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Abstract

Colored dye wastewater occurs as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries. About 700,000 tonnes and 10,000 different types of dyes and pigments are being produced annually across the world. The adsorption process will provide an attractive technology if the sorbent is inexpensive and ready for use. In this study, a typical basic dye, crystal violet, was selected from aqueous solutions using fly ash. The effects of initial dye concentration, stirring time, initial dye solution, pH and adsorbent amount on the efficiency of crystal violet removal have been investigated. The Langmuir, Freundlich and Temkin isotherms were obtained using concentrations of crystal violet ranging 10 to 70 mg/l. The adsorption rate data was analysed according to the the pseudo-first order kinetic, the pseudo-second order kinetic and interparticle diffusion kinetic models.

Keywords: Crystal violet, fly ash, adsorption, isotherm, kinetic

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1. Introduction

Colored dye waswater occurs as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries. The residual dyes in the wastewater of textile industries, even at very low concentrations, are common water pollutants. Therefore removal of dyes from aqueous effluents is a significant environmental issue. (Tekbaş, 2009; Küncek, 2010).

Dyeing effluents are very difficult to treat, due to their resistance to biodegradability, stability to light, heat and oxidizing agents. In general, the treatment of dye-containing effluents is undertaken by adsorption, oxidation-ozonation, biological processes, coagulation-flocculation and membrane processes. Adsorption techniques to remove dyes in solution have been widely used (Fernandez, 2007). Adsorption is an effective and useful process for the removal of dyes from effluents (Liu, 2007; Santos, 2008; El-Maghraby, 2011). The removal of dyes matters from industrial wastewaters using different adsorbents in currently of great interest. However, in order to minimize processing costs for these effluents, recent investigations have focused on the use of low-cost adsorbents. Various low-cost adsorbents were therefore investigated as an alternative to activated carbon (Grillet, 1988; Ramakrishna, 1997). Although activated carbon adsorption is highly effective at removing dyes and pigments, it is often too expensive to be used in developing countries; in such cases, the use of low-cost adsorbents, such as clay minerals, bottom and fly ash, fungi, waste materials from agriculture and elsewhere, might be more appropriate. Fly ash is a waste material originating in large quantities from modern power stations. Although it has been successfully used as a mineral admixture in concrete and brick production, there are still superfluous fly ashes in some countries, causing environmental and disposal problem. The utilization of fly ash as adsorbent for dye removal from industrial wastewater could be rewarding to both environment and economy. Thus many efforts were attempted to make fly ash a cheap adsorbent for dye removal in recent years (Hsu, 2008; Lin, 2008).

In this study, fly ash has been used as an adsorbent for the removal of crystal violet from aqueous solutions. The effects of initial dye concentration, contct time, initial dye solution pH and adsorbent amount on the efficiency of dye removal have been investigated.

2.Materials and methods

2.1. Material

The fly ash sample used for this study was obtained from Soma thermal power plant in Turkey. The chemical composition of the fly ash was evaluated by using X-ray Fluorescence techniques and the results are presented in Table 1. The total amount of SiO_2, Al_2O_3, Fe_2O_3 and CaO content is about 90%.

Table 1. Chemical composition of fly ash sample

Compounds	SiO_2	MgO	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	SO_3	LOI
Weight (%)	22.80	2.60	9.30	4.90	40.60	0.50	0.20	13.40	5.70

2.2. Reagents

A stock solution of the dye was prepared by dissolving 1.0g of dye in 1000 ml distilled water to make a stock solution of 1000 mg/l. Some properties of crystal violet was given in Table 2.

Table 2. Some properties of crystal violet

Basic Dye Properties	**Crystal Violet**
C.I. No	42555
CAS No	548-62-49
Chemical Formula	$C_{25}H_{30}ClN_3$
Molecular Weight	407.98
Melting Point	215 ^{O}C
C.I. Name	Basic Violet 3
λ_{max}	591
Molecular Structure	

2.3. Batch adsorption studies

The adsorption experiments were carried out by a batch method. Adsorption studies were conducted by placing 0.3g of fly ash in contact with 100 ml of crystal violet solution, using several different initial concentrations. Initial dye concentrations were changed in the range of 12.5-200 mg/l. The experiments to determine the optimum pH value were carried out at initial pH values ranging from 2 to 10. The solutions were stirred at 125 rpm for 1 h at room temperature. 0.3 g of fly ash was mixed with 100 ml of 50 mg/l dye solution in conical flask and agitated for 5, 15, 30, 60, 120 and 240 min at 125 rpm. The adsorbent was separated from the solution by the centrifugation at 5000 rpm at 15 min. The concentration of the dye was determined by spectrophotometer, using a UV-visible spectrophotometer at the maximum wavelength of 591 nm. The methylene blue amount in the adsorbent phase was calculated by the following formula;

$$q_t = \frac{(C_o - C_e)V}{m} \qquad (1)$$

where q_t was the amount of dye, adsorbed (mg/g) at time t, C_0 and C_e the initial and equilibrium concentrations (mg/l) of crytal violet in solution, V the volume of the solution (L), and m was the weight of the adsorbent (g). All experiments were carried out in duplicate.

