EQUILIBRIUM AND KINETICS STUDY OF METHYLENE BLUE BY USING LOW COST ADSORBENTS

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ABSTRACT

This work is aimed to study the adsorption capacity of Fuller's Earth (FE), Carbon and Mgo decked Multi Layered Graphene (MDMLG) for Methylene Blue (MB) Dye removal from aqueous solutions. Batch studies were carried out on a laboratory scale by using commercial MB dye as a model pollutant. Methylene Blue is a common basic dye used in every textile industry. The effects of initial dye concentration at different concentrations, contact time, pH and adsorbent dosage on the percentage removal of Methylene Blue dye were investigated. An increase in contact time, adsorbent dose, pH and decrease in initial dye concentration would cause an increase in the removal of Methylene Blue dye.

Keywords: Methylene Blue, Fuller's Earth, Carbon, Mgo Decked Multi Layered Graphene (MDMLG).

I. INTRODUCTION

Dyes are used in large quantities in many industries including paper, textiles, plastics, leather, cosmetics and food industries to color their products. Enormous amounts of different types of dyes and pigments are produced annually. There are more than 100,000 commercially available dyes with over 8 x 10^5 tonnes of dyestuff are produced annually [1]. Many types of dyes are used in textile industries such as direct, reactive, acid and basic dyes. Most of these dyes represent acute problems to the ecological system as they considered toxic and have carcinogenic properties, which make the water inhibitory to aquatic life. Due to their chemical structure, dyes possess a high potential to resist fading on exposure to light and water. The main sources of wastewater generated by the textile industry originate from the washing and bleaching of natural fibers and from the dyeing and finishing steps. Given the great variety of fibers, dyes and process aids, these processes generate wastewater of great chemical complexity and diversity, which are not adequately treated in conventional wastewater treatment plant. In all these processes, dye contamination of water is a huge issue. Decolourisation of dyes in aquatic environment is difficult, as dyes are stable in water and usually resistant to exposure to light and many chemicals. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities.

It was found that colorants may cause problems in water in several ways: (i) dyes can have acute and/or chronic effects on exposed organisms with this depending on the dye concentration and on the exposure time, (ii) dyes are inherently highly visible, minor release of effluent may cause abnormal coloration of surface water which captures the attention of both the public and the authorities, (iii) the ability of dyes to absorb/reflect sunlight entering the water, this has drastic effects on the growth of bacteria and upsets their biological activity, (iv) dyes have many different and complicated molecular structures and therefore, are difficult to treat and interfere with municipal waste treatment operations,(v) dyes in wastewater undergo chemical and biological changes, consume dissolved oxygen from the stream and destroy aquatic life, (vi) dyes have a tendency to sequester metal ions producing micro toxicity to fish and other organisms.

Methods such as chemical coagulation [2], ozonisation [3], membrane filtration [4], electrolysis [5], oxidation [6], and bio-degradation [7] have been widely used for the removal of dyes from water and wastewater. As these established technologies are often unable to adequately reduce contaminants concentration to desired levels [8] a search is on more effective and economic treatment techniques. However, these methods are not widely used due to their high cost and economic disadvantage. In contrast, an adsorption technique is by far the most versatile and widely used. The most common adsorbent materials are: alumina, silica, metal hydroxides and activated carbon. As proved by many researchers, removal of dyes by activated carbon is economically favourable and technically easier. Activated carbon is widely used as an adsorbent due to its high adsorption capacity, high surface area, micro porous structure, and high degree of surface respectively.

Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications. Adsorption has been found to be superior to other techniques 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. The common adsorbent, activated carbon, has good capacity of removal of pollutants. But its main disadvantages are the high price of treatment and difficult regeneration, which increases the cost of wastewater treatment. Thus, there is a demand for other adsorbents, which are of inexpensive material and do not require any expensive additional pre-treatment step. So the adsorption process will become economically viable. A successful adsorption process not only depends on dye adsorption performance of the adsorbents, but also on the constant supply of the materials for the process. So it is preferable to use low cost adsorbents, such as an industrial waste, natural ores, and agricultural by-product. The present work is aimed to study the adsorption capacity of Fuller's Earth (FE), Carbon and MgO decked on multilayered Graphene (MDMLG) for Methylene Blue (MB) dye removal from aqueous solutions. Batch studies were carried out on a laboratory scale by using commercial MB dye as a model pollutant. For the removal of MB, different parameters such as adsorbent dosage, effect of pH, initial dye concentration and contact time were studied.

