PROJECT DETAILS - Department of Chemistry

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2	15BC4161	Deepika S	Chemistry	Physico-chemical analysis of Ground water of selected areas in Nilgiris District.	Mrs. R. Chitradevi, Assistant Professor
3	15BC4163	Elakkiya S	Chemistry	Mild Steel Corrosion Inhibition using Gum Exudates of Azadirachta Indica in Sulphuric Acid	Mrs. M. Malarvizhi, Assistant Professor
4	15BC4164	Gayathiri M	Chemistry	Removal of Methylene Blue dye from aqueous solution by adsorption technique	Dr. M. Indrani, Assistant Professor
5	15BC4165	Geetha D	Chemistry	Green synthesis of silver nano particles using herbal extracts	Dr. E. Vaishnavi, Assistant Professor
6	15BC4168	Kalaivani M	Chemistry	Removal of Malachite Green dye from aqueous solution by adsorption technique	Dr. M. Indrani, Assistant Professor
7	15BC4169	Kalaiyarasi K	Chemistry	Green corrosion inhibition for Carbon Steel in Sulphuric Acid Medium	Mrs. M. Malarvizhi, Assistant Professor
8	15BC4170	Kannirathinam S	Chemistry	Ru(II) Coumarin Complex as Colorimetric Sensor for Detection of Cobalt	Dr. J. Bhuvaneswari, Assistant Professor
9	15BC4171	Kanneeshwari	Chemistry	Ru(II) Coumarin Complex as Colorimetric Sensor for Detection of Cobalt	Dr. J. Bhuvaneswari, Assistant Professor
10	15BC4172	Kavipriya C	Chemistry	Physico-chemical analysis of Ground water of selected areas in Dindugul District.	Mrs. R. Chitradevi, Assistant Professor
11	15BC4173	Kaviya S	Chemistry	A comparative study of photocatalytic decoloration of Congo Red dye by using ZnO, Al-Zn LDH, ZnO/Al-Zn LDH catalyst under sunlight irradiation	Mrs. V. Anitha, Assistant Professor
12	15BC4174	Kayal R	Chemistry	Eco-friendly synthesis and characterization of zinc oxide nanoparticles	Dr. E. Vaishnavi, Assistant Professor
13	15BC4175	Kiruthika D	Chemistry	Corrosion inhibition of carbon steel using natural polysaccharide in sulphuric acid medium	Mrs. M. Malarvizhi, Assistant Professor
14	15BC4176	Latha S	Chemistry	A comparative study of photocatalytic decoloration of Congo Red dye by using ZnO, Al-Zn LDH, ZnO/Al-Zn LDH catalyst under sunlight irradiation	Mrs. V. Anitha, Assistant Professor
15	15BC4177	Lavanya M	Chemistry	Ru(II) Coumarin Complex as Colorimetric Sensor for Detection of Cobalt	Dr. J. Bhuvaneswari, Assistant Professor
16	15BC4178	Madhumitha Sri L	Chemistry	Removal of Malachite Green dye from aqueous solution by adsorption technique	
17	15BC4179	Mahalakshmi M	Chemistry	Green synthesis of iron nanoparticles using Ocimum basilicum extract	Dr. E. Vaishnavi, Assistant Professor
18	15BC4180	Mahalakshmi R	Chemistry	Removal of malachite green dye from aqueous solution by adsorption technique	Mrs. S. Umadevi, Assistant Professor
19	15BC4181	Manjuladevi V	Chemistry	Green corrosion inhibition for Carbon Steel in Sulphuric Acid Medium	Mrs. M. Malarvizhi, Assistant Professor
20	15BC4182	Nandhini S	Chemistry	Phenazine Based Colorimetric Sensor for the Detection of Cobalt Ion	Dr. J. Bhuvaneswari, Assistant Professor
21	15BC4183	Nishara Farveen S	Chemistry	Phenazine Based Colorimetric Sensor for the Detection of Cobalt Ion	Dr. J. Bhuvaneswari, Assistant Professor
22	15BC4184	Nivetha P	Chemistry	Phenazine Based Colorimetric Sensor for the Detection of Cobalt Ion	Dr. J. Bhuvaneswari, Assistant Professor
23	15BC4185	Parameshwari R	Chemistry	A comparative study of photocatalytic decoloration of Congo Red dye by using ZnO, Al-Ca LDH, ZnO/Al-Ca LDH catalyst under sunlight irradiation.	Mrs. V. Anitha, Assistant Professor
24	15BC4186	Pazhaniyammal K	Chemistry	Mild Steel Corrosion Inhibition using Gum Exudates of Azadirachta Indica in Sulphuric Acid	Mrs. M. Malarvizhi, Assistant Professor
25	15BC4187	Periyanayakam N	Chemistry	Removal of Methylene Blue dye from aqueous solution by adsorption technique	Dr. M. Indrani, Assistant Professor
26	15BC4188	Priya K	Chemistry	A comparative study of photocatalytic decoloration of Congo Red dye by using ZnO, Al-Zn LDH, ZnO/Al-Zn LDH catalyst under sunlight irradiation	Mrs. V. Anitha, Assistant Professor
27	15BC4189	Pushpavathi K	Chemistry	Physico-chemical analysis of Ground water of selected areas in Dindugul District.	Mrs. R. Chitradevi, Assistant Professor
28	15BC4190	Ramya A	Chemistry	Physico-chemical analysis of Ground water of selected areas in Tirupur District.	Mrs. R. Chitradevi, Assistant Professor
29	15BC4191	Ramya P	Chemistry	Removal of Malachite Green dye from aqueous solution by adsorption technique	Dr. M. Indrani, Assistant Professor
30	15BC4192	Rasiya Begam M	Chemistry	Removal of congo red dye from aqueous solution by adsorption technique	Mrs. S. Umadevi, Assistant Professor
31	15BC4194	Sabina Z	Chemistry	A comparative study of photocatalytic decoloration of Congo Red dye by using ZnO, Al-Ca LDH, ZnO/Al-Ca LDH catalyst under sunlight irradiation.	Mrs. V. Anitha, Assistant Professor
32	15BC4195	Sangeetha K	Chemistry	Removal of Methylene Blue dye from aqueous solution by adsorption technique	Dr. M. Indrani, Assistant Professor
33	15BC4196	Sangeetha K	Chemistry	Corrosion inhibition of carbon steel using natural polysaccharide in sulphuric acid medium	Mrs. M. Malarvizhi, Assistant Professor
34	15BC4197	Saranya C	Chemistry	A comparative study of photocatalytic decoloration of Congo Red dye by using ZnO, Al-Ca LDH, ZnO/Al-Ca LDH catalyst under sunlight irradiation.	Mrs. V. Anitha, Assistant Professor
35	15BC4200	Savitha P	Chemistry	Physico-chemical analysis of Ground water of selected areas in Tirupur District.	Mrs. R. Chitradevi, Assistant Professor
36	15BC4201	Selvi M	Chemistry	Green synthesis of silver nano particles using herbal extracts	Dr. E. Vaishnavi, Assistant Professor
37	15BC4202	Shahana Banu S	Chemistry	Corrosion inhibition of carbon steel using natural polysaccharide in sulphuric acid medium	Mrs. M. Malarvizhi, Assistant Professor
38	15BC4203	Shanmugapriya V	Chemistry	Removal of Methylene Blue dye from aqueous solution by adsorption technique	Dr. M. Indrani, Assistant Professor
39	15BC4205	Sivaranjini K	Chemistry	Eco-friendly synthesis and characterization of zinc oxide nanoparticles	Dr. E. Vaishnavi, Assistant Professor
40	15BC4206	Sowndarya S	Chemistry	Eco-friendly synthesis and characterization of calcium oxide nanoparticles	Dr. E. Vaishnavi, Assistant Professor
41	15BC4207	Sowdeswari M	Chemistry	Physico-chemical analysis of Ground water of selected areas in Tirupur District.	Mrs. R. Chitradevi, Assistant Professor
42	15BC4208	Sudha R	Chemistry	Ru(II) Coumarin Complex as Colorimetric Sensor for Detection of Cobalt	Dr. J. Bhuvaneswari, Assistant Professor
43	15BC4209	Sumithra D	Chemistry	Removal of malachite green dye from aqueous solution by adsorption technique	Mrs. S. Umadevi, Assistant Professor
44	15BC4210	Susmitha R	Chemistry	Removal of malachite green dye from aqueous solution by adsorption technique	Mrs. S. Umadevi, Assistant Professor
45	15BC4111	Umamagheswari M	Chemistry	Physico-chemical analysis of Ground water of selected areas in Dindugul District.	Mrs. R. Chitradevi, Assistant Professor
46	15BC4212	Vidhya S	Chemistry	Eco-friendly synthesis and characterization of calcium oxide nanoparticles	Dr. E. Vaishnavi, Assistant Professor
47	15BC4213	Vinothini S	Chemistry	Removal of congo red dye from aqueous solution by adsorption technique	Mrs. S. Umadevi, Assistant Professor

A COMPARATIVE STUDY OF PHOTO CATALYTIC DECOLORATION OF CONGO RED DYE BY USING ZnO, Al-Ca LDH, ZnO/Al-Ca LDH CATALYSTS UNDER SUNLIGHT IRRADIATION

Project Report Submitted to

SRI GVG VISALAKSHI COLLEGE FOR WOMEN (AUTONOMOUS) UDUMALPET

(Re-accredited at 'A' Grade CGPA of 3.53 by NAAC
An ISO 9001-2008 Certified Institution
affiliated to Bharathiar University, Coimbatore)

in partial fulfillment of the requirements for the

Degree of

BACHELOR OF SCIENCE

in

CHEMISTRY

by

R. PARAMESHWARI (Reg.No:15BC4173)
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DEPARTMENT OF CHEMISTRY

SRI GVG VISALAKSHI COLLEGE FOR WOMEN (AUTONOMOUS)

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UDUMALPET – 642 128

APRIL - 2018

CERTIFICATE

This is to certify that the project entitled "**A COMPARATIVE STUDY OF PHOTO CATALYTIC DECOLORATION OF CONGO RED DYE BY USING ZnO, Al-Ca LDH, ZnO/Al-Ca LDH CATALYSTS UNDER SUNLIGHT IRRADIATION''** is the bonafide work done by **R. PARAMESHWARI (15BC4185)** in partial fulfilment of the requirements for the award of the degree of Bachelor of Science in Chemistry in Sri GVG Visalakshi College For Women (Autonomous), Udumalpet during the academic year 2017-2018.

Submitted for the viva-voice held on ____________________

Signature of the Guide **Signature of the HOD**

Internal Examiner **External Examiner**

Signature of the Principal

DECLARATION

I hereby declare that the project entitled **"A COMPARATIVE STUDY OF PHOTO CATALYTIC DECOLORATION OF CONGO RED DYE BY USING ZnO, Al-Ca LDH, ZnO/Al-Ca LDH CATALYSTS UNDER SUNLIGHT IRRADIATION"** submitted to the Department of Chemistry, Sri GVG Visalakshi College For Women (Autonomous), Udumalpet in partial fulfillment of the requirements for the award of the Degree of Bachelor of Science in Chemistry, is a record of original project work done by me under the supervision and guidance of **Mrs. V. Anitha M.Sc., B.Ed., M.Phil.,** Assistant professor, Department of Chemistry, Sri GVG Visalakshi College For Women (Autonomous), Udumalpet.

Place: Udumalpet **Signature of the candidate**

Date: **R. PARAMESHWARI**

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CHAPTER 1

INTRODUCTION

1.1Environmental pollution

Environment pollution is a wide-reaching problem and it is likely to influence the health of human populations is great. Pollution reaches its most serious proportions in the densely settled urban-industrial centers of the more developed countries. In poor countries of the world more than 80% polluted water have been used for irrigation with only seventy to eighty percent food and living security in industrial urban and semi urban areas. Pollution can be made by human activity and by natural forces as well [1].

1.2 Dye industry

Recently, there is a growing concern about the damage done to the natural environment due to the human activity. Industry is usually blamed for the introduction of pollutants to the environment. Some of them are resistant to environmental degradation and have the tendency to accumulate in the food chain. Therefore, there is an interest in development of innovative, efficient, cheap and environment friendly techniques for the degradation of these pollutants [2].

1.3 Dyes and their intermediates: Environmental Anxiety

Dye pollutants from the textile industries play a very important liability in contaminating the environment. Environmental pollution by the wastewater containing dyes is setting an ecological problem and hazards to aquatic animals. About 15% of the total world production of the dyes is lost during the dyeing process [3].

1.3.1 Dye:

A dye is a coloured compound, normally used in solution, which is capable of being fixed to a fabric. A dye its colour to the presence of a chromophore and its fixing property to the acidic or basic auxochromic groups such as OH, SO_3H, NH_2, NR_2, *etc*.

1.3.2 Classification of dyes

Dyes may be classified according to the type of *chromophores* present in their structures.

1.3.2.1 Nitro and Nitroso dyes:

The NO_2 and NO groups are chromophores in this class of dyes. Examples are, Naphthol yellow S and Mordant green 4

1.3.2.2 Azo dyes:

The azo dyes contain one or more azo groups, -N=N-, as the primary chromophore. Azo dyes form the largest and most important group of synthetic dyes. They are highly coloured and can prepared by diazotizing an aromatic amine and subsequent coupling with a suitable aromatic phenol or amine. Examples are, Para Red, Methyl Orange, Congo Red and Bismarck Brown

1.3.2.3 Triarylmethene dyes:

In triarylmethene dyes, a central carbon is bonded to three aromatic rings, which is in the quinoid form (chromophore). The auxochromes are $–NH_2$,$-NR_2$ and –OH. Examples are Malachite green, phenolphthalein and Fluorescein

1.3.2.4 Anthraquinone dyes:

The para quinoid chromophore is present in these anthracene types of dyes. Examples are, Alizarin red is a typical anthraquinone dye. Neutral red is a typical anthracene or phenazine group of dye [4].

1.4 Methods for decoloration of Dyes

Various physical, chemical and biological treatments have been widely used to handle the dye removal from wastewaters in order to comply with the environmental regulations, which are becoming more stringent these days. Physical and biological treatments have been successfully applied till now.

Methods adopted to remove the pollutants are given below:

1. Decomposition
2. Coagulation
3. Flocculation followed by precipitation
4. Chemical reduction followed by precipitation
5. Contact filtration
6. Adsorption
7. Biological removal
8. Electrolysis
9. Electro-dialysis
10. Electro-coagulation
11. Reverse osmosis
12. Ion exchange
13. Photocatalytic degradation

But these methods have their own drawbacks. The aerobic treatment process is associated with the formation and disposal of large amounts of biological sludge, while wastewater treated by anaerobic treatment method does not lower down the pollutant contents to a satisfactory level. Activated charcoal adsorption and air stripping methods are non-destructive, since they simply transfer the pollutants from water to another phase.

The disadvantages of biological removal are needed to be used at much higher temperature to be effective, which are costly and cause problems to the environment. The Electro-dialysis process is used for the water pre-treatment. But it forms some disadvantages are, organic matter, colloids and SiO_2 are not removed by ED system. The reverse osmosis (RO) process is applied pressure must exceed the osmotic pressure to obtain product flow and to separate the solute from the solvent .The inherent disadvantage of electrocoagulation is the generation of large quantities of chemical sludge and its classification as hazardous waste. There are certain disadvantages associated with ion exchange, such as calcium sulfate fouling, iron fouling, adsorption of organic matter, organic contamination from the resin, bacterial contamination and chlorine contamination [5].

Many studies have been carried out on the toxicity of dyes and their impact on the eco system as well as the environmental issues associated with the manufacture of dyes.

1.5 Photochemistry

Photochemical reactions form a basis for the development of the world in its present form, having Sun as the central figure. Initially, Sun was the source of energy but with the passage of time, nature developed various other photo biological reactions and thus, provided a way for the self-propagation of life.

Photochemistry is concerned with reactions which are initiated by electronically excited molecules. Excited molecules are produced by the adsorption of suitable radiation in the visible and UV region of the spectrum [6].

1.6 Photocatalysis

Photocatalysis may be termed as a photo induced reaction which is accelerated by the presence of a catalyst. These types of reactions are activated by absorption of a photon with sufficient energy (equals or higher than the band-gap energy (E_{bg}) of the catalyst). The absorption leads to a charge separation due to promotion of an electron (e^-) from the valence band of the semiconductor catalyst to the conduction band, thus generating a hole (h^+) in the valence band [7].

1.7 Photodecoloration

Among the various physical, chemical and biological techniques for treatment of wastewaters, heterogeneous photocatalysis has been considered as a cost-effective alternative for water remediation. Photocatalytic decoloration has been shown to be one of the most promising processes for the wastewater treatment due to its advantages over the traditional techniques, such as quick oxidation, no formation of polycyclic products, oxidation of pollutants in the parts per billion (ppb) ranges, *etc*. The primary mechanism of photodecoloration is the generation of hydroxyl radicals obtained by the reaction of holes with surface hydroxyls or water and their attachment to organic compounds [8].

1.8 Congo red

Congo red [1-naphthalene sulfonic acid, 3,30-(4,40-biphenylenebis (azo)) bis (4-amino) disodium salt, CR] is a benzidine-based anionic disazo dye, i.e. a dye with two azo groups. Synthetic dyes, such as Congo red, are difficult to biodegrade due to their complex aromatic structures, which provide them physicochemical, thermal and optical stability. Therefore, there is an urgent requirement for development of innovative, but low-cost processes, by which dye molecules can be removed.

Adsorption technique is quite popular due to simplicity and high efficiency, as well as the availability of a wide range of adsorbents .Various adsorbents have been tested and used for the removal of dyes from polluted water. A number of non-conventional adsorbents such as montmorillonite, bentonite, rice hull ash, leaf, flyash, activated redmud, rice husk, fungi, coir pith carbon, mesoporous activated carbons, anilinepropylsilica xerogel, Azadirachta indica leaf powder, chitosan, and mesoporous Fe_2O_3, have been used for the removal of CR from aqueous solutions. However, some of these adsorbents do not have good adsorption capacities for anionic dyes [9].

1.9 Clay

One of the major current challenges before chemists is to develop synthetic methods that are less polluting, i.e., to design clean or 'green' chemical transformations. The chemical manufacturing processes should be such that they do not cause permanent damage to the environment or disturb the ecological balance The problem has become more acute in recent times and has received wider attention because of our better understanding of the causes of environmental degradation. The area of chemistry, which is particularly directed to achieve such goals, is termed as 'green chemistry' and is defined, according to an US award programme [10].

In efforts aimed at the development of new drug compounds, pharmaceutical companies and academic research labs also generate a significant amount of chemical waste that is hazardous to the environment. Since the Pollution Prevention Act of 1990 was passed, however, chemists have attempted to minimize waste by designing new, more environmentally friendly methods for synthesizing useful organic compounds. This movement, often referred to as “Green Chemistry,” has produced an array of improved methodologies, including the use of clays as chemical catalysts [11].