3. Results and discussion

3.1. Effect of contact time on dye removal

Fig. 1 shows the effect of contact time on the removal of crytal violet by fly ash. The contact time ranges between 5-240 min. The results showed that the adsorption of crytal violet increases with time rapidly (in the first 15 min) and saturation in about 60-120 min.

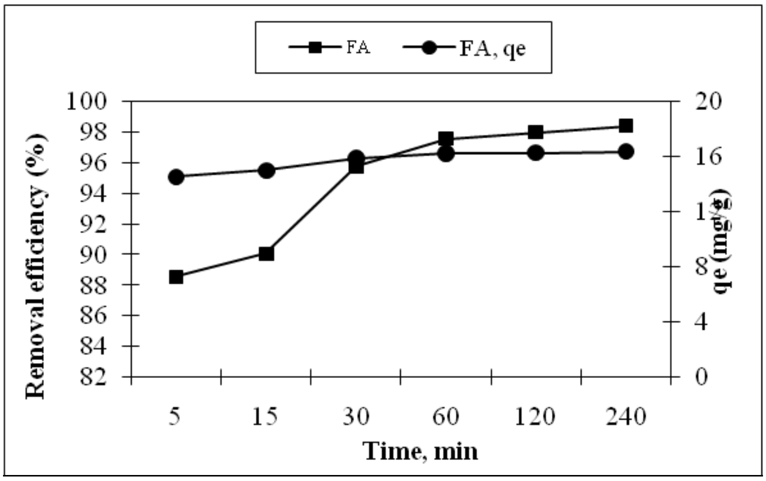

Figure 1. Effect of contact time on crystal violet adsorption (T: 25°C, C_o : 50 mg/l, dosage: 3 g/l)

3.2. Effect of fly ash amount on dye removal

Fig. 2 shows the effect of the amount of fly ash dosage on the crystal violet removal. As the fly ash amounts increased, the removal efficiencies increased. The removal efficiencies for 1 g/l of fly ash samples were found to be 83.58 %, but as the fly ash amounts were increased to 10 g/l, removal efficiencies were found to be 99,60 %. These results showed that removal efficiency increased with increasing amounts of the fly ash. The maximum adsorption capacities (*qe*) of 1.0, 2.0, 3.0, 4.0, 5.0 and 10 g/l fly ash amounts were found to be 41.79, 22.10, 16.32, 12.25, 7.60 and 4.98 mg/g, respectively. From Fig. 2, the decrease the adsorbed amount with the increase in adsorbent dosage may result from the electrostatic interactions, interference between binding sites, and reduced mixing at higher adsorbent densities. Also, the reason for decrease in the sorption capacity was due to the increasing interface area when the suspension was dilute.

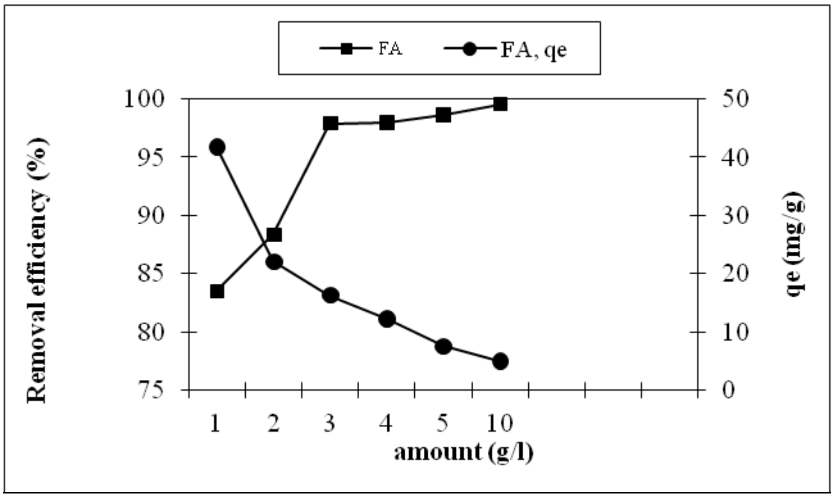

Figure 2. Effect of fly ash amount on crystal violet adsorption (T: 25^{o}C, C_o : 50 mg/l, time: 1 h)

3.3. Effect of initial concentration on dye removal

The effect of initial crystal violet concentration in the range of 12.5- 200 mg/l on the adsorption was investigated under the specified conditions. Fig. 3 shows the adsorption of crystal violet on fly ash as an initial dye concentration. As it can be seen from Fig. 3, increasing the dye concentration led to an increase in the crytal violet adsorption by fly ash.