1.1 Literature Review

Dyes

A dye can generally be described as a coloured substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fibre. Both dyes and pigments appear to be coloured because they absorb some wavelength of light preferentially. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate.

Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminium lake, calcium lake or barium lake pigments.

Classification of dyes

- Natural dyes
- Food dyes
- Synthetic dyes
- Acidic dyes
- Basic dyes
- Direct dyes
- Mordant dyes
- Vat dyes
- Reactive dyes.

1.2 Methylene Blue

Methylene Blue is a contaminant agent and is widely used in colouring, textile industries, and paper as well as in researches related to histology, textile, cytology and bacteriology [9 and 10]. Methylene Blue is used as a counter stain in some staining protocols, colouring all cell nuclei red. This is the classic counter stain in a gram stain. It can also be used for the detection of cartilage, mucins and mast cell granules. Methylene Blue is commonly used for staining Gram negative bacteria red in smears to contrast with the blue Gram positive organisms. For tissue sections it is useful as a red nuclear counter stain, and was popular at one time for staining cartilage met achromatically yellow, against red nuclei on a pink background. Fig.1. displays the chemical structure of the MB.

Usage: Ink Dyestuffs, Paint Dyestuffs, Paper Dyestuffs.

TABLE 1.1

Property	Data
Common name	Methylene Blue, Methylthionate Chloride, Urolene Blue
Suggested name	Swiss blue
C.I name	Basic blue 9, Solvent blue 8
C.I number	52015
Class	Basic
Color	Blue
Empirical formula	$C_{16}H_{18}N_3SCl$
Formula weight	319.9
Dye content	70%

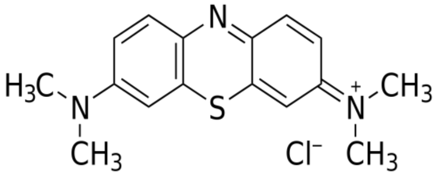

Fig.1.Structure of Methylene Blue

1.3 Chemistry of Fuller's Earth

Fuller's Earth (FE) is a type of sedimentary clay having high magnesium oxide content, used in bleaching and clarifying petroleum and in refining edible oils. Fuller's earth (FE) is used as an adsorbent abundantly available around Mihaliccik region of Turkey. It contains various amounts of dioctahedralsmectities (Ca-montmorillonite), natural zeolites (analcime), and loughlinite, which is a kind of sepiolite [11]. All of these minerals exhibit a strong affinity for hetero aromatic cationic dyes. Smectites are specified as 2:1 layered clays and swell in water. Surface charge of smectites arises from proton adsorption- desorption reactions on surface hydroxyl groups while layer charge results from substitutions in the octahedral alumina layer, which is separated from aqueous solution by a tetrahedral silicate layer. The structure of zeolite channels contains large cages with windows showing different openings. Sepiolite is a fibrous clay mineral with fine channels running parallel to its fibers. It has an open structure exhibiting micro fibrous morphology with a large micro pore volume due to the existence of inter-crystalline cavities. Fuller's Earth is stiff clay with a waxy appearance and it can be blue, grey or yellow in colour. Like most clay, it is mostly made up of silicon and aluminium but it has traces of many other minerals. Its most useful property is that it is an efficient absorber in powder form.

1.4 Instrumental Components

Sources of UV radiation

The power of the radiation source does not change over its wavelength range. The electrical excitation of deuterium at low pressure produces a continuous UV spectrum. The mechanism for this involves formation of an excited molecular species, which breaks up to give two atomic species and an ultraviolet photon.

$$D^2 + \text{Electrical Energy} \rightarrow D^{2*} \rightarrow 2D + h\upsilon$$

II. EXPERIMENTAL METHOD

2.1 Preparation of Dye Solution

A stock solution of 5 x 10^{-3} M was prepared by dissolving the appropriate amount of Methylene Blue dye in 500 ml of distilled water. Methylene Blue absorbs at 663nm. Concentrations ranging from 0.2 x 10^{-5} M to 5.0 x 10^{-5} M were prepared from the stock solution to prepare the standard curve. The study of adsorption was carried out by keeping the dye solution in contact with the adsorbent. The amount of dye adsorbed per gram of the adsorbent (x/m) was calculated. The amount of dye unabsorbed was calculated from the calibration curve of Beer-Lamberts plot for Methylene Blue. All chemicals used throughout the study were analytical-grade reagents. Distilled water was used for preparing all the solutions and reagents and the pH was adjusted with 0.1N HCl or 0.1 N NaOH. All the adsorption experiments were carried out at room temperature.