Clay catalyst is one of the important smectite groups mineral. Clay catalysts have been shown to contain both Brönsted and Lewis acid sites [12, 13] with the Bronsted sites mainly associated with the interlamellar region and the Lewis sites mainly associated with edge sites. The chemical formula of montmorillonite is $Al_2Si_4O_{10}(OH)_2.\ nH_2O$. Montmorillonite (MMT for short) may appear in variety of colors (e.g. yellow-green, yellow-white, gray and white) due to other trace metal elements; it typically forms microscopic or at least very small platy micaceous crystals. The moisture content is variable; in particular, due to swelling effects the volume of MMT crystal may increase several to thirty-fold after absorption of water. The crystalline structure of MMT consists of multiple layers and each layer made up of one octahedral alumina sheet sandwiched between two tetrahedral silica sheets [14] Montmorillonite clay’s are layered silicates and are among the numerous inorganic supports for reagents used in organic synthesis. They can be used as an efficient and versatile catalyst for various organic reactions [15].

1.9.1 Structure of Clay:

Clay minerals are made up of layered silicates. They are crystalline materials of very fine particle size ranging from 150 to less than 1 micron (colloidal form). There are two basic building blocks viz. tetrahedral and octahedral layers, which are common to clay minerals (**Figure 1**).

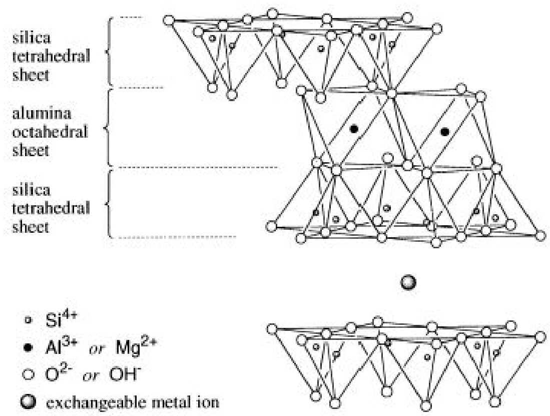


Figure 1 Structure of K10-Montmorillonite clay

1.9.2 Hydrotalcites

Hydrotalcite (a mineral that can be easily crushed into a white powder similar to talc, discovered in Sweden around 1842) is a hydroxycarbonate of magnesium and alumiium and `rs in nature in foliated and contorted plates and/or fibrousmasses. The exact formula for hydrotalcite, $[Mg_6Al_2(OH)_{16}CO_3.4H_2O]$ and of the other isomorphous minerals have been identified by Manasse, at the University of Florence (Italy), who is also the first to recognise that carbonate ions are essential for this type of structure.[16]

On the basis of X-ray investigations, Aminoff and Broome [17] have recognised the existence of two polytypes of hydrotalcites, the first one having rhombohedral symmetry and the second having hexagonal symmetry, which are called manasseite in honour of Manasse. Anionic clays, natural and synthetic layered mixed hydroxides containing exchangeable anions, are less well known and diffuse in nature than cationic clays. Hydrotalcite belongs to the large class of anionic clays. The anionic clays based on hydrotalcite like compounds have found many practical applications (**Figure 2**).

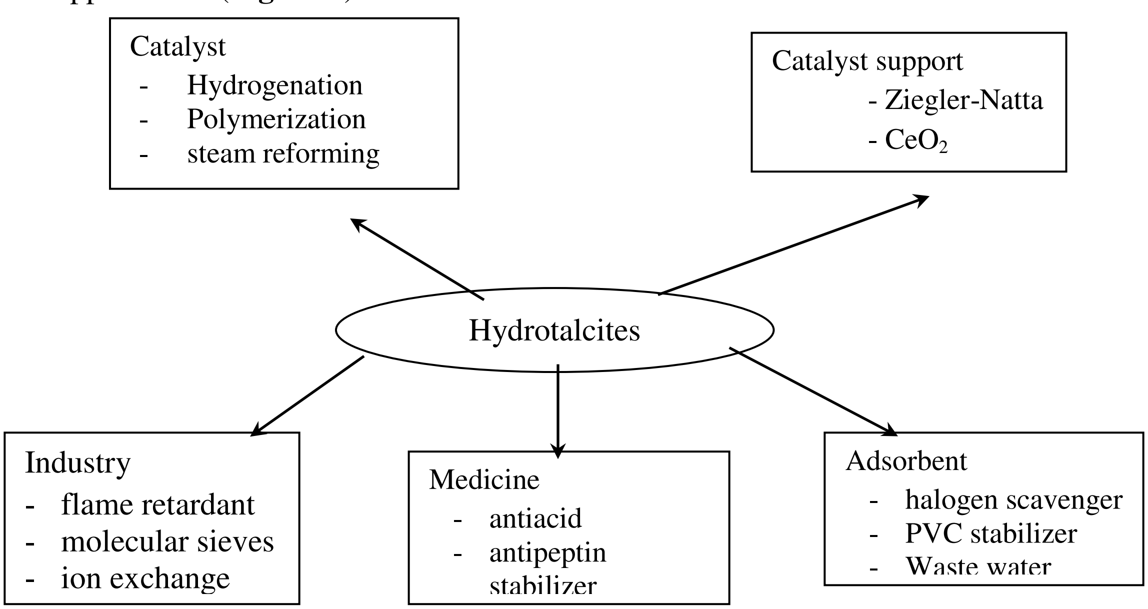


Figure 2 Potential applications of hydrotalcite-like compounds (HTlc)

The hydrotalcites have been used as such or after calcinations. The most interesting properties of the oxides obtained by calcination are the following.

1) High surface area,
2) Basic properties,
3) Formation of homogeneous mixtures of oxides with very small crystal size, which are stable to thermal treatments and
4) "Memory effect" which allows the reconstruction under, mild conditions, of the original hydrotalcite structure when contacting the product of the thermal treatment with water solutions containing various anions.

Properties 1, 2 and 3 have found application in the field of heterogeneous catalysis (hydrogenation, reforming basic catalysts and as support). Properties 1, 2 and 4 are utilized in applications such as the scavenging of chlorine ions and the purification of water containing waste anions (organic and inorganic).

1.9.2.1 Structure of hydrotalcite

To understand the structure of these compounds it is necessary to start from the structure of brucite, $Mg(OH)_2$, where octahedra of Mg^{2+}(6-fold coordination to OH^-) share edges to form infinite sheets (**Figure 3**). These sheets are stacked on top of each other and are held together by hydrogen bonding.

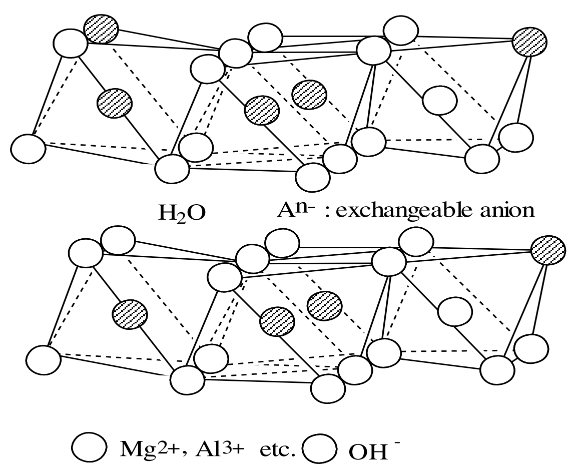


Figure 3 Structure of hydrotalcite

When Mg^{2+} ions are substituted by a trivalent ion having not too different a radius (such as Fe^{3+} for pyroaurite and Al^{3+} for hydrotalcite, respectively), a positive charge is generated in the hydroxyl sheet. The net positive charge is compensated by $(CO_3)^{2-}$ anions which lie in the interlayer region between the two brucite-like sheets. In the free space of this inter-layer the water of crystallization also finds a place.

The sheets containing cations are built as in brucite, where the cations randomly occupy the octahedral holes in the close packed configuration of the OH^- ions. The anion and water are randomly located in the interlayer region, being free to move by breaking their bonds and forming new ones (as in liquid water). The oxygen atoms of the water molecules and of the $(CO_3)^{2-}$ groups are distributed approximately closely around the symmetry axes that pass through the hydroxyl groups (0.56 Å apart) of the adjacent brucite-like sheet.

1.9.2.2 Hydrotalcite–like compounds

Hydrotalcite-like anionic clays (HTlc) constitute a class of extremely useful materials in the field of catalysis. Hydrotalcite-like anionic clays are synthetic (or) natural crystalline materials consisting of positively charged two dimensional sheets with water and exchangeable charge-compensating anions in the interlayer region. Their general formula is

$$\mathbf{[M(II)_{1-x}M(III)_x(OH)_2]^{x+}\ (A^{n-}{}_{x/n}).mH_2O}$$

Where M (II) and M (III) represent divalent and trivalent cations in the brucite type layers, A is the interlayer anion with charge n, x is the fraction of the trivalent cation (x values in the general formula are in the range of 0.20-0.50) and m is the water of crystallization. Because of their structure, HTlcs are also known as layered double hydroxide (LDHs).

The main features of HTlc structures are determined by the nature of the brucite-like sheet, by the position of anions and water in the interlayer region and by the type of stacking of the brucite - like sheets.

CHAPTER II

REVIEW OF LITERATURE

Literature in the field of photo degradation of dyes using varies catalyst was surveyed and summarized in this Chapter II

2.1 Photocatalytic degradation of dyes by busing various photocatalyst

K. Sahel *et al*., performed by photocatalytic efficiency in the degradation of methylene blue and Remazol black dyes was compared with the efficiency of P25 titanium oxide. In the dark, the adsorption of methylene blue on Ti-clays is total and fast. Ag doping of the clay increases this kinetics of adsorption, but does not alter the amount adsorbed [1].

A dye-sensitization technique applied to effective catalysts—TiO_2 and ZnO—under fluorescent light irradiation for Orange II and Methyl Orange degradations. Treatments were carried out at different time periods using 20 mg of catalysts and 30 mL of 5 mg/L of OII and MO. The degradation efficiency increased with increasing irradiation time under irradiation of light was studied *by* **Md. Ashraful Islam Molla** *et al., [2].*

L. **Cottet** *et al.,* was performed by Montmorillonite clay modified with iron oxide was prepared for use as an adsorbent of methylene blue dye. Structural characterization of MtMIO was performed by field-emission scanning electron microscopy, energy-dispersive spectroscopy; surface area measurements, zeta potential analysis and Fourier transform infrared spectroscopy. Batch experiments were carried out under different conditions of initial dye concentration, contact time and temperature to investigate the adsorption of methylene blue [3].

Qi Xiao *et al*., was investigated by photocatalytic degradation rates of methylene blue (MB) under either UV or visible light. The results showed that doping with the samarium ions significantly enhanced the photocatalytic activity for MB degradation under UV or visible light irradiation. This was ascribed to the fact that a small amount of samarium simultaneously increased adsorption capacity and separation efficiency of electron-hole pairs [4].

The photocatalytic decolourisation and degradation of an azo dye Reactive Yellow 14 (RY14) in aqueous solution with TiO_2 as photocatalyst in slurry form have been using solar light. The various photocatalyst on the decolourisation and degradation reveals the following order of reactivity: ZnO > TiO2-P25 > TiO2. CdS, Fe2O3 and SnO2 have negligible activity on RY14 decolourisation and degradation. The effects of various parameters such as catalyst loading and initial dye concentration on decolourisation and degradation have been investigated by **M. Muruganandham** *et al.,* [5].

R. Vinu *et al.,* was performed by catalysts are used for the first time for liquid phase photo catalysis. The photocatalytic degradation of various dyes such as Alizarin Red S, Methylene Blue, Orange G and Rhodamine B and phenol and 4-chlorophenol was investigated under UV exposure. Though Pd-ion substituted Titania has significantly higher photocatalytic activity [6].

Yu Zhiyong *et al., was* studied the discoloration of the azo-dye Orange II was carried out in a concentric coaxial photo-reactor and was a function of the Orange II and ox one concentrations, the solution pH and the recirculation rate. At bio-compatible pH-values, the concentration of Co-ions in solution after photo catalysis (15 min) was found to be between 0.5 and 2 ppm, within the limits allowed for treated waters. The generation of peroxide was observed as long as Orange II was still available in solution. [7].

The photocatalytic degradation of Direct Yellow12 (DY12) a batch process using ZnO as the catalyst on irradiation with light. Experiments were carried out under different conditions of initial dye concentration, contact time and temperature to investigate the adsorption, The influence of pH, catalyst weight and initial concentration of the dye on the degradation of the dye was investigated by **A. Nageswara Rao** *et al*., [8].

Chungshin Lu *et al.*, performed by ZnO-mediated photo catalysis process was used to successfully degrade Basic Blue 11 (BB-11) under solar light irradiation. The effects of influential factors like initial dye concentration, catalyst dosage, and initial pH. The photodegradation of the BB-11 dye with low watt visible light irradiation, a large number of the intermediates resulting from the photodegradation were separated, identified, and characterized [9].

K. Sahel *et al.,* was studied by anionic Remazol black is less adsorbed, and its photodegradation. The comparison of the photocatalytic activity of these materials shows that TiO_2 remains the most efficient catalyst, and decreases the activity in agreement with its lower adsorption capacity. The initial rate of reaction was found to be directly proportional to the results observed using TiO2 powder at low concentration. The photocatalytic degradation of anionic dyes which remains pollutants can be removed by adsorption and photo catalysis [10].

2.2 Scope of the present work

Congo red dye is one of the main effluents present in the waste water of several Industrial therefore the removal of Congo red dye past 20 discharged from this most essential. During the last 20 years ZnO is used as efficient photocatalyst and the applications of ZnO and their modifications to photocatalytic degradation of dyes have been extensively reported. HT and HT like compounds having catalytic activity in organic synthesis and in photodegradation.

Hence it is decided to study the effect of ZnO, HT like compound and ZnO doped HT like compound in the photodegradation of Congo red dye. As sunlight is the major as well as economical source for the study of discoloration of any pollutants. It is planned to investigate the effect of various parameters like concentration of the dye, irradiation time, and dose of the catalysts and pH of the dye solutions under sunlight.

CHAPTER III

EXPERIMENTAL PART

This section deals with the chemicals used and the methodology adopted to estimate the decoloration of dye in sun light.

3.1. Materials

The glass apparatus used for all experiments were well cleaned and rinsed with double distilled water. All the solutions required for the experiments were prepared using double distilled water. To obtained reproducible results and to minimize the experimental errors a high degree of purity of the reagents employed is necessary. Therefore 'Analytical Reagent' grade chemicals were used to the maximum extent.

3.2. List of chemicals

The following chemicals were used for the present study,

- Sodium hydroxide
- Sodium carbonate
- Aluminium nitrate
- Calcium nitrate
- Zinc oxide
- Congo Red

3.3. Preparation of Congo red

The solution of Congo red were prepared by dissolving appropriate amounts (accurate weighed) of dry powered dye in double distilled water to prepare stock solution (1000mgL^{-1}). The experimental solution was obtained by dilutions were made to obtain the working solution at desired concentrations.

3.4.Structure and properties of Congo Red

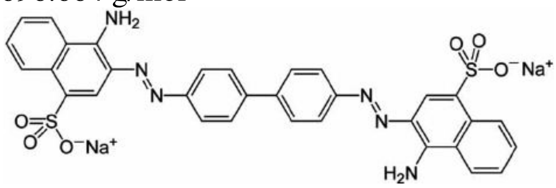
Molecular Formula	$C_{32}H_{22}N_6Na_2O_6S_2$
Synonym	Direct red 28, Benzo Congo Red, Haemomedical, Congo red 4B, 573-580.
Molecular weight	696.664 g/mol
Structure	
λmax	497nm
Solubility	Water
Physical state	Powder
Appearance	Red colour
Toxicity	Carcinogen, mutagen

Table 1 - Structure and physical and chemical properties of Congo Red

3.5. Synthesis of photo catalyst

3.5.1. Precipitation at low super saturation

Co precipitation at low super saturation, at constant pH, is the method most frequently used in the preparation of Layered Double Hydroxide (LDH). The conditions most commonly utilized are the following: pH ranging from 7 to 10, temperature 333-353K, low concentration of reagents and low flow of the two streams. Washing is carried out with warm water, and some aging under the conditions of precipitation is usually done; the drying temperature does not exceed 393K. Low super saturation conditions usually give rise to precipitates which are more crystalline with respect to those obtained at the high super saturation conditions, because in the latter situation the rate of nucleation is higher than the rate of crystal growth. A large number of particles is obtained, which, however, are usually small in size.

3.5.2. Al-Ca LDH Preparation

0.0959 mole of $AlNO_3.9H_2O$ and 0.0925 mole of $Ca(NO_3)_2.6H_2O$ were dissolved in 200 mL of water, a second solution containing 0.3396 mole of Na_2CO_3 and 0.9 mole of NaOH in 200 mL of water was prepared. The two solutions were mixed drop wise in one beaker containing 500 mL water, under stirring, while keeping the pH between 10 and 11 at 333K. The precipitate was filter & and washed with 200 mL of water, and finally dried at 353K for 18 hours.

Formula: $Ca_2Al(OH)_6(NO3)_2.2H_2O$.

3.5.3. Preparation of ZnO/Al-Ca LDH

0.0959 mole of $AlNO_3.9H_2O$, 0.0925 mole of $Ca(NO_3)_2.6H_2O$ and 50 mg of ZnO were dissolved in 200 mL of water, a second solution containing 0.3396 mole of Na_2CO_3 and 0.9 mole of NaOH in 200 mL of water was prepared. The two solutions were mixed dropwise in one beaker containing 500 mL water, under stirring, while keeping the pH between 10 and 11 at 333K. The precipitate was filter & and washed with 200 mL of water, and finally dried at 353K for 18 hours.

Formula: ZnO /$Ca_2Al(OH)_6(NO_3)_2.2H_2O$

3.5.4. Equipmental Analysis

Irradiation was performed with Sun light.

Figure 3.1 Calorimeter

Figure 3.2 Digital pen pH meter

3.6 Methods

In the present work, the photo decoloration as ZnO, Al-Ca LDH, ZnO/Al-Ca LDH was studied in various experimental conditions in order to understand the effect of various experimental parameters under Sun light radiation. Experiments were carried out by employing the photocatalytic degradation technique. Photocatalytic decoloration of Congo Red dye on different photo catalysts such

1. Initial concentration of dye (at constant irradiation time, dose of the catalysts and initial pH).
2. Irradiation time of dye (at optimum initial concentration of the dye, at constant dose of the catalysts and initial pH).
3. Dose of the catalysts (ZnO, Al-Ca LDH, ZnO/Al-Ca LDH) (at optimum initial concentration, irradiation time and initial pH).
4. Initial pH of the dye solution (at optimum initial concentration, irradiation time and dose of the catalysts).

