A

Project Report

On

REMOVAL OF DYES USING CONVENTIONAL AND ADVANCED ADSORBENTS

Submitted by

Kumud Agarwal

(109CH0431)

In partial fulfillment of the requirements for the degree in

Bachelor of Technology in Chemical Engineering

Under the guidance of

Dr. Pradip Chowdhury

DEPARTMENT OF CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

May, 2013

National Institute of Technology Rourkela

CERTIFICATE

*This is to certify that the project report entitled, "**Removal of dyes using conventional and advanced adsorbents**", submitted by **Kumud Agarwal** (109CH0431) in partial fulfillments for the requirements for an award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology Rourkela is prepared by him under my supervision and guidance and this work is not been submitted elsewhere for a degree.*

Date: 6th May , 2013

Place:

Dr. Pradip Chowdhury
(Thesis Supervisor)
Dept. of Chemical Engg
NIT Rourkela

ACKNOWLEDGEMENTS

I consider it as my privilege to express gratitude and respect to all those who guided and inspired me in the completion of my B.Tech project. The undertaking of this project inculcated a strong sense of research inside me and I also came to know about so many new things.

First of all, I would like to acknowledge and extend my heartfelt gratitude to Dr. Pradip Chowdhury, Assistant Professor at Department of Chemical Engineering, National Institute of Technology, Rourkela for his exemplary guidance and constructive criticism, during the undertaking of this project entitled, ”Removal of dyes using conventional and advanced adsorbents”.

I am also thankful to all the faculties and supporting staff of Department of Chemical Engineering and Department of Mechanical Engineering, National Institute of Technology, Rourkela for their constant help and extending the departmental facilities for my project.

I would like to extend my sincere thanks to all my friends and especially my seniors, Mr.Deepak Garg and Mr. Prince George for their unconditional assistance and encouragement. I would also like to keep in record the moral and emotional support provided by my parents and family throughout the period.

Date: 6th May, 2013

Kumud Agarwal

ABSTRACT

Dyes are an important class of pollutants, and can even be identified by the human eye. Disposal of dyes in precious water resources must be avoided, however, and for that various treatment technologies are in use. Among various methods, adsorption occupies a prominent place in dye removal. The growing demand for efficient and low-cost treatment methods and the importance of adsorption has given rise to low-cost alternative adsorbents. This thesis work focused on liquid phase adsorptive removal of organic dyes *viz*. *Crystal violet* and *Coomassie brilliant blue* where they represent the class of a basic and an acid dye respectively. The adsorbents used were: MIL-53 or Fe-BDC (a known Metal Organic Framework), activated carbon and different variants of commercially available zeolites *viz*. 4A, 5A and 13X. The characterization of all the adsorbents were carried out using conventional techniques like scanning electron microscopy (SEM), powder X-ray diffraction analysis (PXRD), thermogravimetric analysis (TGA) and N_2 adsorption analysis (BET). The results with activated carbon showed a high removal percentage (>90%) of both the dyes, irrespective of dosage concentration. The results on the other hand with zeolites were measured to be a function of its concentration. MIL-53 MOF had shown great potential in degrading the organic dyes which can be attributed to its higher percentages of active metal sites and low band gap energy (influencing photocatalysis simultaneously).

.

CONTENTS

PAGE NO.

PAGE NO.

PAGE NO.

LIST OF TABLES AND FIGURE

CHAPTER 1

INTRODUCTION

1.1 Prelude

Saving water to save the planet and to make the future of mankind safe is what we need now. With the growth of mankind, society, science, technology our world is reaching to new high horizons but the cost which we are paying or will pay in near future is surely going to be too high. Among the consequences of this rapid growth is environmental disorder with a big pollution problem. Anthropogenic activities have caused a great harm to the quality of our lifeline, i.e. water. Because of fast depletion of the freshwater resources, there seems to be a crisis of the same. Water pollution is a global concern and, it is the high time that we realize the gravity of the situation. Removing pollutants from water is the crying need of the hour and developing a cost effective and environmentally safe method to achieve the same is a challenging task for chemical engineers. After all, it is the future of mankind, which is at stake.

A dye is a colored substance that has an affinity to the substrate to which it is being applied. Dyes appear to be colored because they absorb some wavelengths of light more than others. Humans are estimated to use dyes for thousands of years and the earliest use of the colorant is believed to be by Neanderthal man about 1,80,000 years ago [1, 2]. The year 1856 witnessed a historic discovery of first synthetic dye, Mauvine, by Perkin [3, 4]. In due course of time, these synthetic dyes gained huge popularity and began to be synthesized on a large scale. In fact, it has reached to a level of annually, over $7.0\text{x}10^5$ and nearly 1000 different types of dyes are produced worldwide [5].

1.2 Background of Present Research

Now-a-days, a large amount of waste water having color is generated by many industries like textile, leather, paper, printing, plastic and so on [6]. The presence of dye materials greatly influence the quality of water and the removal of this kind of pollutant is of prime importance. Owing to their complicated chemical structures, dyes are difficult to treat with municipal waste treatment operations [5]. Even a small quantity of dye does cause high visibility and undesirability. Moreover, the color produced by dyes in water makes it aesthetically unpleasant [6]. They can have acute or chronic effects on exposed organisms, which depend on the concentration of the dye and the exposed time [5]. In addition to that, many dyes are considered to be toxic and even carcinogenic [6-8].

Few decades earlier the dye selection, applications and uses were not given much importance. With the growing health concerns, it was in the 80s that people started paying much attention to the dye wastes [2]. An indication to the magnitude of this problem can be inferred from the fact that two percent of dyes produced are directly discharged into aqueous effluents [9, 10]. With the increased stringent laws on industrial discharge, it has become very important to treat this wastewater. Because of their detriment and large scale distribution in the ecological environment, their separation and determination has become one of the important studies of environmental analysis. Of prime importance is the need for clear information on the safety related properties of the colorants and the measure to be taken for lowering exposure. If all these elements are seriously considered, then the technical use of colorants and the handling involved might be possible without much health danger.

1.3 Research Objectives

Several physical, chemical and biological de-colorization methods such as coagulation/flocculation treatment, biodegradation processes, oxidation methods, membrane filtration and adsorption have been reported to be investigated for the removal of dyes from industrial effluents [11-14]. Among the studied methods, removal of dyes from adsorption is found to be the most competitive one because it does not need a high operating temperature and several coloring materials can be removed simultaneously [6]. The versatility of adsorption is due to its high efficiency, economic feasibility and simplicity of design [8]. As there are various parameters to effect adsorption process such as, charge density and structural stability of the adsorbent so, in the thrust of a comprehensive study, we have selected one basic dye (Crystal Violet) and one acidic dye (Coomassie Blue) for this present study.

Several adsorbents have been used for this purpose such as Zeolites (4A,5A and 13 X). One of the conventional and most studied adsorbent is Activated Carbon (AC). The reasons for this popularity are its high adsorption capacity, high surface area and microporous structure [5]. In fact, Activated Carbon adsorption has been listed by the US Environmental Protection Agency as one of the best available control technologies [17].

Metal-organic frameworks (MOFs) are crystalline materials which are very popular for various applications [18-25]. The special interest in MOFs is due to the easy tunability of its pore size and shape from a microporous to a mesoporous scale [18-20]. MOFs have special interest in the adsorption, separation and storage of gases and vapors [21-24]. The MOF selected for our study is MIL-53. However, there has not been much report on the use of MOFs in the removal of dye materials. But MOFs have certainly, attracted increasing interest due to their rich structural chemistry and tunable physical properties.

Thus our objective is to study the effects of MIL-53(advanced adsorbent), activated carbon and Zeolites (conventional adsorbents) in removing the dyes *viz*. Crystal Violet and Coomissie Blue from aqueous medium.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption Principles

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid, forming a molecular or atomic film. In other words, adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface and this process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It is a surface phenomenon and a consequence of surface energy. The atoms on the surface of the adsorbent are not wholly surrounded by other atoms and thus, can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as follows:

(1) Physisorption: It is a type of adsorption in which the adsorbate adheres to the surface through Van der Walls (weak intermolecular) interactions.
(2) Chemisorption: It is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond.

Adsorption takes place primarily on the walls of the pores or at specific sites inside the particle. As the pores are generally small, the internal surface area is greater than the external area. Separation occurs because differences in molecular weight, shape or polarity cause some molecules to be held more strongly on the surface than others. In many cases, the adsorbate is held strongly enough to allow complete removal of that component from the fluid [26].

2.2 Basics on Dyes

As discussed earlier, dyes are an important class of pollutants and can even be recognized by human eyes. A dye molecule consists of two key components: the ***chromophores***, responsible for producing the color, and the ***auxochromes***, which in addition to support the chromophore, also render the molecule soluble in water and give enhanced affinity toward the fibers. Dyes have high structural diversity and can be classified in many ways [2]. Some properties of dyes are based on their usage and can be broadly classified as [1-3]:

2.2.1 Acid dyes

It is a sodium salt of a sulfonic, carboxylic or phenol organic acid. It is soluble in water and possesses affinity for amphoteric fibres. It is used for nylon, wool, paper, leather, food, cosmetics etc. Most synthetic food colors fall in this category.

2.2.2 Basic dyes

They yield colored cations in solution and this is the reason for calling them cationic dyes. This type of dye finds uses in paper, modified nylons and polyesters, medicine etc.

2.2.3 Direct dyes

These are water soluble anionic dyes. Dyeing is normally carried out in a neutral or slightly alkaline dye bath or at near boiling point, with addition of either sodium chloride or sodium sulphate or sodium carbonate. These are used for dyeing of cotton and rayon, paper, leather etc. They are also used as Ph indicators and as biological stains.

2.2.4 Disperse dyes

These are substantially insoluble nonionic dyes. These are used mainly on polyester and also applied on nylon, cellulose, acrylic fibers etc.

2.2.5 Mordant dyes

These dyes uses a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordants can change the final color significantly. These are basically used for wool.

2.2.6 Sulfur dyes

These types of dyes have intermediate structures. They form a relatively small group of dyes, but the low cost and good wash fastness properties make it very important from the economic point of view. Its main uses are for cotton and rayon.

2.2.7 Reactive dyes

They have a chromophore attached to a substituent that is capable of directly reacting with the fiber substrate. The prime reason to make them classified among the most permanent of dyes is the covalent bond that attaches reactive dyes to natural fibers. They find their uses for cotton, wool and nylon.

2.2.8 Solvent dyes

These type of dyes are generally non-polar or little polar and thus, are water insoluble. They are used for plastics, gasoline, lubricants, oils etc.

2.2.9 Vat dyes

This type of dye is water insoluble and incapable of dyeing fibers directly. But, reduction in alkaline liquor produce the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fiber. These are used mainly for cotton, wool and nylon.

2.3 Reviews on Some Recent Works on Dyes

Several studies have been conducted on the adsorption of different dyes from various adsorbents.

In 2012, the adsorption of acid blue 25, Cd^{2+} and Zn^{2+} on a physically activated bituminous carbon and a phosphoric activated carbon from wood was studied using single and binary (dye/metal) solutions[15]. It was found that the presence of Acid blue 25 (AB25) on dye–metal binary solutions enhanced the adsorption of Zn^{2+} and Cd^{2+} on bituminous and wood commercial ACs in a very similar way, in spite of the differences of the textural and surface chemistry properties of both carbons

In 2012, adsorption of acid dyes on SBA-3 ordered mesoporous silica, ethylenediamine functionalized SBA-3 (SBA-3/EDA), aminopropyl functionalized SBA-3 (SBA-3/APTES) and pentaethylene hexamine functionalized SBA-3 (SBA-3/PEHA) materials was studied[16]. The SBA-3/PEHA was found to have the highest adsorption capacity for all acid dyes. Batch studies were performed to study the effect of various experimental parameters such as chemical modification, contact time, initial concentration, adsorbent dose, agitation speed, solution pH and reaction temperature on the adsorption process. The Freundlich model was found to be fit with the equilibrium isotherm data.

In 2011, dye removal from colored textile wastewater using chitosan in binary system was studied [27]. Here, Direct Red 23 and Acid Green 25 were used as anionic dyes. The adsorption kinetics of dyes on chitosan followed the pseudo second order at different pH values. The experimental data were correlated reasonably well by Tempkin adsorption isotherm. It was concluded that the chitosan is an eco- friendly adsorbent for dye removal from low concentration of acidic colored textile wastewater.

In 2010, chemically modified sugarcane bagasse as a potentially low-cost biosorbent for the removal of methyl red was studied [28]. The kinetics of methyl red adsorption followed the pseudo first order kinetic expression and Langmuir isotherms model fit well. From the study, it was inferred that sugarcane bagasse has a good potential to be used for small scale industries, which produces dyes as their effluent, after it was being pretreated with phosphoric acid.

.In 2010, the removal of reactive red 23, reactive blue 171, acid black 1 and acid blue 193 from aqueous solution using fly ash was studied [31]. The results showed that adsorption was pH dependent, adsorption increased with the initial dye concentration; the reaction was spontaneous and exothermic in nature.

In 2010, the porous magnetic microspheres prepared with sulfonated macroporous polydivinylbenzene as a template and their ability to remove cationic dyes was studied [32]. The results show that methyl violet and basic fuchsin can be successfully removed from the adsorbent used and even the adsorbent is easily regenerated.

2.4 Basic Dye (CRYSTAL VIOLET)

Basic dyes have amino groups, or alkylamino groups, as their auxochromes, and consequently have an overall positive charge. In other words, the colored part of the molecule is the cation. Although the molecule charge is often shown on a specific atom in structural formulae, it is the whole molecule that is charged. They are brilliant and most fluorescent among all synthetic dyes but have poor light and wash fastness.

