

Adsorption of Methylene Blue Dye from Industrial Effluents Using Coal Fly Ash

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Abstract—Industrial Wastewater contains several type of dye, causing serious environmental hazard. The discharge of highly colored effluents into natural water bodies not only is aesthetically displeasing, but also impedes light penetration, thus upsetting biological processes within stream and thus required treatment before discharge into a water body. In the present study, fly ash generated from coal based thermal powers station has been converted into a low-cost adsorbent for the removal of Methylene Blue from effluents of textile industry. Batch studies have been carried out to study the effect of pH, adsorbent doses, adsorbate concentration, temperature and contact time. The results of batch studies reveal that the adsorption of Methylene Blue is strongly pH dependent and maximum Methylene Blue removal is observed at equilibrium pH of 7.0. Optimum adsorbent dose and contact time are found to be 10 g/l and 360 minutes respectively. Kinetic studies have been performed to have an idea of the mechanistic aspects and to obtain the thermodynamic parameters of the process. The results also show that adsorption decreases with increase in temperature thereby showing the process exothermic in nature. Adsorption data have also been correlated with both Langmuir and Freundlich isotherm models.

Keywords—Fly ash, adsorption, Methylene Blue, Langmuir, Freundlich isotherm, adsorbate.

I. INTRODUCTION

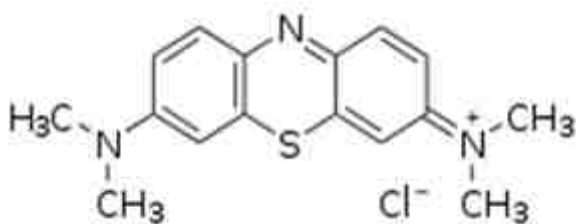
Due to rapid industrialization and urbanization quality of water and air is going to decrease. Dye containing wastewater originates from the textiles, papers, plastics, food and cosmetic industries. Organic dyes are an integral part of many industrial effluents. Most of dyes are toxic, mutagenic and carcinogenic which poses hazard to aquatic life as well as other living organisms [1]. It is estimated that more than 100,000 commercially available dyes with over 7×10^5 tonnes of dye stuff produced annually [2-4]. It is recognized that public perception of water quality is greatly influenced by the colour. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters. Removal of many dyes by conventional waste treatment methods is difficult since these are stable to light and

oxidizing agents and are resistant to aerobic digestion. Possible methods of colour removal from textile effluents include chemical oxidation, froth flotation, adsorption, coagulation etc. Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials [5-7]. Methods of dye wastewater treatment have been reviewed by Pokhrel and Viraraghavan [8], Slokar and Majcen Le Marechal [9], Delee et al. [10], Cooper [11], Crini [12] and Gupta and Suhas [13], Robinson et al. [14] and Banat et al. [15]. Recognizing the high cost of activated carbon, many investigators have studied the feasibility of cheap, commercially available materials as its possible replacements. Such materials range from industrial waste products such as waste tyres, baggasse blast furnace slag, fly ash, zeolites and lignin to agricultural products such as wool, rice husk, coconut husk, saw dust, peat moss etc. [16-24].

Fly ash is a waste substance from thermal power plants, steel mills, etc. and is found in abundance in the world. Since wide scale coal firing for power generation began in the 1920s, many millions of tonnes of ash and related by-products have been created. In India about 160 MT/annum of fly ash is generated from burning of coal in power plants. As a matter of fact, the disposal of fly ash will soon be too costly if not forbidden. Throughout the world, much research is being conducted on the use of such waste materials in order to either avert an increasing toxic threat to the environment or to streamline present waste disposal techniques by making them more affordable. It, therefore, follows logically that an economically viable solution to this problem should include utilization of waste materials in new products for other applications rather than disposal in a landfill. In recent years, utilization of fly ash has gained much attention in public and industry, which will help reduce the environmental burden and enhance economic benefit. Methylene Blue (MB) dye is one of the most commonly used water-soluble cationic dyes in textile, paper, printing and other industries. The structure of Methylene Blue is shown below in scheme 1. It is generally used in dyeing textile specially cotton and silk and in some medical

treatments. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. Though MB is not strongly hazardous, however, on inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, diarrhea, gastritis, mental confusion and methemoglobinemia [25-27].