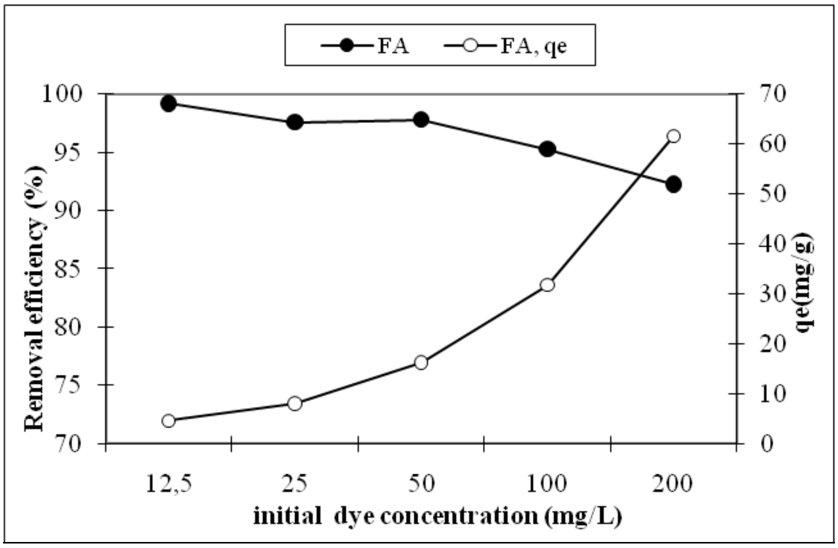

Figure 3. Effect of initial concentration on crytal violet adsorption (T: 25^{o}C, dosage: 3 g/l)

3.4. Effect of pH

The pH of the aqueous solutions is an important variable and controls the adsorption between the adsorbent and aqueous interface. The adsorption extent of dyes is strongly affected by the pH of solution (Wang, 2005; Fernandes, 2007). In order to determine the pH effect on adsorption capacity of materials, solutions were prepared at different pH levels ranging from 3 to 9. The effect of pH on dye removal by different fly ash is illustrated in Fig.4. As can be seen from Fig. 5, adsorption of crystal violet ions by fly ash remained almost unchanged when the initial pH of the solution was increased from 3 to 7. Above pH 7, removal efficiency had a tendency to increase and reached the highest value at above pH 9. The removal efficiencies for 3, 5, 7 and 9 of pH values were found to be 87.2, 88.0, 90.04, and 98.20 %, respectively. The amount of dye sorbed fly ash were almost 14-15 mg/g for 3,5,7 and 9 for pH values.

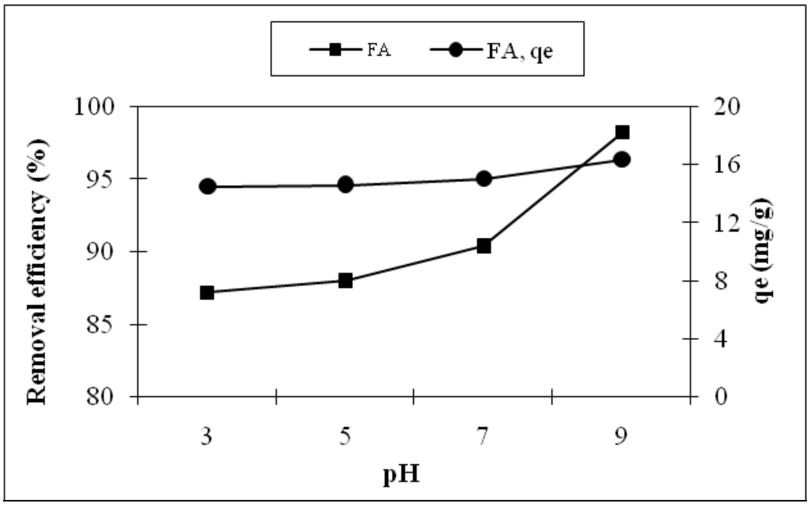

Figure 4. Effect of pH on cyrstal violet adsorption on fly ash (T: 25^{o}C, C_o : 50 mg/l, dosage : 3g/l)

3.5. Adsorption isotherms models

The effect of concentration on sorption was applied to different isotherm models to find a suitable model to instruct the further experimental design. Several isotherm equations are available. In this research, in order to determine the mechanism of crystal violet adsorption on fly ash the experimental data was applied to the Langmuir and Freundlich isotherm equations (Li, 2006; Özdemir, 2006; Lin, 2008).