3.7. General procedure for Photocatalytic decoloration studies

3.7.1. Preparation of stock solution

A stock solution of the Congo Red dye with known initial concentration (1g/L) was prepared and stored in a brown bottle. It was diluted to get different required initial concentration of the dye and used in the photocatalytic decoloration experiments.

3.7.2. Establishing standard curve

20 mL solution of Congo Red dye in different initial concentrations such as 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 ppm were prepared in standard measuring flasks separately by using necessary suitable dilutions of stock solution of the dye (1000 ppm) with the required volume of double distilled water. The absorbance of each dye solution was measured by using calorimneter at 490 nm for Congo Red dye.

A plot of absorbance vs initial concentration (ppm) resulted in a straight line plot (**Figure 3.3**) indicating the applicability of Beer Lambert's law. The plot is considered as standard curve for the estimation of concentration of dye by interpolation technique. The values of absorbance for dye solutions, before and after photo degradation studies were also obtained by using calorimneter at the corresponding λmax value. The corresponding dye concentration was obtained from the standard curve **(Figure 3.3)** by the interpolation technique.

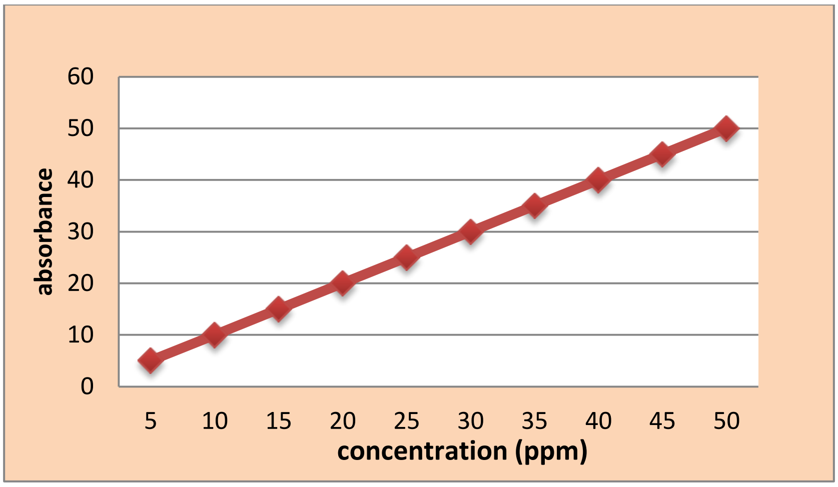


Figure 3.3 Standard curve of Congo Red dye

3.7.3. Photodecoloration Experiments

The stock solution of Congo Red dye was suitably diluted to the required initial concentration with double distilled water. Exactly 20 ml of the dye solution of known initial concentration (C_0) was taken for irradiation under sun light. Required amount of catalysts (ZnO, Al-Ca LDH, ZnO/Al-Ca LDH) was exactly weighed and then transferred to the reaction solution for irradiation under sun light fall into the place. After a definite period of irradiation, the solution was centrifuged immediately for the separation of the suspended solids. The solution was analyzed by measuring the absorbance using calorimeter. The dye solution before and after sun light irradiation is shown in (**Figures 3.4 and 3.5**)

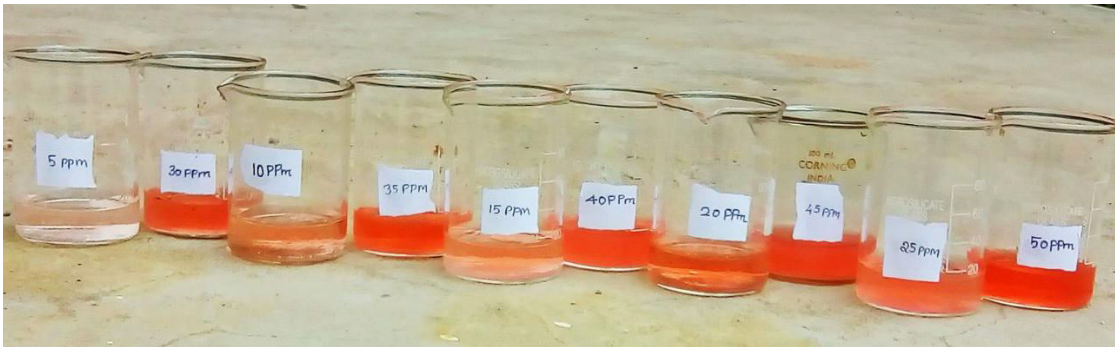


Figure 3.4 Photocatalytic decoloration of Congo Red dye before Sun light radiation (30 min.

Figure 3.5 Photocatalytic decoloration of Congo Red dye after Sun light radiation (30 min.)

3.7.4. Determination of percentage of decoloration

In the photodecoloration experiments, the extent of decoloration of the dye, in terms of the values of percentage decoloration of dye has been calculated using the following relationship:

Percentage of decoloration (R) = 100* ($C_0 - C_t$) / C_0

Where,

C_0 = initial reading of dye (ppm)

C_t = finial reading of dye (ppm) at a given time

In this study, (Table 4.1)

Initial reading of Congo Red = 0.08

Final reading of Congo Red at a given time (30 min) = 0.01

Percentage of decoloration (R) of Congo Red dye = 100 x (0.08- 0.01)/ 0.08

% of R = 87.5

3.7.5. Variation of irradiation time

In order to study the effect of irradiation time on the decoloration of Congo Red dye by photo decolouration experiments were carried out at constant dose of the catalyst (ZnO, Al-Ca LDH, ZnO/Al-Ca LDH) and optimum initial concentration at room temperature.

The decolouration was carried out at constant dose of the catalyst and optimum initial concentration, but varying the contact time. The dye solution was picked out at different time intervals *viz*., 5, 10, 15, 20, 30, 40, 50, 60 minutes and then the solution was centrifuged. The clean transparent solution was analysed by calorimetric by measuring its absorbance. The results were tabulated, and discussed in Chapter IV.

3.7.6. Variation of dose of the catalyst

To study the effect of dose of the catalysts (ZnO, ZnO/Al-Ca LDH, Al-Ca LDH) the initial concentration of the Congo Red dye in each case was kept constant at optimum value and the dose of the, ZnO, ZnO/Al-Ca LDH, Al-Ca LDH was varied from 50, 100, 150, 200, 250 mg. The absorbance of the filtrate was then measured. The results were tabulated and discussed in Chapter IV.

3.7.7. Variation of initial pH

The decoloration experiments were carried out at different initial pH at constant optimum initial concentration of the dye solution, dose of the catalyst (ZnO, Al-Ca LDH, ZnO/Al-Ca LDH) and contact time at room temperature, in order to study the effect of initial pH on the extent of decoloration of cong red dye by photodecoloration.

CHAPTER IV

RESULT AND DISCUSSION

4.1 Photodecoloration of Congo red dye under sun light irradiation

The experimental parameters which affect the extent of photodecoloration of dyes are reported to be initial concentration, irradiation time, dose of the catalysts and initial pH. The effect of these process parameters on the extent of removal of Congo Red dye by photodecoloration on the catalysts like **ZnO, Al-Ca LDH, ZnO/Al-Ca LDH** like compounds under solar light irradiation has been studied in the present investigation. Photocatalytic decoloration experiments are conducted by varying any one of the process parameters like, initial concentration of dye, irradiation time, dose of the catalyst and different initial pH of the medium, by keeping the other experimental parameters constant.

4.2 Effect of concentration dye

Because of considerable wide concentration range of organic pollutants in factual wastewaters, it is needed to consider the effect of dye concentration on the photocatalytic degradation under solar light irradiation.

Photocatalytic decoloration studies on the extent of removal of Congo Red dye by **ZnO, Al-Ca LDH, ZnO/Al-Ca LDH** like compounds are carried out at different initial concentrations (C_0) of Congo Red dye at different pH medium, the range of C_0= 5-50 ppm for the photocatalysts such as **ZnO, Al-Ca LDH, ZnO/Al-Ca LDH** with a fixed dose of the catalysts (50 mg) and 30 minutes of irradiation time for Congo Red dye. The experiments are carried out at sun light and the data obtained are tabulated.

TABULATION: 2

Effect of initial concentration on photo degradation of Congo Red dye on ZnO, Al-Ca LDH, ZnO/Al-Ca LDH under sunlight radiation.

Concentration range : 5-50 ppm

Irradiation time : 30 min

Dose of catalyst : 50 mg/20 ml

Initial Concentration of dye (ppm)	% of Decolorisation		
	ZnO	Al-Ca LDH	ZnO/Al-Ca LDH
5	64.5	72.28	81.77
10	61.3	71.77	79.47
15	59.9	70.73	75.2
20	57.8	69.72	74.98
25	56.9	67.76	72.73
30	55.2	66.42	72.72
35	54.7	65.6	71.01
40	53.9	63.2	69.1
45	52.2	61.54	67.5
50	51.86	60.65	66.6

Table 2: Effect of variation of initial concentration vs % of decoloration

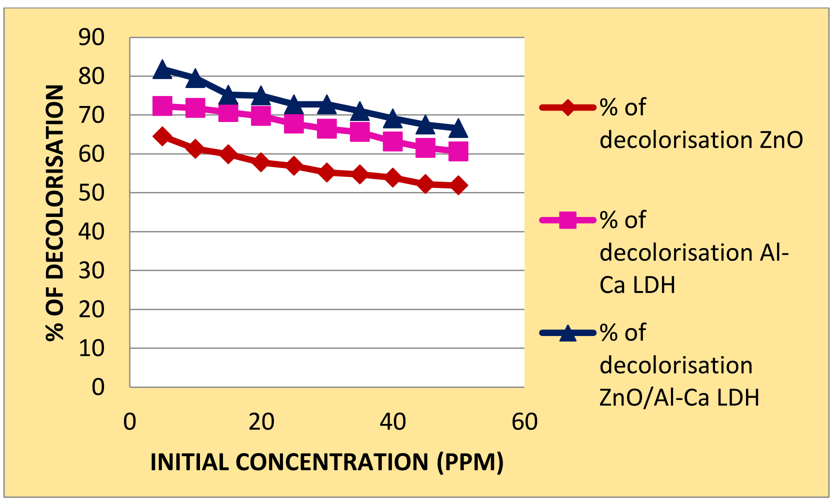


Figure 4.1: Effect of variation of initial concentration vs % of decoloration

The above result revel the percentage of decoloration decrease with increase in initial concentration of Congo Red dye with ZnO, Al-Ca LDH, ZnO/Al-Ca LDH. The possible reason is that, as the initial concentration of the dye is increased and more dye molecules are adsorbed on to the surface of the catalysts (ZnO, Al-Ca LDH, ZnO /Al-Ca LDH). But the adsorbed dye molecules are not decoloured immediately because the intensity of the light and the catalyst amount is constant and also the light penetration was less. Also with an increase in the dye concentration, the solution becomes more intense coloured and the path length of the photons enter the solution is decreased there by fewer photons reached the catalyst surface. Hence, the production of hydroxyl and superoxide radical are limited or reduced. Therefore, the photodecoloration efficiency is reduced. Still at higher concentration of the dye, the path length is further reduced and the photodecoloration are found to be negligible.

4.3 Effect of amount of catalyst

The effect of photocatalyst concentration on the photodegradation rate was studied by employing different concentrations of photo catalyst. As expected, the photodegradation rate was found to increase with the increase in the catalyst concentration. The results showed that ZnO doped exhibits higher photocatalytic activity.

It is well documented that the percentage of photocatalytic decoloration will increase with increase in dose of the catalysts. The increase in the efficiency seems to be due to increase in effective surface of the catalysts area and the absorption of light. At lower amount of catalysts loading, the absorption of light controlled the photocatalytic process due to the limited surface area of the catalyst. However, as the catalyst loading increased, an increase in the active sites of photocatalysts such as **ZnO, Al-Ca LDH, ZnO/Al-Ca LDH** is obtained. The number of photons adsorbed increases and hence the percentage of decoloration also increases.

TABULATION: 3

Effect of catalyst variation on photo degradation of Congo red dye on ZnO, Al-Ca LDH, ZnO/Al-Ca LDH under sunlight radiation

Dose of catalyst range : **50- 250mg / 20 ml**

Optimum concentration : **30ppm**

Irradiation time : **30 min**

Dose of catalyst (mg)	% of decolorisation		
	ZnO	Al-Ca LDH	ZnO Al-Ca LDH
50	61.81	69.18	72.54
100	63.27	72.81	80.18
150	68.09	74.27	83.81
200	70.54	78.09	89.27
250	71.18	80.54	91.09

Table 3: Effect of variation of dose of catalyst vs % of decoloration

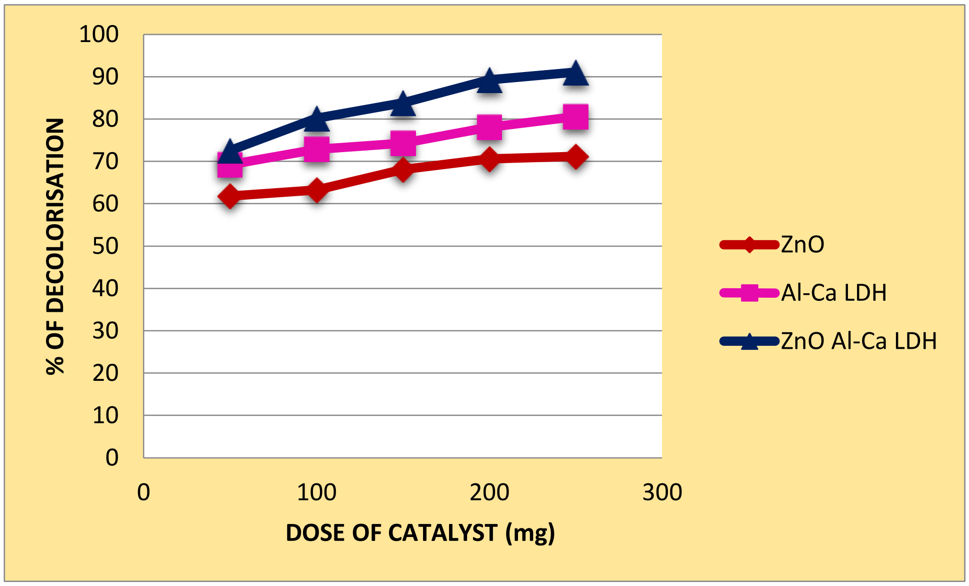


Figure 4.2: Effect of variation of dose of catalyst vs % of decoloration

It is well documented that the percentage of photocatalytic decoloration will increase with increase in dose of the catalysts. The increase in the efficiency seems to be due to increase in effective surface of the catalyst area and the absorption of light. At lower amount of catalyst loading, the absorption of light controlled the photo catalytic process due to the limited surface area of the catalyst. However, as the catalyst loading increased, and increase in the active sites of photo catalyst such as ZnO, Al-Ca LDH, ZnO/Al-Ca LDH is obtained. The number of photons adsorbed increases and hence the percentage of decoloration also increases.

4.4 Effect of pH

The photodegradation rate was found to increase and then decreases with increases in pH. At higher pH values, no photodegradation took place. More efficient formation of hydroxyl radical occurred in alkaline conditions.

At a pH below its pKa value, a dye pollutant is primarily in its molecular form. Above this pKa value, a dye pollutant tends to undergo de-protonation becoming negatively charged. These characteristics can significantly affect the interaction and affinity between both photocatalyst and dye pollutant when a variation of solution pH takes place.

The efficiency of photocatalytic processes strongly depends upon the pH of the reaction solution. Because of the amphoteric behavior of most of the semiconductor oxides, an important parameter governing the rate of reaction takes place on semiconductor surface. Normally, the different behavior of each semiconductor in relation to pH can be explained by unlike modifications of the surface properties, mainly due to the isoelectric point.

TABULATION: 4

Effect of pH on photo degradation of Congo Red dye on ZnO, Al-Ca LDH, ZnO/Al-Ca LDH under sunlight radiation

pH range : **1-13**

Dose of catalyst : **50mg/20 ml**

Optimum concentration : **30 ppm**

Irradiationtime : **30 min**

pH	% of decolorisation		
	ZnO	Al-Ca LDH	ZnO/Al-Ca LDH
1	10.64	11.66	13.04
3	19.01	24	26.66
5	25.04	32.12	39
7.3	45.4	50.9	71.79
9	41.93	46.66	51.27
10	37.42	44.45	47.66
11	34.8	43.27	45.45

Table 4: Effect of variation of pH vs % of decoloration

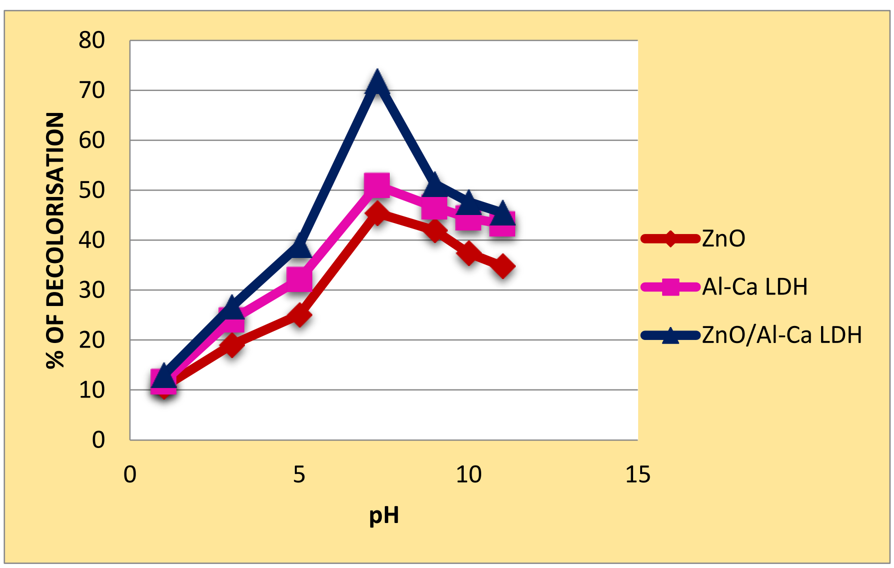


Figure 4.3: Effect of variation of pH vs % of decoloration

In the case of ZnO, The decoloration is gradually increased at pH range 1-7 (94.86% at pH 7) and the decoloration efficiency decreased above pH 7. The rate of Decoloration of Congo Red is maximum at pH 7.0. At pH 7-8, due to metal bound OH^-, negatively charged active sites on the surface of catalyst are preferentially covered by positively charged dye molecule. At lower pH ~3 positively charged active site on the surface of ZnO, Al-Ca LDH, ZnO/Al-Ca LDH, results in lower concentration of positively charged of dye molecule on the surface of ZnO, Al-Ca LDH**,** ZnO/Al-Ca LDH and at higher pH, surface concentration of dye molecules an hydroxyl radicals increases.