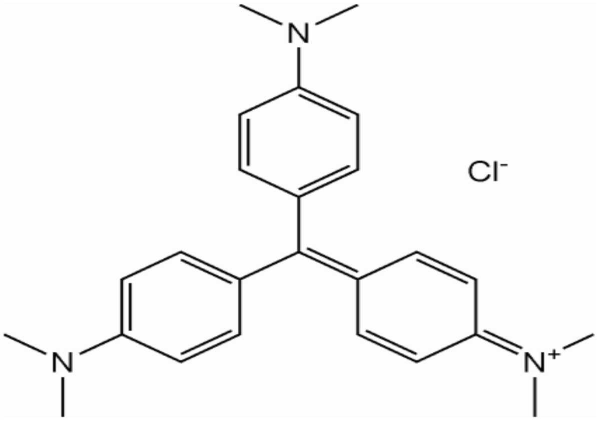

Figure 2.1: Structure of Crystal Violet

IUPAC Name: Tris(4-(dimethylamino)phenyl)methylium chloride

Molecular formula = $C_{25}N_3H_{30}Cl$

Molar mass = 407.979 g mol^{-1}

Appearance = blue-violet colour

Melting point = 205°C(with decomposition)

Crystal Violet is used as dye, especially for paper and as a component of navy blue and black inks for printing, ball-point pens and ink-jet printers. It is also used to colorize diverse products such as fertilizers, anti-freezes, detergents, and leather jackets. The dye is also used as a histological stain, particularly in Gram's method for classifying bacteria. Crystal violet has antibacterial, antifungal, and anthelmintic properties. However, in large quantities, crystal violet may lead to ulceration of a baby's mouth and throat and is linked with mouth cancer. Crystal violet has also been linked to cancer in the digestive tract of animals.

2.5 Acid Dye (Coomassie Blue-R 250)

IUPAC Name: Sodium 3-[[4-[[4-(4-ethoxyanilino)phenyl]-4(ethy)-[3-sulfonate phenyl methyl] azahimylidene] cyclo-hexa-2,5-dien-1-ylidene] methyl]-N-ethylaniline] methyl benzene 2 sulphonate.

Molecular formula = $C_{45}H_{44}N_3NaO_7S_2$ (Sodium salt)

Molar mass = 825.97 g/mol

Appearance = blue colour with a slight reddish tint

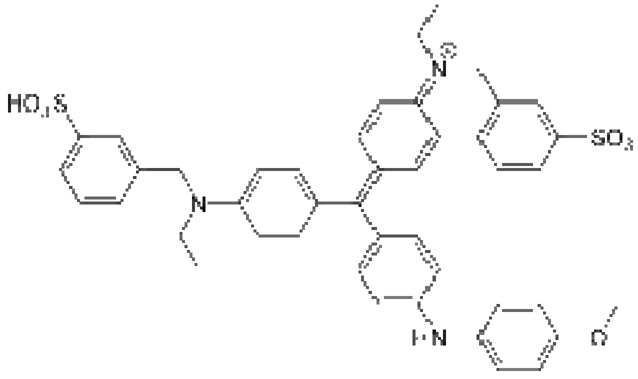

Figure 2.2: Structure of Coomassie Blue

The suffix "R" in the name of Coomassie Brilliant Blue R-250 is an abbreviation for Red as the blue colour of the dye has a slight reddish tint. Coomassie Brilliant Blue R-250 was first used to visualize proteins. Coomassie Brilliant Blue R-250 was used to stain protein samples after electrophoretic separation in a polyacrylamide gel.

In 2011, equilibrium, kinetics and thermodynamics of Crystal Violet (CV) adsorption onto NaOH modified rice husk (NMRH) was investigated [29]. Experiments were carried out as function of contact time, initial solution pH (2–10), adsorbent dose (0.5–5 g) and temperature (293, 303 and 313 K). The adsorption was favoured at higher pHs and lower temperatures. Adsorption data were well described by the Freundlich model, although they could be modelled by the Langmuir model as well. The adsorption process followed the pseudo-second order kinetic model. Thermodynamic parameters suggest that the adsorption is a typical chemical process, spontaneous, and exothermic in nature.

In 2009, The adsorption performance of the materials bottom ash (BA), a power plant waste, and de-oiled soya (DOS), a soya bean industry waste for removal of crystal violet dye, has been investigated through batch and column experiments. It revealed that the adsorption process is endothermic in nature [30].

In 2009, usage of agro-industrial waste for the removal of basic dyes was studied [33]. The experimental data showed that various adsorbents used, such as sawdust and sugarcane fibers were effective in the removal of Rhodamine B and Crystal Violet.

In 2007 three organic dyes namely, Coomassie Blue, Malachite Green and Safranin Orange were removed from solution by adsorption on sand at 298 K [34]. The adsorption kinetics followed the pseudo second order equation for all the three dyes investigated in this work with the *k* values lying in the region of 6.2×105 to 3.0×106. The adsorption behavior of the dyes was also investigated in terms of added cations and anions and it was found that adsorption of Commassie Blue decreased substantially in the presence of sulphate, thiosulphate, acetate, potassium, nickel and zinc ions.

2.6 Metal Organic Frameworks

2.6.1 Definition

Metal organic frameworks or MOFs represent a class of novel adsorbents that have attracted the researches all round the world due to its great diversity in structures resulting from co-ordination bonds between inorganic metal atoms as nodes and organic ligands as linkers. Porosity, crystallinity and product purity are some of the key attributes of MOFs [35]. They consists of a metal ion or clusters coordinated to often rigid organic molecules to form one, two, three dimensional structures that can be porous. MOFs are relatively new microporous structures. The particular interest in MOF is due to due to the easy tunability of their pore size and shape from a micro to a meso scale by changing the connectivity of the inorganic part and the nature of the organic linkers. They can often be considered as expanded versions of typical inorganic structures where organic components act as linkers to connect inorganic clusters, chains or layers. MOFs are known to have many applications [18-25].

Before being explored effectively at industrial level, there are some concerns which need proper attention. It has been observed that surface area and pore volume of the same MOF synthesized by different researches at different parts of the world are different. The same observations have also been found on the different batches of MOF prepared on a single location. The reason behind this anomaly alludes at different synthesis conditions and post- treatment thereafter [35].

2.6.2 MIL-53(Fe) or Fe III (OH)(O_2C-C_6H_4-CO_2)

MIL-53 is one of the widely studied MOF. After it was reported, there was a growing interest in the study of this adsorbent and various methods were developed to improve the synthesis and characterization of this highly promising adsorbent.

There are not much report of the use of MOFs in the removal of dye materials. For the first time in 2010, the study of adsorptive removal of dye (methyl orange) from aqueous solution was studied with MOF (Cr-BDC) [36]. Here, two highly porous MOF materials, MIL-53 and MIL-101 were studied. MIL -101 showed greater values of adsorption capacity and kinetic constant, showing the importance of porosity.

As with the case with other MOFs, MIL-53 also has been majorly studied for gaseous adsorption. However, to the best of our knowledge, less study has been done on the use of MIL-53 for dye removal from aqueous solution.

2.6.3 Activated Carbon

Activated carbon is the conventional and most studied adsorbent. The ability of charcoal to remove odor and taste was observed centuries ago. According to a Sanskrit manuscript from circa 200 BC," it is good to keep water in copper vessels, to expose it in sunlight and to filter it through charcoal." [37, 38]. However, the credit of developing commercial activated carbon goes to Raphael von Ostrezko [39].

Activated carbon is porous material which is commercially used for the removal of liquids and gases pollutants owing to its large surface area. It is a carbonaceous adsorbent and has known to have highly amorphous structure [40]. It has been observed that adsorption on activated carbon is not usually selective as it occurs through weak Van der Walls forces [2].

In 2009, the study of preparation of activated carbon from digested sludge of the tannery industry was done for the removal of a reactive dye [41]. The experimental data correlated well with the Langmuir, Freundlich and Temkin adsorption isotherms.

In 2011, the study was done on the ability of activated carbon in the removal of two anionic dyes (Direct Blue 78 and Direct Red 31) from colored wastewater in single and binary systems [42].

The effects of adsorbent dosage and initial dye concentration were studied at 25°C. The kinetics was found to conform to pseudo second order kinetic model. The equilibrium data fitted well with Langmuir adsorption isotherm. Results indicated that Activated Carbon is an effective adsorbent in this case.

In 2010, competitive adsorption of dyes (congo red, methylene blue, malachite green) on activation carbon was studied [5]. It was found that the percent removal of color increased with the increase in the amount of adsorbent dosage and also with the increase in contact time. It was also observes that the adsorption varies with changing the value of pH of dye solution.

In 2001, the study of methylene blue adsorption on commercial activated carbon and indigenously prepared activation carbon from bamboo dust, coconut shell, groundnut shell, rice husk and straw was done [43]. The effects of various experimental parameters were investigated. The experimental data fitted well with the Langmuir and Freundlich adsorption isotherms. The results also indicated that the indigenous activated carbon can be employed as low cost alternative to the commercial activated carbon.

In 2002, the study was done the removal of a direct dye by adsorption onto coal based adsorbents viz. charfines, lignite coal, bituminous coal and comparing results with activated carbon [44]. The investigation indicated that the coal based sorbents facilitated chemisorption in the process of dye sorption while, activated carbon resulted in physisorption interactions.

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 GLASSWARES AND APPARATUS USED

All glassware (conical flasks, measuring cylinders, beakers, pipettes etc.) were manufactured by Borosil / Rankem. All the instruments and apparatus used in the experiment are listed below:

Table 3.1: list of all instruments used

INSTRUMENT	MANUFACTURER / TYPE	FUNCTION
Electronic weight balance	Sartorius	To measure weight
Oven	Shivaki	To dry the samples / to maintain the temperature
Shaker	Environmental orbital shaker incubator	To shake the samples in dye solutions
Spectrophotometer (UV/ Vis)	Jasco (V 530)	Absorbance
Thermo Gravimetric Analyzer (TGA)	Shimadzu (DTG 60 H)	Thermal analysis
Scanning Electron Microscope((SEM)	JEOL JSM-6480 LV	Morphology
X-Ray Diffractometer (XRD)	Philips Analytical, PW-3040	X-ray diffraction
Brunauer-Emmett Teller (BET)	Quantachrome (Autosorb)	Surface Area Analysis

3.1.2 SYNTHESIS OF MIL-53

Synthesis of MIL-53(Fe) photocatalyst MIL-53(Fe) photocatalyst was prepared according to the report by Férey et al. [21 Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. Science 1999, 283, 1148]. Typically, amixture of iron chloride, terephthalic acid and N,N_-dimethylformamide (DMF) with amolar ratio of 1:1:280 was transferred into a Telfon-lined stainless steel bomb and heated at 150 ◦C for 15 h. The as-obtained yellow MIL-53(Fe) powder was re-heated at 150°C overnight to remove the DMF inside the pores of MIL-53(Fe). After cooling down to room temperature, the solid was then washed with a large volume of

De-ionized water (1 g of MIL-53 in 0.5 l of water) to give the final MIL-53(Fe).

3.1.3 POWDERED ACTIVATED CARBON

The commercial activated was purchased from MERCK. It was used without any improvisation. The adsorbent used was dried at 70°C for 24 hours before use.

3.1.4 POWDERED ZEOLITES

The commercial zeolite was purchased from MERCK. It was used without any improvisation. The adsorbent used was dried at 100°C for 24 hours before use.

3.1.5 DYES

Crystal Violet (λ_{max} = 590nm) was purchased from MERCK, INDIA. It was used without any improvisation or further purification.

Coomassie Blue (λ_{max} = 560 nm) was purchased from MERCK, INDIA. It was used without any improvisation or further purification.

3.2 METHODS

For the experimental work on MIL-53, the stock solution of 220 ppm of coomassie Blue and 40 ppm of Cristal Violet was made .The calculations are shown in ***appendix 1***.

In case of commercial activated carbon and Zeolites the values for stock solution and working solution for both the dyes were 250mg/l and 40 mg/l respectively. The detail calculations are shown in ***appendix 2*** in tabular form.

Dye concentrations were estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, λ_{max}.

3.2.1 Effect of adsorbent dose

50 ml of the working solution was put in each different conical flask. Then, different adsorbent dose was added in each flask. All the flasks were kept inside the shaker at 100 rpm and 25^oC. for 240 minutes, the flasks were withdrawn from the shaker and the dye solutions were separated from adsorbents by using centrifuge at 4000 rpm for 10 minutes at regular intervals. The absorbance of all the solutions was then measured. A graph was plotted with percent removal (% Q) vs. adsorbent dose. D is expressed as,

$$\%Q = \frac{(C_i - C_o)}{C_i} \times 100 \tag{3.1}$$

Where,

$\%Q$ = percentage of dye adsorbed

C_i = initial dye concentration (mg/lit)

C_o = final dye concentration (mg/lit)

3.2.2 Effect of Contact Time

50 ml of the working solution was put in each different conical flask. All the flasks were put in the shaker at 100 rpm and 25^{o}C for a predetermined time period ranging from 10 minutes to 240 minutes. Then, flasks were withdrawn from the shaker, solution was separated from adsorbents by using centrifuge at 4000 rpm for 10 minutes and then absorbance of the solutions was measured. A graph was plotted with $\% \ Q$ vs. contact time.

3.2.3 Effect of temperature

50 ml of the working solution was put in each different conical flask. Three sets of experiments were conducted at temperatures of 25 ^{o}C, 45 ^{o}C and 65 ^{o}C and results were studied.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF ADSORBENTS

Thermal analysis of adsorbents was carried out in detail in a TGA apparatus, SHIMADZU (DTG 60 H). The morphologies of the synthesized MIL-53 product was characterized using a scanning electron microscope (SEM, JEOL JSM-6480 LV) equipped with an energy dispersive X-ray spectrometer (EDX). The synthesized samples were subjected to X-ray diffraction by a diffractometer (XRD, Philips Analytical, PW-3040) equipped with the graphite monochromatized CuKα radiation ($\lambda = 1.5406$ Å) in 2θ angles ranging from 5^o to 50^o with a step size of 0.05 degree and scanning rate 2^o per minute.