The major aim of present research includes evaluation of the removal efficiency of Methylene Blue dye from an aqueous phase by coal based fly ash which is easily available, cheap, and economically advantageous and a solid adsorbents. The performance of fly ash as potential adsorbents to remove dye from waste stream has been investigated. The effects of adsorbent dose, pH, temperature, initial dye concentration, and equilibrium time have been studied on the removal efficiency of methylene blue and results are discussed. Various adsorption isotherm models are experimented to interpret the adsorption data. The coefficients and important parameters of these models were determined.



Scheme 1: Methylene Blue

II. MATERIALS AND METHODS

Methylene Blue dye

Methylene Blue is a cationic dye having chemical formula: C₁₆H₁₈N₃SCl; MW: 319.852 g/mol; IUPAC name: 3,7-Bis (dimethylamino) phenothiazin-5-ium chloride was supplied by Merck, India and used as adsorbate. A stock solution 1000ml was prepared by dissolving a weighed amount (1.0g) of Methylene Blue in one liter distilled water. Different concentrations were prepared by diluting the stock solution with suitable volume of distilled water and the natural pH of the stock solution was around 6.7. All the reagents used were of analytical grade.

Fly ash collection and adsorbent development

A representative sample of the fly ash was collected from H.E.G. Thermal Power Station, Mandideep, and Bhopal, India. The fly ash was in the form of small, spherical grayish black particles. The collected sample was sieved to a desired particle size ranges (150 μm). Sample was washed with distilled water five times to remove the adhering organic materials and then dried in an oven at 110°C for 24 h, and finally stored in vacuum desiccators.

Equipments and characterization of fly ash

The pH measurements were made using a pH meter (model CT Cl-46, Toshniwal Instruments, Delhi, India). The chemical constituents of fly ash were analyzed using Bruker S-8 Tiger WDXRF. The surface area was measured with a model QS-7 Quantasorb surface area analyzer. The specific gravity was determined using specific gravity bottles. The Scanning Electron Microscopy (SEM) was carried out using model LEO 438 VP, UK to study micro structure and qualitative characteristics of the ash of the fly ash. The identification of the mineralogical constituents and phase properties of fly ash was examined by Bruker D-8 advance X-ray diffractometer with a Cu-anode. The diffractometer was operated at 40 kV and 40 mA for 1 h over the range of 2θ from 0° to 80°. The infrared spectrum of the adsorbent was recorded in potassium bromide and Nujol mull in the range of 500-4000⁻¹cm using a Perkin Elmer spectrophotometer. All color measurements were made on a Spectronic 20D+ Thermospectronic spectrophotometer in the visible range in absorbance mode. Absorbance values were recorded at the wavelength of maximum absorbance of dye (Methylene Blue) and dye solution was initially calibrated for concentration in terms of absorbance units. The concentration of dye was measured with a 1cm-path-length cell at a wave length (λ_{max}) of 664 nm.

Sorption procedure

Adsorption of Methylene Blue was carried out by batch technique in aqueous suspensions using fly ash as adsorbent and experiments were conducted to observe the effect of various parameters such as pH, temperature, amount of adsorbent, initial adsorbate concentration, and contact time. Adsorption isotherms were recorded at equilibrium conditions for concentration of dyes over the range 5-50mg/l at a fixed pH (9.0) and temperature (303 K). The selected concentration range was ascertained after a good deal of preliminary examination. Adsorption study was made in a mechanically agitated 100 ml Erlenmeyer flask filled with 20 ml of dye solution of desired concentration along with a known amount of adsorbent. On equilibrium, supernatant was carefully filtered through Whatmann filter paper (No. 41) and analyzed spectrophotometrically by measuring the absorbance at λ_{max} of 664 nm. A stock solution (1g/l) of the dye was diluted to the required volume and concentration. The experiments were performed in duplicate and the average results were reported. The amount of dye adsorbed at time t, q_t (mg/g), was obtained by calculating the difference between the initial and the final Methylene Blue concentration as shown in equation 1:

$$q_e = (C_0 - C_e) \times V/W$$

(1)

Where q_e (mg/g) is the amount of dyes adsorbed, and C_0 (mg/l) is the initial dye concentration, while C_e (mg/l) is the concentration of dye in solution at equilibrium, V (L) is the volume, and W (g) is the weight of adsorbent. The percentage removal of the dye was computed using the following equation:

$$\text{Percentage of removal (\%)} = (C_i - C_e) \times 100 / C_i \quad (2)$$

Where C_i and C_e are the initial and equilibrium concentration of dye (mg/l) in solution.