The Langmuir sorption isotherm is the best known of all isotherms describing sorption and it has been successfully applied to many sorption processes. Thus, the Langmuir isotherm model is given by equation (Alvarez-Ayuso, 2003; Hui, 2005);

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (2)$$

where q_e is the equilibrium adsorbed (mg/g), C_e is the equilibrium liquid-phase concentration (mg/l), q_m and K_L are the Langmuir constants related to sorption capacity and sorption energy, respectively. The values of q_m (mg/g) and K_L (mg^{-1}) can be determined from the linear plot of C_e/q_e versus C_e.

The Freundlich isotherm is an empirical model that is based on adsorption on heterogeneous surface; it is given in Eq. (3),

$$\log q_e = \log K + (1/n)\log C_e \qquad (3)$$

where q_e the amount of metal ions adsorbed per gram of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration in mg/L, K is roughly an indicator of the adsorption capacity (mg/g), $1/n$ is a characteristic constant for the adsorption system (l/g) (Erdem, 2004; Ponnusami, 2008).

The parameters for the Langmuir and Freundlich isotherms obtained from experimental data and the related correlation coefficients are given in Table 3. The data obtained was well fitted with the Freundlich equation as compared to Langmuir equations under the different concentrations studied. The values R^2 are calculated to be 0.9388 and 0.9761 for Langmuir and Freundlich and isotherms, respectively. This suggests that some heterogeneity in the surface or pores of the fly ash will play a role in dye adsorption.

Table 3. Isotherm parameters for the crystal violet adsorption on fly ash

	Langmuir			Freundlich isotherm		
	q_m(mg/g)	K_L(l/mg)	R^2	K	$1/n$ (g/l)	R^2
Fly ash	74.62	0.256	0.9388	13.92	0.524	0.9761

3.6. Adsorption kinetics

Several kinetics models are used to examine the controlling mechanism on the adsorption process such as chemical reaction, mass transfer, and diffusion control. The rate constant of crystal violet removal from the solution was determined using pseudo-second-order, and Elovich rate models, applying those models given in literature (Önal, 2005; Sener, 2005; Zhao, 2008). Pseudo second-order kinetics may be expressed as the following equation;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_e and q_t are the amounts of the heavy metal (mg/g) adsorbed at equilibrium (mg/g), and k_2 (g/mg min.) is the rate constant of the second-order kinetic equations. The second-order kinetic rate constants k_2 and correlation coefficients are presented in Table 3.

The Elovich equation is often valid for systems in which the adsorbing surface is heterogeneous. The rate parameter for the Elovich equation is determined as (Cheung, 2000; Han, 2009):

$$q_t = \beta \ln(\alpha) + \beta \ln t \quad (5)$$

where α ($mgg^{-1}min^{-1}$) and β (gmg^{-1}) are the equilibrium rate constants for Elovich model. The equation constants can be obtained from the slope and intercept of a straight-line plot of q_t against *ln t*. The values of kinetic constants are presented in Table 4. The correlation coefficients for the Pseudo-second-oreder and Elovich models are 0.9985 and 0.8917, respectively.

Table 4. The kinetic constants for the removal of crystal violet by fly ash

	Pseudo-second-order			Elovich		
	q_e (mg/g)	k_2 (g/mg min)	R^2	α (mg/g min)	β (g/mg)	R^2
Fly ash	17.66	0.015	0.9985	$3.7.10^4$	0.519	0.8917

4. Conclusion

The aim of this study was to investigate the potential use of fly ash as a sorbent for removal of crystal violet. The adsorption process is a function of the contact time, adsorbent amount, pH and metal ion concentration. The results show that fly ash was effective in removing crystal violet from aqueous solution. The maximum adsorption capacitiy of fly ash was found to be 74.62 mg/g. The experimental data were well fitted to the Freundlich equation, with good correlation coefficients. The adsorption kinetics of crystal violet ions on fly ash well describe by pseudo second-order model. These results showed that fly ash can be used effectively as an adsorbent material for the removal of crystal violet ions from aqueous solutions and wastewaters.

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