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Adsorption Isotherm Studies in the Removal of Malachite Green Dye from Aqueous Solution by Using Coal Fly Ash

Gopal Gehlot, Sanjay Verma, Sarita Sharma, Neeraj Mehta

Gopal Gehlot
M. Tech Student, Chemical Engineering Department, Ujjain Engineering College, Ujjain–456010 (Madhya Pradesh), India.

Sanjay Verma
Associate Professor, Chemical Engineering Department, Ujjain Engineering College, Ujjain–456010 (Madhya Pradesh), India.

Sarita Sharma
Associate Professor, Chemical Engineering Department, Ujjain Engineering College, Ujjain–456010 (Madhya Pradesh), India.

Neeraj Mehta
M. Tech Student, Chemical Engineering Department, Ujjain Engineering College, Ujjain–456010 (Madhya Pradesh), India.

Correspondence:
Sanjay Verma
Associate Professor, Chemical Engineering Department, Ujjain Engineering College, Ujjain–456010 (Madhya Pradesh), India.

Abstract
In this paper the effectiveness of coal fly ash for the removal of Malachite Green dye from aqueous solution was evaluated using different isotherm models. Adsorption data were modeled using the Langmuir, Freundlich and Temkin adsorption isotherms. The results showed that the optimum conditions for the dye removal at a pH of 8, an adsorbent dose 2 gm, contact time 2 hours and a temperature of 32 °C. Maximum adsorption capacity of coal fly ash was found to be 2.23 mg/g. The result indicated that coal fly ash is an attractive adsorbent for removing basic dye from aqueous solution.

Keywords: Malachite Green Dye, Coal Fly Ash, Adsorption and Isotherm.

1. Introduction
Dyes are highly colored polymers and low biodegradable in nature. Dyes are water pollutants which are generally present in the effluents of the textile, leather, food processing, dyeing, cosmetics, paper, printing and dye manufacturing industries. Textile industries discharge large quantity of dyes (10 to 15%) into water bodies, poses serious ecological problems (Sharma and Nandi, 2013) [7]. Discharge of Malachite Green (MG) into the hydrosphere can cause genotoxic, mutagenic, teratogenic, carcinogenic effects it gives the undesirable color of water and reduces sunlight penetration (Srivastava *et al.,* 2004 and Bhattacharyya and Sharma, 2005) [8, 2].

Removal of undesirable color from dye wastewaters is a complex problem because of difficulty in treating such wastewaters by conventional treatment methods (Kumar *et al.,* 2006) [4]. Among the various treatment methods adsorption technique is a widely used for removal of different contaminants from waste water. This method is efficient and inexpensive so can be operated at large scale (Jirekar *et al.,* 2013) [3].

Coal fly ash is an industrial waste product generated from thermal power plants, which is a major cause of environmental pollution. Many researchers have been used fly ash as adsorbent for the removal of color (Kumar *et al.,* 2004) [5]. In the present study coal fly ash was used as an adsorbent for the removal of MG from aqueous solution and the optimum adsorption data was tested with Freundlich, Langmuir and Temkin isotherm. For obtaining the data batch adsorption studied were conducted.

2. Materials and Methods
2.1 Adsorbent Preparation: Coal-fly ash used in the present study obtained from Grasim Thermal power plant Birla gram Nagda (M.P.) Coal-fly ash produced from combustion of coal. The sample was washed with double distilled water in vertical glass column and oven-dried at 105 ºC for 24 hours and kept in desiccators for further analysis.

2.2 Adsorbate and Chemicals: All the chemicals used in this study were of analytical grade. MG was supplied by Sun Chem. India private limited. The general characteristics of MG ($C_{23}H_{25}ClN_2$) are molar mass = 364.91 g/mol, color index (C.I.) No. = 42000, λmax. = 617 nm. Its stock solution was prepared in double-distilled water. Standard solution of MG was taken from the market. Accurately weighed quantities of the dyes were dissolved in 100 ml distilled water to prepare stock solutions. Experimental solutions of the desired concentration were obtained by dilutions of stock solutions in 100 ml of distilled water. Solution pH was adjusted by adding 0.1 M NaOH and 0.1 M HCl solution. Physical properties of coal fly ash and properties of MG dye are presented in table 1 and table 2 respectively.