Adsorption isotherms

Adsorption isotherms have been investigated to evaluate the applicability of the adsorption process for the removal of methylene Blue dyes from industrial wastewater. The interactions between the adsorbates and adsorbents have been described by several models for the adsorption isotherms [28]. These adsorption models are used to evaluate the performance of the adsorption process, because they represent the surface properties and affinity of the adsorbent towards adsorbate. The most commonly used equilibrium models are Langmuir and Freundlich isotherms [29].

Langmuir isotherm is based on the assumption that maximum adsorption corresponds a saturated monolayer of solute on homogenous adsorbent surface. Once a dye molecule occupies a site, no further transmigration can take place at the same site. It comprised of a finite number of identical sites with homogeneous adsorption energy. The total monolayer capacity of the adsorbent is equal to Q_0 , a Langmuir constant. The rearranged Langmuir isotherm is represented by following equation:

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \quad (3)$$

where, C_e is the equilibrium concentration of dye (mg/l), q_e is the amount of dye adsorbed at equilibrium (mg/g), Q_0 is the monolayer adsorption capacity (mg/g), and b is the constant related to the free energy of adsorption. Hence, a plot of C_e/q_e versus C_e yields a straight line with Q_0 calculated from the slope and the value of b as its intercept.

Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface or surface supporting sites of varied affinities it. Due to variation of interactions between the adsorbed molecules sites with of stronger affinity are occupied first, and in this way multilayer setting of adsorbate molecules takes place. The validity of the Freundlich isotherm model was proved by using following relation and can be written as:

$$q_e = K_F C_e^{1/n} \quad (4)$$

$$\log q_e = \log K_F + 1/n \log (C_e) \quad (5)$$

where, K_F is the constant indicative of the relative adsorption capacity of the adsorbent (m/g), and $1/n$ is the constant indicative of the intensity of the adsorption. The Freundlich equation possesses two constant, K_F and $1/n$. High and low values of K_F and $1/n$ indicate high adsorption throughout the concentration range studied

whereas high values of $1/n$ and low values of K_F show low adsorption. When $1/n = 1$, the adsorption is favorable.

Kinetic studies

Intraparticle diffusion is the most common technique used for identifying the mechanism involved in adsorption process. In order to investigate the mechanism of the Methylene Blue adsorption onto fly ash adsorbent, intraparticle diffusion based mechanism was studied. Kinetic studies were carried out in batch at 10 mg/l of initial dye concentration with a fixed dose of adsorbent dose of 20 g/l at 303 K and pH 9.0. After a fixed time interval the adsorbent was separated by filtration and the filtrate thus obtained was analyzed spectrophotometrically to determine the equilibrium concentration of the dye. The study of kinetics of adsorption describes the solute uptake rate at the solid-solution interface. The rate constant of adsorption of dyes on to fly ash, K_{ad} has been studied using the Lagergren first order rate equation:

$$\log (q_e - q_t) = \log q_e - K_{ad}t / 2.303 \quad (6)$$

where, q_e is the amount of dye adsorbed at equilibrium, and q_t is the amount of dye adsorbed at time t (both in mg/g).

III. RESULTS AND DISCUSSION

Characterization of fly ash

The chemical composition of fly ash determined by WDXRF has been shown in Table 1 which shows that the major constituent of the fly ash is SiO_2 , (55.26 %) followed by Al_2O_3 (22.75 %), Fe_2O_3 (7.12 %), CaO (4.10 %) and MgO (0.63 %). The fly ash predominantly consists of trace metals with the chief constituents being oxides, silicates and aluminosilicates of calcium, iron and other bases. These oxides have a tendency to form metal hydroxide complexes in the solution and the subsequent acidic or basic dissociation of these complexes at the solid-solution interface leads to the development of a positive or negative charge on the surface. The surface area of fly ash is 2.89 m^2/g and specific gravity is 2.2 g/cm^3 .

Table 1: Chemical constituents of the fly ash

Constituents	Weight %
SiO_2	55.26
Al_2O_3	22.75
Fe_2O_3	7.12
CaO	4.10
TiO_2	2.95
K_2O	2.14
P_2O_5	1.65
SO_3	1.58
Na_2O	1.23
MgO	0.63
LOI	4.10

The results of SEM investigation are shown in Fig. 1 which reveals typical fly ash morphology and surface texture. Most of the particles present in the fly ash are sub-angular and spherical in shape. The image also reveals that the particles present in the fly ash are covered with relatively smooth grains of quartz, clusters of iron (Fe-oxide). Irregular surface of glass matrix is observed which may be responsible for an increase in adsorbent pore volume.

