

Removal characteristics of basic dyes from aqueous solution by fly ash in single and tertiary systems

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The use of fly ash as a low cost adsorbent for the removal of three basic dyes from their single and tertiary aqueous solution has been investigated. Batch adsorption experiments were conducted to determine the effect of contact time and adsorbent dosage on adsorption of dyes from aqueous solution. The adsorption isotherm results indicated that the Freundlich adsorption isotherm fitted the data better than the Langmuir adsorption isotherm. The adsorption capacity of fly ash decreases in tertiary system as compared to single system indicates the competitive sorption behaviour of fly ash. Kinetic parameters of adsorption such as the pseudo first order constant and pseudo second order constant were determined. The results of the study demonstrated that the fly ash could be used as an effective low cost adsorbent for the removal of basic dyes from aqueous solution.

Keywords: Fly ash; Adsorption; tertiary system; isotherm; kinetics.

Introduction

Dyes are widely used in industries such as textiles, rubber, paper, plastics, cosmetics, etc. to color their products. It is estimated that 2% of dyes produced annually are discharged in effluent from manufacturing operations while 10% are discharged in effluent from textile and associated industries¹. Basic dyes are the brightest class of soluble dyes used by the textile industry². The release of dyes into waters by various industries poses serious environmental problems due to various dyes persistent and recalcitrant nature. Color in effluents can cause problems in several ways: dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration; dyes are highly visible and undesirable even at very low concentrations in effluent; dyes absorb and reflect sunlight entering water and so can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants; direct discharge of dyes containing effluents into municipal wastewater plants and/or environment may cause the formation of toxic carcinogenic breakdown products¹. The highest rates of toxicity were found amongst basic and diazo direct dyes³. In many developed countries such as the UK and EU countries, environmental policies have

required that zero synthetic chemicals should be released into the marine environment⁴.

The adsorption process is one of the efficient methods to remove dyes from effluent due to its low initial cost, simplicity of design, ease of operation and insensitivity to toxic substances¹. Adsorption onto activated carbon has been found to be superior for wastewater treatment compared to other physical and chemical techniques, such as flocculation, coagulation, precipitation and ozonation as they possess inherent limitations such as high cost, formation of hazardous by-products and intensive energy requirements⁵. Even though activated carbon showed advantages, the main drawback of the activated carbon is the cost and difficulty in regeneration⁶. Therefore, in recent years, this has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors which are mainly industrial and agricultural by-products⁷.

The present study is an attempt to explore a possibility to utilize the low cost adsorbent material, fly ash (FA) an industrial by-product, to remove the basic dyes (Malachite green, Methylene Blue and Crystal Violet) and their tertiary mixtures from aqueous solution. The overall objectives of the present study were (i) to investigate the potential of using FA as low-cost adsorbent for the removal of the three basic dyes (Malachite green (MG), Methylene

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Blue (MB) and Crystal Violet (CV)) and its tertiary composition from aqueous solutions. (ii) To investigate the effects of contact time and adsorbent dosage on dye removal efficiency. (iii) To quantify the adsorption equilibrium through Langmuir and Freundlich isotherms and (iv) to investigate the adsorption mechanisms and potential rate-controlling step through three kinetic models.

Materials and Methods

Adsorbent and its Characterization

The thermal power plant waste material, FA was utilized as potential adsorbents in the study. The adsorbents were obtained from Neyveli Lignite Corporation Limited, Neyveli. The pH value of the FA sample was determined by mixing 2 g of FA with 100 mL of distilled water and recording pH at every 1 hr interval for a period of 24 hr. The loss on ignition (LOI) was determined by heating a pre-weighed dry sample (left at 105 °C in an oven and then cooled in desiccators) to 600 °C over a period of 1 hr⁸. The point of zero charge (PZC) was determined by solid addition method⁹. Chemical solubility characteristics of FA were studied by mixing one gram FA with 200 mL of distilled water for 2 hr⁸. After filtration, the major chemical constituents in the filtrate were measured using atomic absorption spectrophotometer.