4.1.1 Characterization of MIL-53

4.1.1.1 SEM Analysis

The surface morphology studies of synthesized MIL-53 showed octahedral shaped crystals as shown in figure which is similar reports as presented in many literatures.

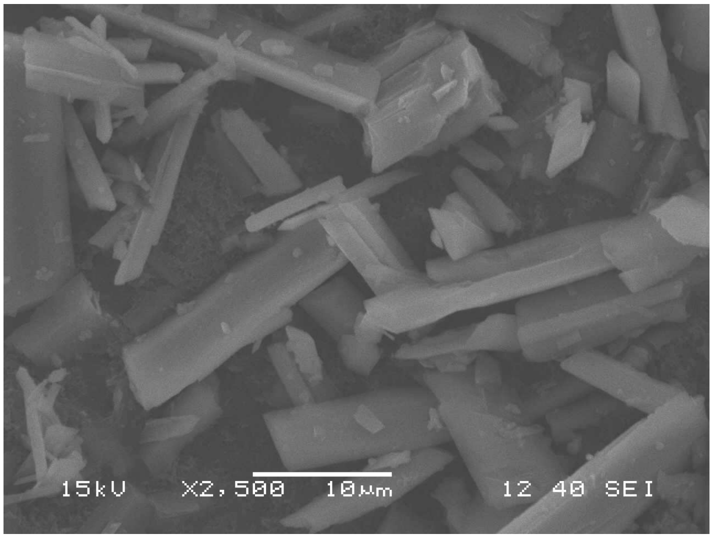

Figure 4.1: SEM Imaging of as-synthesized MIL-53

4.1.1.2 Powder XRD Analysis

The powder XRD pattern as shown in figure 4.2, matches well with the literature reports confirming the product. The sharp peaks are confirmation about the crystallinity of MIL-53. The product synthesized is also very pure since no additional peaks for any foreign impurity is seen in the pattern.

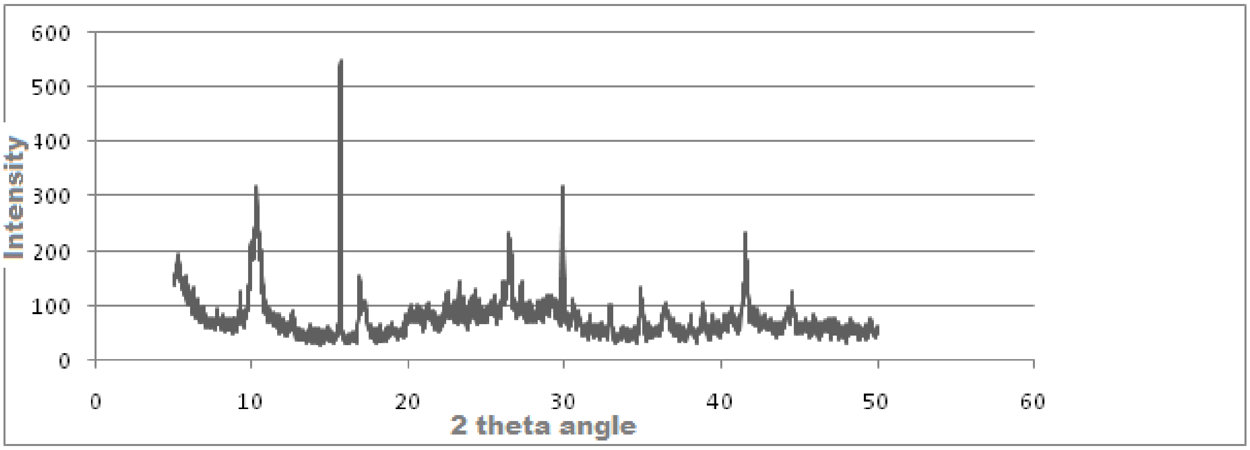

Figure 4.2: Powder XRD Analysis of MIL-53 Sample

4.1.1.3 BET Surface Area Analysis

The BET surface area performed showed a surface area of 121.36 m^2/gm, which is comparatively a reasonable value for the synthesized MOF. It should be worth mentioning that more the surface area, more efficient may be the adsorption of dye from aqueous solution.

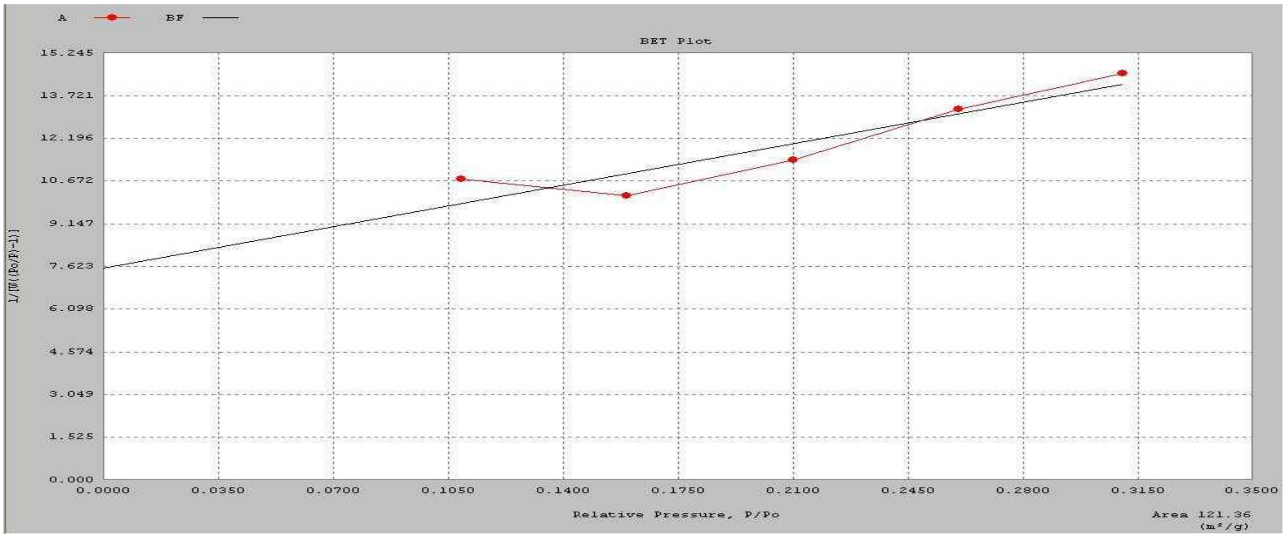

Figure 4.3: BET Surface Area Analysis of MIL-53 Sample

4.1.1.4 TGA Analysis

The TGA profile shows typical weight loss pattern for the MIL-53 MOF and complete degradation of MIL-53 starts around 375°C and by 400°C the degradation is complete. In the range between 50-200°C the weight loss is purely due to removal of moisture and trapped methanol and between 200°C to 300°C where the weight remains fairly constant, is stable zone. Thus, for any experimentation using MIL-53, the system temperature should be regimentally maintained to be between 200-300°C. Figure 4.4 shows the TGA profile.

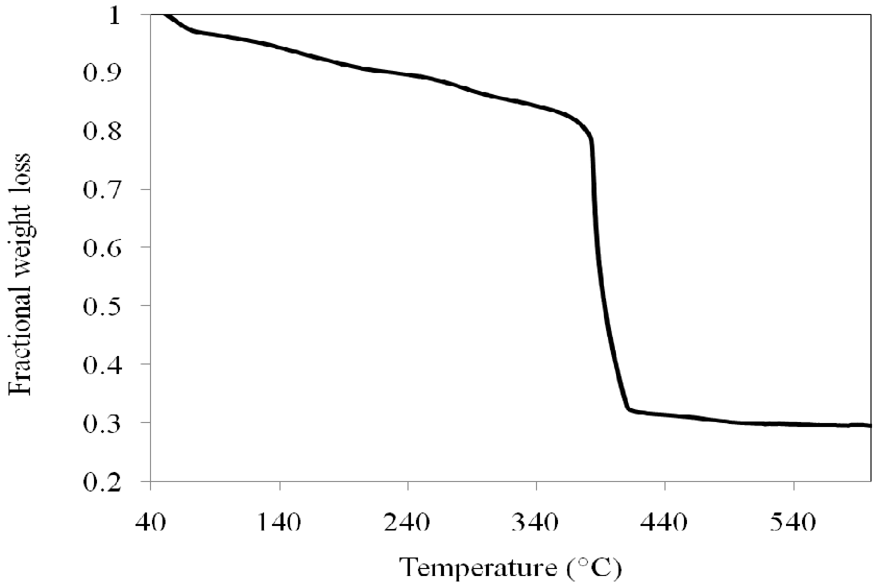

Figure 4.4: TGA Analysis of as-synthesized MIL-53 Sample

4.1.2 Characterization of Activated Carbon

4.1.2.1 SEM Analysis

The SEM image is shown in the following figure. The surface morphology of commercial activated carbon used specifically for this work matches well with various types of activated carbons reported in the literature.

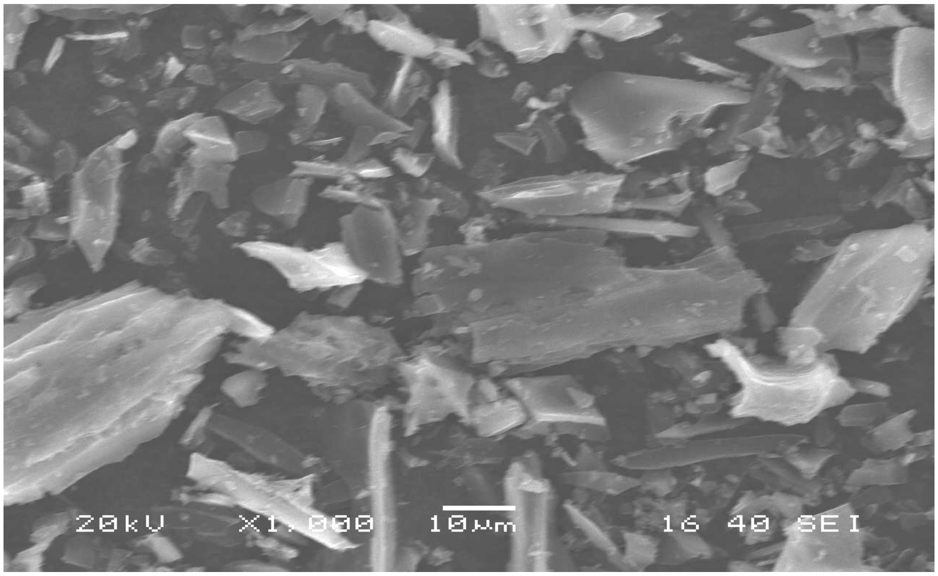

Figure 4.5: SEM Image of Commercial Grade Activated Carbon

4.1.2.2 TGA Analysis

The TGA profile of the activated carbon is shown in figure 4.6. The thermal stability of activated carbon is much higher than Cu-BTC and hence more effective in high temperature applications.

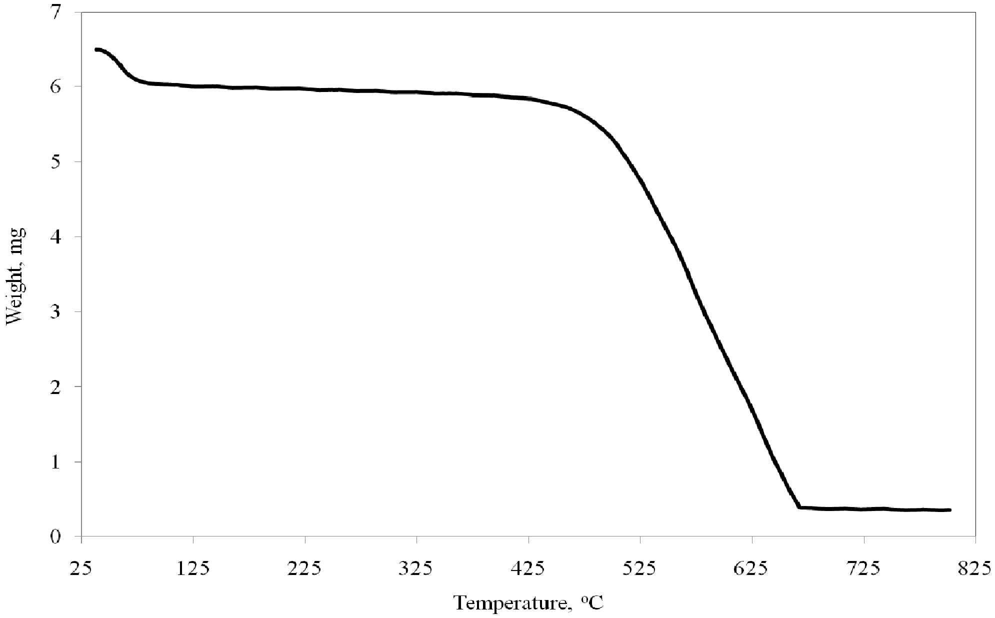

Figure 4.6: TGA profile of activated carbon (Merck)

4.1.2.3 Powder XRD Analysis

Powder X-ray diffraction analysis is shown in figure 4.7. It establishes the amorphous nature of activated carbon.

