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ADSORPTION CHARACTERISTICS OF MALACHITE GREEN AND METHYLENE BLUE DYE ON FLY ASH GENERATED FROM KOLAGHAT THERMAL POWER PLANT: A CASE STUDY

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ABSTRACT

Textile dying industry effluents are highly toxic and carcinogenic in nature as it contains a large number of complex metal dyes which are stable to light and resistant to aerobic digestion. Thus removal of coloured material from dyeing industry effluents and to save the environment remains a challenge to the researchers till today. On the other hand , a large amount of fly ash produced from power plant all over the world requires large dumping sites for their safe disposal. However, the utilization rate of fly ash is still in a relatively low level and the major use of fly ash is as an additive to cement concrete, bricks , also used for land filling purposes. Thus , there is a need to develop alternative uses of fly ash. In this present paper , fly ash obtained from Kolaghat Thermal Power Plant (W. B.) has been used to remove the dye, Methylene Blue and Malachite Green from aqueous solutions . Experiments were done using the solutions with various dyes concentrations of 5 to 40 mg/l. The effect of adsorbent amount , contact time , solute concentration, pH variation and temperature on percent removal of dye has been studied. The percentage of adsorption is determined by spectrophotometer at wave length of 660 nm and 618 nm. Results show that 85- 95% removal of dyes may be achieved using fly ash .

Kinetic studies show the suitability of Pseudo Second order reaction for this adsorption system . The applicability of the rearranged Langmuir isotherm and Freundlich isotherm model has been investigated. The satisfactory values of regression coefficients, and good adsorption capacity show the applicability of the Langmuir and Freundlich model for this *sorption process. Results show that fly ash generated from thermal power plant has good potential as low cost adsorbent.*

Keywords : *Fly ash , Adsorption, , Rejection , Reaction kinetics , isotherms*

Introduction :

Among all other industries textile industry is most polluting as it uses large amount of water during the dyeing process and discharged the effluents loaded with highly toxic metal ions, and non biodegradable substances. The main problem related to the dyes is the color complex present in wastewater decreases the light permeability causing a negative effect on photosynthesis [7]. These highly toxic wastewaters are have a fluctuating pH, high temperature and chemical oxygen demand. Because of their high solubility in water , they can easily be absorbed by the living organisms through the food chain and start to accumulate in the human body and aquatic animals. Since ingestion of heavy metals beyond the permitted concentration can cause serious health disorders, thus it is very much needed to remove these unwanted complexes before their discharge to the environment. Several physicochemical processes like filtration , flocculation, coagulation , biological stabilization , adsorption by activated charcoal and agricultural wastes have been developed . Some of these methods are selective , expensive and may need special infrastructure. Among all these treatment processes adsorption is found to be highly effective because of it's advantages like low cost, ease of operation, efficiency, simplicity of the equipment and mostly because the adsorbent can be chosen from a wide variety of materials, natural, synthetic and wastes . Activated Carbon is a highly porous material with large surface area and intrinsic adsorption properties, but it is non regenerable and expensive in comparison to fly ash. Fly ash is one of the most known waste and the utilization rate of fly ash is still in a relatively low level , it is being used as raw material in cement and bricks industries only. Thus there is a need to develop alternative uses of fly ash . The effective utilization of fly ash as an alternative adsorbent for removal of dyes or hazardous heavy metals from textile wastes and the investigation of its adsorption characteristics is an challenging problem to the researchers .

Colour removal from textile effluent using hard wood and saw dust as adsorbent was tried by Asfour et al [1]. Karunanithi et. al [2] studied the effect of time on Grey and Onion red color removal from effluents using fly ash. In another study [3] they reported that the charcoal obtained from coconut shell is not so effective for dye removal. The potentiality of fly ash as a catalyst in destructive decoluorisation of various dye using Hydrogen Peroxide has been studied by Gupta et. al [4]. Adsorption characteristics of fly ash for removal of Prusian Brill Blue-M-B was also studied by Das and Srikanth et. al [5, 6] . Removal of some selected azo and anthraquinone dyes by adsorption on mixtures of sandy clay loam (SCL) with fly ash and organic matter has been done by Albanis et.al [7]. They also reported 98% color removal from various dye using bacterial strain. Wang et al [8] noted the positive effect of acid treatment on the adsorption capacity of the fly ash . Performance of fly ash for removal of malachite green in a fixed bed , effect of bed height and concentration of solute has been studied by Das et.al. [10]

The present work throws some light on adsorption characteristics of fly ash for the treatment of aqueous solution of Methylene Blue and Malachite Green. Effect of adsorbent amount , solute concentration, and time on removal percentage of dye has been investigated. The potentiality of fly ash as an adsorbent has been studied at various experimental conditions. The effect of temperature on adsorption has been studied. Applicability of Freundlich Isotherm and rearranged Langmuir model and Helfferich first order kinetics for this system has been investigated. It was noted that Langmuir's model and Freundlich's model both are applicable for fly ash –dye adsorption system. An attempt has also been made to find out the rate constants from the experimental result.

