reduce adverse consequences. The Green Chemistry approach strives to achieve sustainability at the molecular level. Because of this goal, it is not surprising it has been applied to all industry sectors. From aerospace, automobile, cosmetic, electronics, energy, household products, pharmaceuticals, agriculture, there are hundreds of examples of successful applications of award winning, economically competitive technologies [7]. The concept of Green Chemistry has had this large impact due to the fact that it goes beyond the laboratory in isolation and has touched industry, education, environment, and the general public. The field of Green Chemistry has demonstrated how chemists can design next generation products and processes so that they are profitable while being good for human health and the environment [8].

II. HISTORY OF GREEN CHEMISTRY

Green Chemistry emerged from a variety of existing ideas and research efforts(such as atom economy and catalysis) in the period leading up to the 1990's, in the context of increasing attention to problems of chemical pollution and resource depletion. The development of green chemistry in Europe and the United States was linked to a shift in environmental problem-solving strategies' moment from command and control regulation and mandated reduction of industrial emissions at the "end of the pipe" toward the active prevention of pollution through the innovative design of production technologies themselves. The set of concepts in the mid-to-late-1990's, along with broader adoption of term "which prevailed over competing terms such as clean and sustainable chemistry"[9,10].In United states, The Environmental Protection Agency played a significant early role in fostering green Chemistry through its pollution prevention programs, funding and professional coordination. At the same time in the United Kingdom, researchers at the University of York contributed to the establishment of the Green Chemistry New work within the Royal Society of Chemistry, and the launch of the journal Green Chemistry.

III. PRINCIPLES OF GREEN CHEMISTRY

Green synthesis can be achieved by following the twelve principles of Green Chemistry as suggested by Paul T. Anastas and John C. Warner, (Green Chemistry, Theory and Practice, Oxford University Press, New York, 1988). The twelve Principles address ways to reduce the environmental and health impacts of chemical production, and also indicate research priorities for the development of green chemistry technologies.

A. The principle covers such concepts as:

- The design of the process to maximize the amount of raw material that ends up in the product.
- The use of renewable material feedstock and energy sources
- The use of safe, environmentally benign substances, including solvents, whenever possible.
- The design of energy efficient processes
- Avoiding the production of waste, which is viewed as the ideal form of waste management.

B. The Twelve Principles of Green Chemistry are:

1. Prevention. Preventing waste is better than treating or cleaning up waste after it is created.
2. Atom Economy. Synthetic methods should try to maximize the incorporation of all materials used in the process into the final product. This means that less waste will be generated as a result.
3. Less hazardous chemical syntheses. Synthetic methods should avoid using or generating substances toxic to humans and/or the environment.
4. Designing safer chemicals. Chemical products should be designed to achieve their desired function while being as non-toxic as possible.
5. Safer solvents and auxiliaries. Auxiliary substances should be avoided wherever possible and as non-hazardous as possible when they must be used.
6. Design for energy efficiency. Energy requirements should be minimized, and processes should be conducted at ambient temperature and pressure whenever possible.
7. Use of renewable feedstocks. Whenever it is practical to do so, renewable feedstock or raw materials are preferable to non-renewable ones.
8. Reduce derivatives. Unnecessary generation of derivatives-such as the use of protecting groups-should be minimized or avoided if possible: such steps require additional reagents and may generate additional waste.
9. Catalysis. Catalytic reagents that can be used in small quantities to repeat a reaction are superior to stoichiometric reagents.
10. Design for degradation. Chemical products should be designed so that they do not pollute the environment: when their function is complete, they should break down into non-harmful products.
11. Real time analysis for pollution prevention. Analytical methodologies need to be further developed to permit real time, in process monitoring and control before hazardous substances form.
12. Inherently safer chemistry for accident prevention. Whenever possible, the substances in process, and the forms of those substances, should be chosen to minimize risks such as explosions, fires, and accidental releases.

C. Goals of Green Chemistry

The principles and guidelines of Green Chemistry are intended to fulfill the following goals for any chemical process, whether industrial or laboratory scale:

- Make better use of available resources for the development of a chemical process.
- Reduce waste generated in any preparation or handling of chemicals.
- Materials should be prepared by improved processes that reduce unwanted effects on the environment.
- Replace toxic reagents and products with others that have the same properties and applications but have less impact on the environment.
- Reduce the energy required to produce substances of interest, either by the use of much faster processes or by the use of renewable energies involving lower energy cost with equal efficiency.
- Reduce toxicity or general danger for a given compound substance and the compound itself.
- Reduce costs by eliminating any manipulation that is not strictly necessary and decreasing time invested in the preparation of a substance.
- Encourage all necessary actions to use chemicals compatible with sustainable development.

D. Parameters to evaluate chemical processes

In Green Chemistry the environmental impact of a reaction or the efficiency of a reaction or a chemical process can be quantified by a number of parameters [11]. Of all those that have been defined, here we will highlight the “E factor” and “atom economy.”

E. E factor

One of the first parameters for evaluating the environmental impact of a chemical transformation is the term “E factor”, which was introduced by R. Sheldon [12]. The concept is quite simple and easy to understand, and it has been applied mainly to the industrial sector. It is a measure of the waste generation in chemical manufacture. The E factor is calculated by dividing the total mass of waste produced in the preparation of a compound by the total mass of product produced or synthesized. Waste is defined as everything but the desired product. Chemical yield is considered together with reagents, solvent losses, all process aids, and, in principle, even fuel used, although this item is often difficult to quantify. There is one exception: water is generally excluded from the calculation of the “E factor.” For example, when considering an aqueous waste stream, only the inorganic salts and organic compounds contained in the water are counted, while the water itself is excluded. The lower the E value, the lower the waste produced and the lower the environmental impact of the process.

E Factor = Total mass of wastes (Kg) /Mass of products (Kg)

Table 1 lists the estimated values of E factors for different chemical industry branches.

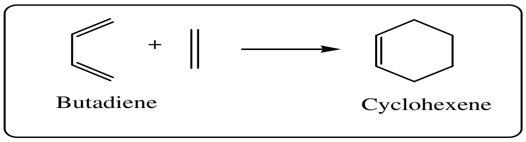
Table 1: E factor.

Industry segment	***Product tonnage***	***E factor (Kg waste/kg product)***
Oil refining	10^{6}-10^{8}	<0.1
Bulk chemicals	10^{4}- 10^{6}	<1-5
Fine chemicals	$10^{2\ -}10^{4}$	5->50
Pharmaceuticals	10-10^{3}	25->100

F. Atom economy

The atom economy concept is due to B. M Trost [13,14]. This is probably one of the most useful parameters for the analysis of reactions, allowing an assessment of the amount of waste generated in a reaction or a sequences of reactions. The atom economy has had a great influence in the further development of organic synthesis as a whole, because it focuses on the design of the synthetic methods according to the concept of sustainability. The calculation of atom economy quantifies the use made of each of the atoms of a reactive, indicating which of them is actually incorporated into the final product. With the concept of atom economy, some approximations are assumed to simplify the calculations. Since it is a measure of how reagents are incorporated to the end products, when calculating, it neither counts the amount of solvent employed, the excess organic reagents, the catalysts, or the inorganic salts that may be added to the reaction nor intervenes in the reaction yield.

Addition reactions



For a simple reaction A + B → C atom economy calculation is as follows:

EA = Molecular weight of C / Σ Molecular weight of reactants (A + B) × 100

As an example of calculating of atom economy, the preparation of ethylene oxide (oxirane) by the traditional method can be considered. Under the assumption that the reaction yield was 100%, the atom economy of the process would be of 25.46%: $C_2H_4 + Cl_2 + Ca(OH)_2 \rightarrow C_2H_4O + CaCl_2 + H_2O$

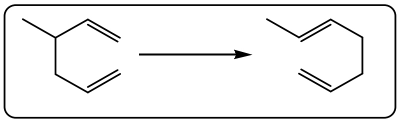
$$EA = \text{Molecular weight of } C_2H_4O / \Sigma \text{ Molecular weight of } C_2H_4 + Cl_2 + Ca(OH)_2 \times 100\%$$

$$EA = 44.05u / \ 28.05u + 70.91u + 74.09u \times 100\% = 25.46\%$$

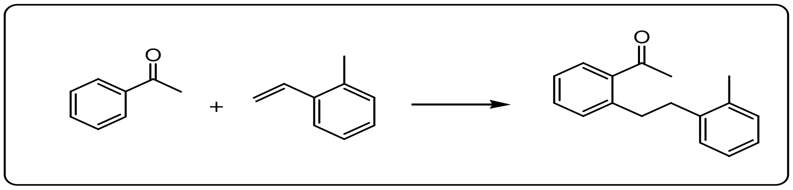
IV. SYNTHESIS

As illustrated in Fig. 1, the synthetic toolbox of organic chemists has been improved by a significant amount of innovative work. Many of the new reactions that have been developed in the past decade add to the already existing green reactions that were discovered during the past century. Reactions based on cycloaddition,[14,15] rearrangement,[16] or multi-component coupling reactions[17] were already known and constitute one category of efficient reactions. Cascade or tandem reactions,[18] C–H activation,[19] metathesis,[20] and enzymatic reactions[21,22] are rather new approaches and illustrate strong examples of cleaner, more efficient synthetic tools available to organic chemists. The Grubbs catalyst, for example, allows alkene metathesis through a mechanism similar to Wittig-type reactions such as the Horner–Wadsworth–Emmons reaction (formation of a four membered ring as reaction intermediate, Fig. 1. It is an essential tool for the construction of larger molecules. However, unlike the Wittig reaction, the metathesis reaction does not produce a large amount of waste. The formation of phosphonium salts in the case of the Wittig reaction is unfortunately unavoidable since it is part of the design of the reaction and is the main driving force.[23]

A. Cope rearrangement



Example of C-H Activation reaction



Alternative synthesis: Grubbs metathesis

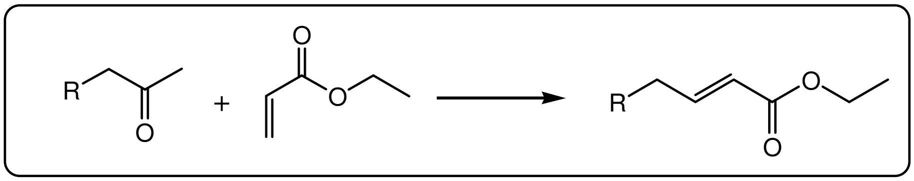


Fig-1: Examples of Green reactions

C–H activation is another relatively new area of chemistry which holds great promise for the future.[24] In traditional coupling reactions, activated carbon–halogen bonds are usually used because of their high reactivity. Since halogenated molecules are rarely natural, it implies additional steps to produce the precursor. The replacement of traditional coupling reactions with C–H activation eliminates the need for halogenated precursors and therefore the halogenated waste byproduct generated. Two famous examples of C–H activation were published in 1993 by Murai31 and in 2007 by Fagnou.[25] In the first case, Murai et al. employed a ruthenium catalyst to couple the inactivated substrates acetophenone and 2-methylstyrene. This work was one of the first examples of C–H activation and represents a milestone in the field. In the second case, Fagnou and Stuart coupled two aromatic compounds selectively without the need for any activating or directing groups. Those examples demonstrate the power of C–H activation in advancing Green Chemistry.

B. Molecular design

While there has been significant focus on designing chemicals for various functions ranging from medicines to materials, there has been a surprising lack of interest in taking into consideration hazard in the design process. Understanding the properties of a molecule that have an impact on the environment and the transformations that take place in the biosphere is essential to sustainability. Through a mastery of this understanding, chemistry will be able to genuinely design molecules that are safer for humans and the environment. Work by Ariens[26] in 1984 and by Garrett and Devito in 1996 showed that designing safer chemicals is not only highly needed for the advancement of Green Chemistry, but is also possible.[27] In recent decades, there has been a significant amount of work in the field of toxicology that has moved it from being a descriptive science to one that has a large mechanistic component,[28] and even more recently progressively towards the incorporation of an in-silico component.[29] Because of that transition, it has been possible to create correlations, equations, and models that relate structure, properties, and function. These approaches provide the basis for the work being pursued in the development of a comprehensive design strategy. For instance the existing understanding of medicinal chemistry can already help establish some ground rules for designing less toxic chemicals via incorporation of specific design features that block their access into humans and many animal organisms.[30]

C. Solvents

Solvents are perhaps the most active area of Green Chemistry research.[31] They represent an important challenge for Green Chemistry because they often account for the vast majority of mass wasted in syntheses and processes.[32]Moreover, many conventional solvents are toxic, flammable, and/or corrosive. Their volatility and solubility have contributed to air, water and land pollution, have increased the risk of workers' exposure, and have led to serious accidents. Recovery and reuse, when possible, is often associated with energy-intensive distillation and sometimes cross contamination. In an effort to address all those shortcomings, chemists started a search for safer solutions. Solvent less systems,[33] water,[34] supercritical fluids[35] (SCF) and more recently ionic liquids[36]are some examples of those new ''green'' answers. Where possible, the ideal situation would be to not use any solvent because the decision to include an auxiliary always implies efforts and energy to remove it from a designated system. Efforts have therefore been devoted to developing solvent less systems.[33] This idea was reinforced by the finding that solvents account for most of the industrial waste.[32] Depending on the physical properties of the reagents used or the desired outcome of the transformation, the approach often requires a new or redesigned chemistry to allow the reaction to proceed without the original solvent. Water is the most abundant molecule on the planet and is sometimes referred to as a benign ''universal solvent.''[34] Being able to run a reaction in or on water therefore has significant advantages. Water is safe and does not pose any hazards. It can be a useful solvent for large scale process chemistry. The properties of water have even led to improved reaction rates through the hydrophobic effect[37] and easier separation since a lot of organic substances do not dissolve in water. The case of an improved Diels–Alder reaction in water is one of the useful examples illustrating the advantages of water as a solvent. One drawback which may slow down industrial applications and has yet to be addressed is the risk of water contamination that can be very energy intensive to clean. SCF are another alternative to traditional organic solvents and have been extensively studied in the past decades.[35] They are substances which have been simultaneously heated and compressed above their critical points (see Fig. 2).

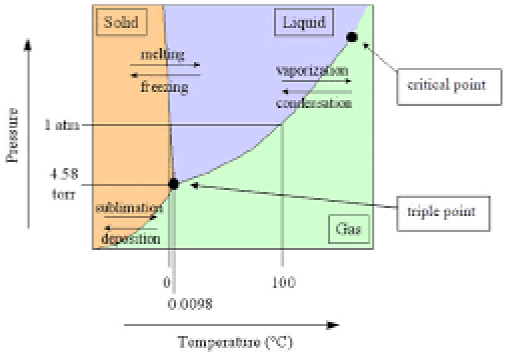


Fig-2 Pressure –temperature phase diagram showing the supercritical region

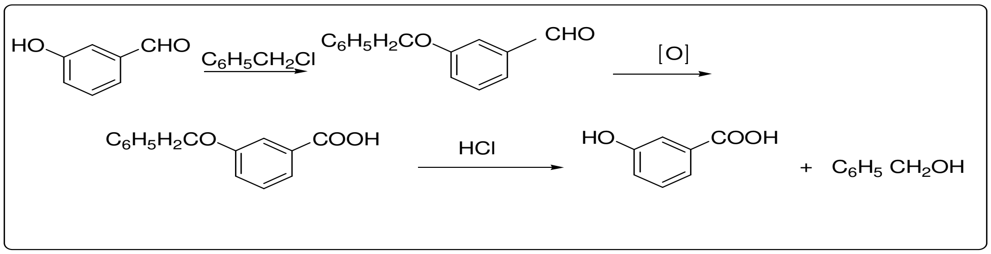
Common SCF are generated from water, carbon dioxide, methane, methanol, ethanol or acetone. Carbon dioxide is one of the most widely used SCF. The resulting scCO_2 has proven to be a versatile solvent, safe and easy to handle, as demonstrated by the work of Poliakoff, Leitner, Jessop, DeSimone, and others.[38] What makes SCF so attractive in general and particularly scCO2 is the change of state that occurs when cooling down the vessel or reducing the pressure. Above critical points, CO_2 will be a liquid in which reactions can be performed and below, it will be a gas. Degassing the system allows the complete removal of the solvent. ScCO_2 has found a wide range of industrial applications with the most famous being the decaffeination of green coffee beans and the replacement of perchloroethylene in dry cleaning.[39] Supercritical fluids have proven to be one valuable alternative to traditional solvents. Another example of greener solvents would be ionic liquids pioneered in modern times by Seddon. As their name highlights, ionic liquids, or sometimes called room temperature ionic liquids, are liquid salts at room temperature. They have virtually no vapor pressure and very low flammability. What was discovered recently by Jessop et al. is a ''switchable'' ionic liquid.[40] A ''smart-obedient solvent'' generated in situ just like the liquid $scCO_2$. Addition of pressurized carbon dioxide into an organic mixture transforms it into an ionic liquid, generating a safer solvent in situ. Releasing the pressure reverses the phenomenon and the ionic liquid is retransformed into the original mixture, thus completely removing the solvent and eliminating tedious purification and extraction steps. Another example based on the same concept is the development of fluorous biphasic catalysis advanced by Horvath.[41] A fluorous phase or solvent containing a catalyst suited for the desired transformation is usually not miscible with organic reagents at ambient temperature. When heated, they form a single media, allowing the reaction to proceed. Upon cooling the organic phase and the fluorous solvent separate, simplifying the purification process. This is an attractive approach with the restriction that fluorous solvents are expensive. These last examples are good illustrations of one of chemistry's major challenges: separation. Apart from certain solvent-less systems, the new improved green solvents remain auxiliaries and therefore must be isolated from the desired product. If their use cannot be avoided then the issue of separation must be taken into consideration when choosing the appropriate solvent.

D. Selection of Starting Materials

Starting materials are those obtained from renewable or non-renewable material. Petrochemicals are mostly obtained from petroleum, which is a non-renewable source in the sense that its formation takes millions of years from vegetable and animal remains. The starting materials which can be obtained from agricultural or biological products are referred to as renewable starting materials. The main concerns about biological or agricultural products however, is that these cannot be obtained in continuous supply due to factors like crop failure etc. Substances like carbon dioxide and methane gas are available in abundance. These are considered as renewable starting materials.

E. Use of protecting groups

In case an organic molecule contains two reactive groups and you want to use only one of these groups, the other group has to be protected, the desired reaction completed and the protecting group removed. For Example



F. Use of Renewable feedstock

The concept of making all our future fuels, chemicals and materials from feedstocks that never deplete is an interesting concept which at first glance seems impracticable. Mankind currently removes fossil fuels, coal, oil and natural gas from the ground and extracts minerals for profit until they are exhausted. In particular, our fossil fuels for carbon-based chemicals and materials are being rapidly depleted in a predictable manner with the expected rise of global populations and expanding energy intensive economies on several continents. The impacts on human health and the environment are significant and present major challenges for our scientists and leaders in the next 50 years.

G. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

A primary goal of green chemistry is the minimization or preferably the elimination of waste in the manufacture of chemicals and allied products: *"prevention is better than cure"*. This necessitates a paradigm shift in the concept of efficiency in organic synthesis, from one that is focused on chemical yield to one that assigns value to minimization of waste. What is the cause of waste? The key lies in the concept of atom economy: *"synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product"*. In the reaction scheme we compare, for example, the reduction of a ketone to the corresponding secondary alcohol using sodium borohydride or molecular hydrogen as the reductant. Reduction with the former has an atom economy of 81% while reduction with the latter is 100% atom economic, that is everything ends up in the product and, in principle, there is no waste(see Fig 3).