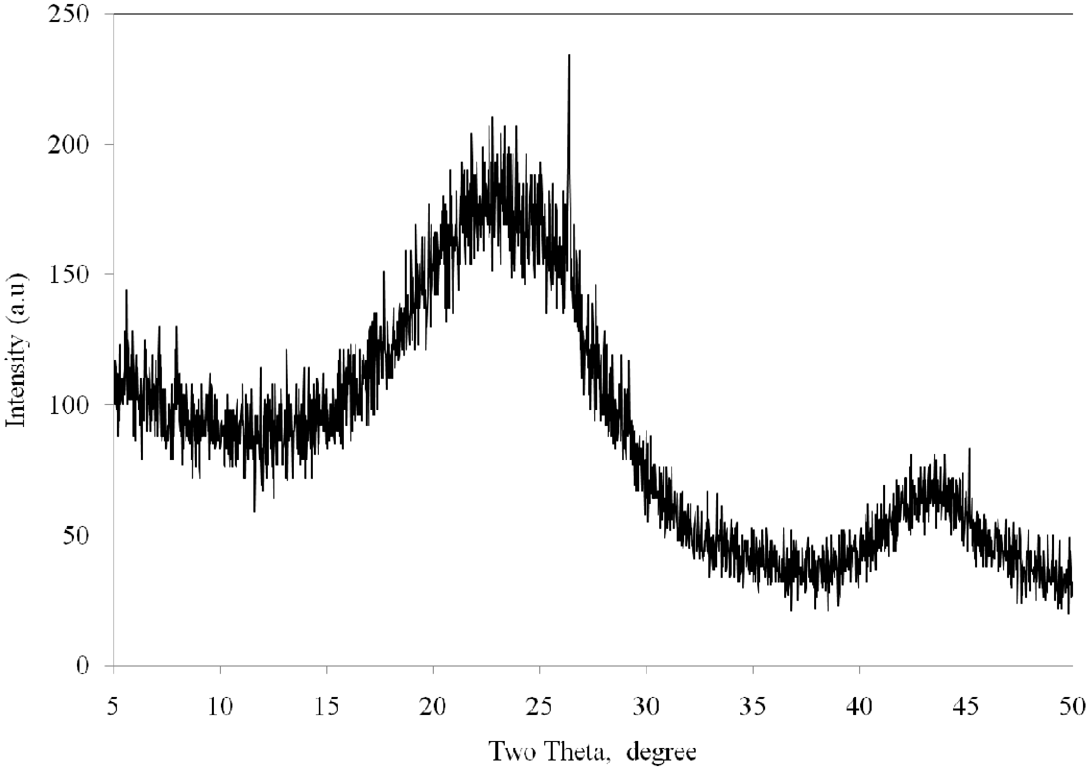

Figure 4.7: Powder XRD pattern of activated carbon (Merck)

4.1.3 Characterization of zeolites

4.1.3.1 characteristics of 4A zeolite:

4.1.3.1.1 SEM Analysis

The SEM image is shown in the following figure. The surface morphology of commercial available zeolite used specifically for this work matches well with the one reported in literatures.

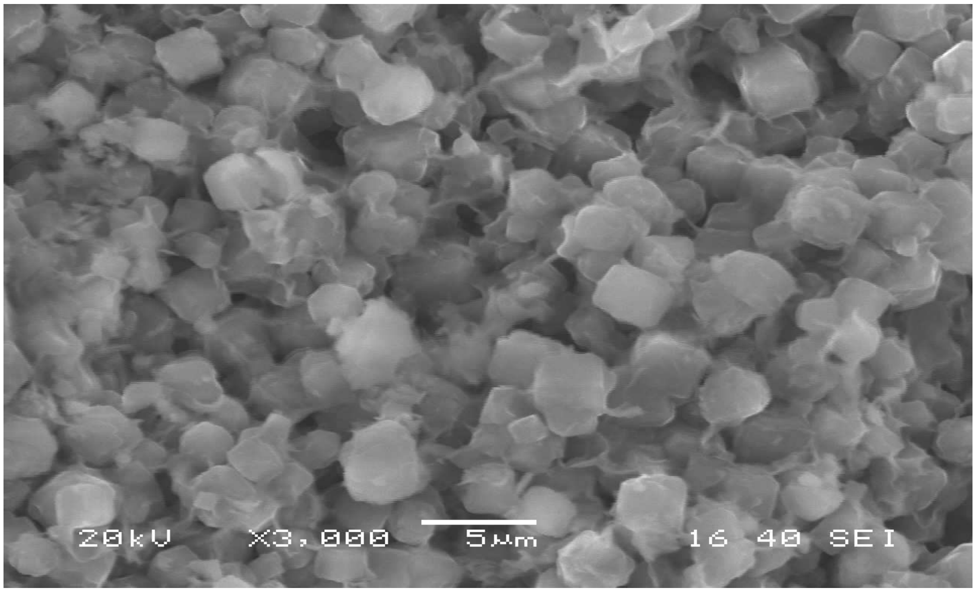

Figure 4.8: SEM Image of Commercial Grade zeolite 4A

4.1.3.1.2 Powder XRD Analysis

Powder X-ray diffraction analysis is shown in figure 4.9. It establishes the crystalline nature of zeolite 4A.

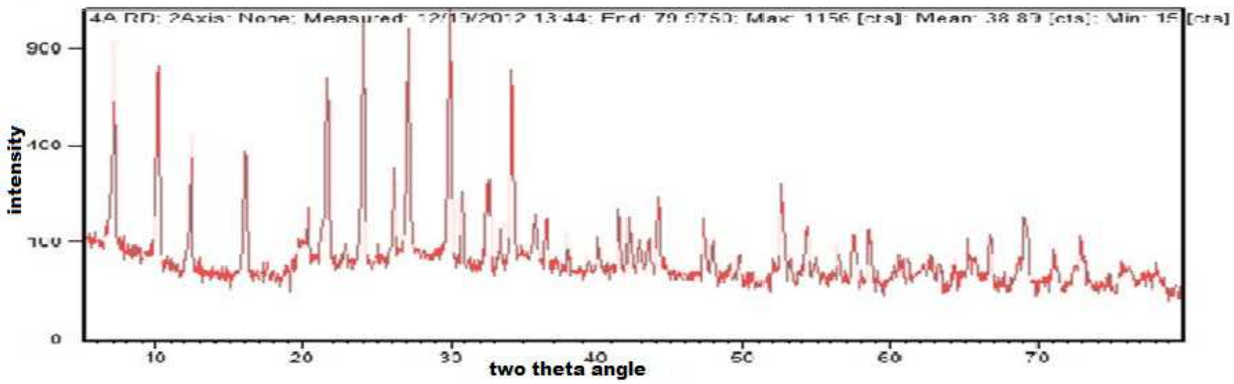

Figure 4.9: Powder XRD pattern of zeolite 4A (Merck)

4.1.3.2 characteristics of 5A zeolite:

4.1.3.2.1 SEM Analysis

The SEM image is shown in the following figure.

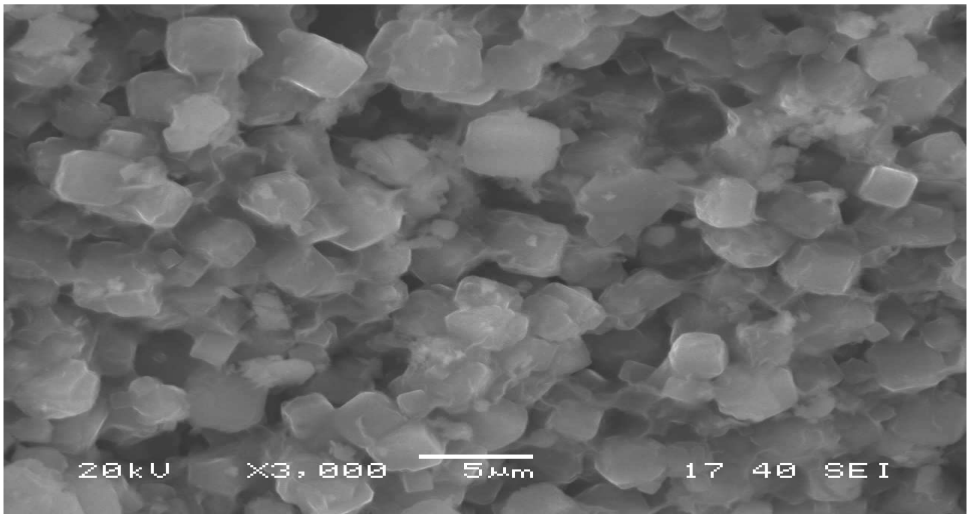

Figure 4.10: SEM Image of Commercial Grade zeolite 5A

4.1.3.2.2 Powder XRD Analysis

Powder X-ray diffraction analysis is shown in figure 4.11. It establishes the crystalline nature of zeolite 5A.

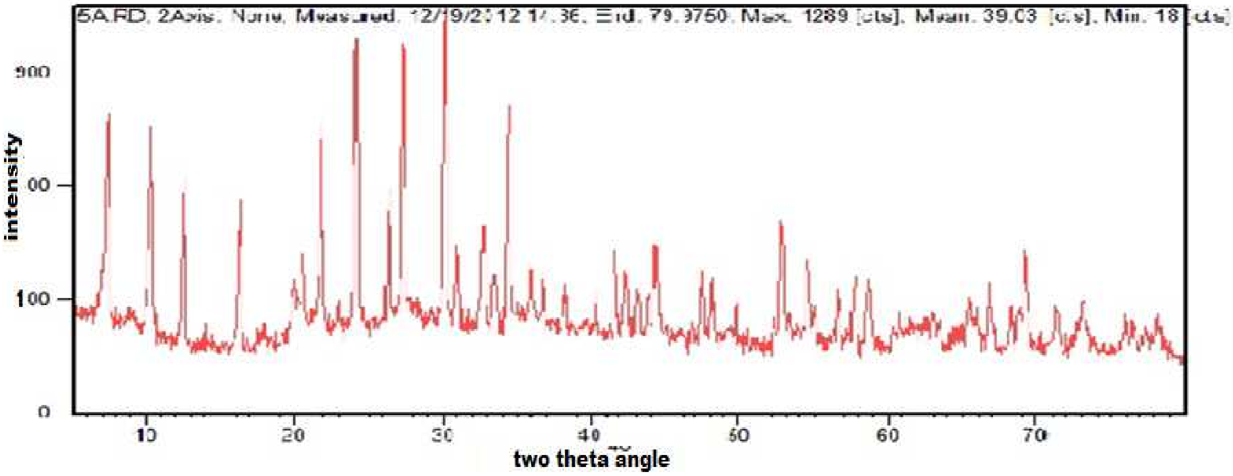

Figure 4.11: Powder XRD pattern of zeolite 5A (Merck)

4.1.3.3 characteristics of 13X zeolite:

4.1.3.3.1 SEM Analysis

The SEM image is shown in the following figure.

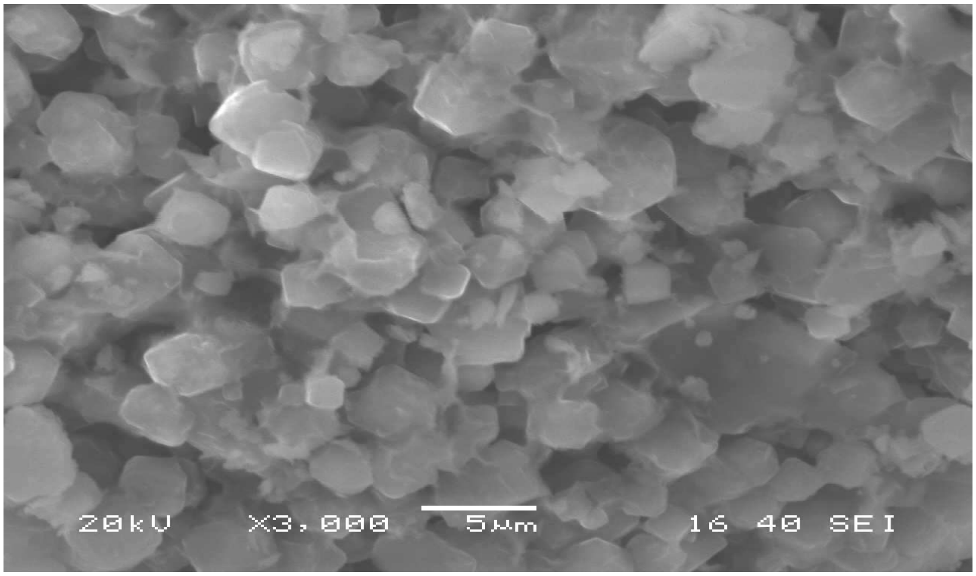

Figure 4.12: SEM Image of Commercial Grade zeolite 13X

4.1.3.3.2 Powder XRD Analysis

Powder X-ray diffraction analysis is shown in figure 4.13. It establishes the crystalline nature of zeolite 13X.