Batch Study

Adsorption studies were carried out by batch process for individual system (MG, MB and CV), tertiary system (MG+CV+MB) for dye concentration of 10 mg/L. The mixture (dye + adsorbent) was shaken well in an orbital shaking incubator at an agitation rate of 150 rpm at a temperature of 30°C. Batch kinetic experiments were carried out at constant pH 8.0. Kinetic study was conducted with the known dosage of adsorbent (0.05 g for individual system and 0.75 g for tertiary system for the 50 mL of dye solution. To study the effect of FA dosage, experiments were carried out by shaking a series of bottles containing different amounts of adsorbents (0.005 to 0.5 g) in 50 mL of dye solution and kept in the shaker for constant duration (equilibrium contact time). The sorbent solution mixtures were then centrifuged at 3600 rpm for 5 minutes and the supernatant was analyzed for the dye concentration.

Desorption Study

1N solutions of H₂SO₄, NaOH, CH₃COOH and NaCl were used as the reagents for desorbing dyes

from the saturated FA (applied for tertiary dye solution). Before the experiments, saturated FA was dried at 75°C for one day in a hot air oven. 1 g of dye adsorbed FA was placed in 100 mL each of the above reagents, taken in a 250 mL conical flask and kept in shaker up to 2 hr. The sorbent solution mixtures were then centrifuged at 3600 rpm for 5 minutes and the supernatant was analyzed for the dye concentration.

Results and Discussion

Characterization of Adsorbent

The FA used in the experiments were collected from the lignite burning thermal power plant, Neyveli, Tamilnadu and analyzed for various physical and chemical properties. PZC, pH, specific gravity and loss on ignition values for FA were obtained as 6.7, 8.36, 2.32 and 1.85% respectively. The value of PZC shows that at pH less than 6.7 the surface of the FA is predominated by positive charges while at pH greater than 6.7 the surface is predominated by negative charges. The solubility concentration of some elements in water from FA is obtained as: Cu of 1.34×10^{-5} mg/g, Na of 3.2×10^{-3} mg/g, K of 2.9×10^{-3} mg/g and Cd of 1.72×10^{-4} mg/g.

Effect of Contact Time

Fig. 1 shows the effect of contact time on the removal of single and tertiary system of basic dyes. From the Fig. 1 (a), it was observed that dye uptake in single system was rapid for the first 5 min in case of MG, 20 min for MB, and 10 min for CV and thereafter it proceeded at a slower rate and finally reached saturation. At the initial stages of adsorption process, adsorbent was filled with active sites. These vacant sites cause the rapid removal of color at initial stages. Such short times coupled with high removals indicate a high degree of affinity for the dye groups pointing towards chemisorption¹⁰. Then the gradual reduction of removal efficiency is due to the reduction in active sites of FA. Also there may be the formation of repulsive forces between the dye molecules on the solid surface and in the bulk phase¹¹. The time required to attain the state of equilibrium (saturation) is termed equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operation conditions¹². At this point, the amount of dye being adsorbed onto the adsorbent was in a state of dynamic equilibrium with the amount of dye desorbed from the adsorbent¹³. The uptakes of MG, MB and CV at equilibrium time were found to be

99%, 17% and 24% at 90 min, 90 min and 60 min respectively. The time profile of dyes uptake is a single, smooth and continuous curve leading to saturation, suggesting also the possible monolayer coverage of dyes on the surface of the FA¹². Similar trends were also observed in tertiary system dye removal (Fig. 1b). The affinity of FA towards basic dyes follows the order of: MG> MB> CV.