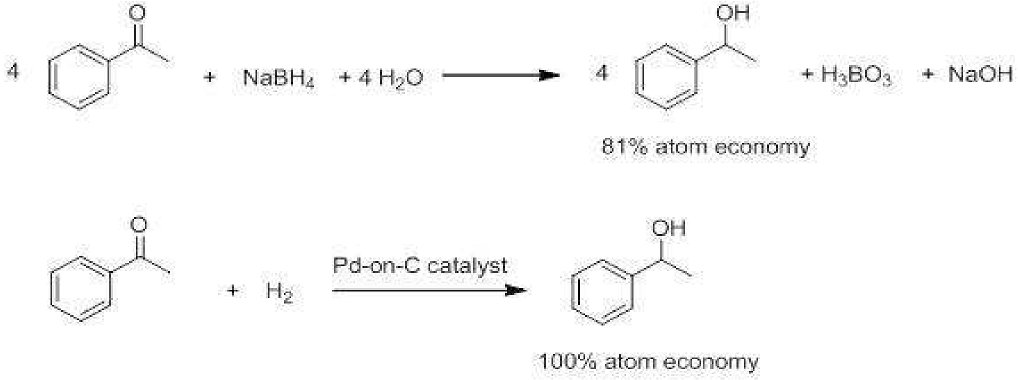


Fig 3:Atom Economy Reaction with Catalyst

Unfortunately, hydrogen does not react with ketones to any extent under normal conditions. For this, we need a catalyst such as palladium-on-charcoal. A catalyst is defined as *"a substance that changes the velocity of a reaction without itself being changed in the process"*. It lowers the activation energy of the reaction but in so doing it is not consumed. This means that in principle at least, it can be used in small amounts and be recycled indefinitely, that is it doesn't generate any waste. Moreover, molecular hydrogen is also the least expensive reductant and, for this reason, catalytic hydrogenations are widely applied in the petrochemical industry, where the use of other reductants is generally not economically viable. It is only in the last two decades, however, following the emergence of green chemistry, that catalysis has been widely applied in the pharmaceutical and fine chemical industries, with the goal of minimizing the enormous amounts of waste generated by the use of stoichiometric inorganic reagents. This involves the use of the full breadth of catalysis: heterogeneous, homogeneous, organocatalysts and, more recently, Nature's own exquisite catalysts: enzymes. The latter are particularly effective at catalyzing highly selective processes with complex substrates under mild conditions and, hence, are finding broad applications in the pharmaceutical and allied industries. Moreover, they are expected to play an important role in the transition from a chemical industry based on non-renewable fossil resources to a more sustainable bio-based economy utilizing renewable biomass as the raw material, yet another noble goal of green chemistry.[41]

H. Products design should be Biodegradable

The problem of products not being biodegradable is encountered particularly in insecticides and polymers

*I. Prevention or Minimization of Hazardous Product*s

The most important principle of green chemistry is to prevent or at least minimize the formulation of hazardous products, which may be toxic or environmentally harmful. The effect of hazardous substances if formed may be minimized for the workers by the use of protective clothing, engineering controls, respirators etc. This however, adds to the cost of production. It is found that sometimes the controls can fail and so there is much more risk involved. Green chemistry, infact, offers a scientific option to deal with such situations.

J. Designing Safer Chemicals

It is of paramount importance that the chemicals synthesized or developed (e.g. dyes, adhesives, cosmetics, pharmaceuticals etc.) should be safe to use. A typical example of an unsafe drug is thalidomide (introduced in 1961) for lessening the effects of nausea and vomiting during pregnancy (morning sickness). The children born to women taking the drug suffered birth defects. Subsequently, the use of thalidomide was banned, the drug withdrawn and strict regulation passed for testing of new drugs, particularly for malformation-including hazards. With the advancement of technology, the designing and production of safer chemicals has become possible. Chemists can now manipulate the molecular structure to achieve this goal.

*K. Strengthening of Analytical Technique*s

Analytical techniques should be so designed that they require the minimum usage of chemicals, like recycling of some unreacted reagent for the completion of a particular reaction. Further, placement of accurate sensors to monitor the generation of hazardous by-products during chemical reactions is also advantageous.

V. CONCLUSION

The growth of green chemistry over the course of the past decade needs to increase at an accelerated pace if molecular science is to meet the challenges of sustainability. It has been said that the revolution of one day becomes the new orthodoxy of the next. When the 12 Principles of Green Chemistry are simply incorporated as an integral part of everyday chemistry, there will no longer be a need for the focusing, highlighting, and moniker of green chemistry. And when that day comes, the challenges that chemistry will meet cannot be imagined.

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Structure and Bonding in Coordination Compounds

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Abstract — *Any of a class of substances with chemical structures in which a core metal atom is surrounded by nonmetal atoms or groups of atoms, known as ligands, that are chemically linked to it.*

Keywords — *Werner's Theory, Crystal Field Theory, Tetrahedral, Square Planar, Octahedral complexes.*

I. INTRODUCTION

Many metal ions aggregate with Lewis bases in solution to produce coordination compounds or complex compounds, which are stable in solution. A complex can be a positive, negative, or neutral ion. It is determined by the metal ion's charge and the donor's charge. $[Co(NH_3)_6]^{+3}$, for example, has an O.N. of +3 while NH_3 is neutral. Iron's O.N. is Fe^{2+}, while the cyanide ion (CN^-) is mono negative. The O.N. of copper is +2 and the glycinate ion is mono negative in $[Cu(H_2NCH_2OO–)_2]$ Chemical species with autonomous existence, such as Co+3, Fe3+, Cu2+, NH3 CN–, etc., are used to make complex compounds. Complexes are chemical compounds that comprise a metal ion that is surrounded by Lewis bases and retains its identity in solution.

II. COORDINATION NUMBER

The coordination number of a metal ion is the number of ligands that surround it. In the event that the number of coordinating centres in polydentate ligands determine the number of coordination Ethylene, for example. A bidentate ligand, diamine, satisfies two coordination position. The most often encountered coordination numbers are 4 and 6.

TABLE I

Complex	*Coordination Number*
$[Ag(NH_3)_2]^+$	2
$[Cu(NH_3)_4]^{2+}$	4
$[Fe(CN)_6]^{4+}$	6
$[CoCl4]^{2+}$	4

III. WERNER'S COORDINATION THEORY

Alfred Werner in the year 1866 – 1919, a Swiss chemist, conducted the first systematic study of coordination chemicals. Werner also used ammonia to make a variety of coloured complexes of Fe^{2+}, Co^{+3}, Ni^{2+}, Pt^{2+}, Pt^{+4}, and other metals. Ammines were and still are metal–ammonia compounds. Co(III) chloride generates a variety of color-changing compounds with NH_3. The following are a few of them:

TABLE II

Complex	*Color*
$CoCl_3.6NH_3$	Yellowish Orange
$CoCl_3.5NH_3$	Purple
$CoCl_3.4NH_3$	Green (trans)

$CoCl_3.4NH_3$	Violet (cis)
$CoCl_3.5NH_3.H_2O$	Red
$CoCl_3.3NH_3$	Blue-Green

Werner proposed the theory based on the following experiments:

A. Complexes reactions

Silver nitrate solution was used to react with cobalt amines. It demonstrates that all chloride ions in $CoCl_3.6NH_3$ are similar. However, there are two types of chlorides in $CoCl_3.5NH_3$ and $CoCl_3.4NH_3$. One kind is comparable to that found in NaCl and precipitates as AgCl, while the other is tightly bound to Co^{+3} and does not.

B. Conductance measurement

The ions present in solutions could be determined using conductance measurements. The electrical conductance of a solution increases as the amount of ions in the solution increases. The conductivities of several complexes with the same conc were compared as a result. It told you how many ions were in each complex and how many of them were present. It was investigated for a number of complexes. The following are some of the findings:

TABLE III

Complex	*No. of ions*	*Conductance*
$CoCl_3.6NH_3$	4	Decreases
$CoCl_3.5NH_3$	3	
$CoCl_3.4NH_3$	2	
$PtCl_4.6NH_3$	5	
$PtCl_4.5NH_3$	4	
$PtCl_4.4NH_3$	3	
$PtCl_4.3NH_3$	2	
$PtCl_4.2NH_3$	0	

From the above observations Werner devised a technique for building coordination complexes. He proposed that it is necessary to keep a complex unit in the square bracket and grs ionizable in the outside bracket. As a result, the aforementioned complexes can be written as, [Complex unit] Ionizable grs.

C. Analysis of isomer

Isomers of coordination compounds, or molecules having the same chemical makeup but distinct structural formulae, are common. Isomerism occurs in a variety of ways in coordination molecules. Some of the more prevalent varieties are listed below.

Isomerism in the cis-trans position

The main difference between cis-trans (geometric) isomers of coordination compounds is how the ligands are placed spatially; for example, in the isomeric pair of diaminedichloroplatinum compounds (Fig.1).

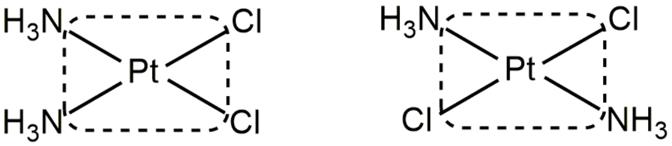

Fig.1 Isomeric Pair of diaminedichloroplatinum

In one isomer, the cis (Latin for "on this side") isomer, the two ammonia molecules and two chlorine atoms are next to each other, whereas in the other, the trans (Latin for "on the other side") isomer, they are across from each other (Fig.2). The cis and trans versions of the tetraamminedichlorocobalt (1+) ion have a similar relationship:

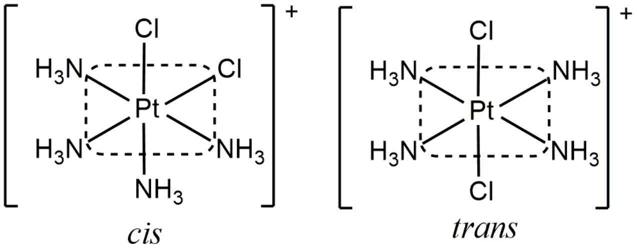

Fig.2 Cis- and Trans-Isomeric Pair of tetramminedichlorocobalt

Diastereomers and enantiomers

Optical isomers (also known as enantiomers) can rotate plane-polarized light in different directions. When the molecules of a substance are mirror images but not superimposable on one another, they are called enantiomers. Enantiomers can form in coordination compounds due to the presence of an asymmetric ligand, such as one isomer of the amino acid alanine (aminopropionic acid),

Familiar examples of the latter variety are octahedral complexes carrying three didentate ligands, such as ethylenediamine, $NH_2CH_2CH_2NH_2$. The two enantiomers corresponding to such a complex are depicted by the structures below (Fig.3).

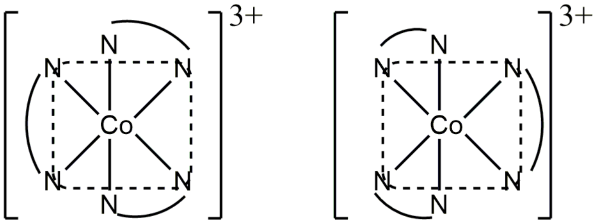

Fig.3 Enantiomeric Pair

IV. Bonding in Coordination Compounds

A. Crystal Field Theory

According to crystal field theory, the electric field produced by ligands can break d or f orbital degeneracy, stabilising the complex.

Key Points

- Due to the static electric field, d- or f-subshell degeneracy is broken when the ligands approach the core metal ion.
- Because electrons resist one other, the d electrons closest to the ligands will have a higher energy than those further away, dividing the d orbitals.

- The stability that follows from ligand binding is known as the crystal field stabilisation energy (CFSE).

The Crystal Field Theory (CFT) is a model for transition metal and ligand bonding interactions. It depicts the impact of the ligand's non-bonding electrons being attracted by the positive charge of the metal cation and the negative charge of the metal cation. Due to the static electric field produced by a surrounding charge distribution, the degeneracy of electronic orbital states, commonly d or f orbitals, is broken as the ligands approach the core metal ion. CFT is able to account for various magnetic characteristics, hues, and hydration energies of transition metal complexes, but it fails to account for bonding.

Due to repulsion between like charges, the electrons in the d orbitals of the core metal ion and those in the ligand repel each other. As a result, the d electrons closest to the ligands will have a larger energy than those further away, dividing the energy of the d orbitals.

Except for the dz2 orbital, which has two opposed lobes and a doughnut of electron density in the centre, all d orbitals have four lobes of electron density. The d orbitals can be further subdivided into two groups. All of the $dx^2–y^2$ and dz^2 points are parallel to the x, y, and z axes. They make up an eg set. The lobes of the dxy, dxz, and dyz, on the other hand, all line up in the quadrants, with no electron density on the axes. The t_2g set is made up of these three orbitals. The d orbitals are usually degenerate, but they can split at times, with the eg and t_2g subsets having differing energies. This is explained by the CFT.

The crystal field stabilization energy (CFSE) is the stability that results from placing a transition metal ion in the crystal field generated by a set of ligands. It arises due to the fact that when the d orbitals are split in a ligand field, some of them become lower in energy than before. For example, in the case of an octahedron, the t_{2g} set becomes lower in energy. As a result, if there are any electrons occupying these orbitals, the metal ion is more stable in the ligand field by the amount known as the CFSE. Conversely, the e_g orbitals are higher in energy. So, putting electrons in them reduces the amount of CFSE.

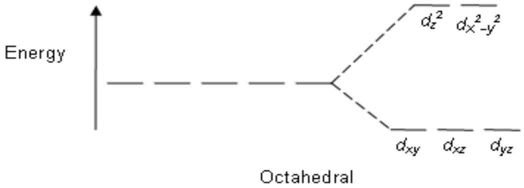

Fig.4 Octahedral CFT Splitting: Electron diagram for octahedral d shell splitting

Transition-metal complexes of all geometries can benefit from crystal field stabilisation. The high amount of crystal field stabilisation that this geometry produces with this number of electrons is why many d8 complexes are square-planar (Fig.4a).

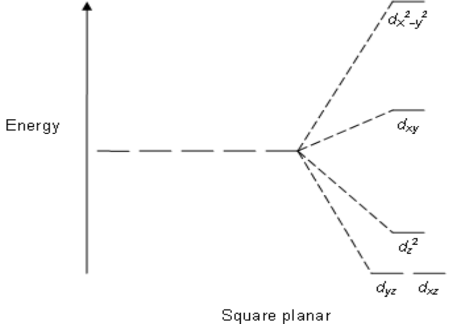

Fig.4a Square Planar CFT Splitting: Electron diagram for Square Planar d subshell splitting

B. Octahedral Complexes

Six ligands are symmetrically placed around a central atom in octahedral complexes, defining the vertices of an octahedron. The shape of compounds with six atoms or groups of atoms or ligands symmetrically grouped around a central atom is referred to as octahedral molecular geometry. The prefix octa- refers to the octahedron's eight faces. Molybdenum hexacarbonyl ($Mo(CO)_6$) is an example of an octahedral compound.

Chemists use the term octahedral loosely, concentrating on the geometry of the bonds to the central atom rather than distinctions among the ligands themselves. For example, $[Co(NH_3)_6]^{3+}$ is referred to as octahedral despite the fact that it is not octahedral in the mathematical sense due to the orientation of the N-H bonds (Fig.5).

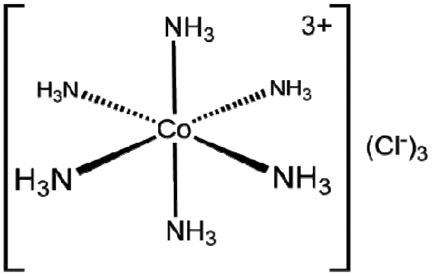

Fig.5 Hexamminecobalt(III)chloride: Examples of an octahedral coordination complex

Isomers can form when two or more types of ligands are coupled to an octahedral metal core. For an octahedral compound with six distinct ligands, the number of potential isomers can reach 30. (in contrast, only two stereoisomers are possible for a tetrahedral complex with four different ligands).

The d orbitals of a free ion, such as gaseous Ni^{2+} or Mo, are degenerate. This degeneracy is lifted in an octahedral compound. The ligand-targeting proteins dz^2 and dx^2y^2 (also known as the eg set) are destabilized. On the other hand, the energy of the dxz, dxy, and dyz orbitals (the so-called t_2g set) decreases.

Given the large range of octahedral complexes available, it's no surprise that a wide range of reactions have been described. The following are the different types of reactions:

- Reactions between ligands (via a variety of mechanisms)
- Protonation and ligand addition reactions (among many others)
- Reverse reactions (in which electrons are gained or lost)
- Rearrangements in which the ligands' relative stereochemistry changes inside the coordination sphere.

Many reactions of octahedral transition metal complexes occur in water. For example, $[Co(NH_3)_5Cl]^{2+}$ slowly equates to give $[Co(NH_3)_5(H_2O)]^{3+}$ in water, especially in the presence of acid or base.

C. Tetrahedral and Square Planar Complexes

A central atom with four substituents exists in both tetrahedral and square planar complexes.

- A central atom is placed at the centre of four substituents that create the corners of a tetrahedron in tetrahedral molecular geometry.
- Tetrahedral geometry is frequent in complexes containing metals with electron configurations of d^0 or d^{10}.
- The dx^2y^2 and dz^2 orbitals are equally low in energy on the CFT diagram for tetrahedral complexes because they are between the ligand axis and suffer little repulsion.
- A centre atom is surrounded by constituent atoms that form the corners of a square on the same plane in square planar molecular geometry.

- For transition metal complexes with the d8 configuration, the square planar geometry is common.
- Although octahedral complexes can be used to create the CFT diagram for square planar complexes, the dx^2-y^2 level is the most destabilised and is left empty..

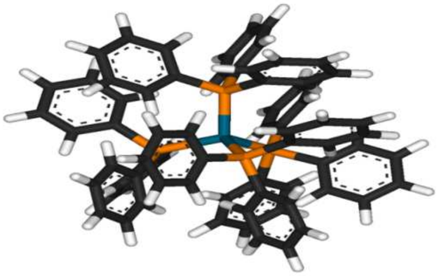

Fig.5a Tetrakis(triphenylphosphine)palladium: 3-dimensional representation of tetrahedral Tetrakis(triphenylphosphine)palladium Chloride

D. Tetrahedral Complexes

A central atom is placed at the centre of four substituent atoms that form the corners of a tetrahedron in tetrahedral molecular geometry. When all four substituents are the same, the bond angles are around 109.5°. This shape is common, especially in complexes with metals in the d^0 or d^{10} electron configuration.

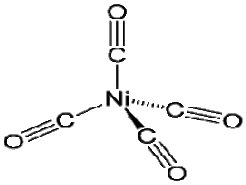

Fig.6 Nickel carbonyl: 2-dimentional representation of tetrahedral nickel carbonyl

Tetrahedral materials include tetrakis(triphenylphosphine)palladium(0), a common catalyst, and nickel carbonyl, a nickel purification intermediate. Many complexes with partially filled d-subshells are also tetrahedral, such as the iron(II), cobalt(II), and nickel tetrahalides (II).

Tetrahedral complexes have ligands in every position that an octahedral complex lacks. As a result, a tetrahedral complex's crystal field splitting diagram is the polar opposite of an octahedral diagram. Because they are located between the ligand axis and experience negligible repulsion, the dx2dy2 and dz2 orbitals should be equally low in energy. The dxy,dyz, and dxz axes, on the other hand, lay right on top of where the ligands go. This increases repulsion while also increasing energy levels.

E. Square Planar Complexes

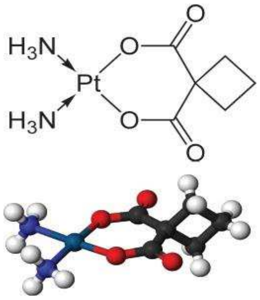

Fig.7 Carboplatin: 2 and 3-dimentional representations of the anti-cancer drug carboplatin

A central atom is surrounded by constituent atoms that form the corners of a square on the same plane in square planar molecular geometry. Transition metal complexes with a d^8 configuration are prone to this shape. Rh(I), Ir(I), Pd(II), Pt(II), and Au are examples of this (III). Cisplatin $[PtCl_2(NH_3)_2]$ and carboplatin are two anticancer medicines that come to mind.

In theory, flattening a tetrahedron can result in square planar geometry. As a result, the interconversion of tetrahedral and square planar geometries provides a route for tetrahedral compounds to be isomerized. Tetrahedral nickel(II) complexes, such as $NiBr_2(PPh_3)_2$, for example, undergo this reversible transition.

The removal of a pair of ligands from the z-axis of an octahedron leaves four ligands in the x-y plane. Therefore, the crystal field splitting diagram for square planar geometry can be derived from the octahedral diagram. The removal of the two ligands stabilizes the d_{z2} level, leaving the d_{x2}-y_2 level as the most destabilized. Consequently, the d_{x2}-y_2 remains unoccupied in complexes of metals with the d^8 configuration. These compounds typically have sixteen valence electrons (eight from ligands, eight from the metal)

Color

The absorption of light causes d-d or change band electron transitions in transition metal complexes, which colour them.

Points to Remember

- Because the d orbitals are not involved in bonding, the colours of metal complexes derive from them.
- If the centre of symmetry is disturbed in a complex, d-d electron transitions are enabled, resulting in a vibronic transition.
- Electrons can be promoted from a metal-based orbital into an empty ligand-based orbital using Metal-to- Ligand Charge Transfer (MLCT).
- An electron can go from a ligand-dominated orbital to a metal-dominated orbital (Ligand-to-Metal Charge Transfer or LMCT). The absorption of complementary colours produces a coordination complex colour.