2.2 Batch Adsorption Studies

2.2.1 Effect of pH

To study the effect of pH on the MB adsorption on FE/Carbon/MDMLG, the experiments were carried out at $4x10^{-4}$M initial dye concentration with 0.1 g/100 ml of FE, 0.07g/100ml of Carbon/MDMLG respectively for 1.30hr equilibrium time. The initial pH values were adjusted to 2, 4, 6, 8, 10 and 12 with 0.1N HCl or 0.1N NaOH. The suspensions were shaken using an orbital shaker.

2.2.2 Effect of adsorbent dose

The effect of sorbent dose on the uptake of Methylene Blue was achieved using FE, Carbon and MDMG doses of 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14 and 0.20g with 4x10-4M.

The experiments were performed by shaking known concentrations of MB with the above different sorbent concentrations to the equilibrium uptake for 1.30hr and the amount of MB adsorbed was determined.

2.2.3 Effect of contact time

To study the effect of contact time on MB adsorption on FE, Carbon and MDMLG, the experiments were carried out from $4x10^{-4}$ M to $6x10^{-4}$ M initial dye concentration with 0.1g/100 ml FE and 0.07g/100 ml Carbon/MDMLG for different intervals from 5 to 60 min. The suspensions were shaken using a mechanical shaker.

2.2.4 Effect of concentration

To study the effect of concentration of MB adsorption on FE, Carbon and MDMLG, the experiments were carried out by varying at $1x10^{-4}$ M to $8x10^{-4}$ M, with 0.1g/100ml FE, 0.07g/100ml Carbon/MDMLG for 1.30hr equilibrium time.

2.3 Batch Equilibrium Adsorption Experiment

Batch adsorption experiments were conducted to study the effects of concentration, adsorbent dose, contact time, and pH for the removal of MB over the surface of FE, Carbon and MDML. Batch experiments were carried out in 250ml conical flasks with 100ml working solution of MB for 90 min (time required for equilibrium to be reached between MB adsorbed and MB in solution) in a mechanical shaker. The pH of dye solution was adjusted by adding few drops of 0.1N HCl or 0.1N NaOH. The solutions were centrifuged at 1000 rpm for 2 min and the absorbance of the supernatant solution was measured to determine the residual concentration at λ_{max} 663 nm by using UV-visible spectrophotometer. Each experimental result was an average of two independent adsorption tests. The amount of dye adsorbed and removal can be determined by using the following relationships.

$$\text{Amount Adsorbed}\,(q_e) = (C_0 - C_e) \times \frac{V}{w} \qquad \text{Percentage removal}\,(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

Where C_0 and C_e (mol/L) are the initial and equilibrium concentrations of the dye solution respectively, V(L) is the volume of dye solution in litres and w (g) is the weight of adsorbent used.

III. RESULTS AND DISCUSSION

3.1 Characterization of Adsorbents

Chemical composition of Fuller's Earth.

Table 3.1.1

Chemical component	Weight percent
SiO_2	71.61
Al_2O_3	12.92
Fe_2O_3	2.87
MgO	2.12
MnO	0.026
CaO	1.38
Na_2O	2.07
K_2O	0.81
TiO_2	1.29
P_2O_5	0.05
Loss on ignition	5.20

3.2 Adsorptive removal of Methylene Blue with Fuller's earth

3.2.1 Calibration curve

Calibration curve is used to estimate equilibrium concentration and constant value. It follows a linear straight line equation. Different concentrations of dye sample solution from stock solution were analysed to draw the calibration curve.

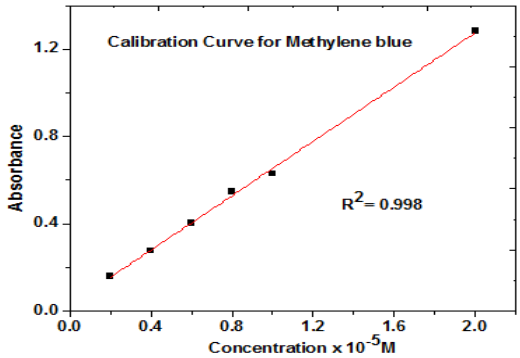

Fig.3.2.1 Calibration curve for Methylene Blue

The above obtained calibration curve shows that the absorbances of the MB dye increases with increase in concentration of MB dye. The maximum wavelength of MB dye is obtained at 663 nm.