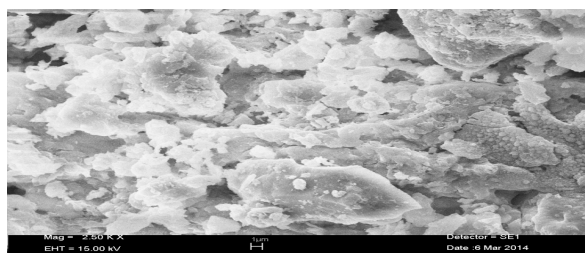


Fig.1: Scanning electron micrograph (SEM) of fly ash

The diffractogram (Figure 2) shows the X-ray diffraction pattern of fly ash for particle size $\leq 45 \mu\text{m}$. It is observed that the fly ash consists mostly of mullite, quartz, hematite and a small amount of hematite and calcium oxide with large characteristic peaks of quartz (SiO_2). This result is similar to that reported for a fly ash investigated by Sarkar et al. [30]. The intensity of quartz is very strong with mullite forming a chemically stable and dense glassy surface layer. The low calcium oxide intensity is characteristic of low-Ca Class-F fly ash.

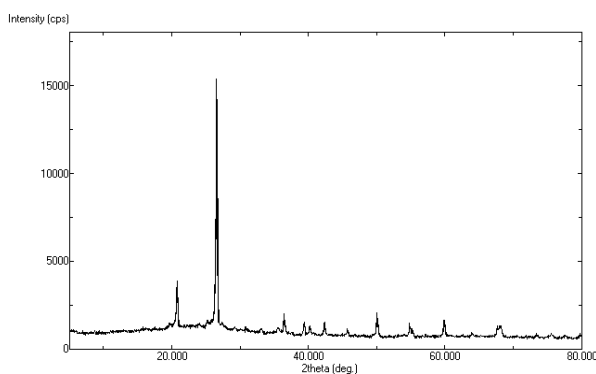


Fig. 2: X-ray diffraction pattern of fly ash

The infrared spectrum of fly ash (Fig. 3) shows broad and weak peaks in the region of $4000\text{-}500 \text{ cm}^{-1}$ associated with the functional groups that are on the surface of coal fly ash. The band appearing at 560 cm^{-1} is associated with octahedral aluminium present in mullite. In addition, bands appearing between $800\text{-}600 \text{ cm}^{-1}$ are associated with tetrahedral vibrations formed which are known as secondary building units and fragments of aluminosilicate system. Band appearing at 2360 cm^{-1} could be attributed due to alkyl groups that are present in clay material of coal fly ash. Bands appearing at $800\text{-}1200 \text{ cm}^{-1}$

and $450\text{-}550 \text{ cm}^{-1}$ assign to asymmetric stretching mode and bending mode of T-O bond respectively. These bands are more or less dependent on the crystal structure. The mid infrared region of the spectrum contains the fundamental framework vibrations of $\text{Si}(\text{Al})\text{O}_4$ groupings. Although some interference can be made about surface functional groups from IR spectra, the weak and broad bands do not provide any definitive information about the nature of the surface oxides. The data, however, indicate the presence of some surface groups on the adsorbent material.