Materials :

Fly ash obtained from Kolaghat Thermal Power Station is used as the absorbent. The samples were collected from ESP-3 which contains less free Sio_2 components as per analysis. Fly ash is a finely divided residue resulting from the combustion of powdered coal or lignite, it is generally acidic in nature. It has a specific surface area which varies from 2500 to 7000 sq. cm/g, particle size range is 120 to 960 microns to less than 5 microns. Specific gravity is found to vary from 2.3 to 2.5 and bulk density 600 to 900 kg/m^3 [5, 6]. Methylene Blue (MB) and Malachite Green (MG) from Qualigens fine chemicals are used as the dye.

Experimental :

Fly ash has been washed with boiling distilled water, filtered and dried at about, 100 ^oC and finally sieved to get 63 mesh size. The mean diameter of the particle was found about 0.0057223 mm. Experiments were carried out by shaking various quantities of adsorbents 10 to 50 gm /L of fly ash and using different concentrations of effluent from 5 ppm to 40 ppm at various temperature. All the samples were kept in a constant temperature shaker which was running at 280 r.p.m. for different contact time of 5 min, 10 min, 15 min, 30 min, 45 min , 60 min and 90 min. The percentage of adsorption is determined by spectrophotometer at wave length of 660 nm and 617 nm for MB and MG respectively.

Results & Discussion :

The effect of adsorbent amount and the time:

The effect of adsorbent amount and the time of contact on the percentage removal of Methylene blue and Malachite Green is shown in figure 1. It shows that percentage removal of dye increases from 80 to 95% with increase of fly ash amount 7.5 gm/L to 30 gm/L and about 85% removal of dye possible in both case using only 10gm/l fly ash. It also shows that adsorption increases with contact time up to certain time, at about 90 minutes it achieved equilibrium concentration.

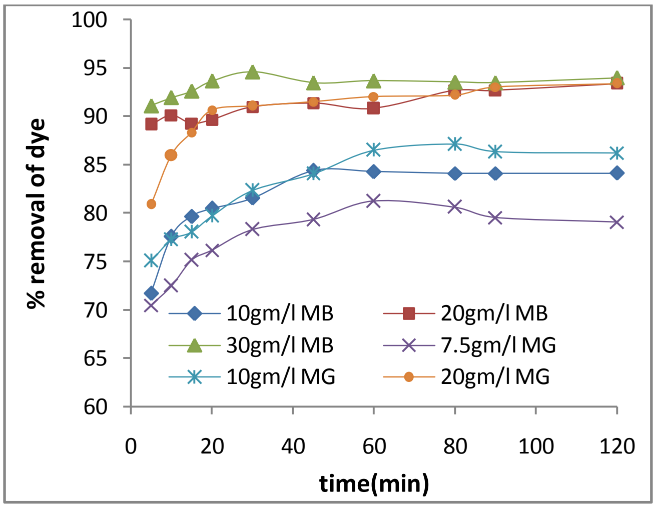

Fig 1 : Effect of adsorbent amount and contact time on removal of dyes

The effect of concentration on removal of dye :

The effect of concentration on removal of dyes is shown in Figure 2. It was noted that percentage removal of dye decreases with increase of concentration for both dyes . This is because at lower concentration, the ratio of available surface area to moles of dye is higher. So adsorption should also be higher as expected for larger amount of adsorbent. But with the increase of solution concentration this ratio decreases due to decreasing adsorption rate. Result shows that removal of 81-95 % may be achieved using 10gm/l fly ash for MG where as 70-90 % for MB for solute concentration range of 10-40 ppm. Similar adsorption characteristics have been reported by other researchers also [5, 8, 14]