3.2.2 Effect of adsorbent dose

The effect of Adsorbent dose is an important parameter to determine the adsorption capacity of adsorbent for a given concentration of MB dye. The absorbance of the unadsorbed MB dye was noted to be decreasing with increase in adsorbent dosage. The effect of adsorbent dosage for the removal of MB dye was carried out in the range of 0.02 to 0.2g and the results are presented in Fig.3. Nearly 25% and 99% adsorption of MB dye was observed with 0.02g and 0.2g of FE dose respectively.

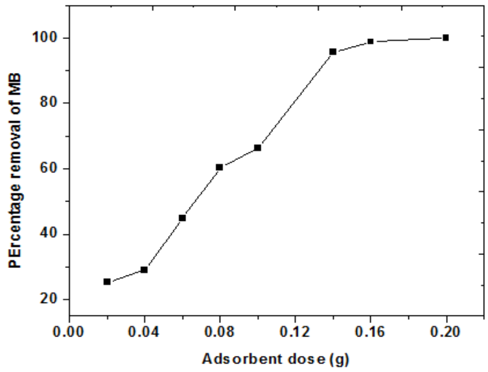

Fig.3.2.2. Effect of adsorbent dose MB dye Concentration 4 x10^{-4}M, Time 1.30hr, dose from 0.02g to 0.2g.

The uptake of MB dye increased with increasing FE dose which might be due to the presence of more surface area and presence of more number of adsorption sites [15]. On the other hand the adsorption capacity of MB dye decreased with increase in adsorbent dose (FE).

3.2.3 Effect of Concentration

Concentrations ranging from 1×10^{-4}M to 8×10^{-4} M of MB were investigated with fixed amount of FE and contact time 90 min**.** The absorbance of left over MB dye was increasing with increase in initial concentration of the dye solution. The effect of initial dye concentration on the adsorption of MB is shown in Fig.3.2.3. It can be inferred that the percentage removal of MB decreased with the increase in initial concentration. The rate of adsorption of MB dye was higher at lower concentrations and lower at higher concentrations. At lower concentrations, few dye molecules are available for the sorption sites, and therefore all the molecules were supposedly Sorbed [16].

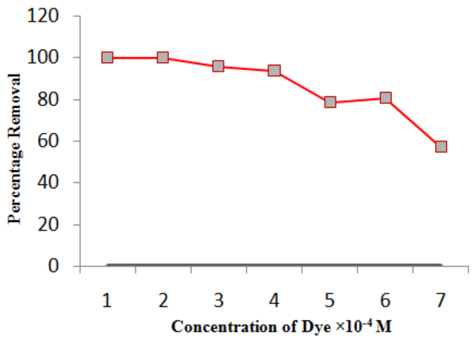

Fig.3.2.3 Effect of MB dye concentration, Time 1.30hr, Dose 0.1g.

3.2.4 Effect of Contact Time

The effects of contact time on the adsorption of MB were studied for different contact times and the results are given in graphical manner. It is clear from Fig 3.2.4 that the contact time needed for MB solutions with the initial concentrations of 4x10^{-4}M, 5x10^{-4}M and 6x10-4M to reach saturation was 90 min. The absorbance of the MB dye was noted to be decreasing with increase in contact time. The contact time is one of the important factors for economical wastewater treatment applications. Short contact time favours the application of the adsorption process [13, 14]. On the other hand the adsorption capacity of MB dye increases with increasing concentration and contact time. Therefore Fuller's earth could be utilized for the removal of MB from aqueous solution.

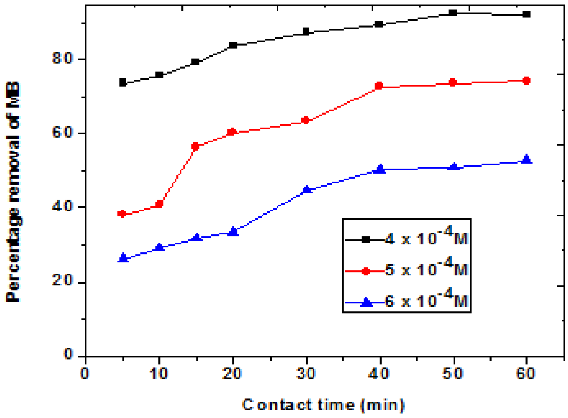

Fig.3.2.4. Effect of contact time: Concentration of MB 4x10-4 M, 5x10-4 M and 6x10-4 M, Time from 5 min to 60min, dose 0.1g

3.2.5 Effect of pH

The pH of a solution plays an important role in the removal of MB dye from aqueous solution on FE. The absorbance of unadsorbed MB dye was decreased with increasing pH from 2 to 12 (Fig.3.2.5). The MB dye removal was investigated over a pH range of 2–12 with an adsorbent dose of 0.1g/L, initial MB concentration $4x10^{-4}$M and contact time 1.30hr as shown in (Fig.3.2.5) and 0.1N NaOH and 0.1 N HCl solutions were employed to adjust the pH of the test solutions. The percentage removal of MB increases slightly as the pH increased from 2 to 12.Metal oxides and non- metal oxides are the main chemical constituents of FE and they form metal-hydroxide complexes in water. At acidic pH, the dissociation of the metal-hydroxide complexes causes the surface to become positively charged. At basic pH, the surface becomes negatively charged [18].