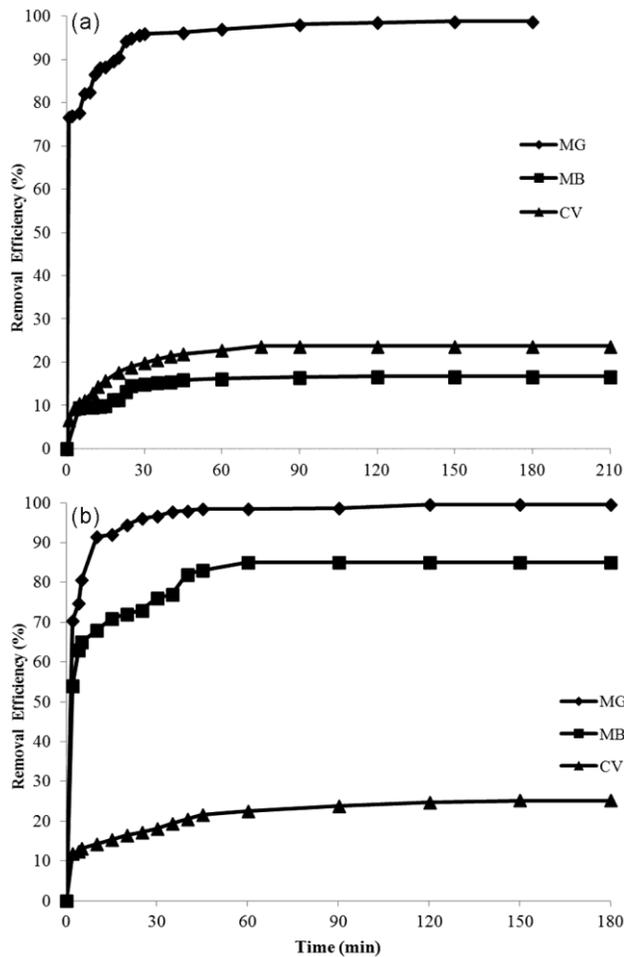


Fig. 1—Effect of contact time for dye removal from (a) single system (b) tertiary systems

This indicates that molecular size of CV is very much higher than MB and MG. For example, the molecular size of the MB and CV are in the range of 135 Å and 461 Å respectively. Therefore, resistance for the penetration of CV in to the small pores of is higher than that of MB and MG. This will reduce the CV adsorption efficiency of FA.

Adsorption Kinetics

In order to find the reaction kinetics, Lagergren’s pseudo first and second order kinetic model were considered and fitted with the experimental data. Based on the comparison between experimental and theoretically calculated q_e values (Table 1), it was found that the pseudo second order model fitted better than pseudo first order model for all systems of MG. It was also found that the pseudo second order model fitted better for tertiary system of MB and CV, except its single system. Figs. 2 (a) and (b) shows the plot of the intra particle diffusion model for adsorption of single and tertiary system of basic dyes. The k_{id} values were obtained from the slope of the linear portions of the curve of different dye system and are given in Table 2. The values of intercept give an idea about the boundary layer thickness such as the larger the intercept, the greater the boundary layer effect¹⁴. But in all the cases the plot is not going through the origin, indicates that intraparticle diffusion is not only the rate limiting steps for dye removal by FA. From the Fig. 2, it is also observed that there are two regions in most of the cases. Initial curve portion is attributed to boundary layer effect while the second linear portion is due to the intraparticle diffusion¹⁵.

Effect of Adsorbent Concentration

Effect of FA concentration on dye removal from their single and tertiary mixture was examined by changing amount of adsorbent (0.005 to 0.5 g) in 50 mL of dye solution at equilibrium time (Fig. 3). From the Fig. 3, it can be observed that the removal

Table 1—Kinetic coefficients for basic dyes removal by fly ash

Dye System	Dyes	Pseudo 1 st order coefficients			Pseudo 2 nd order coefficients			$q_{e,cal}$ (mg/g)
		q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg/min)	R^2	
Single	MG	2.024	0.054	0.903	9.891	0.074	1	9.682
	MB	1.263	0.058	0.953	1.748	0.083	0.9986	0.860
	CV	1.711	0.050	0.999	2.470	0.062	0.999	1.82
Tertiary	MG	2.600	0.075	0.969	0.668	1.398	1	0.645
	MB	3.249	0.057	0.931	0.578	0.718	0.9997	0.484
	CV	1.463	0.028	0.994	0.176	0.614	0.9965	0.166