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Green Chemistry and Environmental Sustainability

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Abstract— *Green chemistry incorporates a new approach to the synthesis, processing and application of chemical substances to reduce threats to health and environment. Today everyone are profoundly interested in the sustainability of the world. Few principles for green chemistry have been laid down to understand environmental sustainability. This article presents selected examples of implementation of green chemistry principles in everyday life in industry, laboratory and in education. A brief note on the principles of green chemistry and future challenges are also mentioned.*

Keywords—*atom economy, green catalyst, green chemistry, solvent, sustainability.*

I. INTRODUCTION

Green chemistry[1,2,3,4] is a new term introduced by Paul T Anastan and John C. Warner from the United States Environmental Protection Agency in 1991. It involves the use of chemicals and design of chemical processes and products which are less harmful to the environment and living beings. Green chemistry involves the use of chemistry for pollution prevention. Sustainability means meeting the needs of the present generation without compromising the needs of future generations. It means preventing pollution before it happens rather than cleaning the mess later. Developments in chemistry also bring new environmental problems and harmful unexpected side effects which result in the need for greener chemical products. Example pesticide DDT. Green chemistry involves preventing pollution on a molecular scale. Chemistry plays a prominent role in our daily lives. New developments in chemistry bring out new environmental problems. Hence the need for greener chemical products is required. Green chemistry involves environmentally friendly chemical processes. We have many renewable and non renewable resources. Due to over utilization of non-renewable resources, renewable resources are being depleted at an unsustainable rate. We must make best use of these without changing the environmental balance.

Today chemical industries use large amounts of chemicals like acids, alkalis, solvents, reagents etc in the manufacture of various products in pharmaceutical industries, food technology, polymer industries, etc. During this process large amounts of byproducts and other harmful substances are produced which cause pollution and affect the environment. Hence there is a need to minimize pollution caused by these chemicals. Environmental chemistry is the study of the effect of pollution on nature whereas green chemistry is the study of steps involved to reduce pollution.

Some of the incidents causing great loss to humans and the environment have to be minimized. Cuyahoga river incident in Ohio, United States in 1969 which caught fire due to pollution which was out of control made environmentalists think and hence the clean water act was passed. Bhopal gas tragedy in India in 1984 released methyl isocyanate killing 4,000 people. Seveso disaster in Italy in 1976 released a toxin poison 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) which killed 30,000 from animals and pets and another 70,000 animals had to be killed to stop dioxin from getting into the food chain. This resulted in long term health problems for many local residents. The pollution prevention act was passed by US environmental law stating that the first choice for preventing pollution is to design industrial processes that do not lead to waste production. This is the approach of green chemistry. Green chemistry promises to lower overall costs associated with environmental health and safety.

Green chemistry involves twelve principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products. These twelve principles are briefly described below:

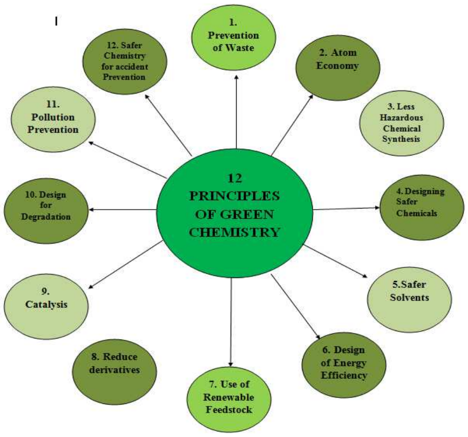

Figure 1: Twelve Principles of Green Chemistry

1. Prevention of waste

It is better to prevent waste than to treat or clean up waste after it is formed thus obeying the old saying “Prevention is better than cure”. Manufacturing processes are so designed either not to produce waste products or they are produced such that they can be recycled or biodegradable. The first step to prevent pollution is the ability of chemists to redesign chemical transformations to minimize the generation of hazardous waste. Glycerin which is produced as a waste from biodiesel production is converted into propylene glycol which is cheap and can even replace ethylene glycol which is a toxic and primary ingredient in automobile antifreeze. This was done by Grubb in his metathesis reaction which involves exchanging the groups attached to double bonds of alkenes which are catalyzed by Grubb"s catalyst. By this method we can reduce hazardous waste. This method of synthesis is a great step in the pharmaceutical and chemical industries.

2. Atom economy

This principle states that it is better to use all the atoms in the process. Methods should be synthesized which maximize the incorporation of all materials used in the process into final products in a more efficient way.

$$\%\ \text{Atom economy} = \frac{\text{Relative molecular mass of desired products}}{\text{Relative molecular mass of all reactants}} \times 100$$

Greater the atom economy [5], less is the waste. The chemical reactions should be designed to get maximum efficiency and yield and minimize the waste. Eg Diels-Alder reaction which involves 100% atom economy.

3. Chemical synthesis with less hazardous products

The aim is to reduce the hazard of the chemicals that are used to make a product. New practicable synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and environment. Now-a-days less hazardous chemicals and reagents are used in the process of making products. Some toxic chemicals are replaced by safer ones. For example, chlorofluorocarbons which contribute to ozone depletion and global warming are replaced by Carbon Dioxide in the manufacture of polystyrene foam sheet packing material.

4. Designing safer chemicals

This principle aims at designing products that are safe and non-toxic. For example chlorine gas which was used for bleaching of paper is now replaced by hydrogen peroxide. Disinfection of water by chlorination kills the pathogens but at the same time forms harmful chlorinated compounds. Therefore another oxidant like ozone is used. Replacing tetraethyl lead with lead free gasoline which is less toxic is preferred. Properties of supercritical Carbon Dioxide make it an effective solvent.

5. Safer solvents

Unnecessary use of solvents by chemists should be avoided. Organic solvents [6] should be replaced by aqueous solvents in chemical manufacturing. We should search for alternate solvents like ionic liquids [7&8] and supercritical fluids [9]. Moreover ionic liquids are nonvolatile and have no vapor pressure Processes involving reduction or elimination of solvents in reaction medium, separation or purification is preferred. If possible, we should encourage dry reactions. For example, tetrachloroethene (C_2Cl_2) which is used as a solvent for dry cleaning contaminates groundwater and is carcinogenic. This is now replaced by liquid Carbon Dioxide which is less harmful to groundwater. Because of the low toxicity and non-inflammability of supercritical Carbon Dioxide fluid, it is used as an industrial solvent in chemical separation. New foam called pyrocool FEF has now been invented to put out fires effectively without producing toxic substances found in other fire fighting materials. Even in the biodiesel production, during the transesterification process, supercritical methanol is used at high temperatures and pressures in a continuous process. In this supercritical state oil and methanol are in a single phase, hence reaction occurs spontaneously and rapidly. Hence use of safer green solvents should be encouraged.

6. Design for energy efficiency

This principle focuses on creating products and materials in a highly efficient manner. Synthetic methods should be conducted at ambient temperature and pressure wherever possible. Processes involving use of renewable energy and energy conservation should be encouraged. Traditional methods of generating energy leading to global warming and other environmental problems should be avoided. Nowadays commercial photochemical processes like synthesis of caprolactam and vitamin D3 are done. Even the use of ionic liquids at ambient conditions works as an excellent solvent. Supercritical carbon dioxide is a boon to chemists. It is a fluid state of carbon dioxide above its critical temperature and pressure. It is less toxic. It acts as a very important solvent especially during extraction.

7. Use of renewable feedstocks

A raw material or feedstock should be renewable rather than depleting where ever technically and economically practical. This principle aims at producing products from renewable materials. For example plastic polylactic acid which is made from renewable feedstocks such as corn and potato waste. Benzene is replaced by glucose in the synthesis of adipic acid [10] used in the manufacture of various polymers [11]. Moreover these reactions are out in water. Levulinic acid which is used as a platform for the synthesis of various chemicals is prepared from paper mill sludge, agricultural residues and waste wood.

8. Reduce derivatives

Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible because such steps require additional reagents and can generate more waste. Moreover the overall yield and atom economy also decreases. reactions involving microwave radiations should be encouraged. These radiations are non-ionizing and do not alter the molecular structure during heating. Reactions involving ultrasonic radiations should also be encouraged.

9. Catalysis

Catalysts are generally used in a chemical process to make a reaction more efficient and reduce energy requirements. A green catalyst is generally preferred as it has high reaction rates, readily regenerated and recycled with low toxicity. For example enzymes or whole cell organisms. These are naturally occurring and water soluble. Nowadays, zeolites and phase transfer catalysts like crown ethers are having more industrial applications.

10. Design for degradable products

This principle aims at designing chemical products so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products. Example sulfonated detergents, chlorofluorocarbons, DDT and plastics do not degrade easily. Hence their manufacture from renewable resources should be preferred so that they can be recycled and reused.

11. Pollution prevention

Real time monitoring and control during synthesis and minimizing or eliminating byproducts helps in prevention of pollution or atleast its control.

12. Safer chemistry for accident prevention:

We should design chemicals to minimize the potential for chemical accidents including releases, explosions and fires. Chemists should try to avoid these chemicals that explode light on fire, air sensitive, etc. Chemical industry accidents should be avoided. There are many incidents where safe chemicals were not used resulting in disasters. One of the most devastating disaster is that of Bhopal, India in 1984 where a poisonous gas leaked from a union carbide factory killing thousands instantly and injuring many more. Thus while creating products, it is better to avoid highly reactive chemicals which have a potential to result in accidents.

CONCLUSIONS

Green chemistry is not a new branch of science but a different method of approaching chemistry which can save energy, minimize resource depletion with minimum global changes, address many food supply issues and reduce the release of non-toxics into the environment. We can deal with green chemistry by changing our mind set and applying the concepts in classrooms, laboratories, manufacturing units and finally the surrounding environment. Government and scientific communities throughout the world are recognizing green chemistry and its applications. There are numerous scholarships and grants offered by the government for researchers and young scholars who are nurturing the goals of green chemistry.

Finally by following these twelve principles let us create a world where the environment doesn’t need any protection.

ACKNOWLEDGEMENTS

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Application of Schiff Bases as Optical Chemical Sensors

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Abstract : *The synthesis, characterization, and activity of Schiff base is an important area of research due to its diversified applications in biology, catalysis, and sensing from its discovery by Hugo Schiff in 1864. A Schiff base is a nitrogen analog of an aldehyde or ketone in which the C=O group is replaced by the C=N-R group. Schiff bases are broadly used as strongly absorbing and colorful chromophores; they are employed as versatile tools in different sensor applications such as fluorescent turn-on/turn-off sensors for the selective determination of cations and anions. In recent years, Schiff base based sensor probes has been developed for the detection of various toxic compounds and imaging of various ions/substances in biological systems in the design of chemosensors. This review focuses on a series of Schiff bases that are used as sensors for metallic cations and anions in environmental and biological applications.*

Keywords— *Schiff base, Chemosensors, Fluorescent, Environmental, Chromophores.*

I. INTRODUCTION:

For health and environmental applications, the need for precise and sensitive identification of pollutant species is in high demand. The threat to human health and the environment due to the discharge of cations and anionic contaminants as a result of industrial and developmental operations. Metal ions are detected using flame atomic absorption spectroscopy, inductively coupled plasma optical emission spectroscopy, stripping voltammetry, X-ray fluorescence spectrometry, and inductively coupled plasma mass spectrometry, but these methods are not accessible to the average person due to low sensitivity or user-unfriendliness. As a result of the constraints, many optical chemosensors have been invented and developed to overcome them. Thus, Schiff base-based structures work exceptionally well in the detection of metal ions. Researchers have been paying close attention to Schiff base ligands due to their ease of use[1].

Schiff bases are generally known as imines or azomethines and act as ligands in several metal complexes. They are formed as condensation products from primary amines and aldehydes or ketones. On the other hand, aldehydes react faster than ketones in condensation reactions due to steric and electronic effects[2]. Several investigations have shown that Schiff bases may be employed as extremely efficient and selective sensing materials for a variety of ion sensors, including optical, electrochemical, and membrane sensors. Due to the unique size of the ion, the electronic configuration of both the ligand and the metal, the charge on the metal ion, the hard-soft acid-base nature of both the metal and donor atom from the Schiff base, and the size of the Schiff base's cavity, these structures exhibited selectivity towards specific metal ions over others, depending on the type of Schiff base[3]. In this article, various Schiff bases have been reviewed as sensing constituents for the finding of metal ions in environmental matrices like water. This chapter provides deep insights into the optical sensors developed from Schiff bases for the resolution of cations, anions and also covers altered Schiff base-based optical sensors for the identification of metallic species in aqueous systems.

II. SCHIFF BASES AS IONIC SENSORS:

Schiff bases have been effectively used to determine a variety of metal ions. For the generation of sensing signals, chemical interactions between Schiff bases and metal ions are crucial[4]. Chemosensors are divided into three types based on the nature of the signal emitted by the detecting materials: colorimetric sensors, fluorogenic sensors, and electrochemical sensors. The sensing signal is produced in Schiff base-based chemosensors by changes in their electronic properties caused by different charge transfer processes. Schiff bases have mostly been investigated as optical metal ion sensors to date. The interactions between metal ions and Schiff bases have a strong influence on the signals of these sensors. Fluorescence resonance charge transfer, excimer-exciplex formation, fluorescence resonance energy transfer, excited-state intra molecular proton transfer, and photoinduced electron transfer, for example, all exaggerate the signals of the fluorescent sensor. Similarly, the detecting signals of an electrochemical sensor are dependent on the redox potential shift[5].

III. DETECTION OF TRIVALENT CATIONS:

The trivalent cation Al^{3+} is the most abundant in nature. If these cations are present in excess, they can contaminate water and have harmful effects on humans. Another trivalent cation that can pollute the environment is Cr^{3+}. Cr^{3+} deficiency in humans can cause problems with glucose and lipid metabolism. In general, altering quantities of these chemicals in humans can have a major impact on the body's regular operations.To avoid any injury, timely and reliable detection of these cations in various fluids is required[6].

In the human body, trivalent cations are engaged in a number of biological activities (e.g., cell functions).

Detection of Aluminium:

Aluminum is the third most common metallic element on the planet.Al^{3+} can also be found in natural water and can be ingested through food and drinking water. The presence of Al^{3+} in excess of the permissible limit might disrupt pulmonary systems and may cause unrecognized health risks such as Alzheimer's and Parkinson's disease, renal failure, and bone softening. Many researchers sought simple, fast, sensitive, and selective detection methods because of the concerns associated with the presence of Al^{3+} beyond the required limit in environmental and biological systems. For example, the Schiff base 7-methoxychromone-3-carbaldehyde-(indole-2-formyl) hydrazone was employed as a selective fluorescent and colorimetric chemosensor for Al^{3+} ion in an ethanol system[7].

The Schiff base (E)-1-((2-aminophenylimino)methyl)naphthalen-2-ol is also very selective for 200 the analysis of Al^{3+} when tested in the presence of water and other metal ions, e.g., Cr^{3+}, Fe^{3+}, Hg^{2+}, and Ag^{+}. Al^{3+} interacted with both the imine group and the oxygen of the antipyrine moiety to form stable complexes with the Schiff base, resulting in a fluorescence switch on[8].

Detection of Iron:

Iron is a crucial component of blood hemoglobin, which transports oxygen to cells and tissues. It can also function as a cofactor in a variety of enzymatic electron transfer and oxidation reactions, as well as DNA synthesis and normal central nervous system function. Iron is required for appropriate myelination in the brain. Iron can induce conjunctivitis, choroiditis, and retinitis if it is absorbed in excess and stays in the tissue. Iron deficiency can also result in a lack of oxygen in the cells (resulting in anemia), a reduction in bodily immunity, and a drop in blood pressure. The interaction of Fe^{3+} with the Z isomer of a Schiff base can result in an enrichment of the Schiff base's structural stiffness and fluorescence[9].

Detection of Chromium:

Chromium has an impact on the metabolism of proteins, carbohydrates, fats, and nucleic acids, among other things. A chromium deficiency can increase the risk of diabetes and cause cardiovascular disease. Furthermore, too much chromium in the body can change the structure and functions of cells. The most common type of chromium released by humans is hexavalent, which is designated as a human carcinogen by numerous agencies. The solubility and oxidation state of chromium dictate the degree of its dangers, which range from low toxicity trivalent metal (e.g., Cr^{3+}) to extremely toxic hexavalent form. In well-lit of such recognitions, a Schiff base derived from 6-aminocoumarin and thiophene-2- carboxaldehyde, i.e., (6E)-6-((thiophene-2-yl)-2H-chromen-2-one, was used for the identification of Cr^{3+} in methanol[10]. Schiff bases 2,3-dimethyl-4-(3-oxo-1,3-diphenylpropylideneamino)-1-phenyl-1,2-dihydropyrazol-5-one (derived from condensation of 4-amino antipyrine and benzil) and 2,3-dimethyl-4-(2-oxo-1,2-diphenylethylideneamino)-1-phenyl-1,2-dihydro pyrazol-5-one (derived from 4-amino antipyrine and 1,3-diphenyl propane-1,3-dione) were synthesized and tested as chemosensors for the determination of Cr^{3+}.

IV. DETECTION OF DIVALENT CATIONS:

Detection of copper

Copper is the third most abundant transition metal found in the human body. Copper participates in various reactions in the human body such as initiating formation of hemoglobin and participation in the usage of iron by the body. A deficiency of copper in the human body can cause heart disease. In contrast, if present in excess levels, it can cause Alzheimer's, Menkes, Parkinson's, and Wilson's diseases[11]. These adverse effects of copper make its detection both in vivo and in the environment critical. The Cu^{2+} exhibited photochromism and fluorescent switching effects (i.e., a reduction in fluorescence intensity) in a few Schiff bases, e.g., 1-(3,5- dimethyl-4-isoxazolyl)-2-{2-methyl-5-[4-hydroxyl-3-(N-butyl-4-hydrazino-1,8-naphthal imide)- phenyl]-3-Thienyl}perfluorocyclopentene.

Detection of Mercury:

Mercury has adverse effects on the environment as well as on human health due to its toxic nature. Excessive exposure to mercury and its derivatives can cause serious heart problems, brain dysfunction, kidney diseases, and diseases associated with the central nervous system. These effects of mercury have helped focus efforts on developing a specific, sensitive, and cost-effective sensor. Schiff bases are promising candidates to develop mercury sensors. An acenaptho[1,2-b]quinoxaline-based thiosemicarbazone displayed aggregation-induced emission enhancement (AIEE) properties for the detection of Hg^{2+} with an "on-off' fluorescent response[12].

Detection of Cobalt:

Cobalt is a trace element found in the human body and is a component of vitamin B12, which aids in iron metabolism and haemoglobin formation. Cobalt levels beyond the allowed limit can cause vasodilation, flushing, cardiomyopathy, significant kidney issues, and respiratory/central nervous system abnormalities[13]. The absence of cobalt in the human body, on the other hand, can result in issues such as growth retardation, anaemia, and weight loss. For the creation of efficient sensors that detect cobalt cations, a variety of Schiff bases have been investigated. For example, in the range of 398 8.0×10^{-7} to 2×10^{-6}, Schiff base 2-((4-(2-hydroxybenzylideneamino) phenylimino) methyl) phenol was used to sense Co^{2+} ions with a DL 0.782 M in ethanol[14].[DL is Detection Limit].

Detection of Nickel:

Nickel is a poisonous and carcinogenic metal. It has the potential to harm the respiratory system, kidneys, and liver, as well as lower body immunity. The optical measurement of Ni^{2+} was also done using Schiff bases. For example, 4-chloro-2-[(3-(4-(dimethylamino)phenyl) allylidene)amino] Schiff base was made by condensing 2-amino-4-chlorophenol and 4-dimethyl aminocinnamaldehyde and was employed as a selective and effective colorimetric Ni^{2+} sensor. For the spectrophotometric measurement of Ni^{2+} from natural food samples, another chromogenic Sch iff base, N,N'-bis(3-methylsalicylidene)-ortho-phenylenediamine, was reported[15,16].

V. DETECTION OF OTHER CATIONS:

Detection of lead:

Lead can induce mental retardation in children, as well as headaches, poor attention, memory loss, dullness, and irritability when discovered in high amounts in the body. Schiff's home base 4-((E)-4-hydroxy By reacting 5,5'- methylenebis(2-hydroxybenzaldehyde) and 2-aminoethanethiol in ethanol, -3-((E)-(2-mercaptoethylimino) methyl) benzyl)-2-((E)-(2-mercaptoethylimino)methyl)phenol was created for lead detection. A fluorescent chemical, 2-hydroxy-1-napthaldehydene-8-aminoquinoline, was synthesized[17] and converted into a sol-gel for the selective identification of lead over a linear detection range of 1.9×10^{-7} to 1.9×10^{-4} M with a DL of 0.083 M.

Detection of Palladium:

Pd^{2+} can bind with proteins, RNA, and DNA, making it cytotoxic and the cause of skin and eye irritation. Schiff base 1,3-(benzo[d]thiol-2-yl)-7- hydroxy-2H-chromen-2-one was synthesized from 2,4-dihydroxy benzaldehyde, O- aminothiophenol, ethylcyanoacetate , and benzoic acid in DMF and was used for naked eye-based color change (e.g., from colorless to sienna) detection of Pd^{2+} with a DL of 29 μM.