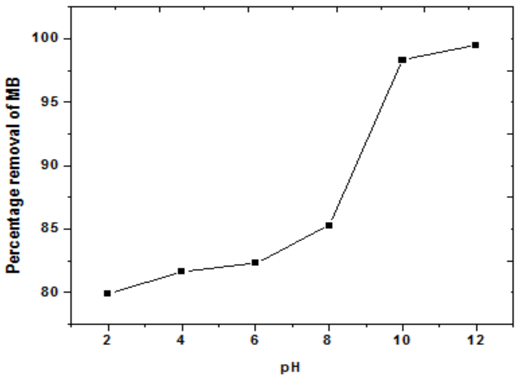

Fig.3.2.5. Effect of pH: Concentration of MB 4 $x10^{-4}$ M, Time 1.30hr and dose 0.1g.

3.3 Adsorptive removal of Methylene Blue with Carbon and MDMLG

3.3.1Effect of adsorbent dose

To determine the effect of adsorbent dose on the percentage removal of Methylene blue dye, the amount of carbon and MDMLG was varied from 0.02 to 0.2g per 100ml of Methylene blue solution keeping the initial dye concentration at 4×10^{-4} M. The percentage removal increased with the adsorbent dosage up to a certain limit and then attained saturation. Dye removal efficiency has increased from 20% to 99% as adsorbent dose increased from 0.02 to 0.2g. The optimum adsorbent dose is 0.07g.

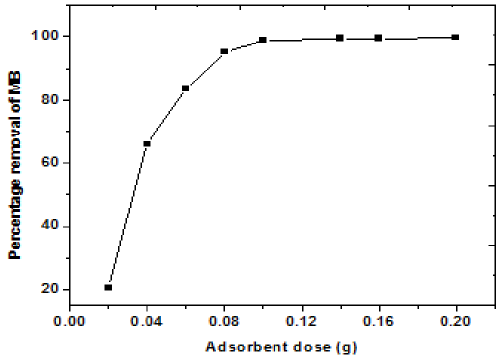

Fig.3.3.1a.Effect of carbon dose: MB dye concentration 4x10-4M, Time 1.30hr

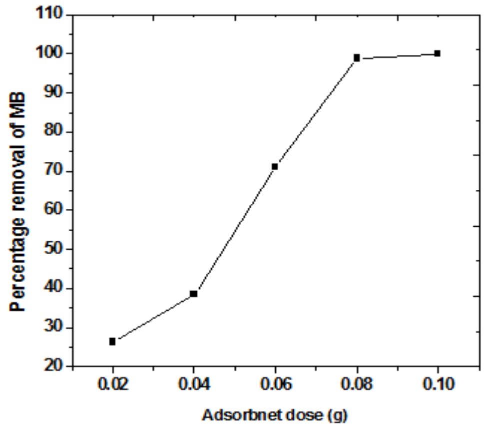

Fig.3.3.1bEffect of MDMLG dose MB dye concentration 4x10-4M, Time 1.30hr

3.3.2. Effect of dye concentration

To determine the effect of initial dye concentration on the adsorption process, the initial concentration of Methylene blue dye was varied from 1×10^{-4} M to 8×10^{-4} M .Adsorbent dose used for this study was the optimum value of 0.07g.The percentage removal of Methylene blue dye decreased as the molar concentration increased(fig.3.3.2). The percentage removal of Methylene blue decreased due to the non-availability of adsorption sites for the increased number of Methylene blue molecules. The inference from this study is that for 0.07g of adsorbent dose and Methylene blue dye's concentration of 4×10^{-4} M will result in more than 80% of Methylene blue dye removal.