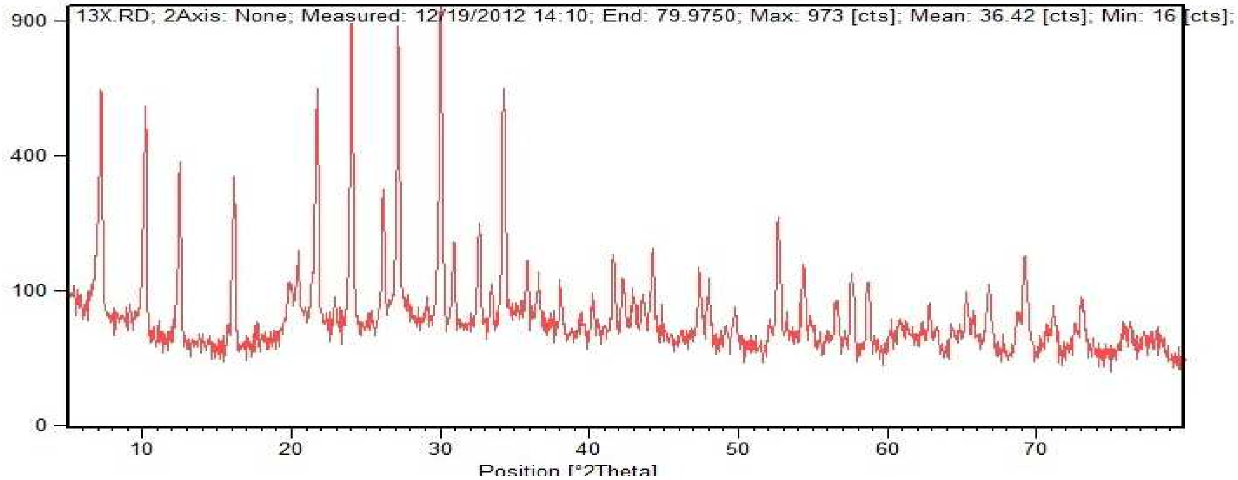

Figure 4.13: Powder XRD pattern of zeolite 13X (Merck)

4.2 DYE REMOVAL STUDY WITH ACTIVATED CARBON

4.2.1 STUDY ON CRYSTAL VIOLET

4.2.1.1 Effect of Contact Time

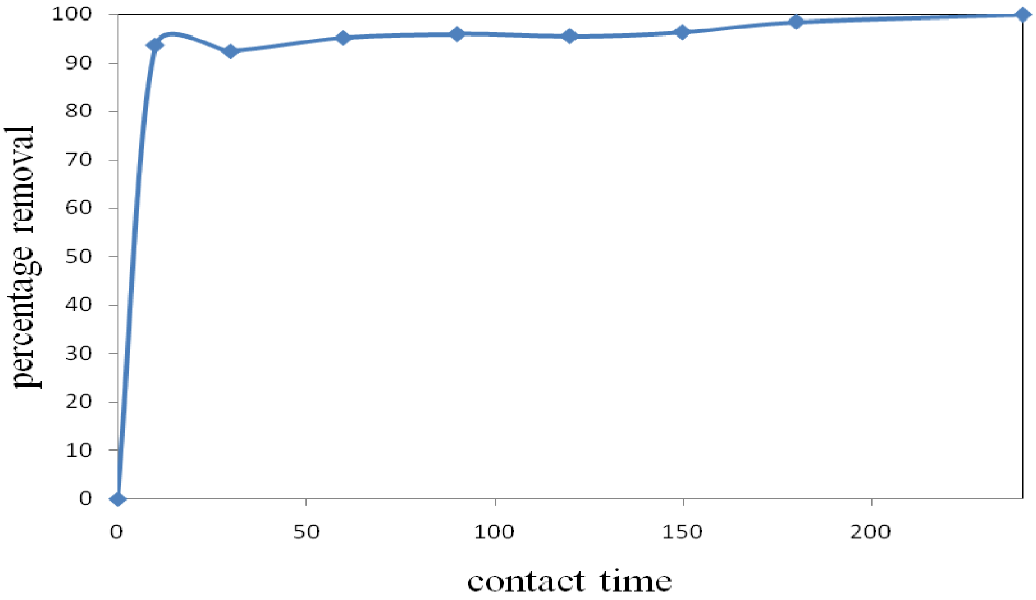

Figure 4.14: Effect of contact time (Crystal Violet on Commercial Activated Carbon)

The values of percentage removal for different time intervals are shown in ***appendix 3***.

As can be seen from the figure above that adsorption increases more rapidly at the initial time period and rate of adsorption decreases as we proceed to the saturation limit. The equilibrium can be assumed to have achieved after 100 minutes as, the final dye concentration does not seem to increase much after this limit. The reason might be the saturation of the active sites which do not allow further adsorption to take place.

4.2.2 STUDY ON COOMASSIE BLUE

4.2.2.1 Effect of Contact Time

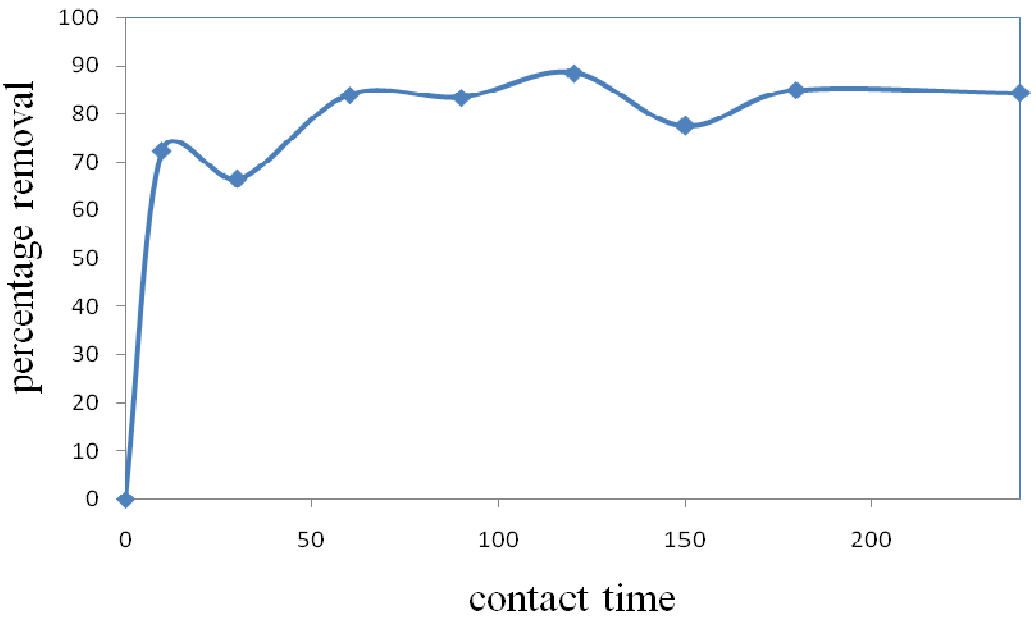

Figure 4.15: Effect of contact time (Coomissie Blue on Commercial Activated Carbon)

The values of percentage removal for different time intervals are given in ***appendix 3***.

From the figure above, it can be estimated that the equilibrium is reached after 70 minutes, as there is not much increase in the percentage removal after this time period.

4.3 DYE REMOVAL STUDY WITH ZEOLITE (4A)

4.3.1 STUDY ON CRYSTAL VIOLET

4.3.1.1 Effect of Contact Time and dosage amount:

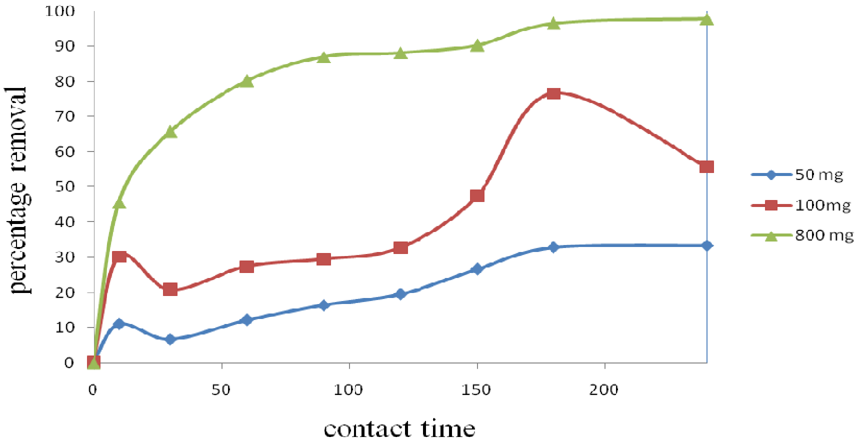

Figure 4.16: Effect of contact time and dosage (Crystal Violet on 4A)

The values of percentage removal for different time intervals are given in ***appendix 4***.

An increase in contact time increases the removal percentage of crystal violet from the liquid solution and the trend is consistent for all concentrations of dosages. The surface area of 4A zeolite is roughly reported to be *ca*. 400-450 m^2/gm, and hence an increase in dosage concentration close to 0.8 g attains close to 98% removal of crystal violet.

4.3.1.1 Effect of temperature :

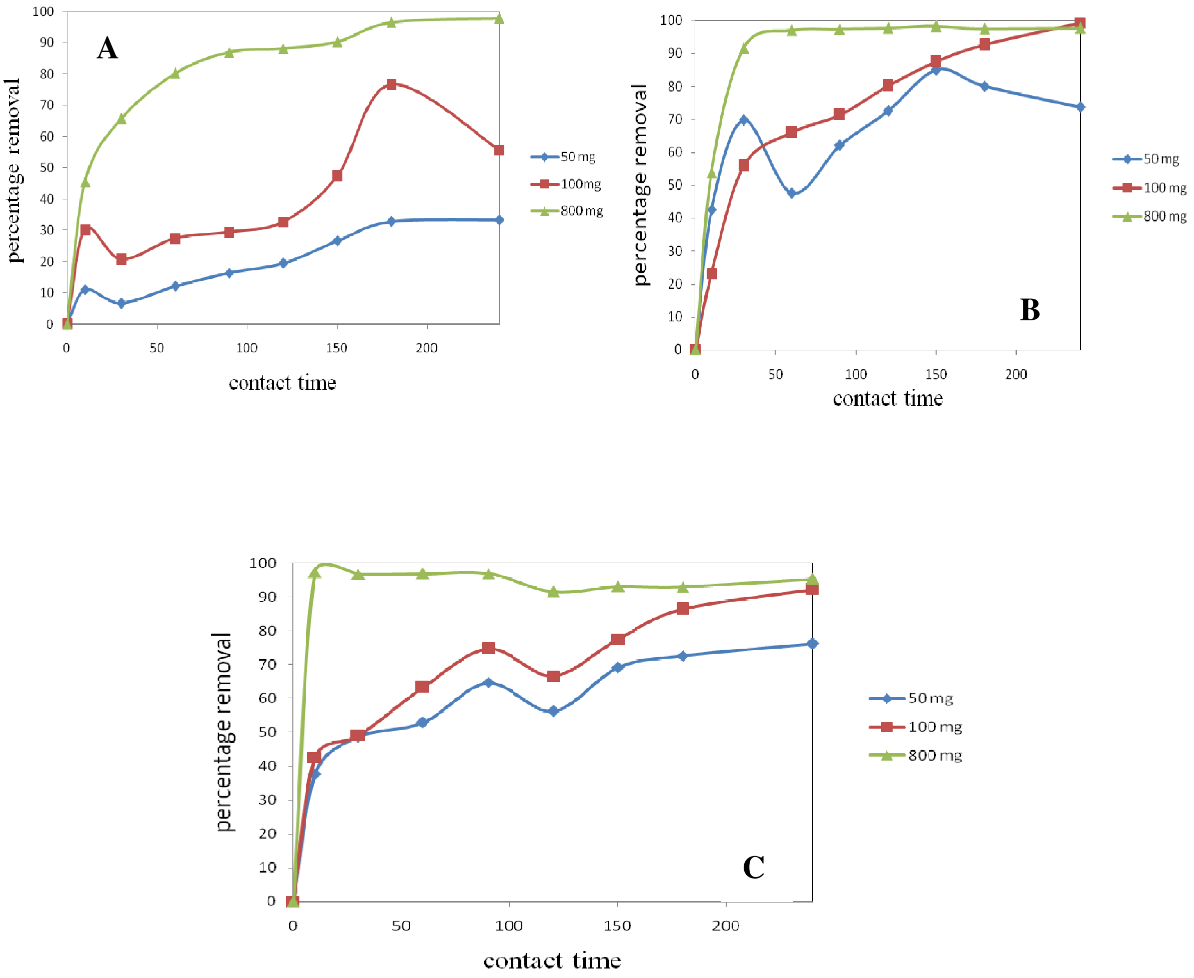

Figure 4.17: Effect of temperature (Crystal Violet on 4A) (**A**) 25 °C (**B**) 45 °C (**C**) 65 °C

With an increase in temperature the dye removal kinetics becomes faster. An increase in temperature probably helps in activating the adsorbent surfaces as well as oxidizes the dyes and facilitates their degradation.

The values of percentage removal for different temperature and time intervals are given in ***appendix 4***.

4.3.2 STUDY ON COOMISSIE BLUE

4.3.2.1 Effect of Contact Time and dosage amount:

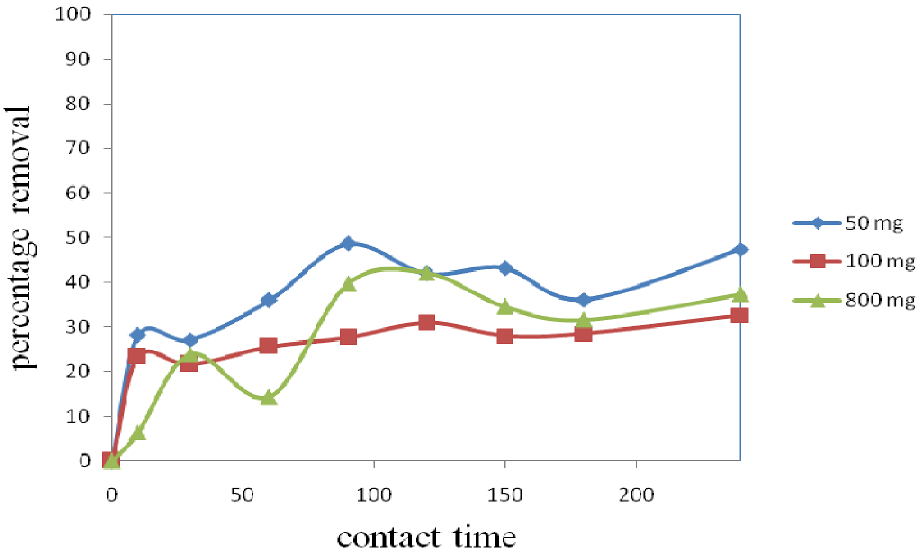

Figure 4.18: Effect of contact time and dosage (Coomassie Blue on 4A)

The values of percentage removal for different time intervals are given in ***appendix 4***.