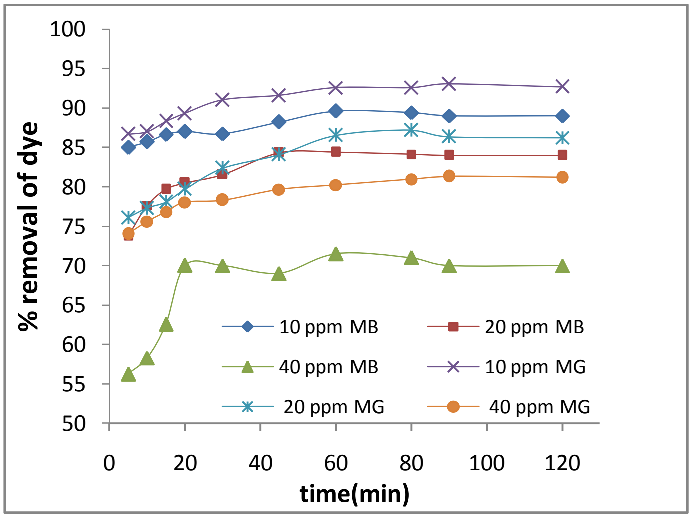

Fig.2 : Effect of solute concentration on removal of dye(MB, MG) using 10gm/L fly ash from various solution.

Effect of temperature on adsorption:

Effect of temperature on adsorption has been shown in the Fig.5. Here adsorption studies were done for 40 ppm solution using 20 gm/L fly ash at four different temperature of 300, 304, 313 and 333 K. Higher adsorption rate at lower temperature for both dyes indicate that the adsorption is exothermic in nature for both dyes .

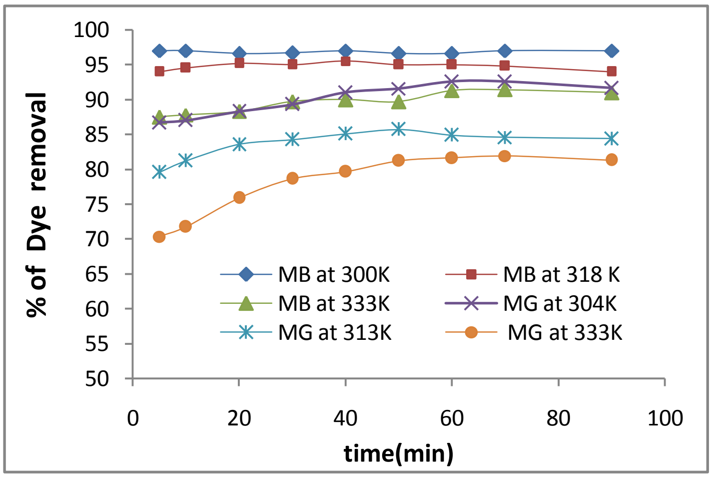

Fig 3 : Effect of temperature on removal of MB and MG (Solute-40 ppm, fly ash - 20gm/l))

Adsorption Process

The adsorption of Methylene Blue or malachite Green dye "A" from solution on fly ash "B" may be considered as reversible reaction [Das et al 11, Y.S.Ho et al 15]

$$A \underset{K_2}{\overset{K_1}{\rightleftarrows}} B$$

Considering C_{A0} as the initial concentration of dye in the solution, in moles / litre , C_A as concentration of dye in the solution at time " t", in moles /litre , and C_B is the concentration of dye on the adsorbent, fly ash at time " t", in moles /litre. If the equilibrium concentration of solute in the solution and on adsorbent are indicated by C_{Aeq} and $C_{B\,eq}$, then the rate equation will be as

$$- d\,C_A/ dt = K_1C_A - K_2\,C_B \quad \ldots\ldots\ldots\ldots (1)$$

$$K_C = K_1 / K_2 = C_{B\,eq} / C_{Aeq} \quad \ldots\ldots\ldots\ldots (2)$$

$$C_B = C_{A0} - C_A \quad \ldots\ldots\ldots\ldots (3)$$

From eqn. (1 & 3) the rate equation for the above reaction can be written as

$$- d\,C_A/ dt = K_1C_A - K_2\,(C_{A0} - C_A)$$

$$- d\,C_A/ dt = K_T\,(C_A - K_2/ K_T.\ C_{A0}) \quad \ldots\ldots\ldots (4)$$

Where K_T is $(K_1 + K_2)$

Integrating the eqn. (4) with limit C_{A0} to C_A for time " 0" to "t" we get

$$\mathrm{Ln}\ [(C_A - K_2/ K_T.\ C_{A0})/ C_{A0}(1-K_2/K_T)] = - K_T.t$$

$$\mathrm{Ln}\ [\{ C_A/C_{A0} - 1/ (K_C + 1)\} / \{K_C / (1+ K_C)\}] = - K_T.t \quad (\text{ from eqn. } 2)$$

$$\mathrm{Ln}\ [\{ C_A/C_{A0} - 1/ (C_{Beq}/C_{Aeq} + 1)\} / \{(C_{Beq}/C_{Aeq}) / (1+ C_{Beq}/C_{Aeq}) \}] = - K_T.t,$$