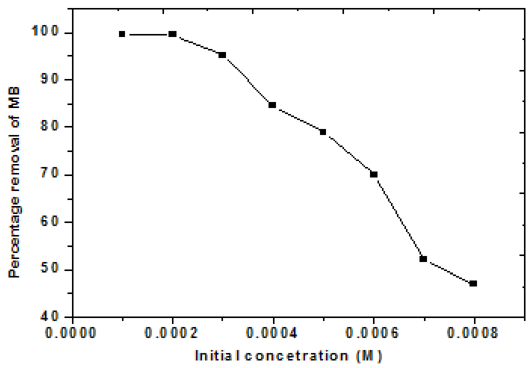

Fig.3.3.2aEffect of MB dye concentration: Time1.30hr, dose 0.07g. MDMLG

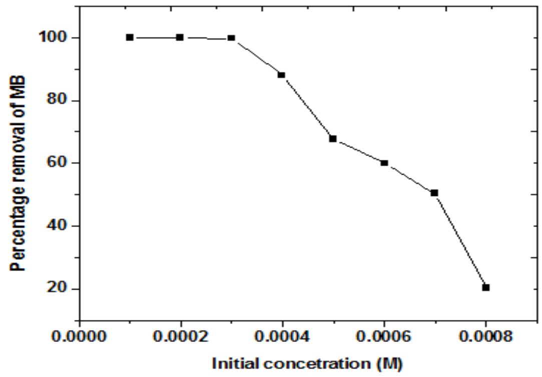

Fig.3.3.2b Effect of MB dye concentration: Time1.30hr, dose 0.07g.

3.3.3Effect of Contact Time

To determine the effect of contact time on the adsorption process adsorption experiments with a fixed adsorbent dose of 0.07 g and methylene blue dye concentration 4.0×10^{-4} is conducted for different contact times.The results are shown in fig3.3.3.It was found that more than 70% removal of methylene blue dye occured in the first 20 min and thereafter the rate of adsorption was found to be slow but effective,that the adsorption of methylene blue dye onto Carbon,MDMLG incresed with increase of contact time.

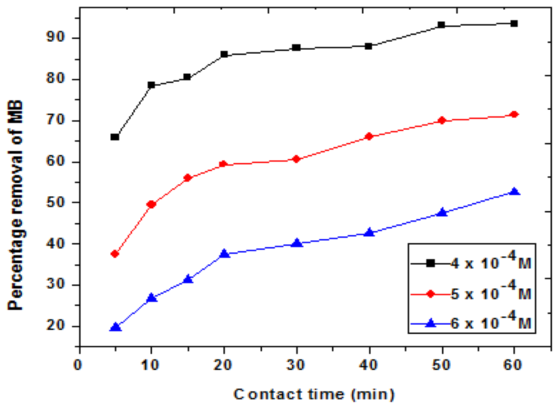

Fig.3.3.3a Effect of contact time: Time from 5 min to 60min, dose 0.07g.

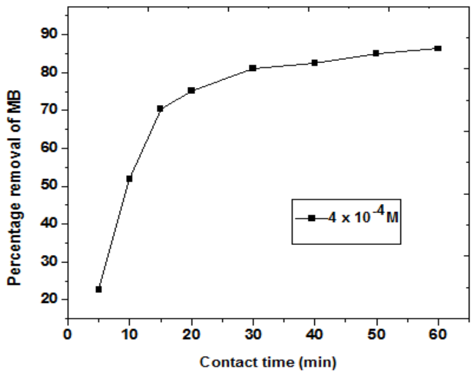

Fig.3.3.3b Effect of contact time: Time from 5 min to 60min, dose 0.07g.

3.3.4 Effect of pH

The effect of pH was studied with MB dye concentration of4.0 _ 10_4 M, adsorbent dose of 0.07 g/100 ml and varying the pH by adding 0.1 N of NaOH or HCl solutions and then shaking the solution until equilibrium was reached. 3.3.4(d) shows that as the pH of the MB dye solution increased from 2 to 12 the percentage adsorption of MB dye onto Carbon and MDMLG increased from 89% to 98%. At low pH, MB dye may be protonated and therefore only partial adsorption occurred. As the pH increased, [H+] plausibly decreased resulting in less protonation of MB onto Carbon and MDMLG.

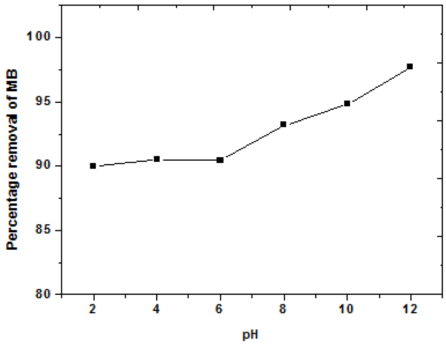

Fig.3.3.4a Effect of pH: Concentration of MB 4 x10-4 M, Time 1.30hr and dose 0.07g.