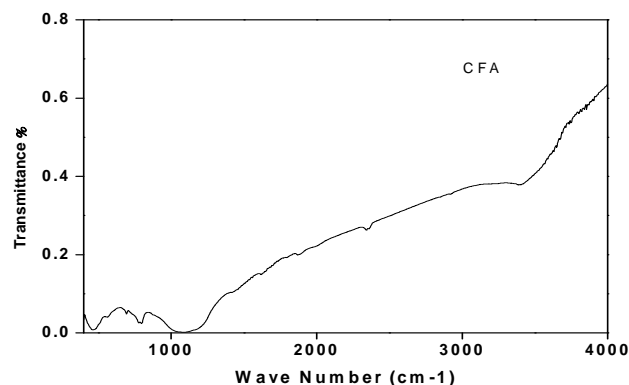


Fig.3: FTIR of coal fly ash

Sorption studies

Effect of contact time

The effect of contact time on Methylene Blue dye adsorption behavior was studied on two concentrations (2 and 4 mg/l) with a fixed adsorbent dose of 5 g/l at 303 K and at a natural pH of 6.7. The contact time was varied from 30 min to 420 min for both the concentrations studied. The percentage efficiency of dye adsorption was calculated and adsorption data for the removal of MB versus contact time at different concentrations are presented in Figure 4. The dye removal percentage increases with the increase in contact time and remains constant after reaching to equilibrium. A perusal of Fig. 4 also indicates that the efficiency of dye absorbed is rapid in initial stage up to 360 min and after that decreases due to saturation of the active site which do not allow further adsorption to take place. It is also observed that at higher concentration of Methylene Blue (4 mg/l), the absorption efficiency is high (78.5 %) as compare to the maximum efficiency of 72.2% for 2 mg/l after 360 min of contact time. The change in the rate of adsorption might be due to fact that initially all the adsorbent sites are vacant and solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in number of vacant sites of adsorbent and dye concentrations. The observed increase in the adsorption of dyestuffs with increasing concentration may be due to availability sufficient adsorption sites at adsorbent [31]. The decreased adsorption rate, particularly, toward the end of

experiments, indicates the possible monolayer formation of MB on the adsorbent surface. This may be attributed to the lack of available active sites required for further uptake after attaining the equilibrium [32]. The optimal contact time to attain equilibrium was experimentally found to be about 360 min.

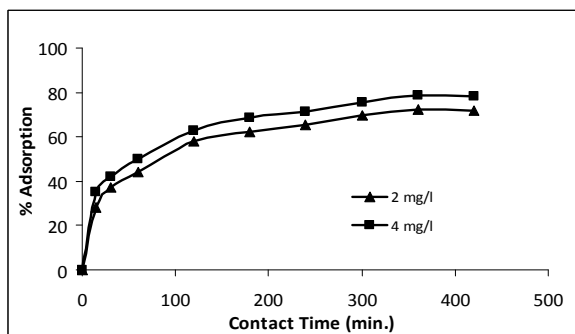


Fig. 4: Effect of contact time on Methylene Blue dye adsorption

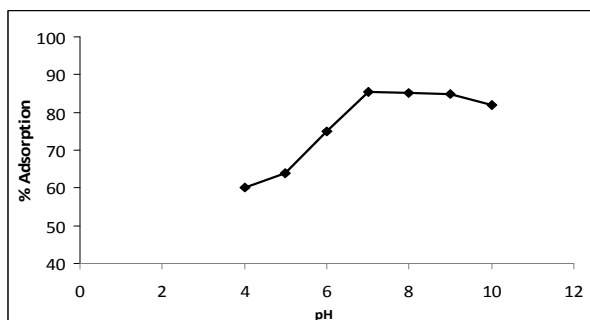


Fig.5: Effect of pH on Methylene Blue dye adsorption

Effect of pH

To determine the optimum pH conditions for the adsorption of Methylene Blue on fly ash, the effect of pH was observed over the pH range (4.0–10.0). The studies were conducted at a fixed concentration of adsorbate (4 mg/l), contact time (360 min) and adsorbent dose 5 g/l at 303 K and pH was adjusted by adding either 0.1M HCl or 0.1M NaOH. The results obtained are presented in Fig. 5, which show that adsorption of Methylene Blue increases with increase in pH from 4.0 to 7.0 and after that a decrease in absorption capacity has been observed on further increase in pH to 10.0. Maximum adsorption of Methylene Blue is 85.5 % at an optimum pH of 7.0. The variation of adsorption with pH can be explained by considering the difference in the structure of the dyes, as well as the point of zero charge of the fly ash (which is 5.8). The main constituents of fly ash are silica and alumina. The ZPC (a concept; related to the adsorption process; describes the condition when the electrical charge density on a surface is zero) of silica is 2.3, while that of alumina is 8.2, and as such the surface of fly ash would have high positive charge density below pH value of 5.8, i.e. ZPC of the fly ash. Under these conditions the

uptake of positively charged dyes would be low; with increasing pH, the negative-charge density on the surface increases resulting in enhanced removal.