Table 2—Intraparticle diffusion constants for different dyes System

Systems	Dyes	$K_{i,1}$	$K_{i,2}$	C_1	C_2	R_1^2	R_2^2
Single System	MG	1.060	0.026	4.665	9.487	0.864	0.775
	MB	0.276	0.008	0.442	2.272	0.987	0.826
	CV	0.182	0.007	0.413	1.577	0.894	0.776
Tertiary System	MG	0.044	0.002	0.430	0.644	0.892	0.888
	MB	0.031	0.001	0.348	0.552	0.952	0.839
	CV	0.012	0.003	0.059	0.113	0.979	0.916

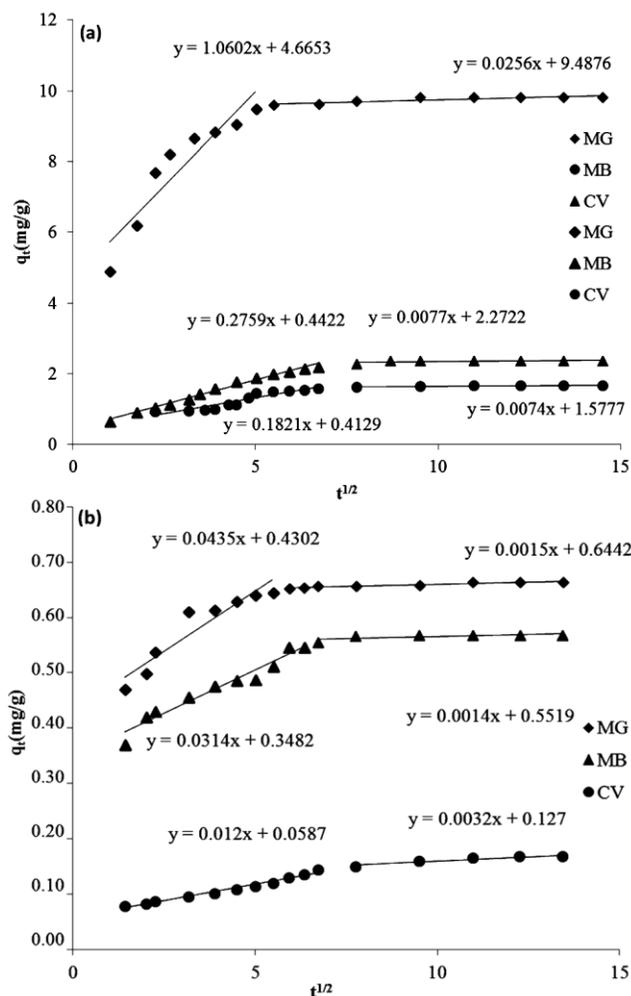


Fig. 2—Intraparticle diffusion for (a) Single System (b) Tertiary System

efficiency increases up to a certain level and beyond that it is more or less constant. With increase in FA concentration, effective surface area and active site concentration also increases and causes the increase in dye removal rate. After that the increase in dye(s) removal is insignificant with respect to increase in dose of FA. This is due to at higher FA concentration; there is a very fast superficial adsorption onto the FA surface that produces a lower solute concentration in