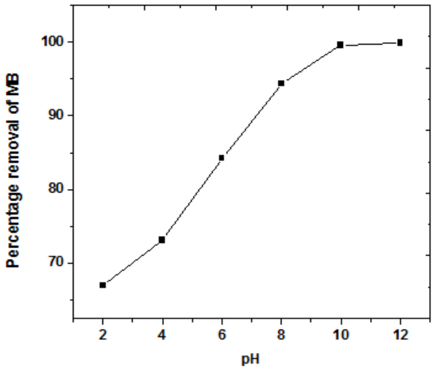

Fig.3.3.4b Effect of pH: Concentration of MB 4 x10-4 M, Time 1.30hr and dose 0.07g.

IV. BACKGROUND WORK

4.1 Adsorption isotherms

The adsorption capacity of any adsorbent and adsorption mechanism can be predicted from equilibrium adsorption isotherms [22]. Langmuir adsorption isotherm assumes that monolayer adsorption occurs at the binding sites of uniform surface [23]. Equation representing Langmuir adsorption is:

$$\frac{C_e}{q_e} = \frac{1}{Q_m\, K_L} + \frac{1}{Q_m} C_e \qquad (3)$$

Where, qe (mol/g) and Ce (M) are the amount of dye adsorbed per unit weight of adsorbent and the concentration of the dye solution at equilibrium, respectively. Qm (mol/g) is the adsorption capacity and K_L (L/mol) is the Langmuir equilibrium constant. The values of Qm and K_L are calculated from the intercept and slope of the linear plot of Ce vs $\frac{C_e}{q_e}$

Freundlich adsorption isotherm is empirical in nature and assumes heterogeneous adsorbent surface (that is adsorption sites at varied energy levels). Equation representing Freundlich adsorption can be expressed as [24]

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e) \qquad (4)$$

Where, qe and Ce are the same as discussed above while KF (mol/g) and n (dimensionless) are constants for a given adsorbate and adsorbent combination at a particular temperature. The values of KF and $\frac{1}{n}$ are obtained from the slope and the intercept of the plot of log (qe) vs. log (Ce).

4.2 Adsorption Kinetics Studies

For adsorption kinetics the adsorbent was mixed with dye solution. The mixture was agitated in a orbital shaker. The samples were withdrawn from the shaker at predetermined time intervals and centrifuged at 1000 rpm for 2min. The final concentrations of samples were determined by using standard calibration curve. The amount of dye adsorbed at time t, was calculated from the following equation.

$$\text{Amount absorbed } (q_t) = (C_0\text{-}C_t) \times \frac{V}{w}$$

Where, C_0 and C_t (mol/L)are the initial and at time t(min) concentrations of the dye solution respectively, V(L) is the volume of dye solution in litres and w(g) is the weight of adsorbent used.

V. SUMMARY AND CONCLUSIONS

1. Fullers Earth, Carbon and MDMLG act as good adsorbents or adsorption of Methylene Blue dye from aqueous solution.
2. The percentage removal of Methylene Blue dye was found to vary with adsorbent dose, initial dye concentration, pH and contact time of the adsorbents.
3. Percentage removal was increasing with increase in adsorbent dose because of increasing surface area and availability of active sites.
4. The percentage removal of Methylene blue decreased due to the non-availability of adsorption sites for the increased number of Methylene blue molecules.
5. The rate of adsorption of Methylene Blue onto Fuller's earth, Carbon and MDMLG was very high in the first few minutes and thereafter the rate of adsorption was found to be slow but effective.

VI. ACKNOWLEDGEMENT

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REFERENCES

[1]. Naresh Kumar Rotte, Subbareddy Yerramala, Jeyaraj Boniface, Vadali V.S.S. Srikanth Equilibrium and kinetics of Safranin O dye adsorption on MgO decked multi-layered graphene ,*Chemical Engineering Journal*, 258 (2014) 412–419.

[2]. D. Asma, S. Kahraman, S. Cing, O. Yesilada, Adsorptive removal of textile dyes from aqueous solutions by dead fungal biomass, *J.Basic Microbial*, 46 (2006) 3-9.

[3]. Choi J H, Shin W S, Lee W S, Joo D J, Lee J D and Choi S J,Studies on the Removal of rhodamine B and Malachite Green from aqueous Solution by Activated carbon,*Environ Technol*.22(2001)1025-1033.