Since, $C_{Beq} = C_{A0} - C_{Aeq}$

$$\mathrm{Ln}\ [1 – (C_{A0} - C_A) / (C_{A0} - C_{Aeq})] = - K_T.t,$$

So, $$\mathbf{Ln\ [1 – U(t)] = - K_T.t,} \quad \ldots\ldots\ldots (5)$$

Where U (t) is the fractional attainment of equilibrium and is given by $(C_{A0} - C_A) / (C_{A0} - C_{Aeq})$, K_T is the sum of K_1 and K_2 , where K_1 and K_2 are the rate constant for adsorption and desorption respectively , K_C the equilibrium constant,. C_{Beq} and C_{Aeq} are equilibrium concentrations of dye on adsorbent and in solution respectively in moles/lit.

Using equation (5), ln [1- U (t)] Vs. time " t " were plotted at various temperature and concentrations, The linear plot in Fig.4 indicates that the process involves Helfferich first order kinetics. The slope of the graph give the values of K_T tabulated in Table 1. The negative adsorption tendency of the fly ash with increase of temperature also indicates the exothermic nature of this adsorption process.

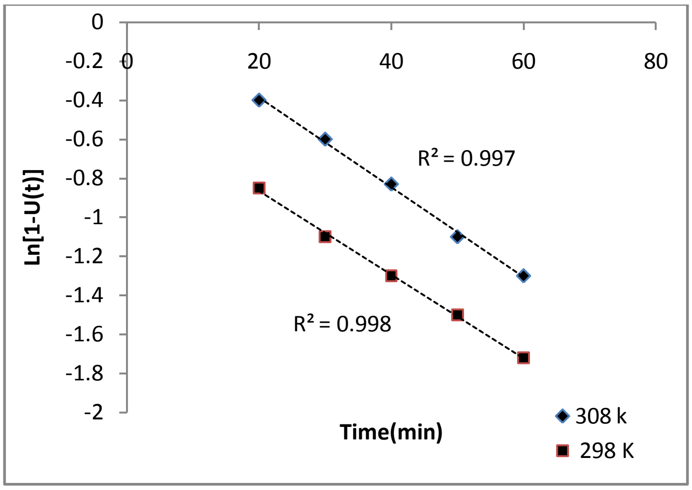

Fig 4: Helfferich first order kinetics for MB - fly ash adsorption process

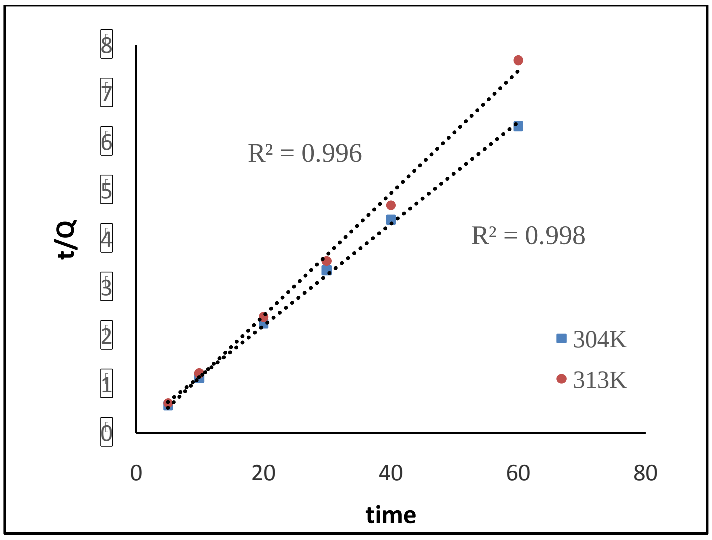

Fig 5 : First order kinetics for MG - fly ash adsorption process.

Table 1. Values of First Order Rate constants and Equilibrium constants(MG)

Temp(K)	**K (g/mg min)**	**h(mg/g min)**	**R^2**
304	2.542	7.496	0.9987
313	4.736	16.583	0.996

The experimental results obtained from flyash –Methylene blue at 298 K have been correlated with the following rearranged Langmuir model of adsorption .

$$C_e / Q_e = 1/ Q^0 b + C_e / Q^0 \text{ --------- } (6)$$

Where C_e is the equilibrium concentrations (in mg/lit.) of dye, and Q_e is the amount of dye adsorbed per gram of adsorbent at equilibrium (mg/gm), Q^0 and b are Langmuir constants related to the capacity and energy of adsorption respectively.