4A zeolite performs relatively poorly in removing an acidic dye like coomassie brilliant blue in comparison with a basic dye. The inherent chemical composition of 4A zeolite can be attributed towards its lack in performance.

4.4 DYE REMOVAL STUDY WITH ZEOLITE (5A)

4.4.1 STUDY ON CRYSTAL VIOLET

4.4.1.1 Effect of Contact Time and dosage amount:

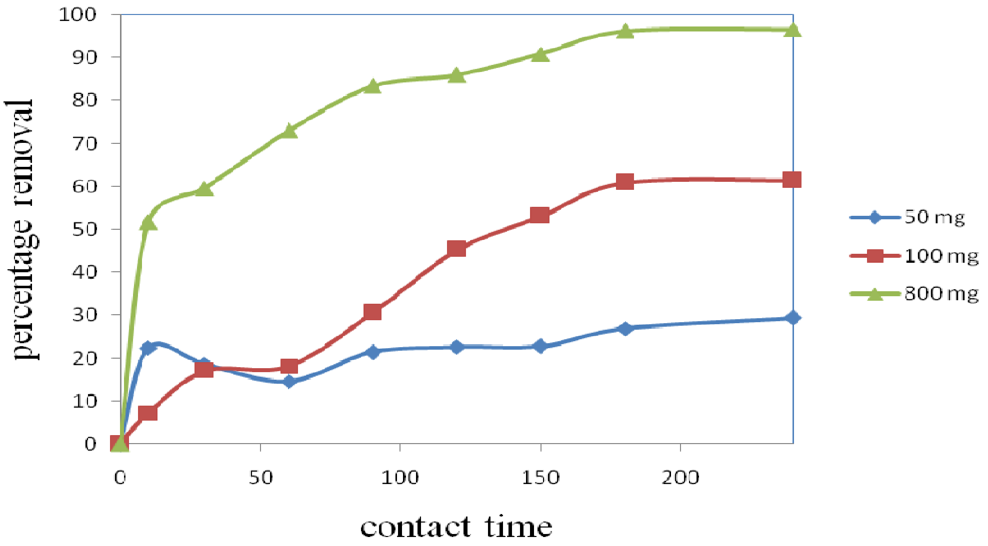

Figure 4.19: Effect of contact time and dosage (Crystal Violet on 5A)

The values of percentage removal for different time intervals are given in ***appendix 5***.

Increase in removal percentage with high concentration of adsorbent may be as a result of an increase in available surface area for the dyes to get adsorbed. The percentage removal trends look very consistent and a dosage close to 0.8 gm almost attains close to 97% removal.

.

4.4.1.2 Effect of temperature :

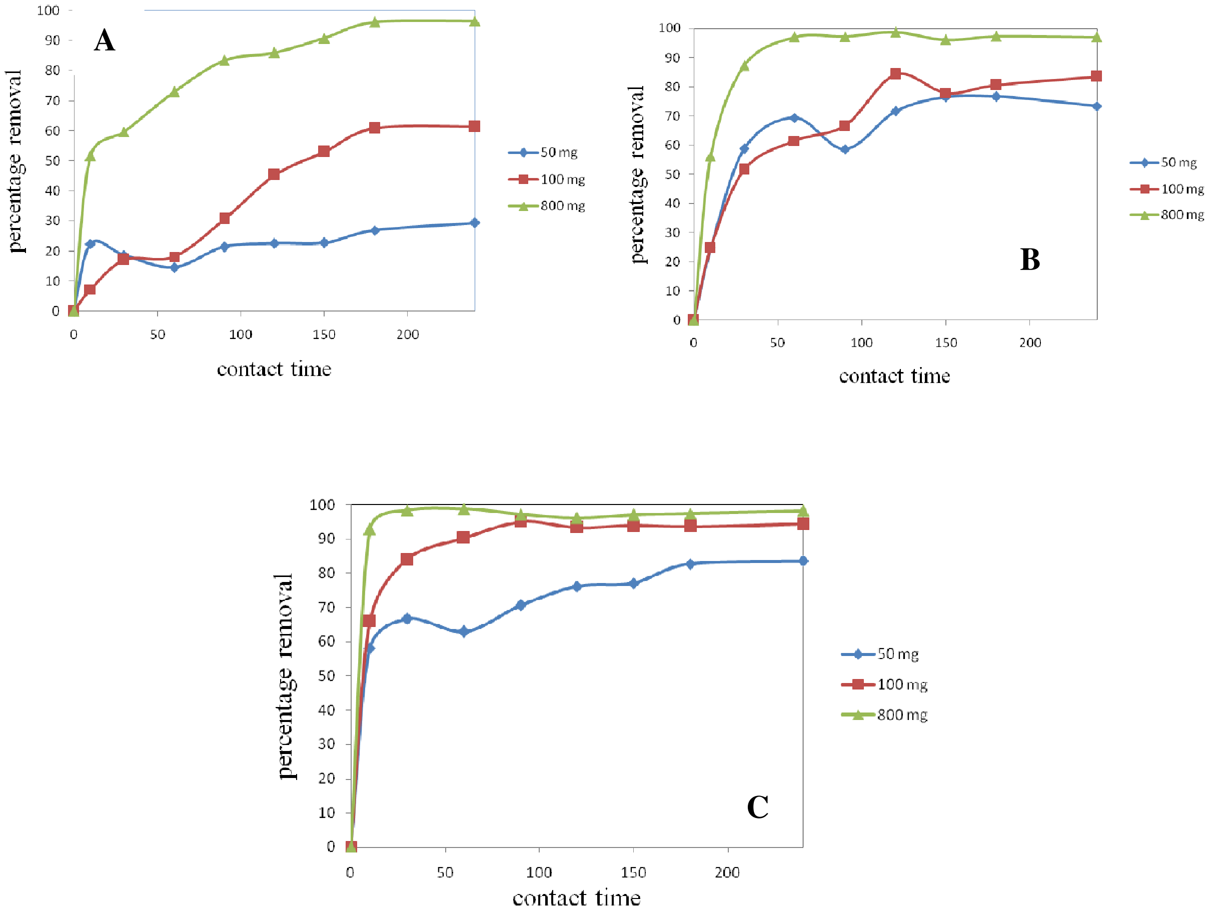

Figure 4.20: Effect of temperature (Crystal Violet on 5A) (**A**) 25 °C (**B**) 45°C (**C**) 65 °C

The values of percentage removal for different temperature and time intervals are given in ***appendix 5***.

With an increase in temperature the dye removal kinetics becomes faster. An increase in temperature probably helps in activating the adsorbent surfaces as well as oxidizes the dyes and facilitates their degradation.

4.4.2 STUDY ON COOMISSIE BLUE

4.4.2.1 Effect of Contact Time and dosage amount:

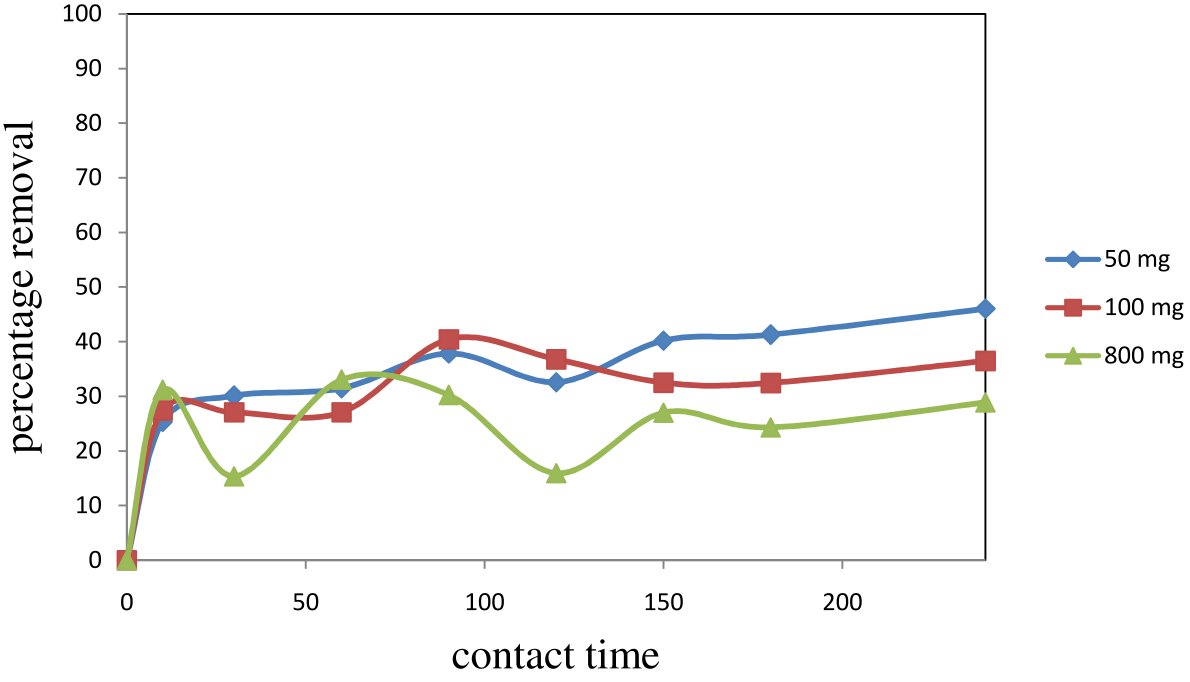

Figure 4.21: Effect of contact time and dosage (Coomassie Blue on 5A)

The values of percentage removal for different time intervals are given in ***appendix 5***.

Like 4A zeolites, the 5A variant too performs relatively poorly in removing an acidic dye like coomassie brilliant blue. The inherent chemical composition of 5A zeolite can be attributed for its lack of performance.

4.5 DYE REMOVAL STUDY WITH ZEOLITE (13X)

4.5.1 STUDY ON CRYSTAL VIOLET

4.5.1.1 Effect of Contact Time and dosage amount:

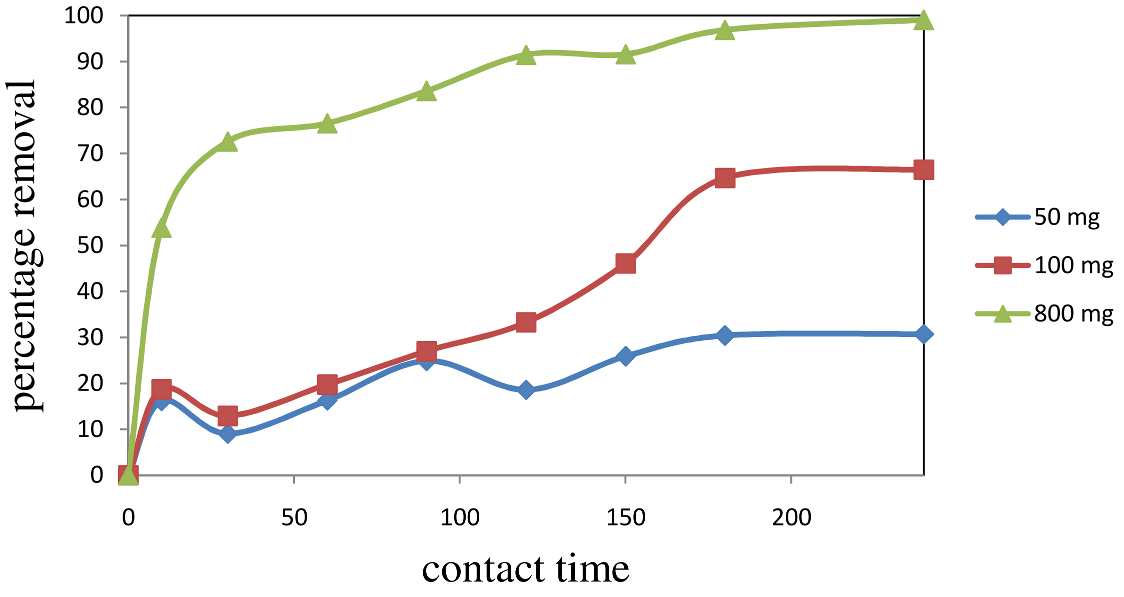

Figure 4.22: Effect of contact time and dosage (Crystal Violet on 13X)

The values of percentage removal for different time intervals are given in ***appendix 6***.

An increase in contact time increases the removal percentage of crystal violet from the liquid solution and the trend is consistent for all concentrations of dosages. The pore/aperture size of 13X zeolite is much bigger than 4A and 5A zeolites. An increase in dosage concentration close to 0.8 g attains close to 98% removal of crystal violet.