Detection of Cadmium:

Cadmium is used in the manufacturing of rechargeable batteries, fertilizers, coloring agents, and electroplating. Renal failure, calcium metabolism abnormalities, and an increased risk of cancer have all been linked to Cadmium exposure. Another study found that persistent Cd^{2+} exposure can impair respiratory function while also lowering olfactory function and bone mineral density. The Schiff base cinnamaldehyde-4-hydoroxybenzoylhydrazone has been created for the selective detection of Cd^{2+} from biological and environmental samples by complexation with a yellow colour[18].

Detection of Manganese:

Regardless of the fact that manganese has also been classified as having low acute toxicity in humans, animals given high amounts of manganese salts in diet have shown neurotoxic consequences. High manganese consumption may cause anaemia due to iron sequestration. A slane-type Schiff base was produced by condensation of ethyl-O-hydroxybenzene with ethylene diamine and ethylenesalicylidine-bisethylenediamine for spectrophotometric detection of Mn^{2+} in pharmaceutical products[19].

VI. DETECTION OF ANIONS:

Only a few Schiff base detectors were produced for anion identification, while many of the receptors synthesised were employed for cation detection. This is discussed in terms of anions' various qualities. Anions are bigger than cations, and the resulting compounds are less stable. The existence of a large number of lone pairs of electrons causes considerable repulsion because different anions have different geometries. As a result, they are well hydrated and maintain a restricted pH range. The majority of the processes used to detect anion species were based on sequential detection, such as the production of metal complexes of a Schiff base, followed by anions, hydrogen bonding, and induced charge transfer. In this section, we'll look at fluorescence and chemosensor techniques that have been developed for use in the field[20].

Detection of Cyanide:

Despite of its capacity to bind to Fe in cytochrome c-oxidase, cyanide is very toxic as it disrupts electron transport. Even with its toxicity, cyanide is widely employed in chemical industries such as fiber and polymer manufacturing, gold mining, and electroplating. Sensors are required to detect the presence of cyanide in extremely low concentrations in order to control the amount of cyanide in environmental samples. Color shifts from yellow to reddish orange were used to test the chemosensor 4-((2,4-dichlorophenyl)diazenyl)-2-(3-hydroxypropylimino) methyl)phenol for CN^- detection. At pH = 7.0, Schiff base N,N'-bis(2-hydroxy-4-diethylamino-1-formylbenzene) had a better DL of 0.15 M and was utilized to identify CN^- in the environment by successive displacement of Cu^{2+} from Schiff base Cu^{2+} complexes[21,22].

Detection of Fluoride:

Despite significant advancements in the population's oral health, there are still issues. Fluoridation of water can result in higher fluoride concentrations, greater the chances of unattractive dental fluorosis. As a result, research on detecting fluoride in the environment using a simple sensor probe is still ongoing. Schiff base f or the colorimetric and turn-on fluorescence detection of F^-, 1-((1H-indol-3-yl) methylene)-2-(4-nitrophenyl) hydrazine was produced. The stoichiometry and binding constant between the metal and the Schiff base were estimated. In the presence of this ion, the Schiff base changed colour from yellow to purple, regardless of the presence of other anions and cations. The charge transfer caused by fluoride between the electrons could be the cause of the spectrum shift[23].

Detection of Phosphate:

The condensation of 3- amino-1-propanol and 1-(3-formyl-4-hydroxyphenylazo)-2,4-dichlorobenzene in ethanol yielded the Schiff base, 4-((2,4-dichloro phenyl)diazenyl)-2-(3-hydroxypropylimino) methyl)phenol for the detection of $H_2PO_4^-$ in the presence of other ions. The phenolic OH functioned as a binding site for anions, causing $H_2PO_4^-$ with a DL of 1.24 M to change colour from yellow to orange[24].

Different methods for the analysis of cations and anions using a variety of Schiff bases were discussed in this chapter. The literature shows that some cations are well detected with one particular Schiff base as opposed to others when the analysis is made using a particular technique. In this subsection, the performance of Schiff bases for sensing diverse metals is discussed, examined various ways for analyzing cations and anions utilizing a range of Schiff bases. For the detection of Al^{3+}, (3, 5-dichloro-2-hydroxybenzylidene) quinolone-2-carbohydrazide using fluorescence spectroscopy was seen to be most sensitive with a DL of 12 nM[25]. In the case of Fe^{3+}, a 4'- hydroxy-3'-{[(2-phenyl-1, 3-thiazol-4-yl)imino]methyl}biphenyl-4-carbo nitrile-based fluorescence spectroscopy technique exhibited the best DL of 109 nM from the five discussed Schiff bases. For the detection of Hg^{2+}, fluorescence spectroscopy and colorimetry were applied using a Schiff base made by condensation of 1, 10-phenanthroline-2, 9-dicarbaldehyde with 1H-indole-2-carbohydrazide out of the three discussed Schiff bases[26]. Fluorescent gold nanoclusters were synthesized and used for the detection of Fe^{3+} with a DL of 0.2 μM by fluorescence quenching[27].

Pb^{2+} driven DNA molecular devices based on a DNA duplex-quadruplex exchange with a DL of 20 nM were created for selective and sensitive detection of Pb^{2+}. This was utilized to detect Pb^{2+} by turning on the fluorescence. Gold nanoparticles functionalized with a dithiocarbamate-modified N-benzyl-4-(pyridin-4-ylmethyl)aniline ligand[28] were utilized to colorimetrically detect Cr^{3+} in an aqueous solution with a DL of 31 ppb; the ligand changed colour from wine red to blue when complexed with Cr^{3+}.

Due to their strong chelating nature, Schiff base has a wide range of applications outside of sensing, including antifungal, anti-inflammatory, anti-oxidant, and anti-cancer compounds. Antibacterial agents, excellent catalysts, and effective medications in the realm of pharmacology[29] have all been discovered to be beneficial in transition-metal complexes of Schiff bases. In comparison to non-Schiff bases, Schiff bases are straightforward to synthesize with high purity products, according to all known evidence[30].

VII. CONCLUSION:

As discussed in this work, Schiff base ligands are useful in a wide range of applications. Schiff bases used as chelating agents are useful in sensing and detecting different ions using a variety of analytical techniques (such as UV-Vis and spectrofluorometry), are discussed. Toxic and poisonous ions can be rapidly identified by demonstrating fluorescence turn-on or turn-off processes when complexed with Schiff base ligands under UV light or by looking at them with the naked eye. Schiff bases have great sensitivity for certain ions in various types of matrices, according to a comparative analysis of sensitivity. Under the same conditions, a single Schiff base can be utilized as a sensor for many ions. Many studies have been conducted employing a Schiff base as optical sensors to detect harmful substances in the environment and biological samples. Among the different recognition alternatives, online detection is a difficult problem that should be addressed. This can be accomplished by designing chemosensor-based electronics probes and connecting the signals with the internet to allow for real-time online mapping of various environmental samples. This will aid in the early detection of pollution and related problems, allowing appropriate control measures to be implemented at the appropriate moment. Schiff bases can also be used to speciate hazardous metal ions such as Cr(III)/Cr (VI). As a result, Schiff base plays a significant role in a variety of industries, including optical sensors and photonics.

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CATALYSIS AND ELIMINATION OF POLLUTANTS

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Abstract — *Environmental pollution is becoming a serious threat to human society, and photocatalysis is recognized as an environmentally benign technology to remediate organic pollutants from aqueous environment. Mainstream research related to pollutant remediation and energy production is based on heterogeneous photocatalysis, a modified advanced oxidation process. This chapter will be a guiding path to understand the photocatalytic process and mechanism for the deterioration of heavy metals, persistent organic pollutants and pathogens from wastewater. Environmental remediation is of crucial importance in the context of human sustainability in the present and future times. The unplanned anthropogenic activities and revolutionary industrialization end up in environmental contamination with noxious organic-inorganic and biogenic pollutants. The photocatalytic disinfection and detoxification is the only solution to preserve and restore the ecological balance.*

Keywords— *Pollution, photocatalysis, heavy metals, ecological*

I. INTRODUCTION

The term “Pollution” can be defined in many ways. It has been recognized for some time now that most of the pollution is with respect to air, water and soil which are the most essential ingredients for life in this earth. It has also been recognized that the present day pollution that we generally conceive is mainly generated by the anxiety of human beings for their comfort. It is no doubt that the pollution has to be completely avoided if that were not to be possible, at least it should be reduced considerably. Each pollutant that has been introduced in the surroundings has its own health risk profile, which makes summarizing all relevant information into a single unit difficult. That is why we have decided to make a series of presentations on various manifestations of this topic. Nevertheless, public health practitioners and decision makers in developing countries need to be aware of the potential health risks caused by air and water pollution and to know where to find the more detailed information required to handle a specific situation. With this objective in mind we have attempted in this compilation some of the aspects of pollution and its control. The presentations are based on some perception that sector wise the problem of pollution can and may be controlled. However this is not the only methodology one has to adopt.

The strategy for automobile exhaust control has been evolved in the form of the catalytic converter. The challenges in this converter are concerned with dealing with opposing oxidation (of carbon monoxide and hydrocarbons) and reduction reaction. Introduction to Pollution Control Strategies (reduction of NOx to N_2) simultaneously and under varying experimental conditions of high space velocity, temperature and lean and rich Air/fuel ratio. Though three way catalyst as a concept has been introduced to carry out all these three reactions (also metal traps if the fuel used were to contain metallic impurities) there are still challenges to be faced in terms of high cost of the noble metal catalysts employed, the operational difficulties that are introduced by the inclusion of a catalytic converter.

Scientists, in their anxiety to popularize their innovations and discoveries, have been pushing hard their achievements too strongly, without much consideration to the after effects that will follow in the years to come. This has been true in each of the scientific discoveries that we have exploited in the last few decades. This has become obvious in the seventies when the Pharmaceutical industry has to find ways and means to make new drugs and medicines for human suffering in ways and means hitherto unknown. This has resulted in new diseases and disorders which were hitherto unknown or at least not detected extensively.

Environmental pollution is mainly the result of many processes and chemical reactions that are being practiced in chemical industries for manufacture of commodities and also due to indiscriminate use of energy sources. It is therefore necessary to understand the unit operations of these chemical industries. The proper understanding of the various unit operations of these chemical industries may provide us with some conceptual framework to combat the pollution of the environment.

Human beings in their anxiety to present themselves with simple easy to adopt solutions to the issues with respect to comfortable living have come up with some possibly undesirable solutions that are not naturally degradable and hence leave some non-degradable marks in nature and this aspect has been addressed at various stages but no viable solution has been found yet meeting the human desire for low cost, simple and elegant methodology.

1.2. What is Catalysis?

Catalysis is the process of modifying a chemical reaction with the use of a catalyst. This process only works with chemicals that have an existing reaction, and it is used to accelerate the reaction for commercial purposes. Catalysis occurs faster than a standard chemical reaction because catalysts require less activation energy, which is the minimum level of energy necessary to initiate a chemical reaction.

1.2.1. Catalysis Working Principle

When a chemical is placed with a compatible catalyst, there is a reduction in the free energy required for the chemical to reach the transition state for that particular reaction. Catalysts can influence the reaction environment, depending on the specific reaction requirements.

For example, catalysts can produce more heat, form specific intermediates that are not created naturally, bind the reagents to polarize bonds or cause the dissociation of reactions back to their reactive forms.

1.2.2. Types of Catalysts

There are two main types of catalysts used for catalysis; heterogeneous or homogeneous. A heterogeneous catalyst has molecules that are not in the same phase as the reactants, whereas a homogeneous catalyst’s molecules are in the same phase as the reactants.

1.3. What is Wastewater Treatment?

Wastewater treatment is the process of converting wastewater – water that is no longer needed or is no longer suitable for use – into bilge water that can be discharged back into the environment. It’s formed by a number of activities including bathing, washing, using the toilet, and rainwater runoff. Wastewater is full of contaminants including bacteria, chemicals and other toxins. Its treatment aims at reducing the contaminants to acceptable levels to make the water safe for discharge back into the environment.

There are two wastewater treatment plants namely chemical or physical treatment plant, and biological wastewater treatment plant.

"Wastewater treatment is a process to convert wastewater – which is water no longer needed or suitable for its most recent use – into an effluent that can be either returned to the water cycle with minimal environmental issues or reused. The latter is called water reclamation and implies avoidance of disposal by use of treated wastewater effluent for various purposes."

Step by Step Wastewater Treatment Process

The following is a step by step process of how wastewater is treated:

1.3.1. Wastewater Collection

This is the first step in the wastewater treatment process. Collection systems are put in place by municipal administration, home owners as well as business owners to ensure that all the wastewater is collected and directed to a central point.

1.3.2. Odor Control

At the treatment plant, odor control is very important. Wastewater contains a lot of dirty substances that cause a foul smell over time.

1.3.3. Screening

This is the next step in the wastewater treatment process. Screening involves the removal of large objects for example nappies, cotton buds, plastics, diapers, rags, sanitary items, nappies, face wipes, broken bottles or bottle tops that in one way or another may damage the equipment.

1.3.4. Primary Treatment

This process involves the separation of macrobiotic solid matter from the wastewater. Primary treatment is done by pouring the wastewater into big tanks for the solid matter to settle at the surface of the tanks.

1.3.5. Secondary Treatment

Also known as the activated sludge process, the secondary treatment stage involves adding seed sludge to the wastewater to ensure that it is broken down further.

1.3.6. Bio-solids handling

The solid matter that settle out after the primary and secondary treatment stages are directed to digesters. The digesters are heated at room temperature.

1.3.7. Tertiary treatment

This stage is similar to the one used by drinking water treatment plants which clean raw water for drinking purposes.

1.3.8. Disinfection

After the primary treatment stage and the secondary treatment process, there are still some diseases causing organisms in the remaining treated wastewater.

1.3.9. Sludge Treatment

The sludge that is produced and collected during the primary and secondary treatment processes requires concentration and thickening to enable further processing. Treatment flexibility.

- Mineralization of parent and intermediate contaminants.
- The final efficiency of wastewater treatment.
- Recycling capacity and potential use of treated water.
- Cost-effectiveness and eco-friendliness.

1.4. Photocatalysis

Photocatalysis presents an alternative to physical adsorption methods in indoor air pollution abatement [1]. The common photocatalysts are primarily metal oxides or sulphides, i.e., TiO_2, ZnO, ZrO_2, SnO_2, WO_3, CeO_2, Fe_2O_3, Al_2O_3, ZnS and CdS [2]. Because of its superior photocatalytic activity, chemical stability, low cost and nontoxicity, TiO_2 has been extensively studied as a photocatalyst [3-5]. The organic and inorganic pollutants in the indoor air such as formaldehyde, acetaldehyde, benzene, toluene, acetone, ammonia and NOx can all be photo-oxidized into CO_2, H_2O and mineral acids on TiO_2 or other photocatalysts [6–9]. Bacteria in the indoor air can also be removed by photocatalytic decomposition [10], which is also important for indoor air purification [11]. Because TiO_2 is only active upon UV excitation, there has been much effort to develop second-generation TiO_2 photocatalysts that can be operated not only under UV but also visible light irradiation [12,13]. Various techniques have been employed to enable it to operate under visible light irradiation. These techniques include surface modification via organic materials and semiconductor coupling, band gap modification by creating oxygen vacancies, and by doping with nonmetals or co-doping with nonmetals and metals [14]. VOCs and bacteria can be photodegraded under visible light irradiation on Fe-TiO_2 [15], N-TiO_2 [16], C-TiO_2 [17,18], CuxO/TiO_2 [19], TiO_2 hybridized with graphite-like carbon [20] and so on. Air-cleaning devices based on photocatalysts require an additional light source. Besides use in air-cleaning devices, indoor wall paint with second-generation TiO_2 photocatalysts have been used for air cleaning under indoor daylight or artificial light [21]. Additionally, the generation of relatively stable reaction intermediates (such as the formation of benzaldehyde, benzoic acid and benzyl alcohol during the photocatalytic oxidation of toluene) may lower the removal rate and even stop the reaction through blocking active sites [22-23].

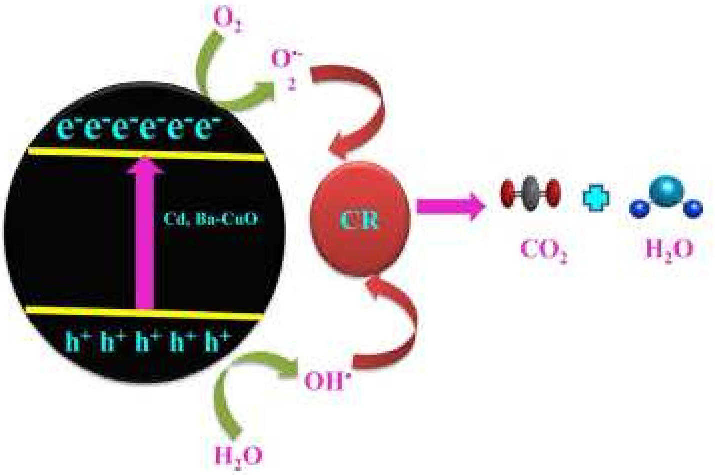
1.4.1. Basic Principles, Mechanism, and Challenges of Photocatalysis

The main and short mechanism of AOPs can be explained as follows:

- Initially, the light energy fall on the surface of a catalyst, the valence band electrons are agitated and move to the conduction band. Holes would be left in the valence band of the catalyst. These holes in the valence band can oxidize donor molecules and react with water molecules to generate hydroxyl radicals

(The hydroxyl radicals have strong oxidizing power responsible for the degradation of pollutants).

- The oxidative reaction of these radicals with organic compounds in the water producing biodegradable intermediates.
- The reaction of biodegradable intermediates with oxidants is referred to as mineralization (i.e., production of water, carbon dioxide, and inorganic ions).



1.4.2. Operating and Affecting Parameters of Photocatalysis

The rate of photo mineralization of an organic compound by photocatalysis method primarily depends on the following parameters: structure, shape, size, and surface area of the catalyst, reaction temperature, pH, light intensity, amount of catalyst, and concentration of wastewater.

1.4.3. Major Advantages of Photocatalysis

The advantages of this photocatalytic technology are as follows (i) Photocatalysis offers a good replacement for the energy-intensive conventional treatment methods (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins) with the capacity for using renewable and pollution-free solar energy. (ii) Photocatalysis leads to the formation of harmless products, unlike conventional treatment measures which transfer pollutants from one phase to another. (iii) The photocatalytic process can be used in the destruction of a variety of hazardous compounds in different wastewater streams. (iv) The reaction conditions for photocatalysis are mild, the reaction time is modest and a lesser chemical input is required. (v) Minimal of secondary waste generation and (vi) It can be applied to hydrogen generation, gaseous phase, and aqueous treatments as well for solid (soil) phase treatments to some extent. Limitations of Photocatalysis The photocatalytic activity depends on the following limitations.

- interfacial charge transfer
- improve the charge separation and
- inhibition of charge carrier recombination. These are essential for enhancing the efficiency of the photocatalytic process.

1.5. Semiconductor Photocatalyst and Its Challenges

Several aspects should be aimed in future research of environmental catalysis for the abatement of major pollutants in air and water. 1) Environment-friendly catalysts have attracted much attention to develop. 2) Significant efforts should be made for the activity and durability of catalysts, and dealing with catalyst fouling for long-term successful treatment. 3) For the selectivity of pollutants transformation to harmfulness should be more concerned by adjusting heterogeneous catalytic processes. 4) Further efforts at materials design or reactor design for pilot- and demonstration-scales. In addition, work is also needed to couple catalytic processes with other treated technologies.

1.6. Methods of Improving Photocatalytic Activity

- Composite System
- Metal Ion Dopants
- Nonmetal Doping
- Dye Sensitization
- Codoping
- Surface modification

1.7. Summary

In this chapter, we concluded that the basic theory of photocatalysis, mechanism, and its advantages clearly indicated that photocatalysis is the simply powerful emerging and promising technology that holds a number of applications in environmental systems which are effectively utilized for the industrial applications including wastewater treatment, hydrogen generation, air purification, antibacterial activity, and so on. Photocatalysts have several advantages, but however an ideal photocatalyst should be inexpensive, nontoxic, long-term stability, easily reproducible on separation, and also has a highly effective photocatalytic activity.

Most wastewater treatment plants treat wastewater from homes and business places. Industrial plant, refineries and manufacturing plants wastewater is usually treated at the onsite facilities. These facilities are designed to ensure that the wastewater is treated before it can be released to the local environment. Some of the water is used for cooling the machines within the plants and treated again. They try to ensure that nothing is lost. It is illegal for disposing untreated wastewater into rivers, lakes, oceans or into the environment and if found culpable one can be prosecuted.