[4]. Wu J and Wang T,Ozonation of aqueous azo dye in a semi-batch reactor,*Water Res*.35(2001)1093-1099.

[5]. C.A. Buckley Membrane technology for the treatment of dye house effluents,Water Sci Technol.22 (*1992*) 265-274.

[6]. S.H. Lin, C.F.Peng,Continuous treatment of textile wastewater by combined coagulation,*Water Res*.30 (1996) 587-592.

[7]. R. Aplin, T. D. Wait. Comparison of three advanced oxidation processes for degradation of textile dyes, *Water Sci Technol*.42 (2000) 345-354.

[8]. A.L. Henderson, T. C. Schmitt, T.M. Heinze, C. E.Cerniglia,Reduction of malachite green to leucomalachite green by intestinal bacteria,*Appl Environ Microbio*.63 (1997) 4099-4101.

[9]. Lambert S D, Evaluation inorganic adsorbent for the removal of problematic textile dye and pesticides, *Water Technol*.36(1997) 173-180.

[10]. Sh. Shariati, M. Faraji, Y. Yamini, A. A. Rajab, Fe_3O_4 magnetic nanoparticles modified with sodium dodecyl sulfate for removal of safranin O dye from aqueous solutions. Desalination 270 (2011) 160–165.

[11]. M. R. Malekbala, S. Hosseini, S. K. Yazdi, S. M. Soltani, M. R. Malekbala, The study of the potential capability of sugar beet pulp on the removal efficiency of two cationic dyes. Chemical engineering Research and design (2011), doi:10.1016/j.cherd.2011.09.010.

[12]. Atun.G, Hisarli.G, Sheldrick.S.W,Muhler.M, Adsorptive removal of methylene blue from colored effluents on fuller’s earth, *J.Colloid Interface Sci*.261 (2003)32-39.

[13]. P. Maity, D. Hansda, U.Bandyopadhyay, D.K.Mishra ,Biological activities of crude extracts and chemical constituents of Bael Aeglemarmelos (L.) Corr. *Indian Journal of Experimental Biology*. 47(2009) 849-861

[14]. Yuru Wang, Wei Chu, Ind. Eng. Chem. Res, Adsorption and Removal of a Xanthene dye from aqueous solution Using Two Solid Wastes as Adsorbents, *Industrial and engineering chemistry research*. 50 (2011) 8734-8741.

[15]. K.Kadirvelu, C.Karthika, N.Vennilamani, S.Pattabhi, Activated carbon from industrial soilidwaste as an adsorbent for the removal of Rhodamine-B from aqueous solution: Kinetic and Equlibrium studies, *Chemospehere*60 (2005) 1009.

[16]. C. Namasivayam, D. Kavitha, Removal of Congo red from water by adsorption onto activated carbon prepared from coir pith, an agriculture solid waste, *Dyes and pigments*. 54 (2002) 47-58

[17]. S.S. Gupta, K.G. Bhattacharyya, Adsorption of Ni(II) on clays, *J. Colloids Interface Sci*. 295 (2006) 21–32.

[18]. S. M. Ahmed. Studies of the dissociation of oxide surfaces at the liquid-solid interface, *Can J Chem*. 44 (1966) 1663-1670.

[19]. Shaobin Wang, Y. Boyjoo, A. Choueib, Z.H. Zhu Removal of dyes from aqueous solution using fly ash and red mud,*Water Research* 39 (2005) 129–138.

[20]. J. Sarma, A. Sarma, K.G. Bhattacharyya, Biosorption of Commercial Dyes on*AzadirachtaindicaLeaf Powder*: A Case Study with a Basic Dye Rhodamine B, *Ind. Eng. Chem. Res*.47 (2008) 5433–5440.

[21]. E. Bulut, M. Ozacar, I.A. Sengil, Equilibrium and kinetic data and process design for adsorption of Congo red onto bentonite, *J. Hazard. Mater*. 154 (2008) 613–622.

[22]. O. Gok, A. Safa Ozcan, A. Ozcan, Adsorption behavior of a textile dye of reactive blue 19 from aqueous solutions onto modified bentonite, Appl. Sur. Sci. 256(2010) 5439–5443.

[23]. E. Bulut, M. Ozacar, I.A. Sengil, Equilibrium and kinetic data and process design for adsorption of Congo red onto bentonite, J. Hazard. Mater. 154 (2008) 613–622.

[24]. Y. Bulut, H. Aydın, A kinetics and thermodynamics study of methylene blue Adsorption on wheat shells, Desalination 194 (2006) 259–267.