4.5 Effect of time

In order to study the effect of irradiation time (range 5-60 minutes) of Congo Red dye with **ZnO, Al-Ca LDH, ZnO/Al-Ca LDH** like compound catalysts on the extent of decoloration of the dye, the photodecoloration experiments are carried out at constant dose of the catalysts (50 mg). Optimum initial concentration of dye for **ZnO, Al-Ca LDH, ZnO/Al-Ca LDH** like compound is fixed as 30ppm. The percentage of decoloration of CR dye increases with increase in irradiation time during photolysis under solar light radiation.

The experiments are carried out at room temperature and the data obtained are tabulated. The effect of irradiation time of CR dye on the percentage of decoloration of dye **ZnO, Al-Ca LDH, ZnO/Al-Ca LDH** like compound are presented.

TABULATION 5

Effect of time on photo degradation of Congo red dye on ZnO, Al-Ca LDH, ZnO/Al-Ca LDH under sunlight irradiation.

Irradiation time range : 5-60 min

Optimum concentration : 30 ppm

Dose of catalyst : 50mg/20ml

Time (min)	% of decolorisation		
	ZnO	Al-Ca LDH	ZnO/Al-Ca LDH
5	51.45	55.81	61.18
10	54.72	58.45	67.81
15	56.18	62.72	69.45
20	61.81	69.18	71.72
30	64.27	68.81	72.18
40	68.4	71.27	81.81
50	71.18	74.9	87.27
60	73.81	80.87	90

Table 5: Effect of variation of time vs % of decolorisation

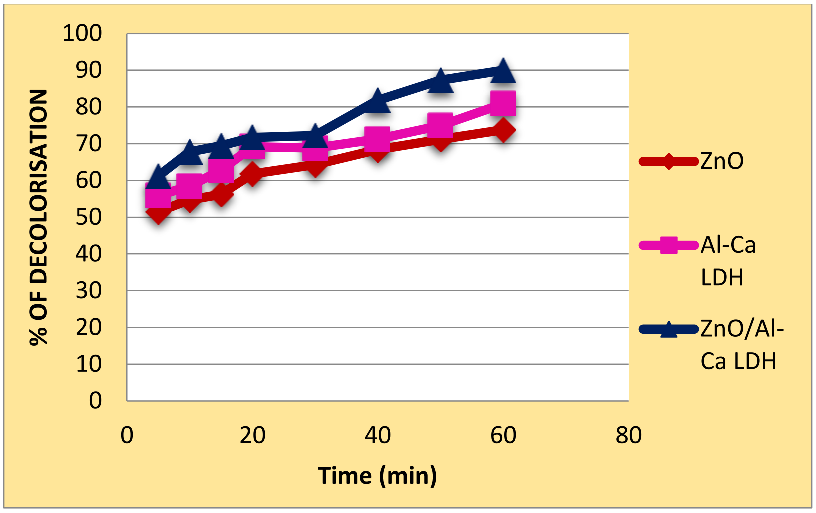


Figure 4.4: Effect of variation of time vs % of decolorisation

The observed data indicate that among these catalysts ZnO/ Al -Ca LDH catalyst is more efficient due to increasing surface area, the number of active sites of catalyst also increases. Hence the photodegradation rate of ZnO/ Al -Ca LDH is higher than bare ZnO.

CHAPTER V

SUMMARY

- The photo catalyst decoloration of Congo Red dye under sunlight has been investigated.
- The effect of various process parameters like concentration of the Congo Red dye, irradiation time, dose of the catalyst and pH of the Congo Red dye with different photo catalyst like ZnO, Al-Ca LDH, ZnO/Al-Ca LDH.
- Comparing the results on the basis of the efficiency of the catalyst it is conclude that, the decoloration of dye proceeds much more rapidly in the presence of ZnO/Al-Ca LDH as compared with other photo catalysts.
- The observed data indicate that among these catalysts ZnO/ Al-Ca LDH catalyst is more efficient due to increasing surface area, the number of active sites of catalyst also increases. Hence the photodegradation rate of ZnO/ Al - Ca LDH is higher than bare ZnO.
- ZnO/Al-Ca LDH is used as the photo catalyst since this material exhibited the highest overall activity for the decoloration of the dye.

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REMOVAL OF MALACHITE GREEN DYE FROM AQUEOUS SOLUTION BY ADSORPTION TECHNIQUE

DBT Funded Project

PROJECT REPORT

Submitted in partial fulfillment of the requirements for the award of the degree of Bachelor of Science in Chemistry

Submitted by

Kalaivani. M

Reg.No:15BC4168

Under the guidance of

Dr. (Mrs.). M.Indrani M.Sc., M.Phil., Ph.D., B.Ed., M.Lisc.,

Assistant Professor, Department of Chemistry.

DEPARTMENT OF CHEMISTRY

SRI GVG VISALAKSHI COLLEGE FOR WOMEN (AUTONOMOUS)

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CERTIFICATE

This is to certify that the project entitled "**Removal of Malachite Green Dye From Aqueous Solution By Adsorption Technique"** is the experimental work done by **M.Kalaivani (15BC4168)**in partial fulfillment of the requirement for the award of the degree of Bachelor of Science in Chemistry in **Sri GVG Visalakshi College For Women (AUTONOMOUS), Udumalpet** during the academic year 2017-2018.

Submitted for the viva-voice held on ____________________

Signature of the SupervisorSignature of the HOD

External Examiner

Signature of the Principal

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INTRODUCTION

One of the offshoots of industrialization and population growth is pollution, which is the waste water discharged by the industries and also solid wastes generated due to human activities as well as industries. Management of solid wastes and liquid effluents are a great menace and has become a formidable social problem. Many countries including India find it difficult to have a control on it. Liquid effluents and solid waste from textiles, paper, plastic, leather, food and cosmetic industries pollute soil and water which are the vital requisites of human life.

SOLID WASTE MANAGEMENT

Solid waste management may be defined as the application of techniques that will ensure the orderly performance of the purpose of collection, processing and disposal of solid waste. These parts are called the three basic functional components of solid waste management. Collection refers to the gathering of solid wastes from places such as residences, commercial, institutional and industrial establishments and public places. Processing refers to the activity applied to solid waste to prepare it for subsequent operation. Disposal refers to the placing of solid waste in its ultimate resting place.

Solid waste can be defined as the waste that is not transported by water but that has been rejected for further usage. Due to rapid urbanization the amount of solid waste problems is also increasing. Glynn Henry & Gary Heinke (2005) stated that solid waste generated from houses increased significantly in quantity and complexity with the advent of the throwaway society and the growth of the packaged and processed food industry. In spite of incurring huge expenditure, the services that are provided towards solid waste management are not fulfilling the requirements thereby causing public health hazard and nuisance. Hence there is a strong need to develop appropriate technology for the proper management of urban as well as rural solid wastes.

IMPACTS DUE TO SOLID WASTE

The municipal portion of the total solid waste generated represents only 5%. It receives most attention because of improper disposal and can have adverse effects on public health and water supplies (both surface water and ground water sources). The bulk of municipal solid waste consisted of ashes and food waste. Few scrap materials such as metals and rags that were recoverable were collected on a casual basis by scavengers. With the shift of burgeoning population to cities, urban population densities increased and society became increasingly industrialization.

INDUSTRIAL EFFLUENTS

Due to massive industrialization and urbanization, the development in printing, dyeing and textile industries has increased multifold. The effluent released proves to be highly hazardous (Gong et al 2005). The untreated effluents cause drastic reduction in the quality of water in the receiving body since they possess strong colors, high pH and large amount of suspended solids, TDS, BOD and COD. Thousands of dyes weighing approximately 0.7 million tons are produced annually for various industrial processes (Pearce al 2003).

DETRIMENTAL EFFECTS OF DYEING EFFLUENT

The complex aromatic frame work of dyes and presence of heavy metal induce toxicity in particular, and they may be mutagenic, teratogenic or carcinogenic (Martin and Holdich 1986, Anne et al 1986) and can cause severe damage to human beings by affecting the kidneys, reproductive system, liver, brain and central nervous system (Atef 2009). The problems with dyes also include haemorrhage, ulceration of skin and mucous membrane and irritation of the tract (Jain et al 1977).

Disposal of highly coloured water of low BOD and high COD into receiving waters can be toxic to aquatic life. The dyes prevent the re-oxygenation of the receiving waters by preventing penetration of sunlight, thus upsetting biological activity in the water bodies. These dyestuffs with toxic metals enter the fishes and rapidly affect the human body through the process of food chain.

Most commercial systems currently use activated carbon as sorbent to remove dyes in waste water because of its excellent adsorption ability. Activated carbon adsorption has seen cited by the US environmental Protection Agency as one of the best available control technologies (Derbyshire et al 2001). However its widespread use is restricted due to its high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents. Hence, the studies for the preparation and utilization of activated carbon adsorbents are warranted immediately.

Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many non-conventional low- cost adsorbents, including natural materials, bio-sorbents and solid waste materials from industry and agriculture, have been proposed by several workers. The materials that could be used as adsorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge), bio-sorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton).

ACTIVATED CARBON

Activated carbon is a micro porous inert carbon with a large internal surface (up to 1500 m^2/g). On this surface organic molecules from liquids or gases can adsorb. Activated carbon contains: (a) bulk atoms that are neutral, (b) surface atoms that are the real 'adsorption' atoms and (c) corner atoms that are very reactive and even react with metals. Activated carbon is capable of adsorbing a wide range of organic substances, oxidizing materials (such as chloride and ozone) and certain heavy metals from liquids and water. Adsorption is the natural phenomenon in which molecules from the gas or liquid phase are attached to the surface of the solid. The micro pores are developed primarily during carbon activation and result in the large surface area for adsorption to occur.

AGRICULTURAL WASTE INTO ACTIVATED CARBON

Abundance and low cost agricultural by-products and municipal waste materials known as putrescible vegetable waste (PVW)(vegetable and fruit peel- off) is a good selection as a precursor for the preparation of activated carbon. Almost any organic matter with a large percentage of carbon could theoretically be activated to enhance its sorptive properties. The major advantages of activated carbons are minimum amount of volatile organic matter, long shelf life, stability under usage, low cost and abundant.

ADSORPTION

Among other processes for removal of dyes from industrial waste water, adsorption process is an economically feasible alternative. Adsorption is a process in which a single or a group of ions/ compounds get accumulated on the surface of another solid or liquid. The substance on which the adsorption takes place is known as adsorbent and the substance, which gets adsorbed, is called adsorbate. Based on the extent of attraction between the adsorbent and adsorbate, the adsorption process can be classified into two types:

- Physical adsorption or Vander Waal's adsorption
- Chemisorption

Adsorption (Mahamudur Islam 2008), which can result from the Vander Waal's force of interaction, is known as physical adsorption or Vander Waal's adsorption. In this type of adsorption, the process heat is of the order of 20-40 KJ/mol. Physical adsorption process is reversible and established rapidly. In chemisorption, the chemical interaction/ electrostatic force of attraction occur between the adsorbent surface and adsorbate molecules. In this process, the heat of adsorption usually varies from 40 to 400 KJ/mol. It is associated with appreciably high activation energy and therefore termed as activated adsorption. It is a relatively slow process. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic in nature.

The adsorption process has many advantages such as (Desai et al 1997):

- Low cost of adsorbent
- Easy available of adsorbent
- Utilization of industrial, biological and domestic wastes as adsorbent
- Low operational cost
- Ease of operational compared to other processes
- Re-use of adsorbent after regeneration
- Capacity of removing dye molecules and heavy metal ions over a wide range of pH and to a much lower level
- Ability to remove complex form of metals that is generally not possible by other conventional method
- Environmental friendly, cost effective and technically feasible alternative due to utilization of biomaterials.

BATCH MODE ADSORPTION

Batch mode adsorption was employed to conduct the experiments which provided the required equilibrium and kinetic data (Stenzel 1993, Hsuen 2000). It helps in designing an efficient water treatment plant. Several advantages of conducting experiments in batch mode techniques are:

- Cheap and less time consuming
- Easy to interpret the results
- Does not depend on number of variables

Hence the study of any adsorption system in batch mode carries prime importance.

REVIEW OF LITERATURE

LOW COST ADSORBENTS FROM VARIOUS ACTIVATION METHODS

Malik (2003) prepared an activated carbon from low-cost mahogany sawdust and rice husk and utilized it for the removal of acid yellow 36 from its aqueous solution. Kadirvelu et al (2003) used freely, abundantly and locally available agricultural solid wastes, silk cotton hull, coconut tree sawdust, sago waste, maize cob and banana pith for the preparation of activated carbon. It involved quantitative removal of adsorbate like Rhodamine-B, Congo red, Methylene blue, Methylene violet, Malachite green, Mercury ($HgCl_2$), and Nickel ($NiSO_4$).

Activated carbons have been prepared from oak cups pulp, a lingo cellulosic waste material by chemical activation with phosphoric acid and zinc chloride as activating agent (Serkan Timur et al 2010). The aqueous adsorption tests showed that the surface chemistry of the activated carbons also played an important role in dye adsorptions as well as textural properties.

Deng et al (2010) prepared activated carbons from cotton stalk by microwave assisted KOH and K_2CO_3 activation method. Nevine Kamal Amina (2008) used bagasse pith, the main waste from sugarcane industry in Egypt, as raw material for the preparation of different activated carbons. Activated carbons were prepared from bagasse pith by chemical activation with 28% H_3PO_4, 50% $ZnCl_2$ followed by pyrolysis at 600^0C and physical activation at 600^0C in the absence of air. Different activated carbons have been used for the removal of reactive orange dye from aqueous solutions.

A study on the preparation of rice bran-based activated carbon was conducted by Suzuki et al (2007) with and without an acid treatment step prior to the activation process. The influence of the activation time on the structure of the activated carbons was evaluated. The acid treatment had a significant positive influence on sorption properties. Activated carbons were prepared from the biomass of oil palm wood via two stages, pyrolysis and physical activation, using an environmentally friendly pyrolysis pilot plant. An activation pilot plant was studied by Ahmad et al (2007). BET surface area of $931.6m^2/g$ was also obtained.

Lata et al (2007) employed adsorbents like sulphuric acid treated Parthenium and phosphoric acid treated Parthenium for the adsorption of methylene blue. The results showed that the adsorbents can be considered as potential adsorbents for methylene blue removal from dilute aqueous solution. A study by Mall et al (2005) Chemosphere dealt with the utilization of bagasse fly ash (generated as a waste material from bagasse fired boilers) and the use of activated carbons-commercial grade and laboratory grade as adsorbents for the removal of Congo red (CR) from aqueous solutions.

Garg et al (2003) employed saw dust collected from Indian rosewood for the preparation of activated carbon. Formaldehyde treated and sulphuric acid treated saw dusts were used to adsorb malachite green at varying dye concentration, adsorbent dose, pH and agitation time. Cassava peel, an agricultural waste (Rajeshwarisivaraj et al 2001) from the food processing industry, was used for the preparation of activated carbons employing physical and chemical methods. They were tested for their efficiency in the removal of dyes and metal ions from aqueous solution. Both the adsorbents were efficient as adsorbents for dyes and metal ions, the material impregnated with H_3PO_4 showed higher efficiency than the heat treated materials.

The adsorption behaviour of Reactive Blue 2, Reactive Red 4 and Reactive Yellow 2 from aqueous solution onto activated carbon was investigated by A1-Degs et al (2008) under various experimental conditions. The adsorption capacity of activated carbon for reactive dyes was found to be relatively high.

Kannan & Sundaram (2001) studied the kinetics and mechanism of methylene blue adsorption on commercial activated carbon and indigenously prepared activated carbons from bamboo dust, coconut shell, groundnut shell, rice husk, and straw have been studied. The results indicated that such carbons could be employed as low cost alternatives to commercial activated carbon in wastewater treatment for the removal of colour and dyes.

Bagasse pith, a waste product from sugarcane industry, has been studied by McKay et al (1987) without any pretreatment, for the removal of two basic dyes and two acidic dyes from aqueous solutions. High adsorptive capacity was observed for the adsorption of basic dyes (158 mg/g for basic blue 69 and 177mg/g for basic red 22), while lower capacity of 23 mg/g and 22 mg/g was observed for acid red 114 and acid blue 25, respectively.

MISCELLANEOUS ADSORBENTS

Powdered metal hydroxide sludge was tested for its adsorption capacity of Reactive Red 2, Reactive Red 120 and Reactive Red 141 by Netpradit et al (2003). The capacity of sludge-based activated carbon was compared with the commercial activated carbon to remove Acid Brown 283, and Direct Red 89 and Direct Black 168 from aqueous solution (Martin et al 2003).

Modified sawdust was used to adsorb Malachite Green (Garg et al 2003) acidic, basic and disperse dyes (Jadhav & Vanjara 2004). Adsorption capacity of shell of hazelnut for Acid Red 183 was comparatively lower than that of commercial activated carbon but was higher than that of raw kaolnite and monotomorillonite (Aydm & Yavuz 2004)

Potentiality of open burnt clay was used as an adsorbent for the removal of Congo red from its aqueous solution and its adsorptive capacity was compared with rice husk, wood charcoal and tea waste (Mumin et al 2007). Natural volcanic ash containing iron and aluminium (Esmaili et al 2003), iron oxide on activated alumina (Huang et al 2000), spent activated clay from an edible oil refinery (Wang et al 2008) and NALCO plant, Orissa, India sand (Mohapatra et al 2009) were employed as effective adsorbents.

Solid wastes from the distillery waste, which is the byproduct of the ammonia-soda process for the production of soda ash, has been used as an alternative adsorbent for removing the anionic dyes from aqueous medium (Sener 2008). Battery industry waste has been investigated for the removal of some metal ions (Pb, Cu, Cr and Zn) from aqueous solution by Bhatnagar et al (2007) and an appreciable sorption potential (33-64 mg/g) of the prepared adsorbent was observed for the metal ions. The adsorption characteristics of basic yellow 28 (BY 28) and basic red 46 (BR 46) onto boron waste (BW), a waste produced from boron processing plant were investigated (Olgun & Atar 2009).