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A Review on the Extraction of Collagen from Fish Waste and its Applications

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Abstract — *Abstract- Collagen, a well-known protein regarded as one of the most useful biomaterials and has wide biomedical applications due to its biocompatibility and biological characteristics. It is the principal structural protein present in the skin, tendon and bones of the vertebrate body. Different types of vertebrate collagens have been identified of which the dominant collagen is Type – I. Collagen is the most studied protein with a wide range of applications including pharmaceutical, biomedical, cosmetics, leather and film industries due to its special characteristics that are high biocompatibility, good bioactivity, and weak antigenicity. The present review article deals with a brief description on the extraction of collagen from fish waste. The extracted collagen is characterized by UV- visible and it's applications on antioxidant and antimicrobial activities.*

Keywords*:* *Collagen, Fish skin, Fish scale, UV-vis spectrum, Applications.*

INTRODUCTION

Collagen is the most abundant protein found in all living organisms. Bones, skins, muscles, hairs of human beings are rich in protein. Collagen can be collected in numerous ways and one of the methods is extraction of collagen from the fish waste. The fish processing industries produces a lot of fish waste such as skin, bones, scales and fins which make up 70% of fish [1]. There are different types of collagens which can be collected of various parts of fish waste. Type I and type V are collected from bones and type II and type XI are collected from cartilage [2]. This review article is to find out various methods used for the extraction of the collagen, techniques used for the characterization and application of fish collagen in our daily life. The importance of fish collagen in our life is increasing day by day. Fish collagens have a lot of applications such as on the field of cosmetology, pharmaceuticals, biomedical films, leather industry etc… this review consists of original article from the time period 2015-2021.

A. Extraction characterization and application of fish collagen.

Samantaray US *et al*. carried out quantitative analysis of nutrition and biochemical evaluation in *Bramidae* fish. It can be used in children's growth and development as well as their heart health [3]. Capati *et al*. studied biological scaffold due to Total Anti-oxidant Capacity *in vitro* on osteoblastic cell. The proliferation and differentiation of typical preofleoblast, MC3T3-E1 cells were investigated using a microarray analysis. It can be used in clinical applications [4].

B. Collagen from whole fish.

Vakkachan A P *et al*. discovered microbial and enzymatic processing from fish waste. In this process, the characterizations performed by using functional screening methodologies for the purpose are still based on activities in non- specific substrates [5]. Husin N F *et al*. found out comparison of microbial growth on fish waste like *European pilchard* and *Atlantic mackerel*. Hydrolysis process played important roles in producing peptone with high protein content. It has the potential to replace existing commercial peptone for microbial growth [6].Kumar S *et al*.

extracted chitin from different sources and studied the IR spectroscopy and scanning electron microscopy and FTIR. Its degree of de-acetylation was determined [7].

C. Collagen from Fish Skin

Bhuimbar MV *et al*. distinguished an extraction of acid soluble collagen the skin of black ruff. SDS-PAGE, UV, FT-IR and SEM analysis confirmed that extracted collagen is native type. This collagen was used for the preparation of collagen- chitosan film which could be used for food packing process [8]. Arumugam *et al*. prepared collagen from *Solea solea* skin waste. SEM (Scanning Electron Microscope) was used to analyse the structure of the extracted collagen. The effect of acetic acid, NaCl solid ratio and time on the extraction of collagen was synthesis One Variable at A Time (OVAT) method using the solution removed cheesecloth [9].Elango *et al*., synthesis collagen from *Selachimorpha*. The viscosity of PSC was gradually decreased in respect to temperature UV absorbance pattern of blue shark skin collagen FTIR spectra [10]. Krishnamoorthi *et al*. synthesized collagen from *Sepia Pharaonis* outer skin. FT-IR spectroscopy was used for samples. Different Scanning Calorimetry (CDSC) and ^{1}H-NMR spectra analysis was used to characterize the source of collagen in industries [11]. Ana A *et al*. characterized Marine - derived collagen extracted from Salmon and Cod Fish skins targeting its inclusion in cosmetic formulations. Chemical and physical characterizations were performed using several techniques such as sodium dodecyl sulphate - polyacrylamide gel electrophoresis (SDS- PAGE), Fourier Transformation Infra-red (FT-IR) spectroscopy rheology, circular dichroism, X-ray diffraction was performed. Thus it is used in the field of dermocosmetic field [12]. Madhuri V *et al*. developed Acid Soluble Collagen from skin of *Centrolophus niger* (Blackruff) commonly referred as Medusa. This is done with lactic acid. The yield of 45% proved to be efficient solvent. SDS-PAGE, UV visible absorbance, FT-IR and SEM analysis confirmed that extracted collagen is native type I and it is used in the development of antibacterial active food packing film [13].

D. Collagen from Fish Scale

Sathiskumar S *et al*. identified the evaluation of Antibacterial, Anti-biofilm activity of synthesized Zinc Hydroxyapatite bio composites from *Labeo rohita* scale waste. Various characterizations were carried out by XRD, FT-IR, SEM, EDX and DLS methods. The presence of zinc was confirmed by EDAX spectra, XRD, FT-IR, SEM and DLS. Zinc Hydroxyapatite biocomposites from *Labeo rohita* scale waste is useful, eco-friendly and antibacterial nature [14]. Bhagwat PK *et al*. isolated ASC (Acid Soluble Collagen) from scales of *Cyprinus Carpio*. The yield of scale remilitarization takes place and treated with EDTA solution. These were characterized by FT-IR analysis, SDS- PAGE. Also the yield of collagen is used in paneer production and for nitrogen fertilizers for plants [15]. Kothai S and Sobana Premlatha T extracted collagen and studied the characterization of collagen from fish scales. The extracted collagen characterized by UV-visible, FTIR and SDS PAGE techniques to confirm it as type I. It shows that it has been used as bio-waste and on numerous fields such as pharmaceutical, medical, biomedical food industry, cosmetics etc [16]. A study by Mufadhar M synthesized and characterized silver nanoparticles (AgNPs) using a rapid green synthesis. UV-Spectroscopy, SEM spectroscopy, EDX spectroscopy, FTIR spectroscopy and DLS were used to characterize the synthesized Silver nano particles (AgNPs). Antibacterial activities of Silver nano particles AgNPs were also evaluated [17].

II. APPLICATIONS OF COLLAGEN

A. Antioxidant Activity of Collagen

Biological oxidation is an essential process that occurs in aerobic organisms, including most animals, plants and many microorganisms. The primary function of oxidation is to provide the organisms with usable energy. However, this process may lead to the formation of reactive oxygen species (ROS) including free radicals and non-free radical species, and reactive nitrogen species (RNS) as end products [18]. High level of free radicals in the body may cause damage to the important classes of biological molecules including proteins, lipids, DNA, enzymes via peroxidation and nitration process. Lipid oxidation products have been associated with many pathophysiological conditions such as heart disease, cancer, arthritis, lung disease, fibromyalgia, diabetes, neurodegenerative diseases like Parkinson's and Alzheimer's, autoimmune diseases, and eye diseases like macular degeneration [19]. In food, lipid oxidation occurs in unsaturated fatty acids containing food such as meat, low moisture food, emulsions, oil and nuts. As a result, this process can lead to food spoilage and the generation of potentially toxic products to the consumers. Normally the body uses endogenous free radical scavenging antioxidants such as α-tocopherol and ascorbic acid, and other natural protective mechanisms for oxidation, but these alone are not enough to retard diseases that occurred due to this process. Some antioxidants including tocopherols, ascorbic acid, and flavonoids are known to be used to supplement the body's antioxidant defence, more are yet to be discovered [20]. In addition to retarding oxidation in the body and slow progress of many chronic diseases, antioxidants can also protect the food from lipid oxidation and thus extend the shelf life of fatty acids containing food [21]. Although many synthetic antioxidants such as butylated hydroxytoluene (BHT), butylated hydroxy anisole (BHA), tert-butylhydroquinone (TBHQ) or propyl gallate are generally used to prevent peroxidation process in the food industry, the substitution of these synthetic antioxidants by natural antioxidants especially from the marine source, has increased interest over a past decade due to health concerns and consumer's preferences. Recently a number of studies have demonstrated that various peptides derived from marine collagen serve as effective antioxidants for both food and animals [22].

B. Antimicrobial Activity of Collagen

The increasing problems of multiple drug resistance to bacteria and the potential health risks of synthetic antimicrobials and chemical food preservatives have led to a search for nature based source of antimicrobial peptides. Marine organisms being one the alternative source, antimicrobial peptides (AMPs) have been isolated and characterized from fishes and various marine invertebrate taxa, including *Demospongiae, Cnidaria*, *Tunicaca*, *Arthropoda* and *Mollusca* [23]. Antibacterial peptides fractions were reported from snow crab (*Chionoecetes opilio*) and Atlantic rock crab (*Cancer irroratus*) by-products with activity against Gram-negative and Gram-positive bacteria. More recently, an AMPs were identified from anchovy cooking wastewater by-product and showed activity against *S. aureus* [24].

III. CONCLUSION

Collagen is a hard, insoluble and fibrous protein that makes up one third of the protein in the human body. The future study needs to investigate the properties of marine collagen and the involvement of factors such as extraction methods based on the properties. This review article represents collagen extraction, characterizations and applications in various fields. A wide range of applications of collagens have been recognized and still many more applications according to various properties of collagen are yet to be discovered. Hence, research in the field of collagen is now going to be an important topic which will make our future life better and good.

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Chemical Profiling and *in-vitro* Antioxidant Activity of *Scoparia dulcis* (Linn.) Plant Aqueous Extract

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Abstract--*The present study aimed to evaluate the chemical composition by GC-MS analysis and Antioxidant activity using DPPH, ABTS assay of Scoparia dulcis (Linn) plant aqueous extract. Scoparia dulcis belongs to the Scrophulariaceae family it's collected from Western Ghats region of South India. Their medicinal uses are cancer, diarrhoea, diabetes, stomach-ache, hepatosis, bronchitis, fever, hypertension and ulcers. The GC-MS analysis of Scoparia dulcis plant aqueous extract revealed the presence of 33 compounds. The presence of major compound was Diethyl Phthalate (91.98%) and the minor compounds are Phthalic acid (1.77%), Lidocaine (0.35%), Eugenol (0.09%) and Eicosane (0.2%). The in-vitro antioxidant activity of Scoparia dulcis extract were studied the concentrations of 20, 40, 60, 80 and 100 µg/mL with compared at standard ascorbic acid by using DPPH, ABTS assay.*

Keywords— ***Scoparia dulcis,*** **GC-MS,** ***Antioxidant Activity, DPPH assay,*** IC_{50}

I. INTRODUCTION

Scoparia dulcis is the widely used traditional medicinal plant which belongs to the family scorphulariaceae. It is branched green color, leafy, odor taste and tough. It is commonly called as sweet broom weed, liquorice weed and it is locally named as Sarokkotthini in Tamil, Kallurukki in Malayalam, and Ghoda Tulsi, Rice Weed in other languages. [1] It is a perennial herb, which is distributed widely in tropical and subtropical Indian regions and it grows upto 1m, which is small, 3 whorled leaves, the stamens and ovary are in green color, the petioles and pedicles are in 9mm. [2] The plant has a rich sources Flavones, Terpenes, Steriods Phenols, Tannis, Saponins, Aminoacids, Coumarins and Carbohydrates of a biochemical compound. The Fresh and dried plants has been used for treating diseases. [3] It is meant famous in treating the kidney stones. The terpenoids in the herb are responsible for the medicine effects. The importance of terpenes in the biomedical field use in the insect repellants, preparation of perfumes & also in cosmetics, it has a property of antimicrobial, anti-tumour activity, anti-hyperglycemic activity, anti-inflammatory and in neuropsychological disorder treatments. [4,5] Zinc oxide nanoparticles (ZnO-NPs) are considered the most significant between the metal oxides NPs due to their unique chemical and physical properties, which hence increase their applicability aspects. [9] In addition, ZnO-NPs interweave with sunscreen and cosmetic care products due to their highly UV-adsorption properties. [11] Moreover, due to the unique properties that arise at the nanoscale structure such as high electron mobility, wide band gap and high visible transparency, ZnO NPs are considered a good semiconductor. In the textile industry, ZnO-NPs are added to finished fabrics to increase their resistance to ultraviolet rays, antibacterial and deodorant activities. [12] As a part of the applications, ZnO NPscan be used for antifungal, concrete production, solar cell, electronics, photocatalysis and electro technology industries [13,14].

Reactive oxygen species (ROS) along with free radicals are also found to play a role in functional changes associated with diseases like cancer, rheumatoid arthritis, cirrhosis etc. Exogenous chemical and endogenous metabolic processes in the human body or in the digestive system might produce highly reactive free radicals, especially oxygen derived radicals, which are capable of oxidizing biomolecules, resulting in cell death and tissue damage. [6] Cells are equipped with enzymes like superoxide dismutase, catalase and also chemicals like vitamin E, vitamin C, polyphenols, carotinoids and glutathione [7] to neutralize the damage caused by the radicals. These are endogenous antioxidants produced within the body to scavenge free radicals are not adequate to remove them fully and to maintain a balance [8]. The use of synthetic antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), Propylgallate (PG) and butylated hydroquinone have often been implicated to achieve immediate result, recent data indicates that these synthetic antioxidants could have carcinogenic effects thus fuelling an intense search for newer and efficient antioxidants. Antioxidant containing natural foods can however be used to reduce the oxidative damage. [9] Scoparia dulcis medicinal uses are cancer, diarrhea, diabetes, stomachache, hepatosis, bronchitis, fever, hypertension and ulcers [10]. The plant also exhibited antibacterial, antidiabetic, antifungal, anti-inflammatory, antiviral and hypercholesterolemic properties. [11]

The present study was carried out to investigate phytochemical constituents by using GC-MS analysis and in-vitro radical scavenging activity of *Scoparia dulcis* plant aqueous extract was evaluated using DPPH, ABTS assay.

II. MATERIALS AND METHODS

A. Plant collection

Fresh leaves of *Scoparia dulcis* were collected from the area near Pollachi, Tamilnadu, South India (geographical coordinates of Pollachi, India, latitude: 10035’12.96” N, longitude: 77014’37.37” E) between the periods of June to July 2021. The plant material was identified and authenticated by a Botanical survey of India, Coimbatore and the voucher specimens have been kept for further reference.

B. Preparation of the plant extract

5g of *Scoparia dulcis* fresh plant (Fig.1) were washed with running tap water followed by Milli-Q water and then cut, and soaked in a 250 mL Erlenmeyer flask containing 100 mL Milli-Q. The solution was boiled at 700C for 8 min. The plant extract was allowed to cool to room temperature, filtered through Whatman number-1 filter paper, and the filtrate was stored for further experimental use.

C. GC-MS Analysis

GC-MS analysis of *Scoparia dulcis* extract was performed using the Clarus 680 GC was used in the analysis employed a fused silica column, packed with Elite-5MS (5% biphenyl 95% dimethylpolysiloxane, 30 m × 0.25 mm ID × 250μm df) and the components were separated using Helium as carrier gas at a constant flow of 1 ml/min. The injector temperature was set at 260°C during the chromatographic run. The 1μL of extract sample injected into the instrument the oven temperature was as follows: 60 °C (2 min); followed by 300 °C at the rate of 10 °C min−1; and 300 °C, where it was held for 6 min. The mass detector conditions were: transfer line temperature 230 °C; ion source temperature 230 °C and ionization mode electron impact at 70 eV, a scan time 0.2 sec and scan interval of 0.1 sec. The fragments from 40 to 600 Da. The spectrums of the chemical components were compared with the database of spectrum of known components stored in the GC-MS NIST library.

Fig: 1.*Scoparia dulcis* plant

D. Antioxidant DPPH Radical Scavenging activity

The in-vitro radical scavenging activity of *Scoparia dulcis* plant aqueous extract was evaluated by using DPPH assay. Different volumes of sample extracts were made up to 40µl with DMSO and 2.96ml DPPH (0.1mM) solution was added. The reaction mixture was incubated in dark condition at room temperature for 20 min. After 20 min, the absorbance of the mixture was read at 517 nm by UV-Vis Spectrophotometer. 3ml of DPPH was taken as control.

$$\% \text{ RSA} = \frac{\text{Abs control} - \text{Abs sample}}{\text{Abs control}} \times 100$$

Where,
RSA is the Radical Scavenging Activity;
Abs control is the absorbance of DPPH radical + ethanol;
Abs sample is the absorbance of DPPH radical + sample extract.

E. ABTS•+ Decolorization Assay:

The in-vitro radical scavenging activity of *Scoparia dulcis* plant aqueous extract was evaluated by using ABTS assay. The working solution of ABTS•+ radical was made by reacting ABTS (9.5 mL, 7 mM) with potassium persulfate (245 µL, 100 mM), and raising the volume to 10 mL with distilled water. The solution was kept in the dark at room temperature for 18 h, and then diluted with potassium phosphate buffer (0.1 M, pH 7.4) to an absorbance of 0.70 (±0.02) at 734 nm. samples were prepared in methanol with different dilutions µg/mL. A sample (10 µL) was placed in a test tube and mixed thoroughly with 2.99 mL ABTS radical working solution. Absorbance of the resulting clear mixture was recorded at 734 nm.

The percent antioxidant activity of the sample was determined using the following formula:

$$\%\text{Antioxidant activity} = [(Ac - As)/Ac] \times 100$$

Where Ac and As are the absorbances of the control and sample, respectively. The control was prepared by adding 10 µL of methanol in place of the sample.

III. RESULTS AND DISCUSSION

A. GC-MS Analysis of Scoparia dulcis plant extract

The presence of Chemical constituents for *Scoparia dulcis* extract was analysed by using GC-MS that reveals the presence of 33 compounds. The major compound was Diethyl Phthalate (91.98%). The presence of minor compounds are Phthalic acid (1.77%), Lidocaine (0.35%), Eugenol (0.09%) and Eicosane (0.2%).

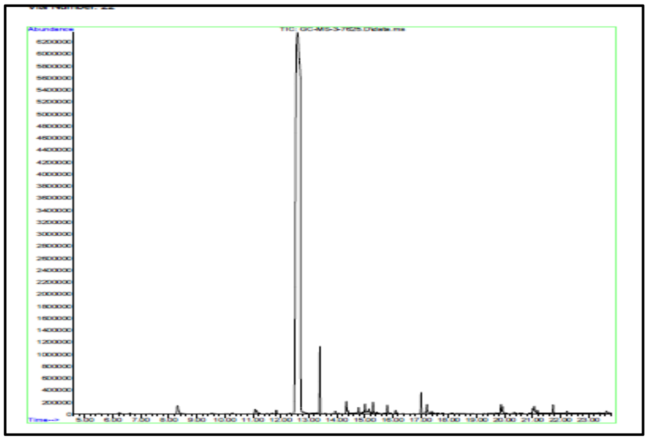

Fig.2: GC-MS Chromatogram of *Scoparia dulcis* extract.

Table - 1: Chemical Constituents Present in the *Scoparia dulcis* extract

S.No	Compound Name	Retention Time	% of the Compound
1.	Propane	6.253	0.16
2.	Butane	6.609	0.06
3.	Benzofuran	8.331	0.83
4.	2-Methoxy-4-vinylphenol	9.531	0.07
5.	Benzaldehyde	10.286	0.07
6.	4-Methoxybenzene-1,2-diol	11.086	0.27
7.	3,5-Dimethylanisole	11.164	0.23
8.	beta - D-Glucopyranose	11.686	0.09
9.	1,2-Benzenedicarboxylic acid	11.842	0.22
10.	Diethyl Phthalate	25.46	91.98
11.	Phthalic acid	13.397	1.77
12.	4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	13.963	0.13
13.	6-Methoxy-2-benzoxazolinone	14.363	0.70
14.	Bicyclo [3.1.1] heptane	14.786	0.19
15.	1,2-Benzenedicarboxylic acid	15.008	0.30
16.	D-Galactose	15.097	0.05
17.	D-Gluconic acid	15.152	0.08
18.	Lidocaine	15.297	0.35
19.	1H-Cycloprop[e]azulene	15.430	0.06
20.	n- Hexadecanoic acid	15.819	0.36
21.	Phenol	16.108	0.23
22.	Isophytol	17.019	0.63
23.	9,12,15-Octadecatrienoic acid	17.230	0.59
24.	Octadecanoic acid	17.396	0.11
25.	Ethyl 9,12,15-octadecatrienoate	17.452	0.05
26.	Hexadecanoic acid	19.874	0.14
27.	1,4,5,7-Tetramethyl-furo[3,4-d]pyridazine	19.929	0.23
28.	Eugenol	20.363	0.09
29.	9,12-Octadecadienoic acid (Z, Z)	21.007	0.22
30.	9,12,15-Octadecatrienoic acid	21.063	0.40
31.	Octadecanoic acid	21.185	0.16
32.	Squalene	21.740	0.30
33.	Eicosane	45.891	0.2

B. in-vitro Antioxidant Activity of Scoparia dulcis Extract

The *in-vitro* antioxidant efficiency of *Scoparia dulcis* extract were performed by DPPH and ABTS scavenging radical activity assay's with IC_{50} values of 66.19µg/mL and 68.91µg/ mL with the concentrations of 20, 40, 60, 80 and 100 µg/mL respectively. Ascorbic acid was used as a standard with IC_{50} values of 13.8 µg/mL and 33.4 µg/mL. It showed a concentration dependent antiradical activity given in the table 2 and table 3 respectively. The percentage inhibitions of the *Scoparia dulcis* extract were shown in fig 3 and fig 4. From the results the *Scoparia dulcis* extract showed significant antioxidant potential which may due the presence of terpenes.