Influence of adsorbent dosage

The adsorption behaviour of methylene blue was investigated by varying mass of adsorbent from 5 to 25 g/l at an initial dye concentration of 2 and 4mg/l. pH of solution was adjusted to 7.0, temperature 303 K and the contact time was kept 360 min. The results plotted in Fig. 6 show that the percentage removal efficiency of Methylene Blue increases initially with increase in adsorbent dose from 5 to 10 g/l and after that a decrease has been observed. The maximum efficiency at a dose of 10 g/l is 86.25 and 89.85% for 2 and 4 mg/l of dye concentration respectively. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase in adsorbent dosage. However, no significant changes in removal efficiency were observed beyond 10g/l of adsorbent dose. Due to conglomeration of adsorbent particles, there is no increase in effective surface area of fly ash [33].

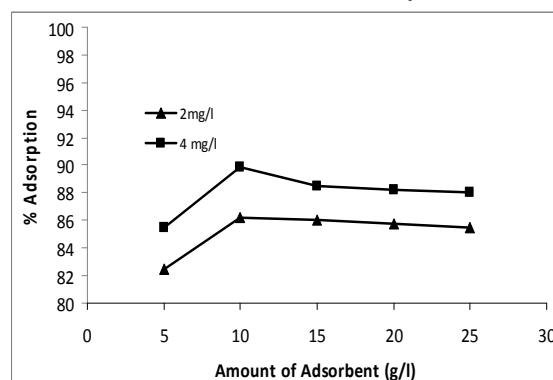


Fig. 6: Effect of adsorbent dose on MB dye adsorption

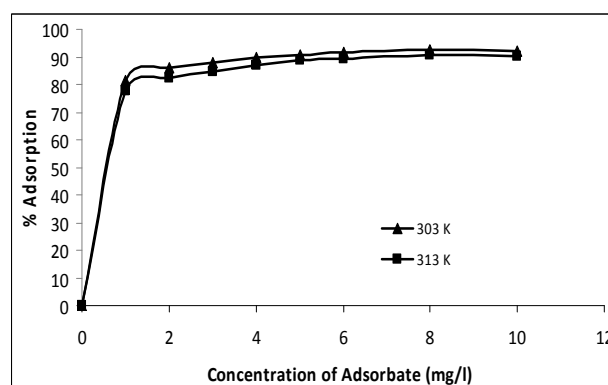


Fig. 7: Effect of adsorbate concentration and temperature on MB dye adsorption

Effect of adsorbate concentration and temperature

The effect of initial concentration of Methylene Blue dye on its adsorption in aqueous solution was investigated in conditions of 10 g/l of adsorbent concentration, pH 7.0, 360 min of contact time and temperature 303 and 313 K.

The results of the studies are shown in Fig. 7 which depict that dye uptake increases with increase in initial Methylene Blue concentration from 2 to 8 mg/l and thereafter equilibrium is achieved in dye uptake efficiency at a concentration of 10 mg/l at 303 and 313 K. However, the uptake of dye was higher at 303 K with a dye uptake efficiency of 0.74 mg/g of adsorbent. Further increase in dye concentration up to 10 mg/l showed no significant changes in removal efficiency. This is due to the fact that with increased dye concentration, the driving force for mass transfer also increases. At low concentrations there will be unoccupied active sites on the adsorbent surface. Above optimal MB concentration, the active sites required for the adsorption of dye will lack [33, 34]. This retards the overall MB adsorption by fly ash. The increment in sorption capacity may be due to the increase of dye concentration which resulted in higher concentration gradient of the dye, thus leading to higher sorption capacity. The rate of uptake of dye was found to decrease with increase in temperature, thereby indicating the process to be exothermic in nature. This decrease in adsorption efficiency on increase in temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate.

Adsorption isotherms

The adsorption of Methylene Blue at equilibrium with increase in initial dye concentration at 303 K has been fitted in Langmuir model and Freundlich isotherms. In Langmuir isotherm, $1/Q_e$ (mg/g) has been plotted against $1/C_e$ (mg/l) a straight line with slope $1/bQ_0$ is obtained as shown in Fig. 8. A perusal of Fig. 8 shows that the adsorption of Methylene Blue follows the Langmuir isotherm. Langmuir constants Q_0 and b are calculated and the values of these constants are given in Table 2 along with coefficient of correlation (R^2). The maximum adsorption capacity (Q_0) was 0.4348mg/g.