POLLUTION DUE TO TEXTILE DYES

Contamination of surface and ground water with the textile industry effluents is a major concern to public health. Synthetic dyes, suspended solids and dissolved organics are the major hazardous material found in textile effluents (Benkli et al 2005). These materials can affect the physical and chemical properties of fresh water. In addition to the undesirable colors of textile effluents, some dyes may degrade to produce carcinogens and toxic products (Shawabkeh & Tutunji 2003). Furthermore, the coloured effluents reduce light penetration and potentially prevent photosynthesis (Gong et al 2005, Kharisheh et al 2005). Thus it is necessary to treat the dyeing effluents prior to their discharge into fresh water bodies.

Acid Dyes

Acid dyes are sodium salts of organic sulfonic acids. Brightly coloured, water soluble and reactive, acid dyes are composed of ionizable anionic groups such as sulphonates, carboxylates or sulphates. Acid dyes have a direct affinity towards polyamide and protein fibers in an acidic dye bath. Hence these dyes are commonly used for dyeing polyamide fibers as well as silk, wood and modified acrylics.

Acid dyes are used in textile industry for dyeing textile fibers and as a consequence, studies have been conducted to reduce the colour of the dye-containing effluents through treatments involving adsorption onto low-cost materials. Acidic pH (pH 3-5) and high temperatures (95^0-105^0C) are the ideal conditions for the adsorption / biosorption of acid dyes (Attia et al 2006, Alaton & Teksoy 2007, Malik 2003).

Basic Dyes

Basic dyes are the brightest class of soluble dyes used by the textile industry, as their tinctorial value is very high (Stephen Inbaraj & Sulochana 2006). Cationic dyes are the most commonly used for colouring purpose, especially methylene blue, a thiazine (cationic) dye, which is used in large amounts among all other dyes of its category. These dyes are generally used for dyeing cotton, wool and silk (Chandrasekar & Pramada 2006).

In addition to their use in dyeing of various products, dyes like Rhodamine B are widely as biological stains in many biomedical laboratories. If swallowed, the dye causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhoea. It is likely to cause irritation to the skin (Senthilkumar et al 2005). Hence it is necessary to remove basic dyes before they are let out into water bodies.

Reactive Dyes

Reactive dyes are azo-based chromophores combined with different types of reactive groups. They are bright coloured and form covalent link with oxygen, nitrogen or sulphur atoms from fibers and provide greater stability to the fabric colour (Trotman 1984). It is reported that reactive dyes are highly soluble in water (Dantas et al 2004). It is difficult to remove reactive dyes using chemical coagulation due to its high solubility in water (Baskaralingam et al 2006). Adsorption appears to be the best prospect for elimination of this dye.

Direct Dyes

The use of direct dyes has continuously increased in the textile industry and finishing processes since the development of synthetic fibers. Direct dye is commonly used in the printing process of the textile industry. Most of the printing processes in textile factories belong to the small factory group (Gupta et al 1992, Graca et al 2001). Direct azo dyes cause environmental concern due to their widespread use and their degradation products such as toxic aromatic amines as well as their slow removal rate during aerobic waste treatment.

CONVENTIONAL TREATMENT METHODS

Several treatment methods have been reported for the decolorisation of dyeing industry waste water. Some of the important technologies available are discussed as follows:

Primary Treatment Processes

The primary treatment processes include screening, sedimentation, flotation, flocculation or coagulation and are used to remove suspended solids from water and further for separation and concentration of sludge.

Coagulation / Flocculation

Coagulation-flocculation is a way to agglomerate fine particles and colloids dispersed stably in water by means of coagulating and flocculating chemicals, and to separate them as large flocs. The inorganic coagulants (lime, Mg and Fe salts), organic coagulants (cationic polymers, polyelectrolytes) and some natural anionic polyelectrolytes like Tamarindus Indica seed extract are used for the removal of different classes of dyes like acid, direct, basic, disperse etc.

The advantages of using the chemical coagulation / flocculation approach are that they require relatively a simple equipment, relatively rapid removal of color and significant reduction of chemical oxygen demand and, if combined with filteration, it also removes suspended solids (Peter Cooper 1995). The disadvantages are dependence on chemicals and generation of considerable volume of sludge and higher operative cost.

Electrocoagulation

Electrochemical processes (electrolysis and electrocoagulation) have been successfully demonstrated for removing pollutants in various industrial wastewaters (Vlyssides et al 2001). Removal mechanisms reported in the electrolysis process generally include oxidation, reduction and decomposition, whereas the mechanisms in the electrocoagulation process include coagulation adsorption, precipitation and flotation (Grimm et al 1998). The electro-generated flocs separate rapidly and remove color, and turbidity from dyeing wastewater (Lin & Peng 1994).

Batch removal of the reactive textile dye Remazol Red RB 133 from an aqueous medium by the electrocoagulation method using aluminium electrodes has been reported (Can et al 2003). It is a simple and efficient method for the treatment of many water and wastewater systems. It has not been widely accepted because of high initial costs as compared to other treatment technologies.

SECONDARY OR BIOLOGICAL TREATMENT PROCESS

Aerobic Digestion

Conventional aerobic biological digestion is the basis of most sewage treatment. It uses a biomass to convert the incoming BOD into CO_2 and sludge, which is frequently transferred to an anaerobic digester for further treatment before finally being disposed to various applications including spreading on fields as fertilizer. One major disadvantage of an aerobic digester is that it generates considerable amount of sludge, which may contain adsorbed species that have passed through the treatment without being retained.

Anaerobic Digestion

Anaerobic digester converts pollutants via a series of metabolic reactions to end products that are mainly gaseous (methane and CO_2). The conversion of organic pollutant depends on the presence of several species of bacteria, each interdependent on the others. Anaerobic systems are very expensive to install but do not require the large energy requirements of an aerobic system and generate only a relatively small volume of sludge.

TERTIARY OR ADVANCED TREATMENT PROCESSES

Wastewater contains significant quantities of non-biodegradable chemicals and polymeric compounds. When the conventional treatment methods are inadequate, the need for efficient tertiary treatment process becomes apparent. Tertiary treatment includes ion-exchange, reverse osmosis, electro-dialysis, hyper filtration, adsorption, oxidation techniques etc.

Oxidation Process

This is the most commonly used method of decolorisation by chemical means due to its simplicity of application. The main oxidizing agent is usually hydrogen peroxide (H_2O_2), which needs to be activated by some means, for example, ultraviolet light. Many methods of chemical decolorisation vary depending on the ways in which the H_2O_2 is activated. Removal of dye from dye-containing effluent occurs by oxidation resulting in aromatic ring cleavage of dye molecules. Kinetics of oxidation of the direct dye, Durazol Blue 8G with H_2O_2 was studied spectrophotometrically in different media (E1-Daly et al 2003).

Ion Exchange

Most ion exchange resins used in wastewater treatment are synthetic ones, made by polymerization of organic compounds into a porous three-dimensional structure. The functional ionic groups are usually introduced by allowing the polymeric matrix to react with chemical compounds containing the desired group. The number of functional groups per unit mass of resin determines exchange capacity. Exchangers approaching exhaustion are regenerated and reused. Ion exchange has not been widely used for the treatment of dye-containing effluents, mainly due to the opinion that ion exchangers cannot accommodate a wide range of dyes.

Electrochemical Destruction

This is relatively a new technique, which was developed in the mid-1990s. It has some significant advantages for use as an effective method for dye removal. There is little or no consumption of chemicals and no sludge build up. The breakdown metabolites are generally non-hazardous leaving it safe for treated wastewaters to be released back into waterways. This is an efficient and economical removal of dyes and a method for colour removal and degradation of recalcitrant pollutants.

Filtration

Filtration is a mechanical method for separation. Its main goal in water treatment is the removal of suspended solids or flocks resulting from coagulation/flocculation operations. This method consists of forcing the flow through a porous filter which will retain the particles bigger than the porous dimension. The removal of particles from water by filtration depends greatly on the size of the particles. For bigger particles, it is easier to apply, but for the smaller ones, filtration is not justifiable. There are different types of filtration equipment, but mostly sand and rotary filters are commonly used in wastewater treatment.

Nano Filtration

Nano filtration is a membrane liquid separation technology that is positioned between reverse osmosis (RO) and ultrafiltration (Xu & Lebrun 1999, Koyuncu et al 2004). Commercially available nano filtration membrane has been used to treat cotton dye house effluents. It retains most pollutants inside the membrane but allows water and some small salts and organics to pass through. The major disadvantages of nano filtration are similar to that of reverse osmosis.

Reverse Osmosis

Reverse osmosis is suitable for removing ions and larger species from dye bath effluents. Conventional reverse osmosis for treatment of textile effluents has limitations based on physical conditions, such as pH and temperature, and chemical properties such as membrane-chemical interactions and fouling. The reverse osmosis on its own has the disadvantage of high capital cost. At least 20% of the total effluent is not treated and the concentrate contains virtually of all the impurities from the effluent. The concentrate has to be treated by some other technology and the purified stream might still contain high levels of impurities for recycling.

Photochemical Degradation

In this process, when the photoactive catalysts are illuminated with UV-light, they generate highly reactive radicals that can decompose organic compounds (Crihenden et al 1997). This method degrades dye molecules to CO_2 and H_2O (Yang et al 1998, Nepppolian et al 2002) in the presence of H_2O_2, Kuo & Ho (2001) employed this technique for decolorisation of the organic dye, Methylene Blue.

Adsorption

Adsorption involves the interphase accumulation or concentration of substances at a surface or interface. Such a process can occur at an interface of any two phases, such as liquid-liquid, gas-liquid, gas-solid or liquid-solid interfaces. Sorption on solids particularly activated carbon, has become a widely used operation for purification of water and wastewaters. Adsorption results in the formation of monolayer of the adsorbate on the surface of adsorbent. This kind of adsorption is called physical adsorption. It involves relatively weak forces, and is therefore reversible. Thus, desorption of the adsorbed solution can occur. Adsorption has been found to be an efficient and economically cheap process for removing dyes (Desai et al 1997).

AIMS AND OBJECTIVES OF THE STUDY

A survey of past literature reveals that many adsorption media have been used successfully to remove pollutants from waste water. Hence an attempt has been made in the present study which reports the feasibility of dye adsorption by using low- cost adsorbents prepared from agricultural solid wastes. To achieve the desired result the present work has been started with the following objectives:

1. To prepare the low- cost adsorbent from abundantly available putrescible vegetable waste.
2. To convert putrescible vegetable waste into activated carbon using different activation methods.
3. To use batch mode adsorption technique for the removal of acidic and basic dyes like Methylene blue, Malachite green, Methyl violet Acid red 52, Acid orange 8 and Reactive violet from their aqueous solutions.

Materials and Methods

Collection of Carbon Source Materials:

In the present study activated carbon was prepared using saw dust which was collected from timber shop.

Carbonisation of H_2SO_4

The dried material was treated with 50% sulphuric acid solution, charring of the material occurred, accompanied by evolution of heat and fumes when the reaction subsided, the product was washed with large volume of water to remove free acid and the product was left in an air oven maintained at 140-160˚C for a period of 24 hours and was kept in a muffle furnace at 400˚C for 10 minutes. Thus sulphuric acid treated activated carbon (SAC) was prepared.

Particle Size Separation

The dried activated carbon was ground and sieved in a mechanical sieve in order to get the carbon with uniform particle size.

Langmuir Isotherm

The Langmuir isotherm plays an important role in the determination of the maximum adsorption capacity of an adsorbent the form of Langmuir isotherm equation is expressed as follows.

$$q_e = \frac{QmKaCe}{1+KaCe}$$

where Q_m is the theoretical maximum adsorption capacity per unit weight adsorbent (mg/g), K_a is Langmuir adsorption constant (L/mg), $C_e$andqeare concentration and amount adsorbed at equilibrium respectively.

The Langmuir isotherm equation can be linearized into the following form.

$$\frac{Ce}{qe} = \frac{1}{QmKa} + \frac{1}{Qm * Ce}$$

A plot of C_e/q_e versus C_e should be indicate a straight line of slope $1/Q_m$ and an intercept of $1/(K_aQ_m)$. The essential characteristics of Langmuir isotherm can also be described by an dimensionless separation factor R_L or R^2 which is defined by the following equation.

$$R_L = \frac{1}{1+ bLC0}$$

The value of separation factor R_L indicates the nature of the adsorption process as given below.

$R_L>1$ → Unfavourable

$R_L = 1$ → Linear

$0 < R_L< 1$ → Favourable

$R_L = 0$ → Irreversible

Freundlich Isotherm

The Freundlich (1906) isotherm model is the earliest known equation describing the adsorption process. It is an empirical equation which can be used for non- ideal sorption that involves heterogeneous sorption. A Freundlich isotherm can be derived assuming a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites and is commonly given by the following non-linear equation:

$q_e = k_fC_e^{1/n}$

where k_f is a constant for the system, related to the bonding energy. K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. 1/n is indicating the adsorption intensity of dye onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/n below 1 indicates a normal Freundlich isotherm while 1/n above 1 is indicative of cooperative adsorption.

Linear form of the equation is

$\text{Log } q_e = \log k_f + 1/n \log C_e$

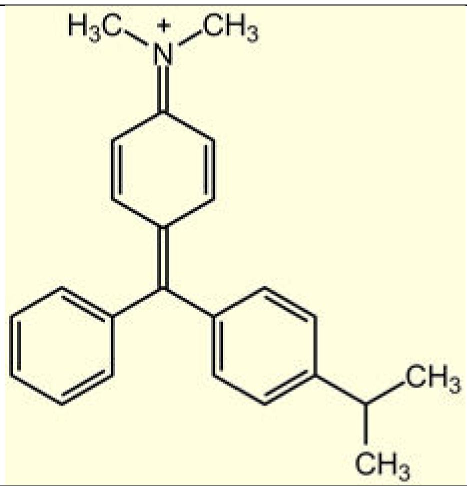
Freundlich model is suitable if the surface is heterogeneous but can describe the adsorption data over a restricted range only. It is often found that the equation is fitted poor to data at higher and intermediate concentrations since the Freundlich equation does not approach Henry's law of ideal dilute solutions.

Preparation of dye solution:

Stock solution of the dye was prepared by dissolving 1g of the dye in 1000ml of double distilled water. Different initial concentration was prepared by diluting the stock solution. Double distilled water was employed throughout the study as solvent. The structure of the dye selected for adsorption study are shown in Table

Structure of Dyes

S.NO	Name of the dye	Structure

1.	Malachite Green λ_{max}=630 nm $C_{23}H_{25}N_2Cl$	

Batch mode adsorption studies:

Batch mode adsorption study was carried out by taking 50ml of dye solution and required amount of activated carbon in a 250ml stopped bottle. Dye solution was agitated at 120 ppm in a mechanical shaker at different temperature. The adsorbate and adsorbent were separated by centrifugation at 1000ppm for 5 minutes. Effect of adsorbent on dye concentration was carried out with aqueous solution.

Isotherm data for the adsorption of Malachite green onto Adsorbent prepared from saw dust: Initial concentration variation at 30^{o}C

Conditions:

Volume of dye solution = 50 mL

Carbon dosage = 200 mg

Temperature = 30°C

Equilibrium time = 130 min

S.No	Concentration	% of dye adsorbed	C_e	q_e	C_e/q_e	log C_e	log q_e	ln q_e	ln C_e
1	10	98.78	0.122	4.939	0.0247	0.6936	-1.6075	1.597	-2.1041
2	20	97.35	0.531	9.7345	0.0545	0.9883	-1.2632	2.275	-0.633
3	30	96.28	1.117	14.441	0.0773	1.1596	-1.1116	2.67	0.1107
4	40	94.94	2.0253	18.987	0.1067	1.2785	-0.972	2.943	0.7057
5	50	91.7	4.148	22.926	0.1809	1.3603	-0.7425	3.132	1.4226
6	60	81.27	11.235	24.382	0.4608	1.3871	-0.3365	3.193	2.419
7	70	77.98	15.412	27.293	0.5647	1.4361	-0.2482	3.306	2.7352
8	80	75.24	19.809	30.095	0.6582	1.4785	-0.1816	3.404	2.9862
9	90	63.88	32.509	28.745	1.131	1.4586	0.0534	3.358	3.4815
10	100	61.65	38.351	30.824	1.2442	1.4889	0.0949	3.428	3.6468

Isotherm data for the adsorption of Malachite green onto Adsorbent prepared from saw dust: Initial concentration variation at 40°C

Conditions:

Volume of dye solution = 50 mL

Carbon dosage = 200 mg

Temperature = 40°C

Equilibrium time = 130 min

S.No	Concen tration	% of dye adsorbed	C_e	q_e	C_e/q_e	log C_e	log q_e	ln q_e	ln C_e
1	10	99.39	0.0915	4.9543	0.0185	-1.0388	0.695	1.603	-2.3918
2	20	98.23	0.354	9.823	0.0361	-0.451	0.9922	2.284	-1.0385
3	30	96.28	0.9574	14.521	0.0659	-0.0189	1.162	2.67	-0.0435
4	40	94.94	2.7342	18.632	0.1467	0.4368	1.2703	2.943	1.0058
5	50	93.27	3.3632	23.318	0.1442	0.5268	1.3677	3.149	1.2129
6	60	85.26	8.8446	25.577	0.3458	0.9467	1.4079	3.241	2.1798
7	70	80.01	14.001	28.001	0.5001	1.1461	1.4472	3.332	2.6391
8	80	76.19	19.047	30.476	0.625	1.2798	1.484	3.416	2.9469
9	90	76.55	21.102	34.448	0.6126	1.3243	1.5372	3.539	3.0494
10	100	73.6	26.403	36.798	0.7175	1.4217	1.5658	3.605	3.2735

Isotherm data for the adsorption of Malachite green onto Adsorbent prepared from saw dust: Initial concentration variation at 50°c

Conditions:

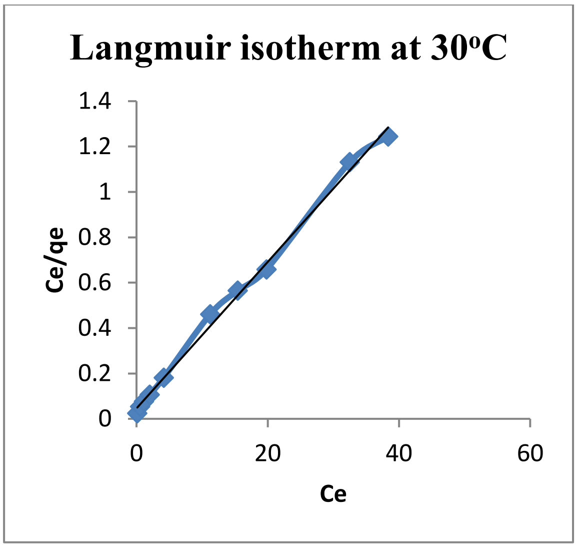
Volume of dye solution = 50 mL

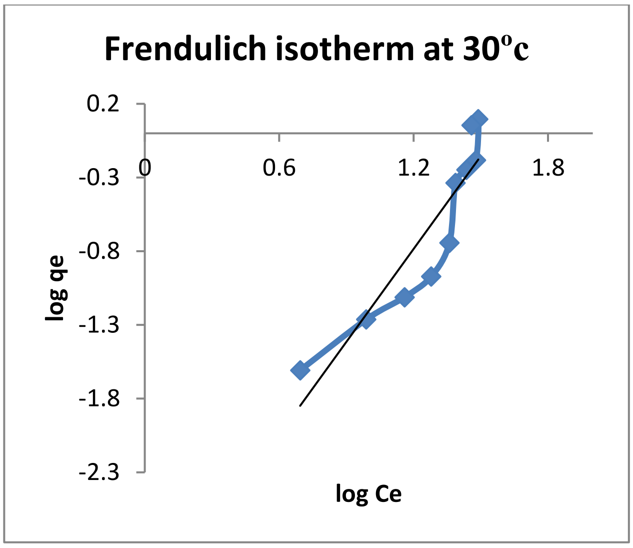
Carbon dosage = 200 mg

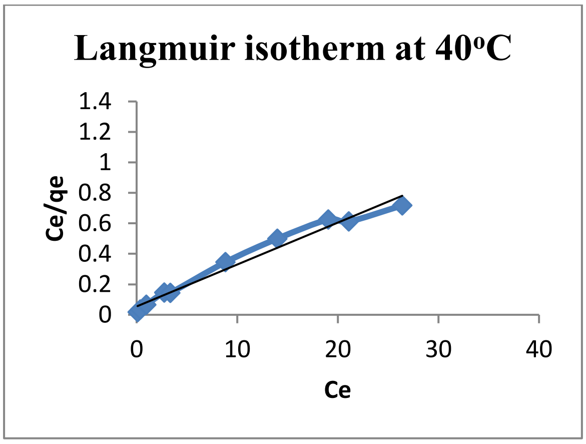
Temperature = 50°C

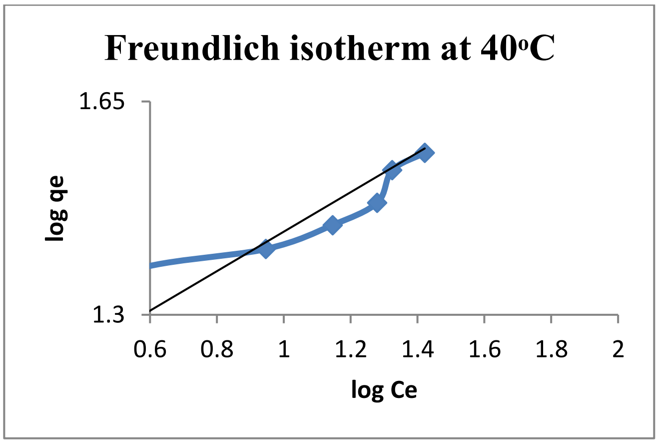
Equilibrium time = 130 min

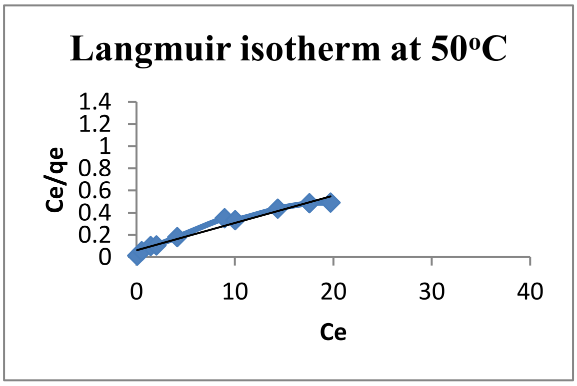
S.No	Concentration	% of dye adsorbed	C_e	q_e	C_e/q_e	log C_e	log q_e	ln q_e	ln C_e
1	10	99.39	0.0611	4.9695	0.0123	-1.2148	0.6963	1.603	-2.7973
2	20	97.35	0.5311	9.7345	0.0545	-0.2749	0.9883	2.275	-0.6331
3	30	95.21	1.4362	14.281	0.1006	0.1572	1.1548	2.659	0.3621
4	40	94.94	2.0253	18.987	0.1067	0.3065	1.2785	2.943	0.7057
5	50	91.7	4.1481	22.926	0.1809	0.6178	1.3603	3.132	1.4226
6	60	85.06	8.9641	25.517	0.3513	0.9525	1.4068	3.239	2.1932
7	70	85.69	10.018	29.991	0.3341	1.0008	1.4771	3.401	2.3044
8	80	82.06	14.349	32.825	0.4371	1.1568	1.5162	3.491	2.6637
9	90	80.48	17.566	36.216	0.4851	1.2447	1.5589	3.589	2.8661
10	100	80.29	19.713	40.143	0.4911	1.2948	1.6036	3.692	2.9813

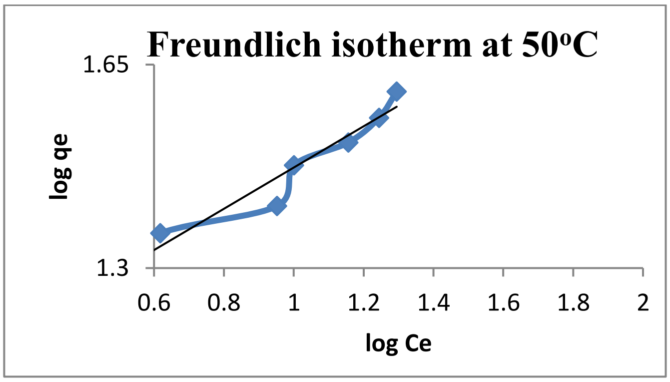

Langmuir isotherm at 30ºC
Ce/qe
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
20
40
60
Ce


Frendulich isotherm at 30ºc
log qe
0.2
-0.3
-0.8
-1.3
-1.8
-2.3
0
0.6
1.2
1.8
log Ce


Langmuir isotherm at 40ºC
Ce/qe
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
Ce


Freundlich isotherm at 40ºC
log qe
1.65
1.3
0.6
0.8
1
1.2
1.4
1.6
1.8
2
log Ce


Langmuir isotherm at 50ºC
Ce/qe
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
Ce


Freundlich isotherm at 50ºC
log qe
1.65
1.3
0.6
0.8
1
1.2
1.4
1.6
1.8
2
log Ce

Results and Discussion

Effect of temperature on adsorption of Malachite Green

Removal of Malachite Green from the aqueous solution was done by varying the temperature from 30^0C - 50^0C. When the temperature was increased, the removal percentage of Malachite Green also increased due to an endothermic process. With an initial dye concentration of 25 mg/L, at various temperature 30^0C, 40^0C, and 50^0C, the maximum percentage of removal increases from 98.2 to 99.41.

The enhancement in adsorption with temperature is due to the decrease in the thickness of the boundary layer surrounding the adsorbent, so that the mass transfer resistance of adsorbate in the boundary layer decreases.

This might be due to the increase in the mobility of dye molecule with increase in temperature and also increase in intra particle diffusion of adsorbate.

Adsorption Isotherms

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherms. The equilibrium data for the removal of Malachite Green by saw dust were analyzed by Langmuir, Freundlich.

Langmuir Isotherm

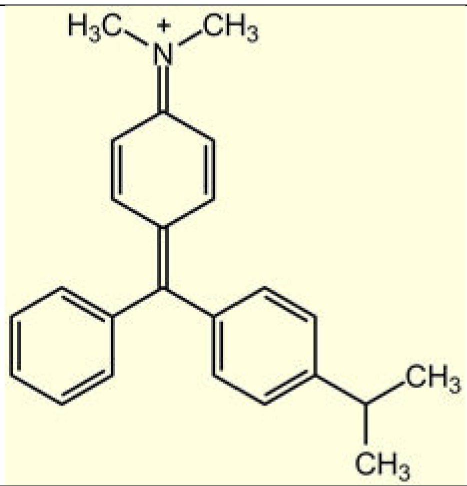
The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface (Langmuir 1996). A base assumption is that sorption takes place at specific homogeneous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption can take place at that site. On plotting a graph between C_e/q_e vs C_e at 30ºC, 40ºC and 50ºC isotherm was found to be linear over entire concentration range with a regression coefficient R^2 ranging from 0.9796 to 0.9979.

The Langmuir parameters are given in Table. The monolayer adsorption capacity at 50ºC was found to be the highest with the value of 40.57 mg/gm. The fact that Langmuir isotherm fits the experimental data very well confirms monolayer coverage of dye on to adsorbent particles and also the homogeneous distribution of active sites on the material, since the Langmuir equation assumes that the surface is homogeneous.

Freundlich isotherm

Freundlich adsorption isotherm was obtained in a linear form by plotting the graph between log q_e versus log C_e. Freundlich coefficients K_f, adsorption capacity and n, the intensity of adsorption were calculated and presented in Table.

Structure of Malachite Green

S.NO	Name of the dye	Structure
1.	Malachite Green λ_{max}=630 nm $C_{23}H_{25}N_2Cl$	

Picture of saw dust

Results of isotherm models for the adsorption of Malachite Green onto Adsorbent prepared from Saw dust

Parameters	Temperature ℃		
	30℃	40℃	50℃
Langmuir isotherm			
Qm (mg/g)	30.985	36.142	40.57
B (L/mg)	0.4031	0.5398	0.701
K_L	21.72	19.51	16.36
R^2	0.9979	0.9886	0.9796

Freundlich isotherm			
N	3.367	3.212	2.818
K_f ($mg^{1-1/n}L^{1/n}g^{-1}$)	12.089	13.413	13.215
R^2	0.9597	0.9885	0.9945

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Conclusion

Both Freundlich and Langmuir isotherm models explained the adsorption systems completely. For most of the dyes employed in the study Langmuir isotherm model was found to be the better one.

REMOVAL OF CONGO RED DYE FROM AQUEOUS SOLUTION BY ADSORPTION TECHNIQUE

DBT Funded Project

PROJECT REPORT

Submitted in partial fulfillment of the requirements for the award of the degree of
Bachelor of Science in Chemistry

Submitted by

Vinothini.S

Reg.No:15BC4213

Under the guidance of

(Mrs.). S.Umadevi M.Sc., M.Phil., M.Ed.,

Assistant Professor, Department of Chemistry.

DEPARTMENT OF CHEMISTRY

SRI GVG VISALAKSHI COLLEGE FOR WOMEN (AUTONOMOUS)

Re-accredited at ‘A’ Grade CGPA of 3.53 by NAAC

An ISO 9001-2008 Certified Institution

Udumalpet-642 128

(2017-2018)

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CERTIFICATE

This is to certify that the project entitled "**Removal of Congo Red Dye From Aqueous Solution By Adsorption Technique"** is the experimental work done by **S.Vinothini (15BC4213)**in partial fulfillment of the requirement for the award of the degree of Bachelor of Science in Chemistry in **Sri GVG Visalakshi College For Women (AUTONOMOUS), Udumalpet** during the academic year 2017-2018.

Submitted for the viva-voice held on ____________________

Signature of the SupervisorSignature of the HOD

External Examiner

Signature of the Principal

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INTRODUCTION

The earth is the only planet where liquid water exists in substantial quantities. Water is the essential component of life. Water plays a key role for our existence, in forming earth surface, moderating the climate and diluting the pollutants. About 97.4% of water is found in ocean as salt water and only 2.6% of the planets abundant water supply is readily available to us as fresh water, locked up in polar ice caps and exist as underground water. (http://oceanservice.noaa.gov/ facts/oceanwaters.html)

Despite its importance, water is one of our most poorly managed resources. Rapid pace of industrialization, population expansion and unplanned urbanization have largely contributed to the severe water pollution. Because of human activities, our planet is contaminated by organic and inorganic pollutants which lead to a real threat to a healthy development of mankind, animal and plants.

Synthetic substances produced by man have been more abundant in the environment only for the past few decades. Improper disposal methods and inadequate control of toxic effluents from different industries have lead to the wide contamination of surface as well as ground water. Many manufacturing industries such as Paper, Plastic, Cosmetics, Textile and Food use dyes for colouring their products(Namasivayam *et al*., 1996) Industrial effluents containing hazardous contaminants such as chlorinated organic compounds, Phenolic compounds, toxic heavy metals and dyes which are present even at low concentrations cause negative impact on the environment (Ramakrishnan *et al*., 2009). Color is the most obvious indicator of water pollution.

The discharge of colored wastes into stream not only affect their aesthetic nature but also interferes with the transmission of sunlight into streams and therefore reduces photo synthetic action (Annadurai *et al*.,2002).The presence of very small amounts of dyes in water (less than 1ppm for some dyes) is highly visible and undesirable (Robinson *et al*., 2001). Some dyes are carcinogenic and mutagenic (Namasivayam *et al*)

Over 1,00,000 commercially available dyes exists and more than $7x10^5$ tones per year are produced annually (Pearce et al.,2003,Lee et a1.,2007). Due to their good solubility, synthetic dyes are common water pollutants. About 12% synthetic textiles dyes used in each year are wasted during manufacturing and processing operations (Mohammed *et al*.,2012). It is assumed that a loss of l-2% dye in production and 1-l0% loss in use (after being garment) are a fair estimate, [Forgacs.E,2004]. For reactive dyes this figure can be about 10-20% due to low fixation.

Dyes and Dye pollution:-

The first synthetic dye mauveine was discovered by the English man, William Hendry Perkin by chance in 1856. Since then the dye stuffs industry has developed. [Hunger.K, 2003]. Not all colored compounds are dye stuffs because they may not have suitable application on a substrate (textile, fibres, foodstuffs etc.,) and it will not have retaining power on the substrate. eg: $CuSO_4$ cannot be termed as a dye. But Congo red is a typical dye. Since it can be retained on the fibre. In dyes chromophores and auxochromes are the major component element of dye molecule.

Hunger *et al* mentioned that dyes are classified into two types. The main classification is based on the chemical structure of dyes and another classification is based on their usage (or) application. The varies types of dyes used in industries include Anionic- acid, direct, and reactive dyes; Cationic-basic dyes; Non ionic disperse dyes. (Zollinger *et al*.,1987).

Anionic (Acid dyes):-

These are water soluble dyes applied on nylon, wool, silk, paper, leather, food and cosmetics. Apart from mentioned above, there are water insoluble vat dyes, sulphur dyes, solvent dyes, mordant dyes, ingrain dyes, and pigments. As a result they generate a considerable amount of colored waste water.

Direct dyes:-

In the presence of electrolytes, these anionic dyes are water soluble in aqueous solution. These are poly azo compounds along with some stilbenes, phthalocyanines and oxazines. To improve wash fastness, frequently chelation with metal (CuandCr) salts are applied to the dye stuffs. They have high affinity to cellulose fibres.eg : Benzidine dyes, Anionic dyes, Direct dye 81, Direct green23, Direct Brown 44(Poly azo), Direct Yellow12 (Stilbene dye).

Reactive dyes:-

They contains azo group which includes metalized azo, triphendioxazine, phthalocyanine, formazan, and anthraquinone dyes. The structure of these dyes are simpler than direct dyes and they produced brighter shades than direct dyes. Reactive dyes are primarily used for dying and printing of cotton fibres.eg Trichlorotriazines remain a popular platform for reactive dyes.eg: Ramazol black B.

Cationic (Basic dyes):-

These dyes are cationic and water soluble. They are applied on paper, polyacrylonitrile, modified nylon poly esters, silk, wood and tannin mordant cotton.eg Methylene blue, Crystal Violet.

Disperse dyes:-

These are water insoluble nonionic dyes applied to hydrophobic fibers such as polyester, polyamide, nylon and acrylic fibers. They contain azo and anthroquinoid groups.eg Disperse blue, Disperse blue7, Disperse Yellow3

The main sector contributing to water pollution is that of chemical pretreatment, where the processing of woolen, cotton and cotton blend fabrics results in the removal of natural impurities. The dyeing operation also release considerable amount of toxic effluent in the adjoining water bodies(Dutta.,l994). These wastes carry high dissolved salts, significant level of Cl^-,SO_4^{2-},SO_3^{2-} ions, Phenolic compounds and heavy metals at pH between 4 to 12 discharged into the environment every year (Meyer *et al*., I992).

A large quantity of salt is used in the dyeing process and the processed waste water is highly saline and also contaminate with variety of chemicals. Also dyes are stable to light heat, and oxidizing agents and biologically non-biodegradable. Hence removal of color from the waste water is most challenging and perplexing problem. In India as in other developing countries due to technological and economic reasons, mostly concentrated (or) partially treated effluents containing dyes are released into nearby water bodies (or) agricultural lands. These effluents import color and turbidity not only to the reactive water bodies [Ranjani et al., 1998] but also to the other water sources in the surrounding areas through soil seepage causing soil pollution as well as ground water pollution. Intake of such detrimental water results in many physiological and pathological effects.

Objective of the study:

- To prepare a low-cost and eco-friendly activated carbon from Ripened *Bauhenia Tomentosa* seed pod
- To determine the effect of variation of initial concentration of Congo red dye solution .
- To determine the effect of optimum contact time for the effective adsorption of Congo red dye from aqueous solution .
- To find out the variation of adsorbent dosage on the removal of Congo red dye from aqueous solution .
- To interpret the results of the study in terms of
    - Langergren kinetic equation
    - Pseudo second order kinetic equation

Review of literature

Dyes are used in textile, paper, pulp, leather and plastic industries. These industries use large amount of water for their process and produce waste water containing large amount of dyes. Most of the dyes are completely resistant to biodegradation and also toxic in nature. Hence their removal before disposal of the waste water necessary.

Treatment of dye wastes:-

The conventional methods for the treatment of colored wastewater are physical, chemical and biological treatments. At large scale, most of these conventional methods are not applicable because of the high cost and disposal problems as large amount of sludge is been generated at the end of the process. (Ghoreishi S.M *et al*.,2003).

Physical methods:

Physical treatment methods includes Membrane filtration process, Reverse osmosis, Electrodialysis and Adsorption techniques. However these methods have advantages and disadvantages. Among all the physical treatments, adsorption process has been reported to be the most effective method for water decontamination. (Dą browski *et al*.,2001).

CHEMICAL METHODS:-

1. Coagulation/Flocculation: -

This process involves chemical treatment of dye waste water with FeCl.6H2O as coagulant (Papic *et al*., 2000).This is very simple and economically feasible process. But accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem because of excessive chemical use.

2. Oxidation techniques : -

A variety of oxidising agents can be used to decolourise the waste water.

Chlorine is a strong oxidizing agent used and may also be applied as calcium hypochlorite and sodium hypochlorite. In addition to being the most widely used disinfectant for water treatment, it is extensively used for reduction of colour like pulp and textile bleaching. Reactive, acid, direct and metal complex dyes, which are water soluble are decolourised readily by hypochlorite, but water-insoluble disperse and vat dyes are resistant to decolourisation in this process (Namboodri et al., 1994a,b).