Table - 2: Antioxidant activity of *Scoparia dulcis* extract by DPPH assay

S.No	Concentration (µg/ml)	% of Zone of Inhibition	
		Scoparia dulcis	Ascorbic acid
1.	20	14.2	78.1
2.	40	28.7	84.3
3.	60	44.8	87.4
4.	80	58.7	93.2
5.	100	78.9	95.6
6.	**IC50 (µg/mL)**	**66.19 µg/mL**	**13.8 µg/mL**

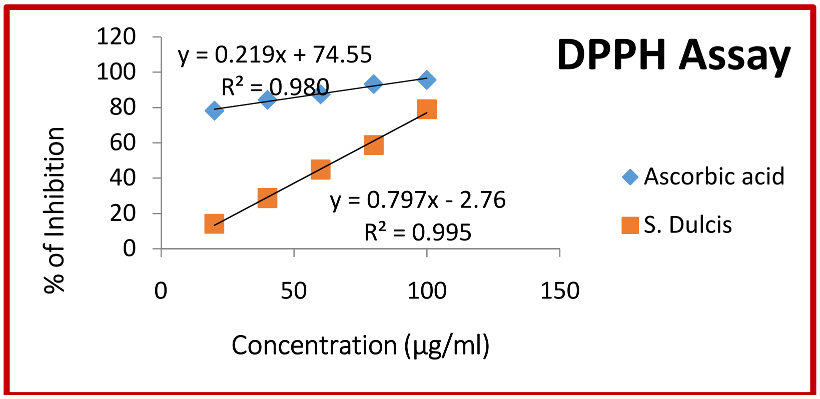

Fig.3: Antioxidant activity of *Scoparia dulcis* plant extract by DPPH assay

Table - 3: Antioxidant activity of *Scoparia dulcis* extract by ABTS assay

S.No	Concentration (µg/ml)	% of Zone of Inhibition	
		Scoparia dulcis	Ascorbic acid
1.	20	18.9	32.3
2.	40	25.4	58.5
3.	60	41.7	78.3
4.	80	59.8	89.4
5.	100	72.6	94.2
6.	**IC50 (µg/mL)**	**68.91 µg/mL**	**33.4 µg/mL**

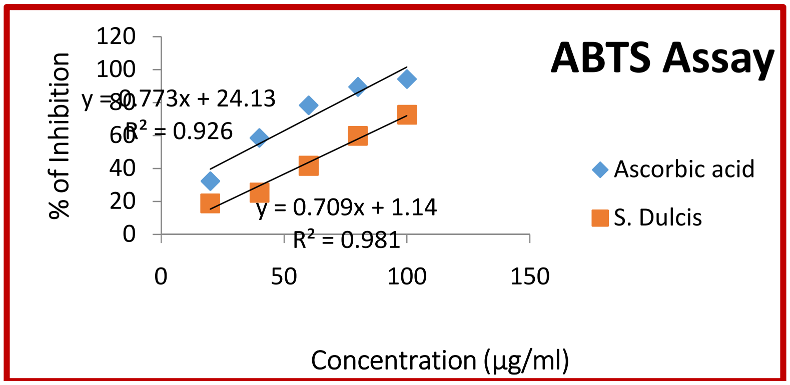

Fig.4: Antioxidant activity of *Scoparia dulcis* plant extract by ABTS assay

IV. CONCLUSION

The chemical composition of *Scoparia dulcis* (Linn) plant extract was analyzed by GC/MS method. A total of 33 components were identified. The presence of chemical constituents was in the climatic condition and soil nature of the area. The in vitro antioxidant activity of *Scoparia dulcis* (Linn) plant extract was tested. The *S.dulcis* showed a concentration dependent activity with IC50 value of 66.19µg/mL for DPPH assay and 68.91µg/mL for ABTS assay. From the results of the DPPH assay and ABTS assay of extract showed significant in vitro antioxidant property

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Studies on the Cellulolytic Microorganisms and their Application on Recycling of Organic Wastes from Pollachi Taluk

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Abstract — *The micro-organisms involved in the possibility of converting organic waste available such as leaf litters, biomasses, and waste into nutrient-rich manure by the environment-friendly method. In this present study locally available six samples were used for biodegradation namely Neem, Vaaagai, paddy straw, sugarcane bagasse, Mixed sample (Neem, Vaagai, Paddy straw, Sugarcane bagasse) and Mixed sample without inoculum. Microorganisms break organic materials into compost. The essential elements required by the composting microorganisms are carbon, nitrogen, oxygen and moisture. The composting process converts much of the biodegradable component to gaseous carbon dioxide. The decomposition process was enhanced by the presence of an aerobic bacterial population. Pseudomonas and Cellulomonas sp. were considered to be the microflora responsible for the reduction of these biomasses.*

Keywords— *Organic wastes, Pseudomonas sp, Cellulomonas sp, recycling*

I. INTRODUCTION

"Agriculture is the mother of all industry and the maintenance of human life" The great significance of agriculture in the country, life and economy is well borne out by the fact that it is the main study of the people as about 70% are dependent on land for their living (1). Agricultural operations produce a variety of waste by-products, and producers are often faced with the challenge of finding economical, environmentally-friendly ways of managing waste. Composting is one technique that is seen by many as a viable approach to agricultural waste management. Composted products are easier to handle than raw wastes, are effective soil conditioners, and can be sold for profit. Composting also helps reduce nuisance odours, groundwater pollution and the spread of pathogens (2). Composting has become a very popular option for the recycling of organic solid waste (3). Unlike, industrial waste, which is produced from clearly identified point sources, and is regulated by government agencies, solid waste is generated by everyone. Further, due to increasing population pressure on the land and over increasing loads of waste generated every minute of the day (4). The only way in which solid waste can be managed is to find ways and means of utilizing such waste at household level and by very simple technology (5).

Intensive use of chemical fertilizer could result in deterioration of food quality, destruction of natural soil fertility, pollute ground and surface water. To solve the problem of impact of fertilizers and toxicity of pesticides, there arise bio-composting which is potential manure. The microorganisms were found to be quality components in the degradation of raw wastes (6).

Biodegradation is the process of converting all biodegradable into organic manure. In the composting process certain input should be made into waste to convert the process in a short time (3). The major input in the composting process is microbial inoculant for composting. The microbial inoculant contains microbial consortia with different microorganisms targeting different substrates. The promising microbes are *Pleurotus, Trichoderma*, *Bacillus*, *Pseudomonas* and *cellulomonas*. It is largely a microbiological and biochemical process based upon the activities of several bacteria, actinomycetes, and fungi. The by-products are carbon dioxide, water and heat (6).

The nutrient value of composts varies widely, depending upon the nature of the feedstock composted. If the initial material contains grass clippings, weeds, or manure, it will be richer in nitrogen and other nutrients than if it contains mainly straw, litter, dirt or corn stalks (7). Aerobic composting is a dynamic process in which the work is done by combined activities of a wide succession of mixed bacterial, actinomycetes, fungal, and other biological populations (6).

In the present study locally available substrates like Sugarcane bagasse, Neem leaves, Vaagai leaves and Paddy straw were used for the bio degradation of organic wastes. This is solid waste treatment, recycling nutrients in hygienic way by using microbes. Further, to study the nutrient availability and enzyme activity in the composted material.

II. MATERIALS AND METHODS

A. *Source of sample*

Agricultural wastes were collected in polythene bag from in and around of Pollachi taluk. Agricultural waste is the mixture of straw and waste part of trees (such as Neem, Vaagai, Paddy straw, Sugarcane bagasse, a mixed sample of vaagai, paddy straw and sugarcane bagasse, etc).

B. *Isolation of bacteria*

Serial dilution technique (8) was used for the isolation of bacteria from soil. For isolation of effective cellulolytic bacteria, samples (soil) were collected from in and around of pollachi taluk where waste materials from relevant area of pollachi, were collected. The samples were taken from 10-15 cm depth with sterile spoons and collected in sterile polythene bags which were transported to the laboratory and stored at 4°C until used.

C. *Identification of isolated bacteria*

The isolated bacteria with strong cellulolytic property were purified according to the procedure described by Pečiulytė, (9). In this method, single colony was inoculated into an autoclaved test tube containing filter paper and distilled water and incubated at 37°C for 15 days. Cellulolytic bacterial strain degraded filter paper in compare to control tube (without bacteria). Finally, the isolated and purified cellulolytic bacterial strains, designated as R1 and R2 were identified by means of morphological examination, cultural studies and biochemical characterization according to the methods of Buchanon and Gibbons (10).

D. *Biodegradation parameter study*

pH and electroconductivity change of treated agricultural wastes were observed . Water holding capacity was measured using the procedure of Skipnes et al., 2007. Nitrogen was estimated by the method of Micro Kjeldal (11). Total phosphorous was estimated by the colorimetric method (12). Potassium was estimated by using Flame photometry (13) and carbon estimation by walkely and rapid titration method (11).

E. *Estimation of Enzymes*

Amylase, Cellulase , Dehydrogenase and Acid phosphatase were estimated according to the methods described by Considine (14) and Grunda (15).

III. RESULTS

Identification of R1 and R2

By comparing the results of morphological, physiological, and biochemical characteristics with literature (16-18), the isolated R1 and R2 were identified as *Pseudomonas sp* and *Cellulomonas sp.* (Plate-1.1 and 1.2)

There are six samples were taken for further all studies. Namely Neem, Vaagai, Paddy straw, Sugarcane bagasse, Mixed Sample (Neem, Vaagai, Paddy straw, Sugarcane bagasse) and Mixed sample without innoculum. There were two organisms *Cellulomonas* (Plate 1.1) and

Pseudomonas (Plate 1.2) are added for efficient degradation. Samples were taken for analysis of all the work.

Water Holding Capacity:

Samples were taken for analysis of water holding capacity. Water holding capacity was measured after 45 days of the entire six samples. Mixed sample having high amount of water holding capacity (58%) (Table 1). Whereas 45% of Water holding capacity seen in the mixed sample without innoculum (Table 1).

Determination of pH and Electrical Conductivity (E.C.)

The pH of different samples is calculated. The samples are incubated for 2 hrs and the pH value was determined. After biodegradation (ABD) the samples pH value were different from before biodegradation (BBD) samples value. Mainly the samples contain increase in pH value. Mixed sample pH value is high as 7.1(Table 1). Mixed sample uninoculated pH value is low as 6.0 (Table 1). Before biodegradation samples containing low amount of E.C. value. After biodegradation the E.C. value was in increase amount. The comparison of 6 samples mixed sample containing E.C. value 2.01microsimens /cm (Table 1). Mixed sample uninoculated containing low amount of E.C. value as 0.62microsimens/cm (Table 1).

Estimation of organic Carbon, Nitrogen, Phosphorous and Potassium

Samples were taken for analysis of organic carbon, nitrogen, phosphours and potassium. After biodegradation the organic carbon value was decreased compared to before biodegradation. The comparison of 6 samples neem leaves containing low amount of organic carbon value 21.3% (Table 2). Mixed sample uninoculated containing high amount of organic carbon value 27.4% (Table 2). After biodegradation the nitrogen value was increased compared to before biodegradation. Mixed sample containing high amount of nitrogen value 1.40% (Table 2). Mixed sample uninoculated containing low amount of nitrogen 1.02% (Table 2). After biodegradation the phosphorus value was increased compared to before biodegradation. Mixed sample containing high amount of phosphorus 1.41% (Table 2). Mixed sample uninoculated containing low amount of phosphorus 0.78% (Table 2). The amount of potassium can get increased after biodegradation. Sugarcane bagasse containing high amount of potassium as 0.82% (Table 2). Mixed sample uninoculated containing low amount of potassium as 0.51% (Table 2). The C:N ratio can be calculated by the results of carbon and nitrogen. After biodegradation the C:N ratio would decrease compared to before biodegradation (Table 2).

Estimation of Amylase, Cellulase, Dehydrogenase, and Phosphatase Activity

Samples were taken for analysis of amylase activity, cellulase activity, dehydrogenase activity, and acid phosphatase activity. After biodegradation amylase activity differ from before biodegradation. Mixed sample containing a high amount of amylase activity as 132.1 h^{-1} g^{-1} (Table 3). Mixed sample uninoculated containing a low amount of amylase activity as 78.9 h^{-1} g^{-1} (Table 3). After biodegradation cellulase activity differs from before biodegradation. Mixed sample containing a high amount of cellulase activity as 143.1 h^{-1} g^{-1} (Table 3). Mixed sample uninoculated containing low amount of cellulase activity 99.9 h^{-1} g^{-1} (Table 3). After biodegradation dehydrogenase activity differ from before biodegradation. Mixed sample containing high amount of dehydrogenase activity 2.45 h^{-1} g^{-1} (Table 3). Mixed sample uninoculated containing low amount of dehydrogenase activity 1.83 h^{-1} g^{-1} (Table 3). After biodegradation acid phosphatase activity differ from before biodegradation. Sugarcane bagasse containing high amount of activity 8.1 h^{-1} g^{-1} (Table 3). Mixed sample uninoculated containing low amount of acid phosphatase activity 4.0 h^{-1} g^{-1} (Table 3).

Table 1 -Water Holding Capacity, determination of pH and E.C

S. No	*Sample*	*Water Holding Capacity (%)*	*pH*		*EC (microsimens/cm)*	
			BBD	ABD	BBD	ABD
1	Neem leaves	47	5.3	6.3	0.57	0.89
2	Vaagai leaves	51	5.1	6.2	0.53	0.71
3	Paddy straw	54	5.4	6.7	0.67	1.29
4	Sugarcane bagasse	56	5.5	7.0	0.70	1.21
5	Mixed sample	58	5.6	7.1	0.76	2.01
6	Mixed sample (Un inoculated)	45	5.2	6.0	0.50	0.62

ABD- After biodegradation BBD- Before biodegradation

Table 2-Estimation of Carbon, Nitrogen, Phosphorus, Potassium and C-N Ratio

S. No	*Sample*	*Organic carbon (%)*		*Total Nitrogen (%)*		*Total Phosphorus (%)*		*Total Potassium (%)*		*C-N Ratio*	
		BBD	**ABD**	**BBD**	**ABD**	**BBD**	**ABD**	**BBD**	**ABD**	**BBD**	**ABD**
1	Neem leaves	23.9	21.3	0.50	1.28	0.95	1.21	0.30	0.52	47.80:1	16.64:1
2	Vaagai leaves	26.7	23.1	0.46	1.23	0.63	0.96	0.25	0.41	58.04:1	18.78:1
3	Paddy straw	29.8	26.3	0.61	1.30	0.42	0.89	0.53	0.67	48.85:1	20.23:1
4	Sugarcane bagasse	29.0	26.4	0.79	1.35	0.51	1.01	0.61	0.82	36.70:1	19.55:1
5	Mixed sample	30.5	25.2	0.81	1.40	1.19	1.41	0.45	0.73	37.65:1	18:1
6	Mixed sample (Un inoculated)	29.0	27.4	0.80	1.02	0.61	0.78	0.32	0.51	36.25:1	26.86:1

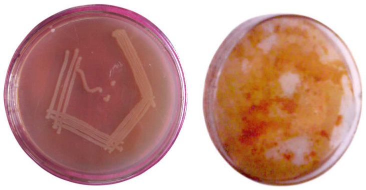
ABD- After biodegradation BBD- Before biodegradation

Table 3- Estimation of Amylase, Cellulase, Dehydrogenase and Phosphatase Activity

S. No	Sample	Amylase activity expressed as µg of glucose released h^{-1}g^{-1}		Cellulase activity expressed as µg of glucose released h^{-1}g^{-1}		Dehydrogenase activity expressed as µg of glucose released h^{-1}g^{-1}		Acid phosphatase activity expressed as µg of glucose released h^{-1} g^{-1}	
		BBD	ABD	BBD	ABD	BBD	ABD	BBD	ABD
1	Neem leaves	50.9	98.3	103.6	135.4	1.12	1.90	2.5	4.1
2	Vaagai leaves	56.3	100.8	99.7	127.0	1.54	2.09	2.6	5.0
3	Paddy straw	60.9	85.6	96.4	129.1	1.32	1.96	3.0	6.0
4	Sugarcane bagasse	58.0	124.3	100.2	135.4	1.45	2.14	4.1	8.1
5	Mixed sample	69.1	132.1	99.3	143.7	1.68	2.45	3.6	7.3
6	Mixed sample (Un inoculated)	68.0	78.9	98.1	99.9	1.65	1.83	3.0	4.0

ABD- After biodegradation BBD- Before biodegradation

PLATE -1 CULTURES



1.1.Pseudomonas

PLATE– 2 SAMPLES

1.2. Cellulomonas

PLATE-3 AFTER BIODEGRADATION

PLATE-4 COMPOSTING METHOD

1.Neem sample 2.Vaagai sample 3.Sugarcane Bagasse 4.Paddy Straw 5.mixed sample 6.Mixed sample uninnoculated

IV. DISCUSSON

There was a change in pH indicated the maturity of compost. The cellulose concentration on maturity was gradually decreasing in *Oscillatoria* sp Hemicelluose content of coir waste was rapidly decreasing in *Phormidium* sp. The rapid reduction of C: N ratio occurs in *Anabaena azollae* sp. Decomposition of coir waste by these three organisms yield good organic manure, which contained high amount of NPK values like organic manure (19). The present study also indicating pH change in a maturity of the compost and reduction of C: N ratio can also occur at the final compost.

The concentration of N was very low at day 0, and this level remained unchanged during the first 35 days of composting suggesting that N was lost during composting. After 40 days the N value was increase. The narrow C: N ratio (<20:1) The total organic C mass decreased with composting time (20). Therefore the present study confirms the after 40 days N value was increased. The C: N ratio (<20:1). And also the total organic C mass decreased with composting time.

Oxidoreductase enzymes, such as dehydrogenase were higher. Phosphatase activity was increased. This is attributed to the microbial stimulation by the organic C and is correlated with the increase in dehydrogenase and amylase activities. The amylase activity After Biodegradation increased averagely about 101.35 $h^{-1}g^{-1}$. The cellouse activity increased averagely about 128.34 h^{-}

^{1}g^{-1}. The dehydrogenase activity and phosphatase activity can also increase slightly. This indicating the microbial biomass can correlate with increase in enzyme activity.

Composting would appear to be a cost effective solution to this problem, but in its entirety, composting is an inherently lengthy and variable process and is restrictive in terms of the demand on resources and space in composting plants (21). The presence study can also prove the efficient degradation by *cellulomonas* and *pseudomonas*. The composting can increase the nutrient availability. It was found that the essential nutrients were found to be increased in the samples comparing the control samples, which indicated the high plant growth.

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Thermophysical Properties of Binary Mixtures of ethyl butyrate + 1,3-butanediol - A Temperature Dependent Study

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Abstract — *The experimental values of densities (ρ) and speeds of sound (u) of ethyl butyrate + 1,3-butanediol binary mixtures have been used to calculate the internal pressure (π_i), free volume (V_f), enthalpy (H), entropy (T_s), excess internal pressure (π_i^E), excess free volume (V_f^E), excess enthalpy (H^E), excess free energy (G^E) and excess entropy (T_s^E) at temperatures 303.15, 308.15, 313.15 and 318.15K over the entire composition range. The results have been discussed in terms of molecular interactions due to physical, chemical and structural effects between the unlike molecules.*

Keywords - *Thermodynamic properties, Internal pressure, Excess Gibbs energy of activation, Molecular interactions, 1,3-butanediol, ethyl butyrate*

I. INTRODUCTION

The speed of sound, *u*, is a property that can be experimentally determined with great precision over a broad range of temperature and pressure. Since *u* can be related to the first pressure partial derivative of density, accurate sound-speed data can be used to enhance the development of the equation of state. Furthermore, it is a very useful source of information for computing values of other thermodynamic properties which are difficult to obtain at extreme experimental conditions, such as calorimetric data at high pressures.