Table 2: Freundlich and Langmuir isotherm parameters at 303 K

Freundlich parameters			Langmuir parameters		
K_F	$1/n$	R^2	Q_0 (mg/g)	b	R^2
0.27	0.337	0.98	0.434	1.927	0.
54	7	9	8	4	97
					5

The equilibrium adsorption data has also been data fitted in the linear form of Freundlich isotherm model and the plots of $\log q_e$ against $\log C_e$ shown in Fig. 9 are linear and the values of K_F and $1/n$, calculated from intercept and slope of the plot (Figure 9), respectively, are given in Table 2. The calculated values of n are less than 1, which suggest the favorable adsorption of dye onto the fly ash. The values of the regression coefficients indicate that the

data satisfactorily follow both Langmuir and Freundlich models but the Freundlich isotherm fits the experimental data better.

Kinetic studies

The graph (Fig. 10) obtained for $\log(q_e - q_t)$ versus time (t) in minutes exhibits straight lines and confirm the adsorption process to follow first order rate kinetics in each case. The K_{ad} value calculated from slope of the plot ($K_{ad}/2.303$) is 0.0092 min^{-1} .

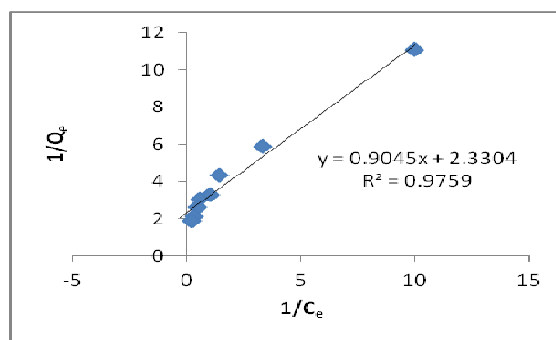


Fig.8: Langmuir isotherm plot of MB dye adsorption

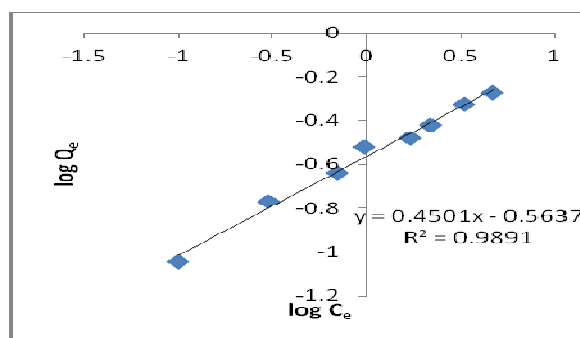


Fig.9: Freundlich isotherm plot of MB dye adsorption

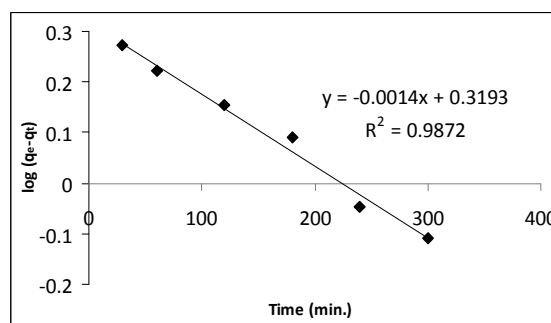


Fig.10: Lagergren's plot of Methylene Blue dye adsorption on fly ash

IV. CONCLUSIOINS

Studies carried out show promising adsorption capacity of fly ash as an adsorbent for methylene blue dye. The studies presented reveal that fly ash from thermal power plants can be fruitfully employed as adsorbent for the removal of Methylene Blue dye. Removal of methylene blue dye is pH dependent and the maximum removal is attain at pH 7.0. The maximum removal of Methylene

Blue, a cationic dye is about 92 % at 4mg/l with a dose of adsorbent of 10 g/l and contact time 360 min at a temperature of 303 K. The adsorption process is of first order, physical and exothermic in nature. Equilibrium data have been fitted in the Langmuir and Freundlich isotherm models which confirmed that the sorption is homogeneous and occurred through physico-chemical interactions. The equilibrium data are best described by Langmuir model isotherms with maximum adsorption capacity of 0.434mg/g. The fitness of Langmuir model indicates the monolayer coverage of the adsorbate on the surface of the adsorbent. As an adsorbent, fly ash is quite cheaper than other commercially available adsorbents. Utilization of fly ash will solve not only its disposal problems and environmental hazards, but also help as potential adsorbent for removal of dyes from waste waters.

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