Ozonation carried out by ozone generated from oxygen has been studied by various workers and has been found to be an very effective way of decolourizing textile effluents (Perkins et al., 1996; Soares et al., 2006; Wu et al., 2008b). Sundrarajan et al. (2007) studied the ozonation for colour removal (reactive dyes) and found that colour removal of the effluent can be achieved in 5 min of contact time for yellow and blue shades at an ozone consumption of 37.5 and 36 mg L_1, respectively and suggested that ozonation is efficient in decolourization of exhausted dye bath effluents con-taining conventional reactive dyes

3. Reverse osmosis and electrodialysis

It works without addition of chemicals. The major disadvantage of the membrane process is that they have a limited life time before membrane fouling occurs and the cost of periodical replacement must be included in any analysis of their economic viability.

4. Destruction Technique

Aerobic digestion (oxidation) and anaerobic digestion techniques are used for the waste water treatment processes. But these are expansive and cause sludge disposal problem. Anaerobic decolourisation of reactive dye has been extensively studied by (lcarliell *et al* 1994). Adsorption and biological decolourisation of azo dye, reactive red in semi continuous anaerobic reaction has been investigated (Van der zee 2001)' Microbial degradation involves biodegradation of dyes by microorganism. Generally dyes are resistant to biodegradation by microorganism However recent research has shown that a variety of microorganisms and approaches hold promise for the development of effective systems for the treatment of water contamination with these colourents (Moreira *et al*.,2000). Studies carried on the decolourisation of textile azo dyes by newly isolated halophilic and Palototerant bacteria isolated from effluents of textile industries showed remarkable ability in decolourising the widely utilized azodyes (Asad 2007).Dead fungal biomass prepared from pheanerochaetechrysosporium and Funaliatrogii was tested for their efficiency in removal of textile dye (Asma *et al*.,2006).

5. Enzyme degradation

Enzyme are highly selective catalysts to degrade targeted substances from waste waters. Congo red was decolourised in the presence of a crude preparation of lignin peroxidase and H_2O_2 by P.Chrysosporium (Tatarko *et al*.,1998).

6. Photocatalytic degradation

It is the process which can destroy the organic compound and it employs photoactive catalysts illuminated with uv light to generate highly reactive radicals which can convert organic compounds to non toxic forms such as $CO_2$and H_2O's. (Crittendens *et al*., l997). Photochemical oxidation of reactive blue dyes in textile waste water be UV/$K_2S_2O_8$ has been investigated by [Rezaee,2008].

7. Sludge treatment

Sludge treatment has been found to remove or degrade the colourants. Sludge from sewage has been successfully used for the degradation of dye stuffs (lshuklu *et al*., 1991. Ganesh *et al*.,1994)have reported the activated sludge degradation of dyes and the fate of azo dyes in sludge.

8) Ion exchange /polyuric resin

Two commercial anion exchange membranes, strong basic (SB6407) and weak basic (DE8l) were evaluated for the removal of anionic reactive dyes, Cibacron blue 3GA and cibacron red 3BA from water in a study (Liu *et al*.,2007) A bio polymer, polygamma-glutamic acid (gamma-PGA) derived from bacterial sources (Bacillus species) was evaluated for its efficiency in removing basic dyes from aqueous solution(Inbaraj et al., 2006).

The use of chemical or electro coagulation treatment process followed by ion-exchange process of textile dye effluent has also been investigated (Raghu *et al*., 2007). The removal of methyl violet 2B., a cationic dye from water using two kinds of strong acid cation exchange membranes was investigated (Jeng-shiou Wu *et al*.,2008).

Biological methods:

Biological treatment of wastewater is an alternative and most economical method as compare to physical and chemical methods. Biodegradation methods such as adsorption by (living or dead) microbial biomass, fungal decolorization, bioremediation systems and microbial degradation are commonly used in the treatment of industrial effluents. Microorganism such as yeasts, bacteria, fungi and algae are able to accumulate and degrade different pollutants, but due to some technical constraints their applications is often restricted **(**Bekchanov *et al*.,2012; Fu et al.,2002; Banat *et al*.,2003). Biological treatment may be aerobic and anaerobic **(**Bhattacharyya *et al*.,2004). But the major drawback is that, it requires substantial land area and is constrained by sensitivity toward diurnal variation as well as toxicity of chemicals (Crini *et al*.,2006). Moreover, contradictory findings were reported in review of current technologies(Robinson *et al*., 2001) which states that, with current conventional technology, biological treatment is incapable of obtaining satisfactory color elimination. Furthermore, dyes such as (azo dyes) are not easily degradable due to their complex chemical structure, synthetic organic origin and xenobiotic nature(Ravi Kumar *et al*.,1998).

Adsorption

The general term sorption includes adsorption, the process by which a solute clings to a solid surface and absorption the process by which the solute diffuses into a porous solid and clings to interior surfaces. Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications (Dabrowski, 2001). Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances.

Activated carbon

The use of carbon extends so far back into history that its origin is impossible to document. Charcoal was used for drinking water filtration by ancient Hindus in India, and carbonized wood was used as a medicinal adsorbent and purifying agent by the Egyptians as early as l500B. (Cheremisinoff *et al*., 1980). Modern development and use has been documented more precisely. Activated carbon was first generated industrially at the first part of the twentieth century when carbon activated from vegetable material was produced for use in sugar refining (Bausal and Roopet *et al*., 1988). The first document use of activated carbon in a large scale water treatment application was in 19th century England, where it was used to remove undesirable odours and tastes from drinking water (Cheremisinoff 1980). In recent years, the use of activated carbon for the removal of priority organic pollutants has become very common.

Today, hundreds of brands of activated carbon are manufactured for a large variety of purposes. Most commercial systems currently use activated carbon as sorbent to remove dyes in waste water because of as excellent adsorption ability. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies (Derbyshine *et al*., 2001) The widespread use of a particular raw material as a source of activated carbon is obviously limited by the supply of that material. As a result wood (at 130000 tons/year) is by far the most common source of activated carbon. This is followed closely by coal (100000tons); coconut shell (35000tons) and peat (35000tons). which are also used in large quantities (www.aboutchemistry.com). However although activated carbon is a preferred sorbent, its widespread use is restricted due to high cost. In order to decrease the cost of treatment attempts have been made to find in expensive alternative adsorbents. Many non-conventional low-cost adsorbents, including natural materials, bio sorbents and waste materials from industry and agriculture, have been proposed by several workers. Some of the recently reported sorbents and their adsorption capacities provide information about the use of low-cost materials as sorbents. However, the reported adsorption capacities must be taken as an example of values that can be achieved under specific conditions since adsorption capacities of the sorbents presented vary depending on the characteristics of the materials, the experimental conditions, and also the extent of chemical modifications.

Non conventional low cost adsorbents and Removal of dyes:-

Different low cost sorbents have been explored by various researchers for dye removal from wastewater. These include Palm kernel fibre (El-Sayed, 2011), rice husk (Gupta et al., 2006; Lakshmi et al., 2009), sawdust (Batzias and Sidiras, 2007; Khattri and Singh, 2009), tea waste (Uddin et al., 2009), peanut shell (Tanyildizi, 2011), orange peels (Khaled et al., 2009; Arami et al., 2008), wheat shell (Bulut and Aydin, 2006), pineapple stem (Hameed et al., 2009), and coconut basedsorbent; babassu coconut mesocarp (Vieira et al., 2009), coconut husk (Jain and Shrivastava, 2008; Low and Lee, 1990; Gupta et al., 2010), coconut shell fibre (de Sousa et al., 2010; Babel and Kurniawan, 2004), coconut copra meal (Ho and Ofomaja, 2006), coconut coir pith (Namasivayam et al., 2001)and coconut bunch waste (Hameed et al., 2008)

These wastes are renewable, available in large amounts and less expensive as compared to other materials used as adsorbents. They are better than other adsorbents because the agricultural wastes are usually used without or with a minimum of processing (washing, drying, grinding) and thus reduce production costs by using a cheap raw material and eliminating energy costs associated with thermal treatment (Franca et al., 2009).

- ❖ A.Asfaram et al (2016) studied biosorption of congo red dye by novel biosorbentyarrowialipolytica using response surface methodology. The influence of parameters such as initial pH, dye concentration, temperature and time were carried out. The nature of biomass dye interactions was evaluated by FT-IR analysis and maximum CR removal (99.88%) was obtained under optimum conditions. The maximum adsorption capacity for biosorption was found around the pH range 6.5-7.5
- ❖ Haochun Shi et al (2013) investigated methylene blue adsorption from aqueous solution by magnetic cellulose/ grapheme oxide composite: Equilibrium, kinetics and thermodynamics studies were carried out. The morphology and chemical structure of the MCGO composite were characterized by the FT-IR spectrometer, X-ray diffraction and SEM. The influence of parameters such as initial concentration of MB, contact time, adsorbent dose and pH value were evaluated experimentally. The adsorption isotherm followed Langmuir isotherm model. The adsorption kinetics were fitted by a pseudo-second order kinetics model. Thermodynamics parameters such as ΔG0, ΔH0& ΔS0 values spontaneous, favorable and exothermic in nature.
- ❖ Mylsamy Shanker et al (2012) investigated adsorption of reactive dye using low cost adsorbent: cocoa (Theobromo cocoa) shell. The parameters such as initial dye concentration, contact time, effect of solution pH and adsorbent dosage influenced the adsorption capacity. Experimental isotherm data was represented with Langmuir, Freundlich, Temkin and Harkins-Jura isotherm models. The adsorption data were found to follow the Langmuir model better than the other model. The data were also fitted to kinetic models such as pseudo first order, pseudo second order, elovich and intra particle diffusion models.

- Feilian et al (2016) studied one-step synthesis of a novel N-doped microporous biochar derived from crop straws with high dye adsorption capacity. The products exhibit high microporosity (71.5), atomic percentage of nitrogen (8.81%) and adsorption capacity to dyes 15-20 times higher than original biochar. Sample NBC800-3 pyrolyzed at 800°c in NH_3 for 3h, its adsorption capacity of acid orange7(Ao7 anionic) and methyl blue (MB, cationic) is upto292mgg-1, 436mgg-1.
- Ayesha wasti et al (2014) studied the adsorption of textile dye onto modified immobilized activated alumina. Parameters like contact time, stirring rate, initial concentration and adsorbent dose of MIAA were investigated both Langmuir and freundlich adsorption isotherms which fitted the data with R2 value of 0.99. Thermal regeneration was achieved at 450°c.
- Vaishakh Nair & R. Vinu (2016) analysed peroxide-assisted microwave activation of pyrolysis char for adsorption of dyes from wastewater. Adsorption parameters such as initial pH of the dye solution and adsorbent dosage were also optimized. Langmuir and Langmuir, Freundlich isotherms described the adsorption equilibrium, while pseudo second order model described the kinetics of adsorption
- Ruiping Li et al (2016) studied the visible-light photocatalytic degradation of azo dyes in water by Ag3PO4. An unusual dependency between adsorption and the degradation rate on pH value was observed. It is determined by FTIR spectroscopy.
- Aparna Roy et al (2013) examined the equilibrium, kinetic and thermodynamic studies of azo dye adsorption from aqueous solution by chemically modified Lignocellulosic jute fiber. It is determined by solid state NMR spectroscopy, FTIR spectroscopy and SEM. The experimental data followed by Langmuir isotherm model. The efficiency of modified JF for the spontaneous and exothermic adsorption of azo dye is attributed to the copious availability of hydroxyl and other polar functional groups on the fibre surface.
- Khalid M Mousa et al (2015) studied the adsorption reactive blue dye on to natural and modified wheat straw. The parameters such as pH values and initial dye concentration influence the adsorption studies. Equilibrium isotherm experiment were carried at different dosages to predict isotherm model, Langmuir, Freundlich and BET. The experimental data should that reactive blue is fitted with freundlich isotherm and

Langmuir isotherm. Thru kinetic model, were selected to fit the kinetic data; pseudo first, second order and intra particle diffusion.

- Maytham Kadhim Obaid et al (2016) investigated the removal of reactive orange dye from aqueous solution by using modified kenaf core fiber. The effective parameter such as adsorbent dose, pH contact time and initial dye concentration of adsorption by modified kenaf core fiber was investigated. In addition, isotherms and kinetic adsorption studies were used. The result also showed that the equilibrium data were represented by freundlich isotherm and the kinetic study followed dye the pseudo-second order kinetic model.
- H.E. Reynel Avila et al (2016) studied relevance of anionic dye properties on water depolarization performance using bone char. Kinetics, isotherms and break through curves for the adsorption of acid blue25 (AB25) acid blue74 (AB74) and reactive blue 4 (RB4) on bone char. Dye adsorption and intra-partial diffusion rates, adsorption capacities, equilibrium constants, enthalpy& breakthrough curve parameters were calculated & correlated with dye molecular properties. FTIR characterization of bone char supported an anionic dye removal mechanism based on electrostatic interactions.
- Khadijah Khalid et al (2015) studied the performance of rubber leaf powder treated with phosphoric acid in the removal of Acid Blue 25 (AB25) from aqueous solution. The parameters affect adsorption capacities such as pH, agitation period; adsorbent dosage & different initial concentration of AB25 were examined. The maximum adsorption capacity determined from Langmuir isotherm was 28.09 mg/g at 320k. Two kinetics models including pseudo-first order & pseudo-second order were used to analyze the adsorption of AB25 dye. The pseudo-second order model fitted well with correlation coefficients greater than 0.99.
- Qingwen Lin et al (2016) studied grafting dimethyl diallylammonium chloride for cationic and anionic dyes. It microspheres showed pH-sensitive and could adsorbed cationic dye methylene blue(MB) or anionic dye orange II at near neutral ($pH > 4$) or acidic ($pH < 3$) condition. It desorbed within 20 min. The pseudo-second-order kinetic model and Langmuir isotherm provide better correlation.
- Mohammed Bassim Aalqaragully (2014) studied removal of textile dyes such as maxilon blue (GRC) and methyl orange (MO) by date stocks activated carbon. The influence of

various experimental factors such as initial dye concentration, adsorbent dosage, temperature and pH of dye solution were investigated. The adsorption equilibrium was represented with Langmuir, Freundlichand Tempkin isotherm models. Adsorption process was spontaneous and exothermic in nature of MO dye, while endothermic in nature of GRL dye.

- DaroudBalara et al (2015) investigated the application of low cost adsorbent Lemna minor for removal of reactive blue 19 dye from aqueous solution. The effect of various parameters including contact time, solution pH, adsorbent dosage and dye concentration was investigated It was found that the equilibrium data followed by Langmuier isotherm. Also, the pseudo-second-kinetic model was best applicable for RB 19 dye adsorption.

MATERIALS AND METHODS

The present investigation has been carried out to study the efficiency of a low-cost, eco-friendly adsorbent prepared from Bauhinia Tomentosa for the removal of a basic dye, Congo red by adsorption technique. Batch adsorption studies were carried out by varying the initial concentration of dye solution, pH and Adsorbent dosage.

Description of the adsorbent

Common Name	:	Yellow Bell Orchid
Botanical Name	:	Bauhinia Tomentosa
Family	:	Fabaceae
Tamil Name	:	Mandare

Preparation of the adsorbent

Ripened Bauhenia Tomentosa seed pods (Fig 1) were collected in and around udumalpet area then washed with water to remove the duet particle and cut into small pieces, dried in sunlight for 10 days and further dried in hot air oven 600C for 24 hours. The completely dried material was powdered well. The powdered raw material was chemically activated by treating it with conc.Sulphuric acid with constant stirring and kept for 24 hours. The carbonized material obtained was washed well with plenty of water several times to remove excess acid and then dried at 105^{0}C – 110^{0}C in a hot air oven. The adsorbent thus obtained was ground well and sieved through a 250 mesh and kept in air tight container for future.

Fig 1 Bauhenia Tomentosa Tree with seed pods and Flowers

Preparation of the adsorbate

The dye solution was prepared by dissolving 1g of Congo red in distilled water and diluted to 1000ml. The stock solution was diluted to appropriate concentrations.(Fig 2)

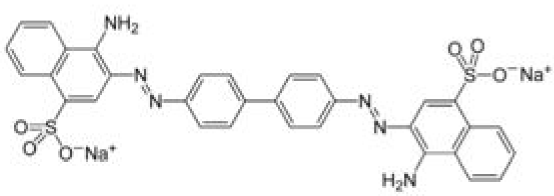


Fig 2 Structure of Congo red dye and crystals of Congo red

Congo Red is one type of acid dyes. Acid dyes are brightest class of dyes and are applied widely in industries. Congo Red is a heterocyclic aromatic chemical compound with molecular formula, C32H22N6Na2O6S2. Figure 1 shows the structure of Congo Red. Its chemical name is sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid. Its formula is illustrated in Figure 1, and molecular weight is 696.66 g/mol. It is a secondary diazo dye having the color index number of 11313. Due to a color change from blue to red at pH 3.0-5.0, Congo Red can be used as a pH indicator. It has a strong affinity to cellulose fibers. However, the use of Congo Red in the cellulose industries (cotton textiles, wood pulp, and paper industry) has long been abandoned, primarily because of its tendency to change color when touched by sweaty fingers, to run, and because of its toxicity. It can be also used for diagnosis purpose [9].

Applications and toxicity of Congo red dye

Applications

It is used for the dyeing of cotton, paper, jute, silk, wool, leather products and acrylic industries Antiseptic and fungicidal for humans Antiparasitical, antibacterial and antifungal in aquaculture and commercial fish hatchery industries It is also used as a food coloring agent, food additive, a medical disinfectant, and anthelminthic.

Toxicity

Environmentally persistent Damage to nervous system, brain and liver when ingested Eye burns, fast breathing, profuse sweating and cancer of different parts of the body Acutely toxic to a wide range of aquatic and terrestrial animals Decreases food intake, growth and fertility rates Causes damage to the liver, spleen, kidney and heart Inflicts lesions on the skin, eyes, lungs and bones Produces teratogenic effects Cytotoxic to mammalian cells Acts as a respiratory enzyme poison Decreasing RBC count (Dyscrasia), Hb (Anemia), and HTC (%) Increasing WBC count (Leukocytosis) and delay in blood coagulation Its presence in the hydrosphere reduces photosynthesis by obstructing light penetration and adversely affects aquatic life.(Raval et al.,2017)

Adsorption studies

Batch mode experiments were performed to study the effect of various parameters such as contact time, dye concentration and adsorbent dose affecting the adsorptive removal of CR dye. In the adsorption experiments 50 ml of the dye solutions of the desired concentration and pH were taken in Pyrex bottles containing pre-determined weighed amounts of adsorbent. The pyrex bottles containing adsorbent and adsorbate were equilibrated by shaking the contents at room temperature using thermostated rotary shaker (200 rpm) for different time intervals (10,20,30,40,50,60,80,100,120,140,160 and 180 minutes). Then the solutions were filtered using Whatmann 40 filter paper and the filtrates were analysed for the residual CR dye concentration spectrophotometrically at a wavelength of 497 nm against a reagent blank.

$$\text{Percentage removal of CR dye} = \frac{C_o - C_e}{C_0} \times 100 \quad (1)$$

Were C_o andC_e(mg/L) are the initial and equilibrium concentration of CR dye respectively. The amount of dye adsorbed at equilibrium (q_e) was calculated from the following equation.