4.4.1.2 Effect of temperature:

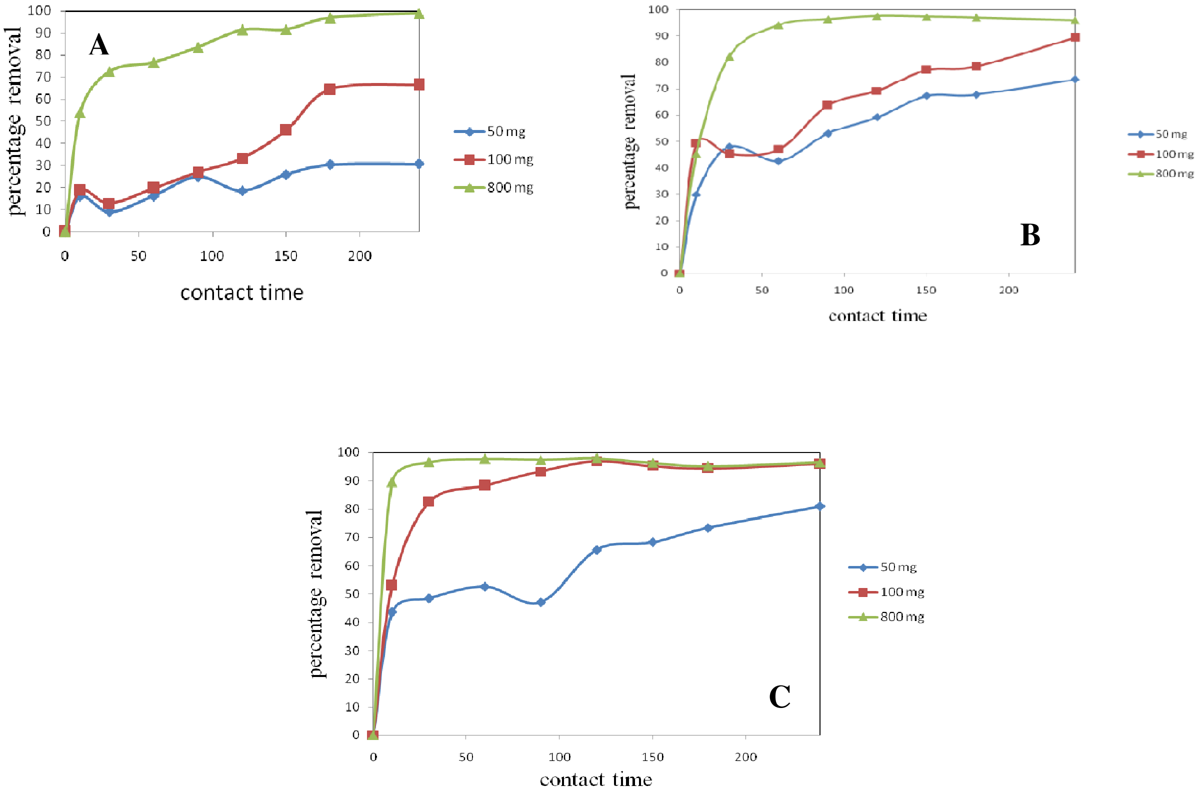

Figure 4.23: Effect of temperature (Crystal Violet on 13X) (**A**) 25 °C (**B**) 45°C (**C**) 65 °C

The values of percentage removal for different temperature and time intervals are given in ***appendix 6***.

With an increase in temperature the dye removal kinetics becomes faster. An increase in temperature probably helps in activating the adsorbent surfaces as well as oxidizes the dyes and facilitates their degradation.

4.5.2 STUDY ON COOMISSIE BLUE

4.5.2.1 Effect of Contact Time and dosage amount:

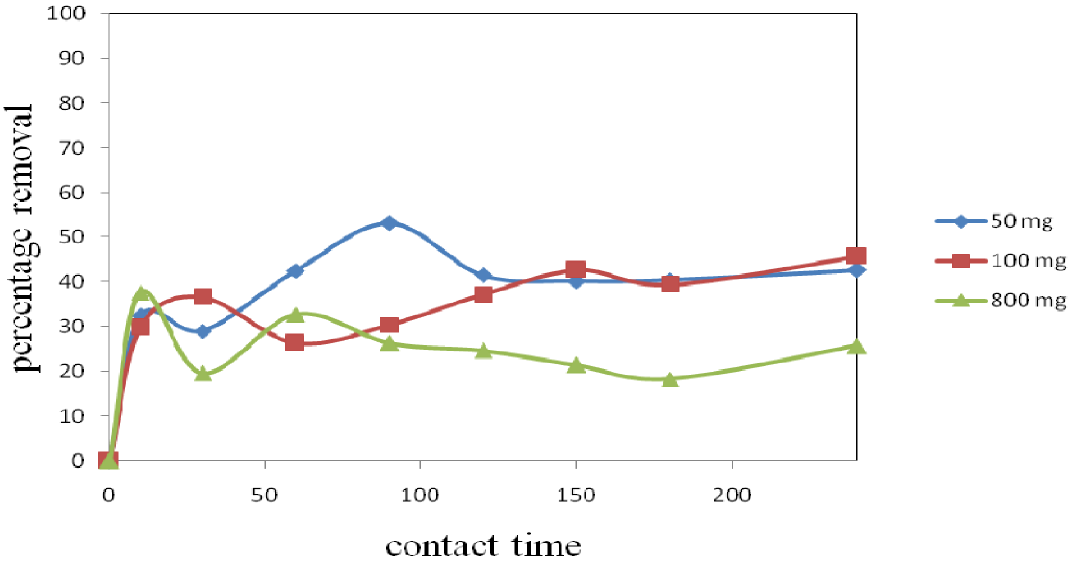

Figure 4.24: Effect of contact time and dosage (Coomassie Blue on 13X)

The values of percentage removal for different time intervals are given in ***appendix 6***.

Like 4A and 5A zeolites, 13X as well performs relatively poorly in removing an acidic dye like coomassie brilliant blue. The inherent chemical composition of 13 X zeolite can be attributed for its lack of performance.

4.6 DYE REMOVAL STUDY WITH MIL-53

4.6.1 STUDY ON CRYSTAL VIOLET:

4.6.1.1 Effect of Contact Time and dosage amount:

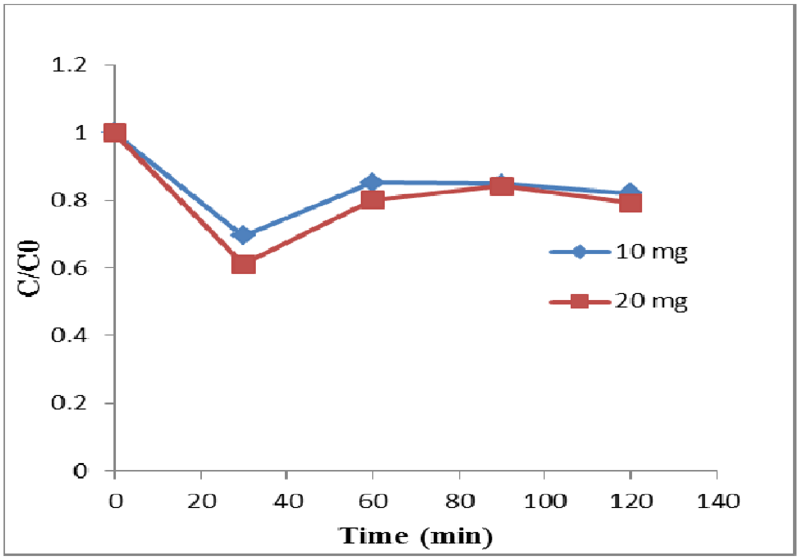

Figure 4.25: Degradation kinetics of Crystal Violet

The values of C/C0 for different time intervals are given in ***appendix*** *7*.

From the above figure, it could be explained that initially the concentration of the dye dropped due to the presence of hydroxyl radicals in system. Further, depletion of free radicals helped in formation of reaction intermediates. After a particular interval of time, degradation proceeded with the change in color of the dye solution from violet to pink and then the intensity of pink faded out to colorless. The active sites of MIL-53 together with its photocatalytic features contributed towards the degradation of the dye.

4.6.1 STUDY ON COOMASSIE BLUE:

4.6.1.1 Effect of Contact Time and dosage amount:

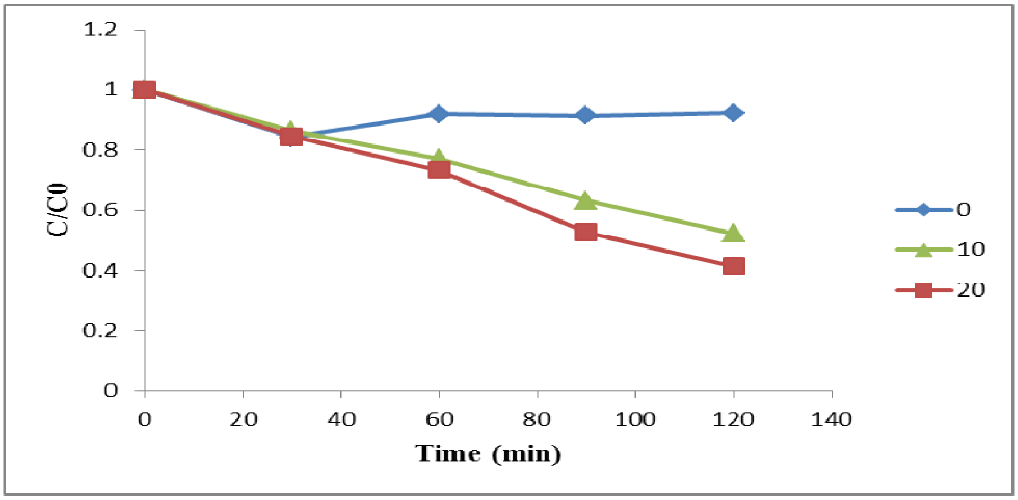

Figure 4.26: Degradation kinetics of Coomassie Blue

The values of C/C0 for different time intervals are given in ***appendix*** *7*.

Just like the above, same justification can be applied for this case as well. From the above figure, it could be explained that initially the concentration of the dye dropped due to the presence of hydroxyl radicals in system. Further, depletion of free radicals helped in formation of reaction intermediates. The active sites of MIL-53 together with its photocatalytic features (owing to low band gap energy) contributed towards the degradation of the dye.

CHAPTER 5

CONCLUSIONS AND FUTURE WORKS

5.1 Conclusions

This thesis work focused on liquid phase adsorptive removal of organic dyes *viz. Crystal violet* and *Coomassie brilliant blue* where they represent the class of a basic and an acid dye respectively. The adsorbents used were: MIL-53 or Fe-BDC (a known Metal Organic Framework), activated carbon and different variants of commercially available zeolites *viz.* 4A, 5A and 13X. MIL-53 was successfully synthesized using the hydrothermal route. The characterization of all the adsorbents were carried out using conventional techniques like scanning electron microscopy (SEM), powder X-ray diffraction analysis (PXRD), thermogravimetric analysis (TGA) and N_2 adsorption analysis (BET). The results with activated carbon showed a high removal percentage (>90%) of both the dyes, irrespective of dosage concentration. The results on the other hand with zeolites were measured to be a function of its concentration. All the zeolite variants performed relatively well in removing the basic dye whereas their poor performance towards acidic dye could be attributed towards their inherent chemical composition. MIL-53 MOF had shown great potential in degrading the organic dyes which can be attributed to its higher percentages of active metal sites and low band gap energy (influencing photocatalysis simultaneously).

5.2 Future Works

The major future endeavors which can be proposed based on this present work are:

(a) Development of a continuous process including dye degradation setup coupled with membrane filtration module to recover the catalysts for reuse.

(b) Experimenting degradation profiles in artificial lights (like Hg vapor lamps) to study the removal efficiencies.

(c) Synthesizing mixed matrix of suitable adsorbents to exploit various alternatives.

REFERENCES

[1] R.M.Christie, Environmental aspects of textile dyeing,Woodhead, Boca Raton, Cambridge, (2007).

[2] V.K.Gupta, Suhas, Application of low-cost adsorbents for dye removal: a review, J. Environmental Management 90 (2009) 2313-2342.

[3] K.Hunger, Industrial dyes: chemistry, properties, applications, Wiley-VCH, Weinheim, Cambridge, (2003).

[4] K.Venkataraman, The chemistry of synthetic dyes, Academic press Inc., New York, (1965).

[5] B.Dash, Competitive adsorption of dyes (congo red, methylene blue, malachite green) on activated carbon, B.Tech thesis, 2010.

[6] G.Crini, Non-conventional low-cost adsorbents for dye removal: a review, Bioresour, Technol.97 (2006) 1061-1085.

[7] A. Mittal, A. Malviya, D. Kaur, J. Mittal, L. Kurup, Studies on the adsorption kinetics and isotherms for the removal and recovery of Methyl Orange from wastewaters using waste materials, J. Hazard, Mater. 148 (2007) 229-240.

[8] S. Chen, J. Zhang, C. Zhang, Q. Yue, Y. Li, C. Li, Equilibrium and kinetics studies of methyl orange and methyl violet adsorption on activated carbon derived from phragmitesaustralis, Desalination 252 (2010) 149-156.

[9] C.I.Pearce, J.R.Lloyd, J.T.Guthrie, The removal of colour from textile wastewater using whole bacteria cells: a review, Dyes pigments 58 (2003) 179-196.

[10] T.Robinson, G.Mcmullan, R.Marchant, P.Nigam, Remedition of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternatives, Bioresour, Technol.77 (2001) 247-255.

[11] Y.Anjanyeulu, N.Sreedhara, D.Chary, Suman Raj Samuel, De-colourization of industrial effluents-available methods and emerging technologies- a review, Rev. Environ. Sci. Biotechnol.4 (2005) 245-273.

[12] H.SinghRai, M.S.Bhattacharyya, J.Singh, T.K.Bansal, P.Vats, U.C.Banerjee, Removal of dyes from the effluent of textile and dyestuff manufacturing industry: a review of emerging techniques with reference to biological treatment, Crit. Rev. Environ. Sci. Technol.35 (2005) 219-235.

[12] G.Crini. P.M.Badot, N.M.Crini, G.Torri, Wastewater treatment processes: a recent review of the available methods, in: Press universitaires de Franche-Comte (PUFC), (2007) 16-62.

[14] F.Gimbert, N.M.Crini, F.Renault, P.M.Badot, G.Crini, Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: error analysis, J. Hazard, Mater,157 (2008) 34-46.