Table 1: Physical properties of Coal Fly ash

Properties	Specific gravity	Dry density (g/cm^3)	Moisture content	Fine sand size	Silt size	Clay size
Values	2.09	1.38	15 %	17%	73%	10%

Table 2: Properties of Malachite Green dye3

Chemical Name	Formula	Molecular Weight	λ_{max}	Color Index No.
N-(4-{[4-(dimethylamino) phenyl] (phenyl) methylidene} cyclohexa-2,5-dien-1-ylidene) -N-methylmethanaminium chloride	$C_{23}H_{25}ClN_2$	364.91 (g/mol)	617-619 (nm)	42000

2.3 Adsorption Isotherm Models: The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process is allowed to reach at equilibrium. Type of an adsorption isotherm model is very important in order to understand the adsorptive behavior for solid-liquid adsorption systems. To optimize the adsorbent's usage, the adsorption isotherm is applied successfully for describing how solutes interact with adsorbents. There are different isotherm equations and three important isotherms are selected in present study namely, Langmuir, Freundlich and Temkin adsorption isotherms. The applicability of these three isotherms was compared by evaluating the correlation coefficients (R^2) values.

2.3.1 Langmuir Isotherm Model: Langmuir isotherm refers to adsorption of a homogeneous monolayer to a surface holding a limited number of adsorption sites with identical qualities and with no transmigration of adsorbate in the plane of the surface. The equation for Langmuir model is given as follows (Uddin *et al*., 2013) [9]

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \quad \text{-------------- (1)}$$

where, q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration (mg/l), while q_{max} and K_L are the Langmuir isotherm constants related to adsorption capacity and rate of adsorption, respectively.

The separation factor is given by

$$R_L = \frac{1}{1+K_L C_0} \quad \text{---------------------- (2)}$$

where R_L is the dimensionless separation factor and C_0 is the initial solution concentration (mg/l). The parameter suggests the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$) (Bozlur *et al.,* 2010) [1]. The parameter indicates the shape of the isotherm.

2.3.2 Freundlich Isotherm Model: The Freundlich model involves the formation of multilayer and heterogeneous surfaces. Linear form of Freundlich adsorption isotherm is given by the following equation (Wu *et al.,* 2012) [10]

$$\ln(q_e) = \ln(K_f) + \frac{1}{n_f}\ln(C_e) \quad \text{-------------------- (3)}$$

where K_f and n_f are the Freundlich constants and represent the adsorption capacity and measure of heterogeneity, respectively. When log q_e is plotted against log C_e and the data are analyzed by linear regression, 1/n and K_f constants are determined from the slope and intercept respectively. The favorability and the nature of adsorption process can be identified from the value of 1/n. The type of isotherm can be irreversible (1/n=0), favorable ($0 < 1/n < 1$) and unfavorable ($1/n > 1$).

2.3.3 Temkin Isotherm Model: This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed q_e against ln C_e and the constants were determined from the slope and intercept. The model is given by the following equation (Paul and Chavan, 2013) [6]

$$q_e = B\ln A + B\ln C_e \quad \text{---------------------- (4)}$$

where B and A known as heat of sorption (j/mol) and equilibrium binding constant (l/g) respectively.

2.4 Batch adsorption Experimentation

Batch adsorption experimentation was carried out at room temperature. Stock solution of Malachite Green dye was prepared in distilled water. The batch adsorption was carried in 250 ml Borosil conical flasks by mixing 2 mg amount of the adsorbent with 100 ml of aqueous dye solution of different concentration such as 10 mg/l, 20 mg/l, 30 mg/l and 40 mg/l. The conical flasks were kept on a magnetic stirrer and were agitated at 120 rpm constant speed. After adsorption was over, the mixture was allowed to settle for 1 hour and filtered with filter paper. The dye remaining unabsorbed was determined spectrophotometrically. Their absorbances were determined using UV spectrophotometer ($\lambda_{max.} = 617$). These values were used to calculate C_e and q_e values and curves for Langmuir, Freundlich and Temkin isotherm were plotted.

3. Results and Discussions

From adsorption study of MG on coal fly ash optimum conditions of pH, contact time and adsorbent dose was determined. Various adsorption parameters at optimum conditions are shown in table 3.