We have previously reported the excess molar volumes, excess isentropic compressibility, excess partial molar volume, excess partial molar compressibility in binary mixtures of ethyl butyrate with butanediol [1]. This work forms part of an investigation into the thermodynamic properties of ethyl butyrate and its mixtures.

Our literature survey shows that no measurements on above parameters have been reported for the mixtures investigated in this work. For examining the nature of inter- and intramolecular interactions, characterizing the thermodynamic and physic-chemical aspects of binary liquid mixtures such as molecular association and dissociation, the study of propagation of ultrasonic waves in liquids and liquid mixtures is of great importance [2]-[5]. These studies find several applications in industries. Such studies as variations in concentration and temperature are useful in giving insight into structure and various bonding of associated molecular complexes and other related molecular processes [6]-[8].

1,3-butanediol is a clear viscous liquid that's miscible with water and most of the polar organic solvents. The presence of two hydroxyl groups in vicinal positions (on the positions 1 and 3) of this diol makes it suitable as a useful chemical intermediate within the manufacture of many chemical merchandise [9], [10]. Volatile natural Acids including Ethyl butyrate (EtBu) is constituted of low-cost biomass wastes [11]. So, they're diagnosed as opportunity bio energy fuels. Generally, these acids have not been used in inner combustion engines due to the resistance of materials. Ethyl acetate, ethyl propionate and ethyl butyrate had been shown to be suitable fuels for a Homogeneous rate Compression Ignition (HCCI) engine, though they ignite slower than ethanol and those are acidogenesis merchandise. Acidogenesis is generally used to decrease terrible ecological results of polluting compounds. The smaller ignition delay of EtBu may want to assist reduce the inlet temperature and make using these esters as transportation fuels [12]. A success implementation of those fuels may additionally require to combine them with other fuels or to use diverse compositions to control the engine.

From the experimental values of density and speed of sound the internal pressure (π_i), free volume (V_f), enthalpy (H), entropy (Ts), excess internal pressure (π_i^E), excess free volume (V_f^E), excess enthalpy (H^E), excess free energy (G^E) and excess entropy (T_s^E) at temperatures (303.15, 308.15, 313.15 and 318.15) K over the entire composition range have been evaluated. The results are fitted to the Redlich-Kister polynomial equation.

II. EXPERIMENTAL

Ethyl butyrate and 1,4-butanediol (Sigma-Aldrich, mass fraction purity > 0.99) used in this work were purified through the use of the usual strategies [13,14]. Earlier than use, the chemicals are degassed via ultrasound to reduce the water content. All chemical compounds had been used without additional purification because density and speeds of sound were determined in desirable agreement with literature of NIST ThermoLit records.

The procedure for sample preparation and measurements of density and speeds of sound are described elsewhere [1].

III. RESULTS AND DISCUSSION

The internal pressure of a fluid is related to the thermal pressure coefficient $(\square\square/\square\square)_{\square}$ by the following well-known thermodynamic equation of state [15],

$$\pi_i = \left(\frac{\square\square}{\square\square}\right)_{\square} = T\left(\frac{\square\square}{\square\square}\right)_{\square} - \square = \square\left(\frac{\square_{\square}}{\square_{\square}}\right) - \square \quad \ldots (1)$$

where α_P is the isobaric expansivity and k_T is the isothermal compressibility of the mixture. For most of the liquids, the thermal pressure coefficient multiplied by absolute temperature, i.e., $T(\alpha_P/k_T)$ is very high so that the external pressure (P) becomes negligible in comparison [16], therefore it may be neglected in Eq.(1) in the present calculations. Thus, the internal pressure can be shown to be equal to the following relationship [17,18].

$$\square_{\square} = \frac{\square_{\square}}{\square_{\square}}\square \quad \ldots (2)$$

The free volume, V_f of the mixtures are calculated from the relation [19,20]

$$\square_{\square} = \frac{\square\square}{(\square + \square_{\square})} \quad \ldots (3)$$

since P is very small as compared to π_i, it has been neglected in the Eq.(3) in the present calculations. k_T is calculated using the well-known thermodynamic relationship[21,22]

$$\square_{\square} = \square_{\square} + \frac{\square\square\square_{\square}^{2}}{\square_{\square}} \quad \ldots (4)$$

where $k_s[=1/(\rho u^2)]$ is isentropic compressibility, V is the molar volume and C_p is the heat capacity of the mixture. The α_p values for the mixtures were evaluated from temperature dependence of density data [1]. The C_p values of pure liquids have been taken from the literature [1], [22] and the C_p values for the mixtures have been calculated by using the following relationship.

$$C_p = x_1C_{p,1} + x_2C_{p,2} \quad \ldots (5)$$

The values of various parameters, C_p, α_p, k_s and k_T of pure liquids used in the calculations are taken from our earlier paper[1]. The π_i^E and V_f^E of binary mixtures have been calculated using the relationship,

$$Y^E = Y - (x_1Y_1 + x_2Y_2) \quad \ldots (6)$$

where Y is π_i or V_f and subscripts 1 and 2 refers to pure ethyl butyrate and 1,3-butanediol, respectively. The excess enthalpies (H^E) and excess entropies (T_S^E) are calculated from π_i and V_f by using the following relations based on regular solution theory [19,20,23].

$$H^E = \pi_iV - [x_1\pi_{i,1}V_1 + x_2\pi_{i,2}V_2] \quad \ldots (7)$$

$$T_S^E = R\,[x_1\ln V_{f,1} + x_2\ln V_{f,2} - \ln V_f] \quad \ldots (8)$$

The excess free energy (G^E) of mixtures is given by the relationship,

$G^E = H^E - T_s^E$ … (9)

The values of π_i^E, V_f^E, H^E, T_S^E and G^E were fitted to a Redlich-Kister [24] type polynomial equation

$Y^E = x_1(1 - x_1)\sum_{i=1}^{n} A_i(2x_1 - 1)^{i-1}$ … (10)

where Y^E is π_i^E or V_f^E or H^E or T_S^E or G^E. The values of coefficients, A_i in Eq.(10) were evaluated by using least-square method with all points weighted equally. The standard deviations, σ of fit have been calculated by using the relation

$\sigma (Y^E) = [\sum(Y_{obs}^E - Y_{cal}^E)^2/(m - n)]^{1/2}$ …(11)

where, m is the total number of experimental points and n is the number of coefficients.

The values of u, ρ, π_i, H, and V_f for the binary mixtures of ethyl butyrate + 1,3-butanediol as function of mole fraction, x_1 of ethyl butyrate at various temperatures are listed in Table 1. The values of coefficients, A_i of Eq.(10) for the excess functions and the corresponding standard deviations, σ are listed in Table 2. The variation of π_i^E, V_f^E, H^E, T_S^E and G^E with composition and temperature of the mixtures are presented graphically in Figs 1 - 5, respectively.

TABLE 1 - Values of u, ρ, π_i, H, and V_f for the Binary Mixtures of Ethyl Butyrate + 1,3-Butanediol as Function of Mole Fraction, x_1 of 1,3-Butanediol at Various Temperatures.

x_1	u (m s^{-1})	ρ (kg m^{-3})	π_i (10^8 N m^{-2})	H (10^6 k J mol^{-1})	V_f (10^{-6} m^3 mol^{-1})	u (m s^{-1})	ρ (kg m^{-3})	π_i (10^8 N m^{-2})	H (10^6 k J mol^{-1})	V_f (10^{-6} m^3 mol^{-1})
	T = 303.15 K					T = 308.15 K				
0.0000	1514.0	998.41	4.237	90.26	5.949	1500.1	994.94	4.233	90.58	6.053
0.1034	1476.5	985.01	4.235	94.22	5.951	1461.9	981.34	4.227	94.58	6.061
0.2030	1440.3	972.10	4.204	98.15	5.996	1425.0	968.23	4.190	98.54	6.115
0.3050	1403.3	958.89	4.145	102.27	6.081	1387.2	954.82	4.125	102.70	6.210
0.3835	1374.8	948.71	4.084	105.52	6.171	1358.2	944.49	4.061	105.99	6.309
0.4936	1334.8	934.45	3.980	110.20	6.333	1317.4	930.01	3.950	110.72	6.485
0.5811	1303.1	923.12	3.884	114.02	6.489	1285.1	918.51	3.850	114.59	6.655
0.6878	1264.3	909.28	3.754	118.81	6.714	1245.5	904.47	3.714	119.44	6.898
0.7997	1223.7	894.79	3.606	123.99	6.989	1204.1	889.75	3.560	124.69	7.196
0.8818	1193.9	884.14	3.492	127.90	7.218	1173.7	878.94	3.442	128.66	7.444
1.0000	1151.1	868.85	3.321	133.69	7.589	1130.2	863.40	3.266	134.54	7.844
	T = 313.15 K					T = 318.15 K				
0.0000	1486.2	991.49	4.227	90.89	6.160	1472.3	988.02	4.219	91.21	6.269
0.1034	1447.2	977.69	4.216	94.93	6.176	1432.6	974.01	4.203	95.29	6.293
0.2030	1409.6	964.38	4.174	98.93	6.237	1394.3	960.49	4.156	99.33	6.364
0.3050	1371.2	950.77	4.105	103.14	6.343	1355.1	946.68	4.081	103.58	6.481
0.3835	1341.5	940.28	4.035	106.47	6.452	1324.9	936.03	4.008	106.95	6.600
0.4936	1300.0	925.59	3.919	111.25	6.644	1282.6	921.10	3.885	111.79	6.808
0.5811	1267.0	913.91	3.813	115.17	6.828	1249.0	909.25	3.775	115.76	7.007
0.6878	1226.8	899.66	3.672	120.08	7.090	1208.0	894.78	3.628	120.73	7.290
0.7997	1184.6	884.72	3.513	125.40	7.412	1165.0	879.61	3.463	126.13	7.638
0.8818	1153.6	873.76	3.390	129.42	7.680	1133.4	868.48	3.336	130.21	7.928
1.0000	1109.0	857.94	3.208	135.39	8.117	1088.0	852.49	3.149	136.26	8.400

TABLE 2 – Coefficients (A_i) of Eq. (10) for π_i^E, V_f^E, H^E, T_s^E and G^E along with standard deviations (σ) for Ethyl butyrate + 1,3-butanediol binary mixtures at different temperatures.

Property	T(K)	A_1	A_2	A_3	A_4	σ
π_i^E (10^8 N m^{-2})	303.15	1.5038	-0.5648	0.1589	0.0008	1.0000
	308.15	1.5579	-0.6037	0.1751	0.0011	1.0000
	313.15	1.6169	-0.6387	0.2010	0.0010	1.0000
	318.15	1.6729	-0.6816	0.2201	0.0012	1.0000
V_f^E (10^{-6} m^3 mol^{-1})	303.15	-1.7037	0.0638	-0.0794	0.0003	1.0000
	308.15	-1.8081	0.0499	-0.0817	0.0005	1.0000
	313.15	-1.9278	0.0181	-0.1041	0.0002	1.0000
	318.15	-2.0517	-0.0013	-0.1081	0.0003	1.0000

H^E (10^6 k J mol^{-1})	303.15	-10.2988	1.0625	0.0576	0.0008	1.0000
	308.15	-10.5406	1.1388	0.0717	0.0018	1.0000
	313.15	-10.8101	1.1313	-0.0122	0.0015	1.0000
	318.15	-11.0542	1.1962	-0.0126	0.0006	1.0000
T_S^E (10^{-2} J mol^{-1})	303.15	-0.5807	0.1009	-0.0219	0.0001	1.0000
	308.15	-0.6035	0.1039	-0.0223	0.0002	1.0000
	313.15	-0.6291	0.1012	-0.0287	0.0001	1.0000
	318.15	-0.6543	0.1039	-0.0285	0.0001	1.0000
G^E (k J mol^{-1})	303.15	-9.7183	0.9615	0.0798	0.0008	1.0000
	308.15	-9.9372	1.0349	0.0940	0.0017	1.0000
	313.15	-10.1808	1.0298	0.0160	0.0015	1.0000
	318.15	-10.3998	1.0918	0.0158	0.0006	1.0000

The internal pressure (also known as the cohesion pressure or energy-volume coefficient) is an interesting and valuable quantity that describes the macroscopic result of molecular interactions. The internal pressure is the cohesive force which is the resultant of forces of attraction and forces of repulsion between molecules in a liquid, and considerable information can be gained by simply observing and comparing internal pressure-volume curves for pure liquids [25,26].

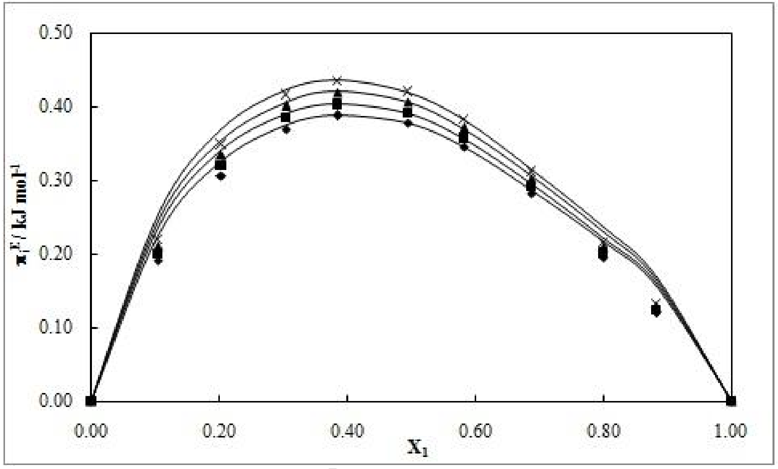

FIGURE 1 - Variation of excess internal pressure, π_i^E with mole fraction of 1,4-butanediol for the binary mixture ethyl butyrate + 1,3-butanediol at temperatures: 303.15K(♦), 308.15K(■), 313.15K (▲) and 318.15K(x).

From Fig. 1, the π_i^E values are observed to be positive over the entire composition range and at all investigated temperatures. With increase in temperature the increase in π_i^E values can also be observed. It has been established that the sign and magnitude of excess functions give a good estimate of the strength of the unlike interactions in a binary mixture. A closer packing of molecules, resulting in a contraction in volume of the mixture, leading to an increase in the internal pressure of the mixture, hence, positive π_i^E values.

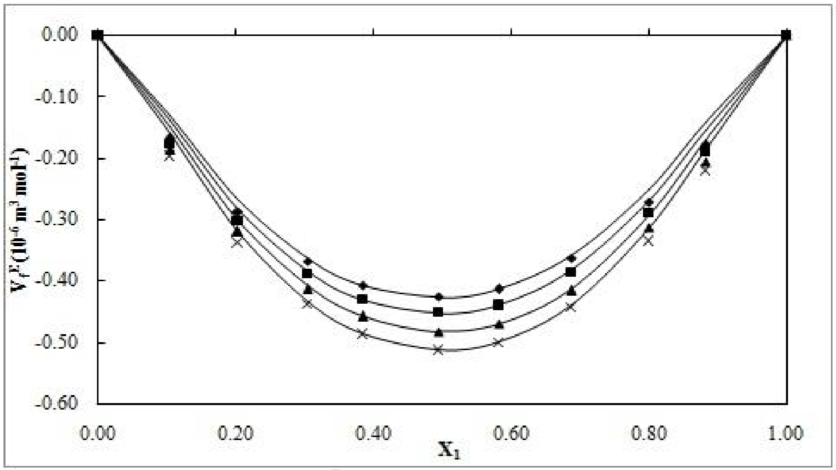

FIGURE 2 -Variation of excess free volume, V_f^E with mole fraction of 1,4-butanediol for the binary mixture ethyl butyrate + 1,3-butanediol at temperatures : 303.15K(♦), 308.15K(■), 313.15K (♠) and 318.15K(x).

Free volume is a central concept in considering both equilibrium thermodynamic properties and transport properties in liquids. The V_f^E values are observed (Fig. 2) to be negative for the binary mixtures at all the temperatures studied. The decrease in V_f^E can also be observed from the same figures with the increase in temperature. The observed negative trend in V_f^E values indicates specific interactions between the molecules of the mixtures. The negative values of excess free volume in the binary system assert that the combined effects of the factors are responsible for volume contraction and vice-versa [27]. According to these investigations, the negative values of excess free volume may be attributed to the packing effect and ion-dipole interaction of solvent molecules with the 1,3-BD in these mixtures [28,29].

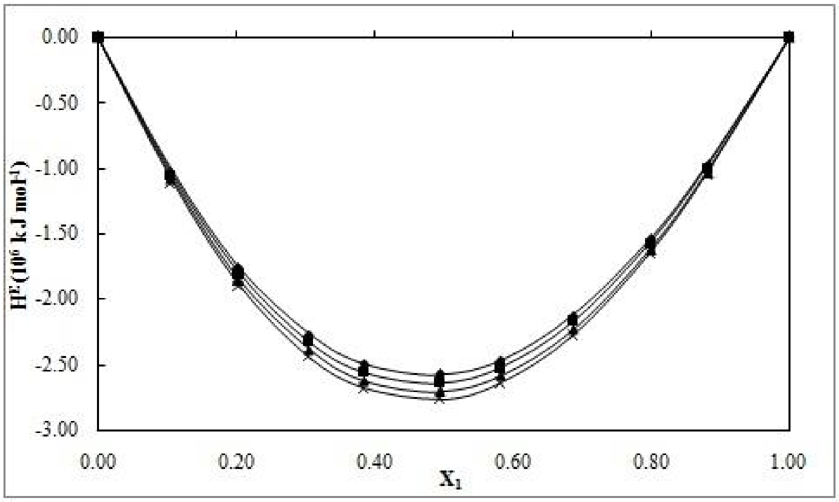

FIGURE 3 -Variation of excess enthalpy, H^E with mole fraction of 1,4-butanediol for the binary mixture ethyl butyrate + 1,3-butanediol at temperatures : 303.15K(♦), 308.15K(■), 313.15K (♠) and 318.15K(x).

From Fig. 3, the H^E values are observed to be negative for the binary mixtures at all the temperatures studied. It can also be observed from the same figures that with the increase in temperature, the H^E values are decreased. In general, H^E values of mixing depend upon the relative enthalpies of endothermic and exothermic effects that arise on mixing of the components. The factors that cause endothermic effect on mixing are:

a) Strong specific interactions, usually some type of chemical interactions,

b) Favorable geometrical fitting of component molecules due to occupation of void spaces of one component by the other when the molecular sizes of the unlike molecules differ by a large magnitude, and,

c) ion-dipole interactions of solvent molecules with the 1,3-BD molecules.

The factors that cause exothermic effect on mixing of the components are:

a) breakdown of the solvent self-associated molecules from each other,

b) Breakdown of the 1,3-BD ion pairs, and,

c) Formation of weaker 1,3-BD-solvent bonds than 1,3-BD-1,3-BD and solvent-solvent bonds.

It can be observed that the negative value of H^E indicates exothermic process [30] in the mixing of the ethyl butyrate + 1,3-butanediol system. The negative H^E values may be attributed to dipole-dipole or ion-ion interactions between the solvent molecules and 1,3-BD and are dominant over the ion-dipole interaction between unlike molecules.

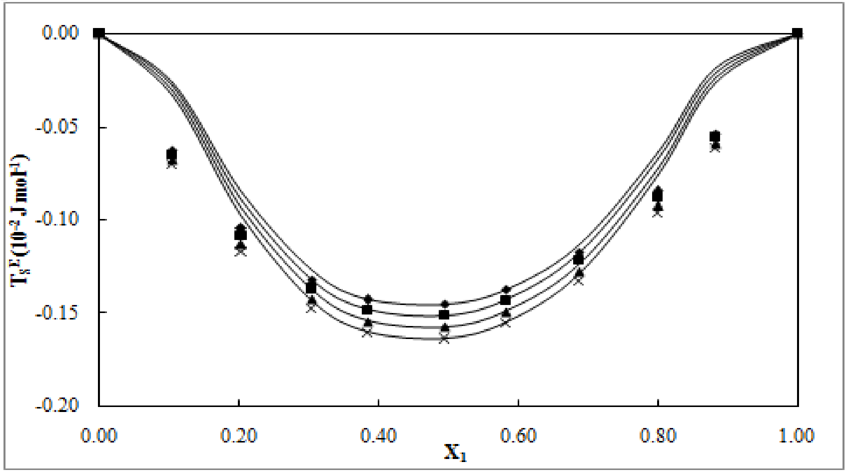

FIGURE 4 -Variation of excess entropy, T_s^E with mole fraction of 1,4-butanediol for the binary mixture ethyl butyrate + 1,3-butanediol at temperatures : 303.15K(♦), 308.15K(■), 313.15K (♠) and 318.15K(x).

From Fig. 4, the T_s^E values are observed to be negative for the binary mixtures at all the temperatures studied. The negative T_s^E values of the mixtures further support the conclusions drawn from the π_i^E and V_f^E values, that the formation of hydrogen bonding between ethyl butyrate molecules and 1,3-BD ions leads to closer packing of molecules, resulting in a contraction in volume. This leads to a decrease in the entropy of the mixture resulting in negative T_s^E values.