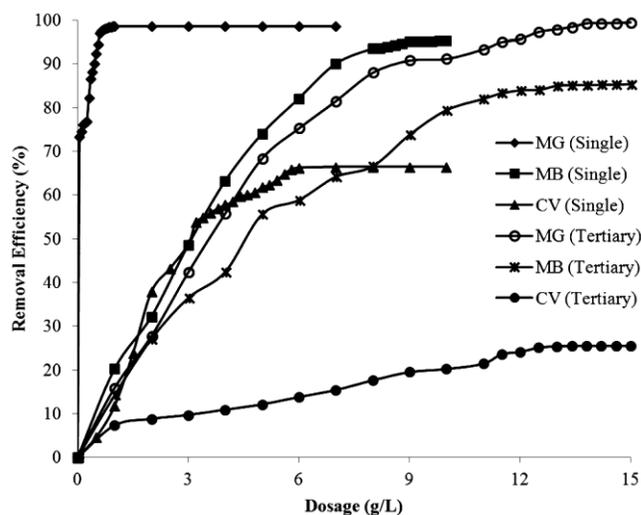


Fig. 3—Optimization of fly ash dosage for single and tertiary systems

the solution than when FA dose is lower¹⁶. Thus with increasing adsorbent dose, the amount of dye(s) adsorbed per unit mass of FA is reduced, thus causing a decrease in removal efficiency¹⁶. The maximum MG removal of 98% was observed at 0.65 g/L, MB removal of 95% was observed at 8.8 g/L and 66% for CV at 5.8 g/L. By comparing the adsorbent dosage corresponding to maximum removal efficiency of the individual system with tertiary system, the dosage requirement was more in the case of tertiary system. In tertiary system, the removal efficiency of CV was affected much more compared to MG and MB. From the Fig. 3, it was found that MG removal of 98% was achieved at 13.8 g/L, 85% of MB removal at 13 g/L and 25.5% for CV at 13.4 g/L.

Equilibrium Modeling

The adsorption data were analyzed by a regression analysis to fit the Freundlich and Langmuir isotherm models (Table 3). In overall, based on numerical values of correlation coefficients the comparison it appeared that the equilibrium data were well described

Table 3—Isotherm constants for dye removal by fly ash

Systems	Dyes	Langmuir coefficients			Freundlich coefficients		
		q_{\max} (mg/g)	b (1/min)	R^2	n	k (mg/g)	R^2
Single System	MG	100.00	0.256	0.936	2.278	23.496	0.8834
	MB	1.384	4.828	0.918	5.917	1.124	0.9714
	CV	-4.682	-0.058	0.9782	0.746	4.562	0.9827
Tertiary System	MG	1.175	3.260	0.9301	4.721	1.134	0.9434
	MB	0.891	1.237	0.9181	4.513	0.536	0.9063
	CV	-2.687	-0.009	0.9328	0.928	0.022	0.9351

by Freundlich model. Also, the value of Freundlich constant 'n' is greater than unity in most of the cases, were favorably adsorbed on FA. As expected with the kinetic studies, the maximum fixation capacity, q_{\max} was obtained at 30°C for MG to be 23.49 mg/g, for MB to be 1.12 mg/g and 4.56 mg/g for CV in single system.

A comparison of adsorption capacity for single system and multi component adsorption of MG, MB and CV has been given in Table 4. Adsorption in multi component systems is much complicated because of the solute–surface interactions and competition of dyes with each other. The effect of dye interaction¹⁷ on the sorption process may be represented by the ratio of the sorption capacity of one dye in the presence of the other dyes, Q_{mix} , to the sorption capacity of same dyes when it is present alone in the solution, Q_0 , such that for:

1. $(Q_{\text{mix}}/Q_0) > 1$ the sorption is promoted by the presence of other dyes,
2. $(Q_{\text{mix}}/Q_0) = 1$ there appears no observable net interaction,
3. $(Q_{\text{mix}}/Q_0) < 1$ the sorption is suppressed by the presence of other dyes.

The values of Q_{mix}/Q_0 are found to be <1 for all dyes (Table 4), indicated that the sorption of individual dye is suppressed by the presence of other dyes. Q_{mix} increased in the order CV < MB < MG for the adsorption of MG, MB and CV in multi component system.