Table 3: Optimum adsorption data from adsorption studies (pH = 8, time = 2 hrs. Adsorbent dose = 2 g/100 ml, Temp. = 32±2)

Conc. (mg/l)	Absorbance (nm)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	ln(q_e)	ln(C_e)
10	0.12	1.0	0.450	2.22	-0.799	0
20	0.42	3.50	0.825	4.24	-0.192	1.25
30	0.73	6.0	1.20	5.00	0.182	1.79
40	1.20	10.0	1.50	6.67	0.405	2.30

Data of table 3 are plotted for the Langmuir, Freundlich and Temkin isotherm. Langmuir isotherm curve C_e/q_e vs. C_e is plotted (Fig. 1), the intercept gives the value $\frac{1}{q_{max}K_L}$ and slope gives the value $\frac{1}{q_{max}}$. Freundlich isotherm curve log (q_e) vs. log (C_e) is plotted (Fig. 2), 1/n and K_f constants are determined from the slope and intercept respectively. Temkin isotherm curve q_e vs. ln (Ce) is plotted (Fig. 3) and Temkin isotherm constant determined from the slope and intercept. These constants are summarized in table 4. As per the regression factor as well as correlation factor of calculated and experimental values indicate that there is better fitting of Freundlich isotherm model than the Langmuir isotherm and Temkin isotherm model for adsorption of MG.

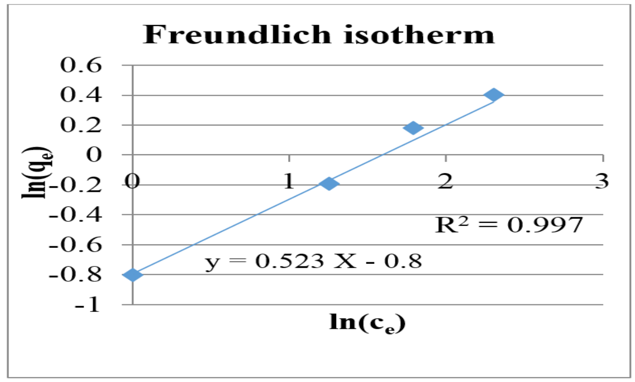

Fig 2: Freundlich isotherm curve

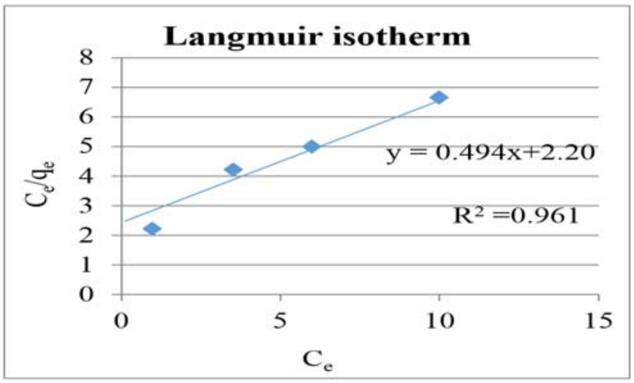

Fig 1: Langmuir isotherm curve

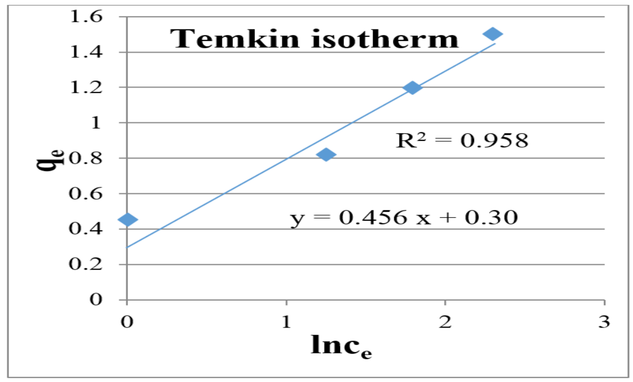

Fig 3: Temkin isotherm curve

Table 4: Isotherm Constants for the Adsorption of MG

Langmuir				Freundlich			Temkin		
$q_{max.}$ (mg/g)	K_L (l/mg)	R_L	R^2	K_f (mg/g)	n_f	R^2	B (j/mol)	A (l/g)	R^2
2.02	4.45	0.0115	0.961	2.23	1.91	0.997	0.456	1.93	0.958

4. Conclusion

The results obtained in present study indicate the CFA can be successfully used for the removal of hazardous dye, malachite green from aqueous solutions. The amount of dye adsorbed was found to be dependent on solution pH, adsorbent dose, and initial dye concentration and contact time. Maximum uptake of dye was observed at pH 8. The optimum conditions of above parameters were tested with three known isotherm models. Based on R squares values obtained from different isotherm models, it was found that Freundlich isotherm give the best data fitting. This result is obvious as Freundlich isotherm fits the best for dilute solutions and shows multilayer heterogeneous surface of adsorbent.

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