[15] I.A. Aguayo-Villarreal, V. Hernández-Montoy, A. Bonilla-Petriciolet, R. Tovar-Gómez E.M. Ramírez-López M.A. Montes-Morán, Role of acid blue 25 dye as active site for the adsorption of $Cd^{2+}$and Zn^{2+} using activated carbons

[16] Mansoor Anbia, Samira Salehi, Removal of acid dyes from aqueous media by adsorption onto amino-functionalized nanoporous silica SBA-3

[17] F.Derbyshire, M.Jagtoyen, R.Andrews, A.Rao, A.M.Gullon, E.Grulke, Carbon materials in environmental, In: Radovic, L.R. (Ed.), Chemistry and physics of carbon, Vol. 27, Marcel Dekker, New York (2001) 1-66.

[18] G.Ferey, Highly porous solids: past, present future, Chem. Soc. Rev. 37 (2008) 191-214.

[19] S.Kitagawa, R.Kitaura, S.-I.Noro, Functional porous coordination polymers, Amgew. Chem. Int. Ed. 43 (2004) 2334-2375.

[20] O.M.Yaghi, M.O'Keeffe, N.W.Ockwig, H.K.Chae, M.Eddaoudi, J.Kim, Reticular synthesis and the design of new materials, Nature 423 (2003) 705-714.

[21] L.J.Murray, M.Dinca, J.R.Long, Hydrogen storage in metal-organic frameworks, Chem. Soc. Rev. 38 (2009) 1294-1314.

[22] D.Farrusseng, S.Aguado, C.Pinel, Metal-organic frameworks: oppurtunities for catalysis, Angew. Chem. Int. Ed. 48 (2009) 7502-7513.

[23] J.Lee, O.K.Farha, J.Roberts, K.A.Scheidt, S.T.Nguyen, J.T.Hupp, Metal-organic framework materials as catalysts, Chem. Soc. Rev. 38 (2009) 1450-1459.

[24] J.-R.Li, R.J.Kuppler, H.-C.Zhou, Selective dye adsorption and separation in metal-organic frameworks, Chem. Soc. Rev. 38 (2009) 1477-1504.

[25] P.Horcajada, C.Serre, G.Maurin, N.A.Ramsahye, F.Balas, M.Vallet-Regi, M.Sebban, F.Taulelle, G.Ferey, Flexible porous metal-organic frameworks for a controlled drug delivery, J. Am. Chem. Soc. 130 (2008) 6774-6790.

[26] W.L.McCabe, J.C.Smith, P.Harriot, Unit operations of chemical engineering, McGraw-Hill, Singapore (2005).

[27] N.M.Mahmoodi, R.Salehi, M.Arami, H.Bahrami, Dye removal from colored textile wastewater using chitosan in binary systems, Desalination 267 (2011) 64-72.

[28] S.A.Saad, K.Md.Isa, R.Bahari, Chemically modified sugarcane bagasse as a potentially low-cost biosorbent for dye removal, Desalination 264 (2010) 123-128.

[29] Sagnik Chakraborty, Shamik Chowdhury∗, Papita Das Saha, Adsorption of Crystal Violet from aqueous solution onto NaOH-modified rice husk.

.

[30] Alok Mittal a, Jyoti Mittal a, Arti Malviya a, Dipika Kaur a, V.K. Gupta, Adsorption of hazardous dye crystal violet from wastewater by waste materials

[31] D.Sun, X.Zhang, Y.Wu, X.Liu, Adsorption of anionic dyes from aqueous solution on fly ash. J. Hazard. Mater. 181 (2010) 335-342.

[32] Q.Liu, L.Wang, A.Xiao, J.Gao, W.Ding, H.Yu, J.Huo, M.Ericson, Templated preparation of porous magnetic microspheres and their application in removal of cationic dyes from wastewater, J. Hazard. Mater. 181 (2010) 586-593.

[33] H.Parab, M.Sudersanan, N.Shenoy, T.Pathare, B.Vaze, Use of agro-industrial wastes for the removal of basic dyes from aqueous solutions. In proceedings of the 2nd international conference and exhibition on water in the environment, Stellenbosch, South Africa, 37,963-969.

[34] M.A. Rauf *, S.B. Bukallah, F.A. Hamour, A.S. Nasir, Adsorption of dyes from aqueous solutions onto sand and their kinetic behavior

[35] P.Khare, Treatment of phenolic water using adsorption, M.Tech thesis, 2011.

[36] E.Haque, J.E.Lee, I.T.Jang, Y.K.Hwang, J.-S.Chang, J.Jegal, S.H.Jhung, Adsorptive removal of methyl orange from aqueous solution using metal-organic frameworks, porous chromium-benzenedicarboxylates, J. Hazard. Mater. 181(2010) 535-542.

[37] H.M.Freeman, Standard handbook of hazardous waste treatment and disposal, second ed. McGraw-Hill, New York (1989).

[38] C.Tein, Adsorption calculations and modeling, Butterworth-Heinemann, Boston (1994).

[39] M.Smisek, S.Cerny, Active carbon manufacture properties and applications, Elsevier publishing company, Amsterdam (1970)

[40] R.C.Bansal, M.Goyal, Activated carbon adsorption, London, Taylor and Francis group, LLC (2005).

[41] S.Govidasami, B.R.Phani Kumar, C.Balamurli Krishna, R.Mayildurai, Equilibrium and isotherm studies of sludge based activation carbon, Ecol. Environ. Conserv. 15 (2009) 817-824.

[42] N.M.Mahmoodi,R.Salehi, M.Arami, Binary system dye removal from colored textile waste water using activated carbon: kinetic and isotherm studies, Desalination 272 (2011) 187-195.

[43] N.Kannan, M.M.Sunderam, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons-a comparative study, Dyes Pigments 51 (2001) 25-40.

[44] S.Venkata Mohan, P.Sailaja, M.Srimurali, J.Karthikeyan, Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study, J. Hazard. Mater. B 90 (2002) 189-204.

APPENDICES

APPENDIX 1

Preparation of solutions to study the effects of MIL-53

Preparation of 100 ml of stock solution

Type of dye	Amount of dye used (mg)	RO water used (ml)
Crystal Violet	25	100 ml
Coomassie Blue	22	100 ml

Preparation of 50 ml of working solution

Type of dye	Stock solution used (ml)	RO water used (ml)
Crystal Violet	8	42
Coomassie Blue	50	0

APPENDIX 2

Preparation of solutions to study the effects of Activated Carbon and zeolites

Preparation of 100 ml of stock solution (250 mg/l)

Amount of dye used (mg)	**RO water used (ml)**
25	100

Preparation of 50 ml of working solution (40 mg/l)

Amount of stock solution (10^{-4} M) used (ml)	**RO water used (ml)**
8	42

APPENDIX 3

Study of Activated Carbon on Removal of Crystal Violet

Effect of contact time

contact time	% removal (50 mg)	% removal (100 mg)	% removal (500 mg)
0	0.0	0.0	0.0
10	93.6	95.9	94.4
30	92.4	91.2	94.2
60	95.2	95.6	93.4
90	95.9	96.7	97.1
120	95.5	94.0	94.6
150	96.3	98.3	98.1
180	98.5	96.9	99.3
240	99.9	99.5	98.5

Study of Activated Carbon on Removal of Coomassie Blue

Effect of contact time

contact time	% removal (50 mg)	% removal (100 mg)	% removal (100 mg)
0	0.0	0.0	0.0
10	72.3	78.6	89.9
30	66.4	74.9	76.5
60	84.0	67.8	76.9
90	83.5	81.5	76.4
120	88.4	86.3	95.0
150	77.5	78.3	71.9
180	84.9	80.5	86.7
240	84.2	82.6	87.9

APPENDIX 4

Study of zeolite 4A on Removal of Crystal Violet

***Effect of contact time at** 25 ^{0}C*:

contact time	% removal 50 mg	% removal 100 mg	% removal 800 mg
0	0.0	0.0	0.0
10	10.9	30.2	45.5
30	6.7	20.7	65.6
60	12.1	27.4	80.2
90	16.4	29.5	87.0
120	19.5	32.7	88.1
150	26.6	47.3	90.3
180	32.8	76.7	96.5
240	33.4	55.6	97.8

Effect of temperature :

At 45 ^{0}C :

contact time	% removal 50 mg	% removal 100 mg	% removal 800 mg
0	0.0	0.0	0.0
10	42.5	23.1	53.9
30	69.7	55.9	91.6
60	47.5	66.1	97.1
90	62.1	71.4	97.4
120	72.6	80.1	97.7
150	85.1	87.6	98.2
180	80.0	92.7	97.5
240	73.7	99.3	97.7

AT 65 ^{0}C

contact time	% removal 50 mg	% removal 100 mg	% removal 800 mg
0	0.0	0.0	0.0
10	37.6	42.6	97.3
30	48.6	48.9	96.7
60	52.9	63.3	96.8
90	64.6	74.6	96.9
120	56.2	66.6	91.5
150	69.1	77.4	93.0
180	72.6	86.4	93.0
240	76.2	92.2	95.3

Study of zeolite 4A on Removal of Coomassie Blue

Effect of contact time at *25* ^{0}C

contact time	% removal 50 mg	% removal 100 mg	% removal 800 mg
0	0.0	0.0	0.0
10	28.1	23.4	6.3
30	27.1	21.6	23.9
60	36.0	25.6	14.3
90	48.6	27.6	39.7
120	42.0	30.9	42.1
150	43.2	28.0	34.6
180	36.1	28.5	31.5
240	47.4	32.7	37.3

APPENDIX 5

Study of zeolite 5A on Removal of Crystal Violet

***Effect of contact time at** 25* ^{0}C:

contact time	% removal (50 mg)	% removal (100 mg)	% removal (800 mg)
0	0.0	0.0	0.0
10	22.5	7.3	51.8
30	18.6	17.1	59.7
60	14.6	18.2	73.0
90	21.4	30.6	83.5
120	22.6	45.3	86.0
150	22.8	53.1	90.9
180	26.9	60.9	96.2
240	29.4	61.5	96.6

Effect of temperature

At 45 ^{0}C

contact time	% removal (50 mg)	% removal (100 mg)	% removal (800 mg)
0	0.0	0.0	0.0
10	24.7	24.8	56.2
30	58.8	51.6	87.2
60	69.3	61.4	97.0
90	58.6	66.8	97.2
120	71.6	84.2	98.7
150	76.4	77.9	96.1
180	76.6	80.6	97.3
240	73.4	83.5	97.1

At 65 ^{0}C

contact time	% removal (50 mg)	% removal (100 mg)	% removal (800 mg)
0	0.0	0.0	0.0
10	58.1	66.0	93.0
30	66.7	84.2	98.5
60	63.0	90.4	98.9
90	70.6	95.1	97.3
120	76.2	93.4	96.2
150	77.2	94.0	97.2
180	82.7	93.6	97.5
240	83.7	94.5	98.3

Study of zeolite 5A on Removal of Coomassie Blue

Effect of contact time at *25* ^{0}C

contact time	% removal (50 mg)	% removal (100 mg)	% removal (800 mg)
0	0.0	0.0	0.0
10	25.3	27.4	31.2
30	30.1	27.1	15.4
60	31.5	27.1	33.0
90	37.9	40.4	30.2
120	32.6	36.8	16.0
150	40.2	32.5	27.0
180	41.3	32.5	24.3
240	46.1	36.5	28.9

APPENDIX 6

Study of zeolite 13X on Removal of Crystal Violet

***Effect of contact time at** 25* ^{0}C:

contact time	% removal (50 mg)	% removal (100 mg)	% removal (800 mg)
0	0.0	0.0	0.0
10	16.1	18.7	53.9
30	9.0	12.9	72.6
60	16.3	19.7	76.6
90	24.9	27.0	83.6
120	18.6	33.3	91.5
150	25.9	46.1	91.6
180	30.4	64.7	96.9
240	30.7	66.5	99.0

Effect of temperature

At 45 ^{0}C

contact time	% removal (50 mg)	% removal (100 mg)	% removal (800 mg)
0	0.0	0.0	0.0
10	29.9	49.4	45.5
30	48.0	45.1	82.1
60	42.6	46.9	94.1
90	53.0	63.7	96.3
120	59.2	69.2	97.5
150	67.3	77.0	97.3
180	67.7	78.4	97.0
240	73.5	89.4	95.9

At 65 ^{0}C

contact time	% removal (50 mg)	% removal (100 mg)	% removal (800 mg)
0	0.0	0.0	0.0
10	43.5	53.0	89.5
30	48.4	82.5	96.6
60	52.7	88.3	97.7
90	47.1	93.3	97.4
120	65.6	97.0	98.0
150	68.3	95.2	96.5
180	73.4	94.4	95.2
240	80.9	96.0	96.5

Study of zeolite 13X on Removal of Coomassie Blue

Effect of contact time at *25* ^{0}C

contact time	% removal (50 mg)	% removal (100 mg)	% removal (800 mg)
0	0.0	0.0	0.0
10	32.4	29.8	37.6
30	29.1	36.6	19.5
60	42.6	26.3	32.7
90	53.1	30.4	26.3
120	41.4	37.1	24.7
150	40.3	42.6	21.5
180	40.5	39.4	18.3
240	42.7	45.7	25.7

APPENDIX 7

Study of MIL-53 on Removal of Crystal Violet

TIME	C/C0 for 10 mg	C/C0 for 20 mg
0	1	1
30	0.62	0.58
60	0.83	0.77
90	0.81	0.80
120	0.79	0.77

Study of MIL-53 on Removal of Coomassie Blue

TIME	C/C0 for 0 mg	C/C0 for 10 mg	C/C0 for 20 mg
0	1	1	1
30	0.82	0.81	0.80
60	0.91	0.78	0.76
90	0.89	0.61	0.53
120	0.90	0.52	0.42