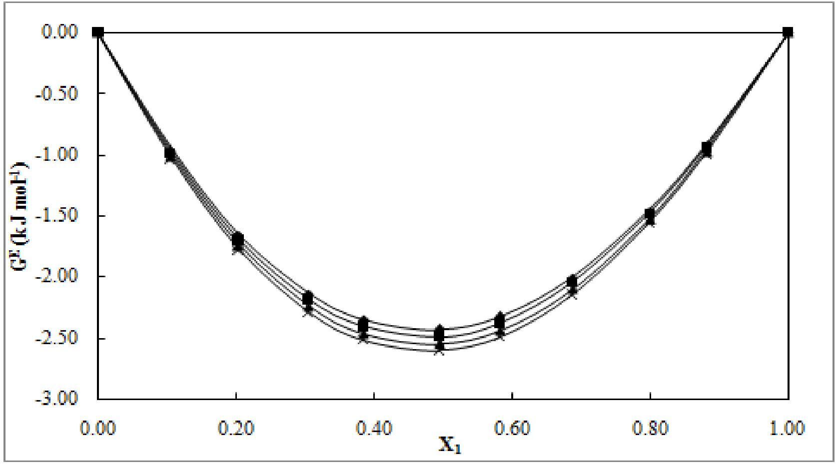

FIGURE 5 -Variation of excess free energy, G^E with mole fraction of 1,4-butanediol for the binary mixture ethyl butyrate + 1,3-butanediol at temperatures: 303.15K(♦), 308.15K(■), 313.15K (▲) and 318.15K(x).

The G^E values are observed to be negative at all the temperatures studied (Fig. 5). It can also be observed from the same figure that with the increase in temperature, the G^E values are decreased. The negative values of G^E may be attributed to the effective geometrical packing effect.

IV. CONCLUSION

In this paper, densities, and speeds of sound of binary mixtures of ethyl butyrate with 1,3-butanediol along with those of pure liquids at temperatures T = (303.15 to 318.15) K at the atmospheric pressure 0.1MPa, have been reported. Values of the excess internal pressure (π_i^E), excess free volume (V_f^E), excess enthalpy (H^E), excess free energy (G^E) and excess entropy (T_s^E) were obtained from experimentally measured values of densities and speeds of sound. Values of V_f^E, H^E, G^E and T_s^E are negative and become less negative with increase in temperature. The overall negative behavior of V_f^E, H^E, G^E and T_s^E may be attributed to strong dipole-dipole interaction and easy accommodation of 1,3-butanediol in the voids of ethyl butyrate molecules.

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Recent Developments in the Synthesis of Schiff Bases and Its Applications

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Abstract - *Schiff bases are some of the most widely used organic compounds. They are widely used for industrial purposes and also exhibit a broad range of biological activities. Schiff bases can be synthesized from an aliphatic or aromatic amine by an addition reaction. The first preparation of imines was reported in the 19th century by Schiff (1864). Schiff base (also known as imine or azomethine) is an analog of a ketone or aldehyde in which the carbonyl group (C=O) has been replaced by an imine or azomethine group. Schiff base exhibit useful biological activities such as anti-inflammatory, analgesic, anti-microbial, anti-convulsant, anti-glycation, and anti-depressant activities. Schiff bases are also used as catalysts, pigments, and dyes, intermediates in organic synthesis, polymer stabilizers, and corrosion inhibitors. The review article is about the various synthesis of Schiff base compounds and their preparation method and properties.*

Keywords*:* *Schiff bases, Application Studies, Characterization, Biological Activity.*

I. INTRODUCTION

Schiff bases were discovered by a German chemist, Nobel Hugo Schiff. (1) A Schiff base is a compound with a functional group that contains a carbon-nitrogen double bond with a nitrogen atom connected to an aryl or alkyl group. It is usually formed by the condensation of an aldehyde or ketone with a primary amine. (2) Schiff base has a typical imine group (-C=N), which is formed from the elimination addition reaction from primary amine ($R-NH_2$) and active group of carbonyl compound using an acid catalyst. Schiff base complexes show excellent catalytic activity in various reactions. (3) Schiff base compound has pharmacological activities as anti-oxidant, anti-cancer, anti-tumor, anti-inflammatory, anti-bacterial, and anti-tuberculosis. (4) Schiff base can be synthesized from an aliphatic or aromatic amine and a carbonyl compound by nucleophilic addition. (5) The classical synthesis reported by Schiff involves the condensation of a carbonyl compound with amine under azeotropic distillation.

II. REVIEW OF LITERATURE

Dief A M A *et al* (6) have synthesized Schiff bases. They are formed when amine reacts with aldehyde or ketone under specific conditions. Schiff base complexes have anti-fungal, anti-bacterial, anti-malarial, and anti-viral and has several other properties. Nowadays Schiff base has gotten more attention from medicinal chemists. The review is about the various Schiff base complexes and their biological importance. Schiff bases were derived from 2 thiophene carboxaldehyde and 2 aminobenzoic acids. Four platinum Schiff bases complex containing of salicylaldehyde and 2 furaldehyde with *o* and *p* phenylenediamine and several compounds has several antibacterial activities.

Yadav P *et al* (7) have synthesized that Schiff bases ligands show various medicinal applications. The review is about the Schiff base amino acid complex are obtained from 5-bromosalicylaldehyde, amino acid, L-phenylalanine, L-aspartic acid and also obtained from 5-bromosalicyaldehyde and amino-methyl-thiophene has various biological activities. The article reviewed also the antifungal activities of Schiff base metal complexes. The synthesized Schiff base ligands have good anti-fungal activities and were detected by the good diffusion method.

Kumar R *et al* (8) explained a variety of methods for the synthesis of imines and application of Schiff base complexes. The catalytic activities of complexes are observed. Isatin-derived Schiff bases have been reported to possess antibacterial activity. The importance of Schiff base complexes for bioinorganic chemistry, biomedical applications, and material science has been recognized and reviewed.

Gupta D *et al* (9) have reviewed that the Schiff bases are the most widely used organic compounds. They have been used in various industrial applications and biological properties. Schiff base is a compound having the common structure R-C-NR'. Schiff base is the sub-class of imines. Schiff bases can act as anti-inflammatory, anti-cancer, anti-covalent, and anti-microbial.

Amarasekera A S *et al* (10) reviewed about the synthesis of divannillin. Schiff base is used in the synthesis of organometallic polymers. The compound ortho-vanillin has been used in the synthesis of organometallic polymers. The phenolic aldehyde isolated from the vanilla extract is used for common food flavoring. They actually synthesized the 6, 6'-Dihydroxy-5,5-dimethoxy-(1,1'-biphenyl)-3,3'-carboxaldehyde or compound commonly known as divanillin can be easily prepared from vanillin by fecl3

Ahmed F *et al* (11) reviewed about chitosan is a natural polymer derived from chitin by alkaline de-acetylation. They synthesized the Schiff base of 4, 4- diaminodiphenyl ether (vanillin). It can be used in the biological and medicinal industries. He categorized various tests and find dense surface, uniformity, and regularity.

Zhong G Q *et al* (12) have reviewed that Schiff bases are a series of organic compounds which contain methane group (-C=N-). The use of Schiff base as ligands in transition metal complexes has been studied. They synthesized the zinc and nickel complexes of the glycine-vanillin Schiff base ligand and studied the crystal structure and antibacterial activity.

Prakash V *et al* (13) reviewed that vanillin is a naturally occurring food compound found in plants and is used by the manufacturer of Schiff base chelates. Schiff bases are synthesized by the condensation of primary amine and a carbonyl compound. They reviewed the application of vanillin Schiff bases with antibacterial and antifungal properties with different structures and reviewed vanillin Schiff bases in water purification, heterocyclic compounds, therapy, and catalyst.

Marufah L *et al* (14) reviewed that synthesis was carried out by using vanillin and p-aminoacetophenone by grinding method. In the synthesis, lime juice is used as a catalyst (citrus aurantifolia). The product was characterized using NaOH. The characterization was carried by reacting the product with NaOH. Corrosion inhibitor efficiency test was also carried out. The product synthesized was 1-(4{4-hydroxy-3-methoxy-benzylidene)-amine}-phenyl-ethanone.

Baluja S *et al* (15) reviewed the density, ultrasonic velocity and viscosity of vanillin Schiff bases derivatives has been studied in methanol and tetrahydrofuran (THF) at 308.15K. The results are interpreted in terms of molecular interactions occurring in the solution. In solutions of vanillin Schiff bases, compound – solvent interaction exist. These concluded that these compounds are more bonded to solvent.

III. CONCLUSION

Schiff base compounds and their metal complexes are one of the most important chemical classes of compounds having a common integral feature of variety, structural diversity, and of active medicinal reagents. (16) Schiff base and their metal complexes are interesting research subject that constantly provides us with new information about created compounds. Schiff base derivatives are finally in the various process promoted by the researchers for designing novel heterocyclic /aryl Schiff bases for the development of new eco-friendly technology. The review reflects the contribution of Schiff base to the design and development of various compounds and their properties. (17)

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Chemical Profile and Biological activity of Essential oil from *Artabortrys Hexapetalus* (L.f.) Bhandari Grown in Southern parts of Western Ghats

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Abstract— *Essential oils are volatile compounds having the oily fragrance obtained from various plant parts including the flowers, leaves, stem, bark and roots, plant extracts. The essential oil obtained by hydrodistillation from the leaves of Artabortrys hexapetalus grown in Southern parts of Western Ghats were analyzed by gas chromatography (GC) coupled with mass spectrometry (GC/MS). The GC-MS analysis reveals that the presence of 34 compounds. The major compounds are Caryophyllene (17.2%), Copaene (12.9%), α - Bisabolene (8.3%), Biocyclogermacrene (6.3%), α –Cadinol (6.2%), β-Myrcene (5.7%), δ- 3-Carene (5.3%), γ- Muurolene (4.9%) and the minor compounds are β - Gurjunene (3.5%), Longipinane (3.5%), α –Patchoulene (3.1%), Trans cadina (2.8%), Ledol (1.4%), α - Phellandrene (1.3%), Patchouli alcohol (1.3%), were present in A. hexapetalus leaves essential oil. The in vitro anticancer potential of essential oil was evaluated by using MCF-7 cell line by MTT assay. The essential oil exhibited significant anticancer activity with IC50 value 66.92 µg/mL. From the results, A. hexapetalus essential oil has significant anticancer properties which can be utilized as natural supplement as anticancer agents in pharmaceutical industries.*

Keywords— *Essential oil, Artabortrys hexapetalus , GC/MS, MTT assay, MCF-7*

I. INTRODUCTION

India has rich resources of medicinal plants with a wide variety of plants, because of the extreme variations in geographical and climatic conditions prevailing in the country [1]. Western Ghats is blessed with many medicinal plants. Southern parts of Western Ghats have great diversity of plants with varied ethno medicinal uses and economic importance [2]. The genus Artabotrys is among the relatively large genera of the family Annonaceae, consisting of at least 100 species which are distributed in Africa and East Asia [3,4] . *Artabortrys hexapetalus* (L.f.) Bhandari is native to India and widely distributed in the southern part of China, and is used in traditional Chinese medicine for the treatment of malaria [5]. The bark and fruit parts are used to treat diarrhea, dysentery, bruises, cuts, pains, sprain, inflammation, gout, helminthiasis, leprosy, skin diseases, wound, ulcers, tumors, amenorrhea, dysmenorrhea, cough, asthma, bronchitis, colic and constipations [6]. A wide range of chemical compounds including alkaloids, sesquiterpenes, flavanoids, fixed oils and volatile oils have been found to possess various pharmacological activities [7]. Human body has several mechanism to counter act oxidative stress by producing enzymes such as superoxide dismutase, catalase and by antioxidant compounds such as ascorbic acid, tocopherols and gluthatione, which are either naturally produced in situ or externally supplied through foods [8].

II. MATERIALS AND METHODS

A. Plant material

Fresh leaves of *A. hexapetalus* (2 kg) were collected near Udumalpet (10.6419°N, 77.2659°E.) in Tamil Nadu, Southern India. The plant sample was identified and authenticated by Dr. P. Sathishkumar, Assistant Professor, Department of Botany, Nallamuthu Gounder Mahalingam College, Pollachi, and the voucher specimen (PCH025) was preserved in the Chemistry department.

B. Isolation of essential oil from A. hexapetalus leaves

About 500 g of fresh leaves were taken in a round bottom flask and hydrodistillated using Clevenger type apparatus for 4h. The essential oil was dried over anhydrous sodium sulphate

(Merck) until the last traces of water were removed and then stored in a container at 4oC before GC/MS analysis. The extraction of the essential oil process was repeated (4 times) for the required amount of oil for further analysis.

C. Gas chromatography-Mass spectrometry analysis

GC-MS analysis was performed using an HP 5MS column (cross-linked 5% methyl phenyl silicone, 30 m x 0.25-mm i.d., 0.25-mm film thickness). The column oven temperature was initially held at 70^o C for 2 rain, then programmed to reach 230^o C at a rate increase of 20^o C and held for 2 min. The total run time was 12 min. The temperatures of the injector port and the interface were set at 250^o C and 280^o C respectively. The carrier gas (helium) flow rate was 1 mL/min. The ionization energy was set at 70 eV. Mass spectra were collected by scanning from mlz 50 to mlz 550 at 2-s intervals [9]. The identification of constituents was performed on the basis of retention indices (RI) determined by co-injection with reference to a homologous series of n-alkanes, under identical experimental conditions. Further identification was performed by comparison of their mass spectra with those from NIST 08 Libraries (on Chem Station HP) and Wiley 9th Version and the home-made MS library built up from pure substances and components of known essential oils, as well as by comparison of their retention indices with literature values [10,11].

III. RESULTS AND DISCUSSION

The presence of phytochemical constituents of essential oil of *A. hexapetalus* leaves was analyzed by GC-MS method. The GC-MS analysis reveals that the presence of 34 compounds. The major compounds are Caryophyllene (17.2%), Copaene (12.9%), α -Bisabolene (8.3%), Biocyclogermacrene (6.3%), α –Cadinol (6.2%), β-Myrcene (5.7%), δ- 3-Carene (5.3%), γ-Muurolene (4.9%) and the minor compounds are β - Gurjunene (3.5%), Longipinane (3.5%), α – Patchoulene (3.1%), Trans cadina (2.8%), Ledol (1.4%), α - Phellandrene (1.3%), Patchouli alcohol (1.3%), were present in *A. hexapetalus* leaves essential oil. The compounds were identified comparison of the retension time of GC peaks. From the collection of literatures, a very few results were found on the GC/MS analysis of the essential oil from *A. hexapetalus* leaves. The essential oil obtained from Bangalore origin contains 2,5-dimethyl tetradeca hydrophenenthrene (33.02%), nonanoic acid (19.25%), 2-amino-3-ethyl biphenyl (19.08%), dibutyl phthalate (16.77%), decanoic acid (14.01%) and the minor compounds are 5-methyl-9-phenylnonan-3-ol (5.43%), 2,5-dimethyl (-1-phenylheptan-1- one (5.48%), 1-phenyl undecane (6.12%). The leaf essential oil from *A. hexapetalus* in southern Karnataka contains major products are 3-Carene (44.91%), β-caryophyllene (19.17%), α- humulene (8.78%), α-copaene (6.59%) and caryophyllene oxide (5.55%) [12].The obtained results are almost similar in Thailand, Bangalore, Vietnam and southern Karnataka origin. However, there were variations in their composition; this may be due to climatic and geographical variations.

Table 1: Chemical composition of essential oil of *A. hexapetalus* leaves

S.NO	NAME OF THE COMPOUND	R.T	RI estimated	RI reported	% Composition
1	β – Myrcene	4.909	982	988	5.7
2	α - Phellandrene	5.242	998	1002	1.3
3	δ- 3-Carene	5.620	1010	1008	5.3
4	α - Terpinene	5.809	1016	1014	0.7
5	β - Ocimene	6.031	1030	1032	0.7
6	Isobutyl hexanoate	6.609	1145	1149	0.2
7	α - Cubebene	7.042	1342	1345	0.8
8	Copaene	7.331	1376	1374	12.9
9	α - Santalene	8.431	1413	1416	0.1
10	β - Gurjunene	9.986	1429	1431	3.5

11	α –Patchoulene	10.375	1450	1454	3.1
12	Caryophyllene	10.542	1463	1466	17.2
13	Geranyl propanoate	10.986	1473	1476	0.2
14	γ- Muurolene	11.364	1481	1478	4.9
15	Bicyclogermacrene	11.508	1502	1500	6.3
16	α -Bisabolene	12.097	1506	1505	8.3
17	Quinoline	12.186	1512	1510	0.7
18	Trans cadina	12.530	1536	1533	2.8
19	Hexenyl benzoate	12.675	1564	1565	0.6
20	Ledol	12.864	1608	1602	1.4
21	aromadendrene epoxide	12.930	1641	1639	0.8
22	Longipinane	13.064	1646	-	3.5
23	α –Cadinol	13.219	1650	1652	6.2
24	Patchouli alcohol	13.375	1658	1656	1.3
25	Cedren-13-ol <8->	13.475	1684	1688	0.9
26	Heptadecane	13.586	1697	1700	0.5
27	Farnesol	13.741	1712	1714	0.3
28	MethyI tetradecanoate	14.119	1724	1722	0.2
29	Nonadecane	14.486	1892	1900	0.5
30	Phytol	15.341	1947	1942	0.7
31	Eicosane	16.174	2012	2000	0.2
32	Heneicosane	17.041	2108	2100	0.4
33	Tetracosane	22.262	2412	2400	0.2
34	Heptacosane	23.685	2691	2700	0.4
	Total identified				92.8
	Monoterpene hydrocarbons (S.No: 1-5)				13.7
	Sesquiterpenes hydrocarbons (S.No: 7-12, 14-16, 18, 20 &22)				64.8
	oxygenated compounds (S.No: 6,13,19,23-25,27,28 & 30)				11.4
	Non-terpenes (17,26,29 & 31-34)				2.9

In-vitro anticancer activity

The current study revealed that the in vitro anticancer potential of *A. hexapetalus* essential oil was tested by MCF-7 cell line by using MTT assay. The viability of the breast cancer cells after incubation with different concentrations of essential oil from *A. hexapetalus* leaves were carried out. The incubation with different concentrations of essential oil of the sample (15, 25, 75, 150,300 µg/ mL) affected the viability of the cancer cell line (MCF-7). The graph was plotted between % cell inhibition and concentrations from which IC_{50} value was calculated and shown in Fig. 1. Essential oil of *A. hexapetalus* leaves showed the anticancer activity on the MCF-7 cancer cell lines in dose dependent pattern. At lower levels, cancer cell decomposition is minimal (15 µg/mL), while almost all cancer cells break down at 300 µg/mL. The IC_{50} was calculated to be 67.15 µg/mL.

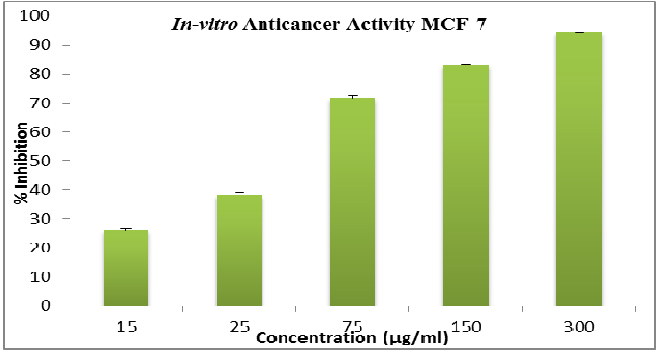

Fig.1. Anticancer activity of Essential oil from *A. hexapetalus* leaves

From the result, the essential oil extracted from *A. hexapetalus* leaves have potent in vitro anticancer property. From the collection of literature, a very few anti-cancer activities were reported from the essential oil of *A. hexapetalus* leaves grown in Taiwan, was tested using crude extract of roots, stems and leaves active against both Hep G2 and 2,2,15 cell lines with IC50 9.1 and 11.0 µg/ml respectively, Taiwan [13].This is the reported for the first time the anticancer potential of essential oil of *A. hexapetalus* leaves grown in South India.

IV. CONCLUSION

The essential oil obtained from the leaves of *A. hexapetalus* were analyzed by GC/MS reveals that the presence of 34 compounds. The in vitro anticancer potential of essential oil was evaluated by using MCF-7 cell line by MTT assay. The essential oil exhibited significant anticancer activity with IC50 value of 66.92 µg/mL. Our work suggests that essential oils from *A. hexapetalus* can be considered as a promising future can be utilized as natural supplement as anticancer agents in pharmaceutical industries.

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