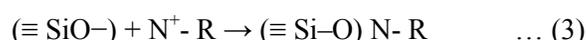
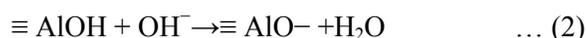
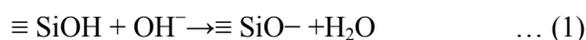
Adsorption mechanism

There were many factors that may influence the biosorption behavior, such as dye structure and size, biosorbent surface properties, steric effect and hydrogen bonding, van der Waals forces etc.¹⁸. Basic dyes used for the present study will form positively charged ions in aqueous solution. It can be

Table 4—Adsorption capacities for individual and tertiary system

Dyes	Adsorption capacity (mg/g)		Q_{mix}/Q_0
	Single system (Q_0)	Tertiary system (Q_{mix})	
MG	23.496	1.134	0.048
MB	1.124	0.536	0.476
CV	4.562	0.022	0.005

notated as +N-R. The present study was conducted at pH of 8. Under this pH, surface of FA is predominated by negative charges (Since PZC =6.7). Also SiO₂ and Al₂O₃ are presented on FA surface¹⁹. The negative charge at an active site on the surface of the FA (Eq. 1 and 2) which allows N⁺-R to be complexed at the surface as in Eq. (3) and (4)²⁰.



Desorption study

The regeneration of dye saturated FA (tertiary mixture) was carried out in batch mode and the results obtained after 2 hr of the experiment is shown in Fig. 4. From the Fig. 4, it can be observed that except NaOH, all other solvents have comparable efficiency for regenerating FA. The obtained dye concentrations after the experiments were in the order of CV > MB > MG. This is opposite to the rate of adsorption of these dyes on FA. This indicates that the bond between FA and dyes follows the order of MG > MB > CV. Because, greater the bond between adsorbent and adsorbate, lesser will be the regeneration of adsorbent.

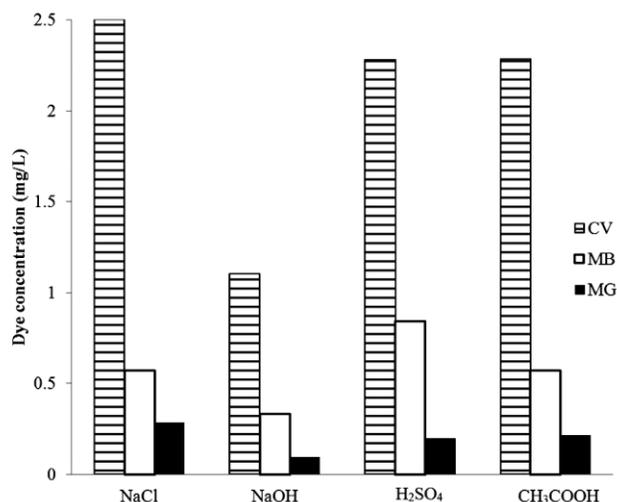


Fig. 4—Dye recovery profiles of various solvents for tertiary system

Conclusion

The present study demonstrated that FA has the ability to remove basic dyes from single and tertiary dye solution. In the single system, the optimum contact time and dose for MG removal was found to be 90 min, 0.65 g/L with the removal efficiency 99%, for MB 90 min, 8.8 g/L with 90% removal and for CV 60 min, 5.8 g/L with 66% removal. In the tertiary system, the optimum contact time and dose for MG was found to be 90 min, 13.8 g/L with the removal efficiency 99%, for MB 90 min, 13 g/L with 85% removal and for CV 60 min, 13.4 g/L with 25% removal. Pseudo 2nd order model fitted better for all system of MG and tertiary systems of MB and tertiary system of CV, all other systems pseudo 1st order model found to be the best fit. From the isotherm study, the adsorption capacity increased in the order of MB<CV<MG for single and CV<MB<MG for tertiary system. It may be concluded that the adsorption capacity of FA decreases in tertiary system as compared to single system.

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