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

Where q_e is the amount of dye adsorbed at equilibrium (mg/g). C_0 and C_e (mg/L) are the initial and equilibrium concentration of CR dye respectively. V is the volume of the solution (L) and M is the mass of the adsorbent used (g).

Effect of variation of initial concentration of the dye on the adsorption

The initial concentration of Congo red dye solution was varied (20,30,40, and 50 ppm) and batch experiment's were carried out by taking 50ml of the Congo red dye solution of specific concentration with fixed adsorbent dosage of 100 mg at pH 6.8. The system was equilibrated by shaking the content's flask at 32^0 C. The solution's were filtered and the dye concentrations of the filtrates were estimated Calorimetrically at 497 nm.

Effect of variation of adsorbent dosage on the adsorption dye

To determine the effect of adsorbent Dose on Congo red dye removal the amount of adsorbent dye was varied (20,30,40, and 50 mg/L) and batch studies were carried out using 50 ml of Congo red dye solution containing 20,30,40, and 50 ppm of the dye at 32^0 C and pH 6.8. The solutions were filtered and the filtrates were analysed Calorimetrically to find the amount of dye adsorbed.

RESULT AND DISCUSSION

Effect of initial dye concentration of CR dye solution on CR dye removal

The initial concentration of CR dye solution was varied (20, 30, 40 and 50 mg/L) and batch experiments were carried out. The results obtained reveal that the percentage removal of CR dye decreases with increase in initial dye concentration and this may be due to the saturation of adsorption sites on the adsorbent surface (Jayarajan et al.,2011) .The amount of dye adsorbed qe (mg/g) increases with increase in contact time at all initial dye concentrations used in this study (Table 1) is on par with the results by various researchers (Marius Sebastian Secula et al.,2011) This is so because the initial dye concentration provides the driving force to overcome the resistance to the mass transfer of dye between the aqueous and the solid phase. (Fig 3)

Table 1. Adsorption of CR dye with variation of initial concentration of CR dye solution
Conditions: Adsorbent dose: 100 mg, pH : 6.8 ± 0.02, Temperature 32^{0}C

Contact time	q(mg/g)			
	20 ppm	30 ppm	40 ppm	50 ppm
10	4.28	6.02	7.42	8.63
20	5.86	8.21	1012.34	12.14
30	7.26	10.12	14.29	14.99
40	8.52	11.71	15.99	16.47
50	9.13	12.88	17.02	17.43
60	9.69	13.24	17.62	19.40
80	9.69	13.65	17.62	21.23
100	9.69	13.65	17.62	21.44
120	9.69	13.65	17.62	21.44

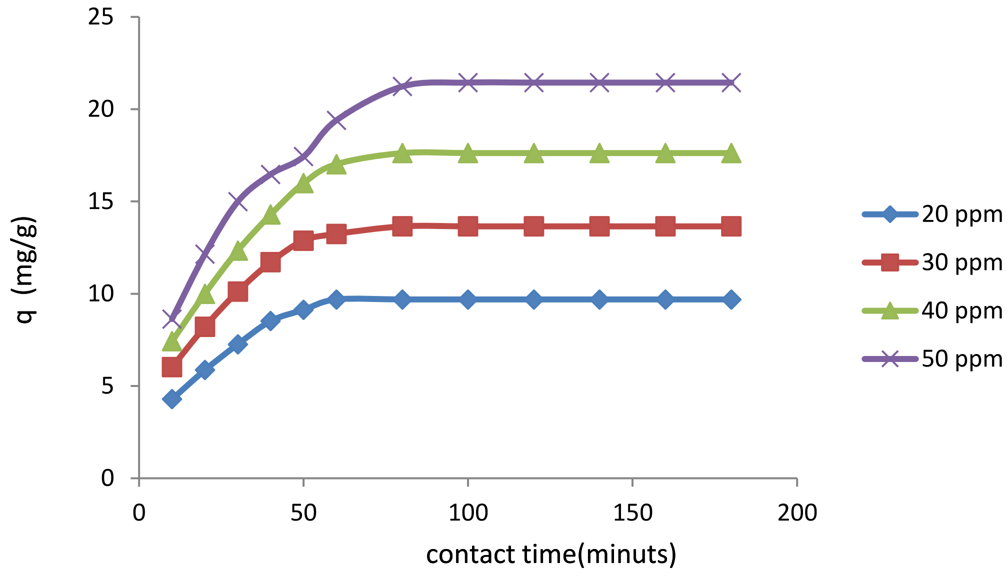


Fig 3 Adsorption of CR dye with variation of initial concentration of CR dye solution

Adsorption Kinetics :

Lagergren'spseudo first order and pseudo second order models were applied to the experimental data obtained in this study.

Lagergren's first order rate equation is given as follows. (Ho YS and MCKay G,1998)

$$\log q_e - q_t = \log q_e - k_1 t / 2.303 \qquad (3)$$

Where q_e and q_t (mg/g) are the amount of dye adsorbed at equilibrium and at time t and k1 (1/min) is the rate constant of the pseudo first order adsorption (Table 2). The plot of values of log (q_e-q_t) Vs. t gives a linear relationship (Figure 4). The values of k_1 and q_e were calculated from the slope and intercept of the plots respectively.

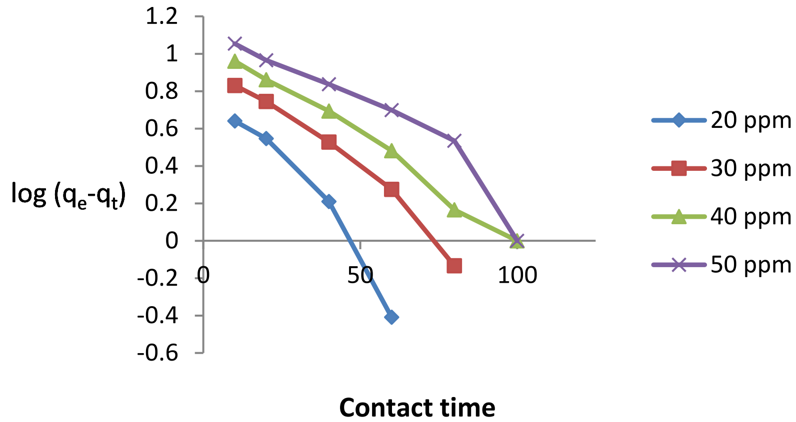


Figure4. Lagergren's plots for Congo red adsorption

Table 2.Kinetic modelling for Congo red adsorption using Lagergren's pseudo first order equation Conditions: Adsorbent dose : 100 mg, pH : 6.8 ± 0.02, Temperature: 32^{0}C

Time (mts)	$Log(q_e-q_t)$			
	20 ppm	30 ppm	40 ppm	50 ppm
10	0.7332	0.8822	1.008	1.1076
20	0.5832	0.7352	0.8816	0.9685
30	0.3856	0.5471	0.7221	0.8095
40	0.0682	0.286	0.5221	0.6963
50	-0.2518	-0.1169	0.2095	0.6031
60		-0.3958	-0.2247	0.3096
80				-0.6778
100				
slope	-0.0248	-0.0263	-0.0239	-0.0232
Intercept	1.0492	1.2437	1.3577	1.5084
R^2	0.9874	0.98654	0.9724	0.9376

The second order Lagergren's equation was given (Ho&Mc Kay,1999) as follows

$t/q_t = 1/K_2 q_e^2 + t/q_e$ (4)

Where K_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo second order adsorption.

From Table 3 and Figure.5 (t/q Vs. t), q_e and K_2 were calculated from the slope and intercept of the plot respectively.

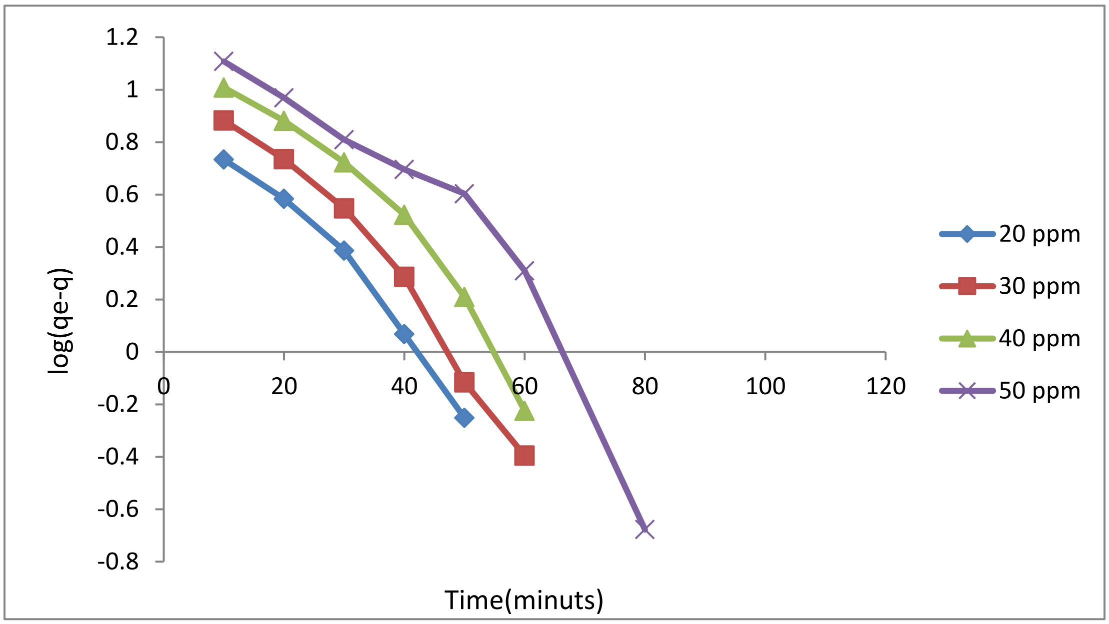
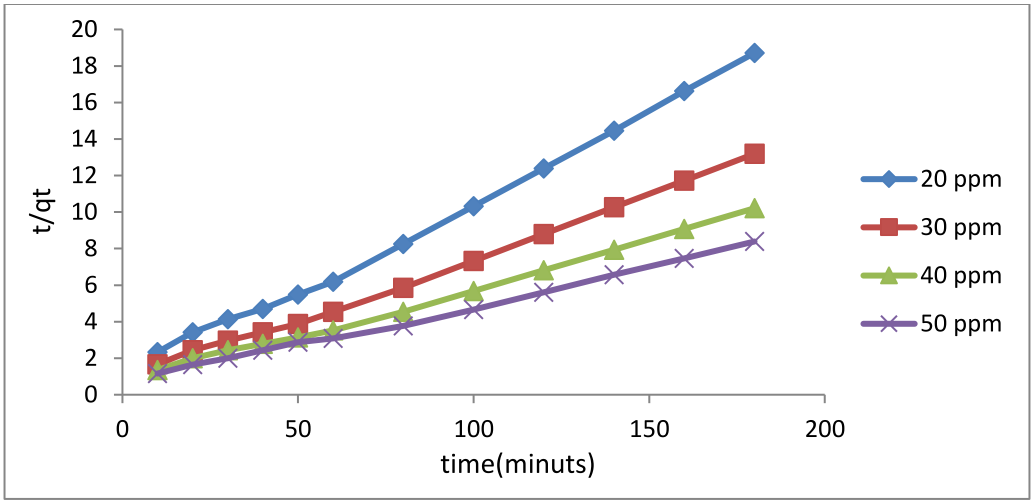


Figure 5.Pseudo second order adsorption

Table 3. Kinetic modelling for Congo red dye adsorption using pseudo second order equation

Conditions: Adsorbent dose : 100 mg, pH : 6.8 ± 0.02, Temperature 32^0C

t(minuts)	t/qt			
	20 ppm	30 ppm	40 ppm	50 ppm
10	2.33	1.66	1.35	1.16
20	3.41	2.43	1.99	1.65
30	4.13	2.96	2.43	2
40	4.69	3.41	2.79	2.43
50	5.48	3.88	3.13	2.87
60	6.19	4.53	3.52	3.09
80	8.25	5.86	4.54	3.77
100	10.32	7.33	5.68	4.66
120	12.38	8.79	6.81	5.6
140	14.45	10.26	7.94	6.57
160	16.63	11.73	9.08	7.46
180	18.71	13.19	10.21	8.39
Slope	0.0964	0.0678	0.0521	0.0418
Intercept	0.9633	0.7451	0,6251	0.6883



The first and second order adsorption rate constants with experimental and calculated q_e values for different initial CR dye solution concentrations are tabulated in Table 4

Table 4.Comparison of pseudo first and second order adsorption rate constants and calculated and experimental qe values for different initial dye concentration

Dye	First order kinetic model				Second order kinetic model		
Conc	q_e (exp)	k_1 x 10^{-2}	q_e (cal)	R^2	k_2 x10^{-3}	q_e (cal)	R^2
(mg/L)	(mg/g)	(1/min)	(mg/g)		(g/mg/min)	(mg/g)	
20	9.69	5.71	11.20	0.9874	9.647	10.37	0.995
30	13.65	6.056	17.53	0.9865	6.169	14.75	0.996
40	17.62	5.50	22.79	0.9724	4.342	19.20	0.995
50	21.44	5.34	32.24	0.9376	2.539	23.92	0.996

The values of R^2 are close to unity in pseudo second order (0.998) than that of pseudo first order. The values of q_e calculated from pseudo second order are in good agreement with q_e experimental values. This indicates that CR adsorption system obeys the pseudo second order kinetic rate equation.

Effect of adsorbent dose on CR dye removal

To determine the effect of adsorbent dose on CR dye removal the amount of adsorbent dye was varied (25, 50, 75,100, 200, 300, 400 and 500 mg) and batch adsorption studies were carried out using 50 ml of CR dye solution containing 20, 30, 40 and 50 mg/L of the dye at 32^0C and at pH 6.8. The percentage dye removal increased with increasing the adsorbent dosage up to a certain limit and then attains saturation. The dye removal efficiency increased from 40 – 96% for an increase in the adsorbent dose from 25mg to 1 mg (Fig.6). The increase in dye removal with increase in adsorbent dose may be due to the increased surface area and the availability of more number of active sites for dye adsorption (Mittal et al., 2010).

Table 4: Effect of adsorbent dose on CR dye removal

Dosage(mg/50 ml)	% Removal			
	(20 ppm)	30 ppm	40 ppm	50 ppm
0	0	0	0	0
25	57.5	56.66	45	40
50	80	78.33	64.2	60
75	88	86.66	76.5	72
100	96	91.66	88.1	84.1
200	100	96	95	93
300	100	100	100	97
400	100	100	100	100
500	100	100	100	100

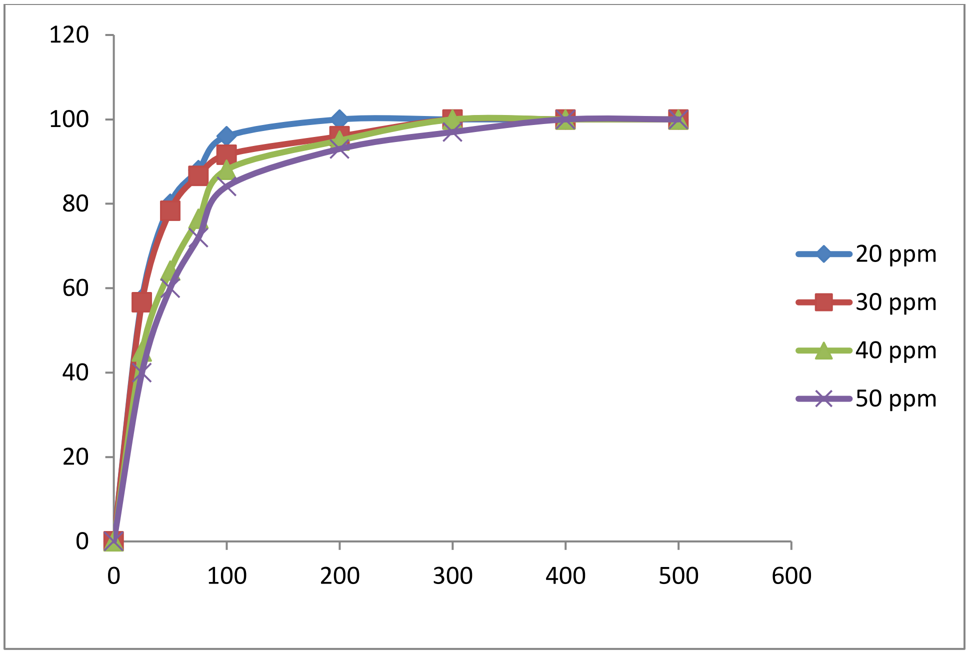


Fig. 6.Effect of adsorbent dose on CR dye removal

Summary And Conclusion

In this study an attempt has been made to prepare a low cost adsorbent from the ripened *Bauhinia Tomentosa* seed pod and it is employed for the removal of Congo red dye from aqueous solution. The efficiency of dye removal by the low cost adsorbent *Bauhinia Tomentosa* seed pod carbon revealed the following:

- The activated carbon derived from the seed pods of *Bauhinia Tomentosa* can be used as an efficient adsorbent for the removal of Congo red dye from aqueous solution.
- The percentage of Congo red dye adsorption increased from 54-98% with the adsorbent *Bauhinia Tomentosa* seed pod carbon in 180 minutes of contact time, when the initial concentration of Congo red dye solution was varied from 20ppm to 50ppm.
- The removal of Congo red dye increased from 31 to 100% when the dosage of adsorbent *Bauhinia Tomentosa* seed pod carbon was varied from 25 to 500mg in 120 minutes of agitation time at 32^0C and P^H 6.8 $\pm$ 0.02 using 50ppm of Congo red dye solution.
- The adsorption kinetics of Congo red dye onto the adsorbent *Bauhinia Tomentosa* seed pod carbon followed pseudo second order rate equation.

Thus it can be concluded that the low cost eco-friendly adsorbent prepared from the ripened *Bauhinia Tomentosa* seed pod carbon may be used for the Congo red dye removal from aqueous solution.

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