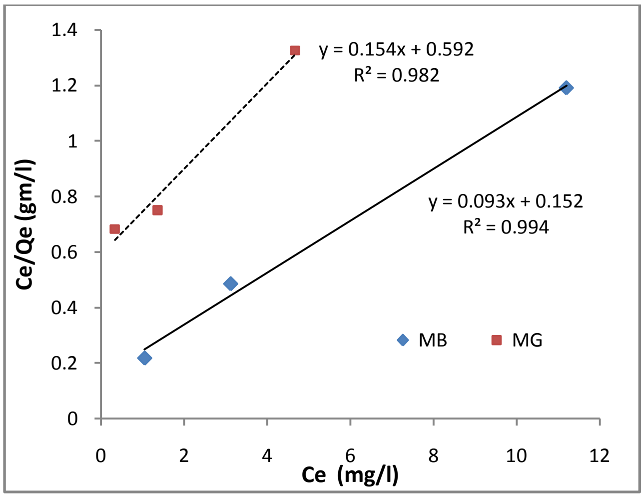

Fig 6. Langmuir Isotherm for fly ash and dye adsorption at 298K

The plot of C_e / Q_e Vs. C_e is shown in fig.6. The linear plot suggest the applicability of the Langmuir Isotherm for this system. It also indicates the formation of monolayer coverage at the outer surface of the adsorbent. The values of Q^0 and b, Langmuir constants are calculated from the slope and intercepts of the graph and reported in Table 2.

Applicability of the Freundlich Isotherm for this present system has also been found out by correlating the results using the following Freundlich equation .

$$X/M = Q_e = K.(C_e)1^{1/n}$$

$$\text{So,} \quad \log (X/M) = \log K + 1/n \log C_e$$

Here X/M or Q_e is surface load in (mg/gm). The linear plot of log (X/M) Vs log C_e in Fig 7. also suggests that the system follows Freundlich Isotherm, The values of 1/n and k , the Freundlich constants are shown in Table 2.

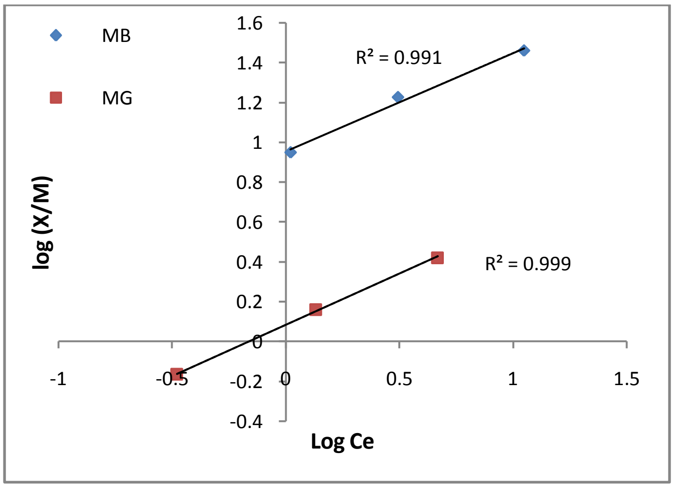

Fig 7. Freundlich Isotherm for fly ash and dye adsorption at 298K

The values of correlation coefficient (R^2) obtained for Langmuir isotherms are 0.982 and 0.994 and for Freundlich isotherm value is 0.991 and 0.999 for Methylene Blue and Malachite Green respectively. Results indicates that Langmuir's model as well as is Freundlich's model both are highly applicable for the present system but isotherm models fit better for MB sorption compare to MG.

Table 2. Values of Langmuir and Freundlich constants :

Tempr	Langmuir's constants		Freundlich's constants	
298 K	Q^0 mg/gm	b Lt/mg	K	n
M.G	6.5	0.26	1.21	1.96
M.B	10.75	0.61	9.01	2.02

Conclusions:

The results obtained from adsorption studies of Methylene Blue and Malachite Green by fly ash at various temperature have been correlated with Freundlich Isotherm and rearranged Langmuir model of adsorption isotherm. The linear plot and the satisfactory value of correlation coefficients suggest the applicability of both Freundlich's as well as Langmuir's model for this adsorption process. The maximum removal percentage of dyes obtained using fly ash was about 96%. Adsorption also depends on various parameters like contact time, adsorbent amount, initial dye concentration and temperature. Since availability of fly-ash is not restricted, regeneration of used up adsorbents is not essential. Thus it may be concluded that fly ash generated from thermal power plant has good potential for waste management, and it may be utilized as low cost adsorbent for dye removal from textile effluents.

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