

Adsorption of anionic dyes from aqueous solution on fly ash

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ABSTRACT

The adsorption behavior of two reactive dyes (Reactive Red 23 and Reactive Blue 171) and two acid dyes (Acid Black 1 and Acid Blue 193) from aqueous solution on fly ash was investigated in order to identify the ability of this waste-material to remove colored textile dyes from wastewater. For this purpose a series of batch tests were carried out as a function of solution pH value, contact time, dye concentration and adsorption temperature. The experimental findings showed that the removal of four dyes on fly ash was a pH-dependent process with the maximum adsorption capacity at the initial solution pH of 7.5–8.5 for reactive dyes and 5–6 for acid dyes. Adsorption equilibria of each anionic dye on fly ash could be reached within 60 min at respective optimum pH at 293 K. An increase in the initial dye concentration enhanced the adsorption capacity, but failed to increase the dye removal efficiency. The adsorption capacity for Reactive Red 23, Reactive Blue 171, Acid Blue 193 and Acid Black 1 was found to be 2.102, 1.860, 10.937 and 10.331 mg g⁻¹, respectively. Kinetic studies of four dyes followed the pseudo-second-order model. Freundlich isotherm described the equilibrium data of acid dyes on fly ash better than Langmuir isotherm, but Langmuir isotherm showed better fit to the equilibrium data of reactive dyes. Different thermodynamic parameters such as the free energy, enthalpy and entropy of adsorption of the dye–fly ash systems were evaluated and it was found that the reaction was spontaneous and endothermic in nature.

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1. Introduction

Synthetic dyes have been increasingly used in textile industries, dye manufacturing industries, paper and pulp mills, tanneries, electroplating factories, food companies, etc. It is reported that approximately 100 tons of dyes are discharged into waste streams by the textile industry per year [1]. Dyes are considered an objectionable type of pollutant on aquatic environment because they give an un-desirable color to the water [2] and reduce light penetration and photosynthesis [3–5]. Most dyes are considered to be non-oxidizable substances by traditional biological and physical treatment [6]. As a result, the conventional techniques of wastewater treatment on the basis of biological oxygen demand removal are largely ineffective in removing colored textile dyes from effluent. Adsorption process is an attractive and effective alternative treatment for dye removal from wastewater, especially if the adsorbent is cheap and readily available. In the past years, numerous investigations have been reported using industrial or agricultural wastes

as adsorbents and the data show that these wastes exhibit more or less adsorption capacity. These include fly ash [7–10], bottom ash [11,12], zeolite [13], rice hull [4], peanut hull [14] and orange peel [15].

Fly ash (FA) is a by-product produced during the combustion of coal in the electricity generation process. Although fly ash has also been used effectively for building materials, soil amendment and fillers, it is unlikely that these applications will result in the reuse of all the fly ash generated. Great efforts are therefore being made to explore other applications prior to disposal. Recently, Ahmaruzzaman [16] has reviewed the utilization of fly ash. Since fly ash is enriched with SiO₂ and contains a portion of unburned carbon, this waste possesses the potentiality of a low-cost adsorbent to remove various hazardous materials from wastewater [7–10,17–20]. Although several investigations have been reported on fly ash for removal of textile dyes, more information is still needed for better understanding of the adsorption behavior of different water-soluble anionic dyes on fly ash. In this work, the removal of two reactive dyes and two acid dyes from aqueous solutions were investigated using a porous fly ash. Adsorption isotherms for the anionic dyes were undertaken to study the effects of initial solution pH, adsorption time, initial dye concentration and adsorption temperature.

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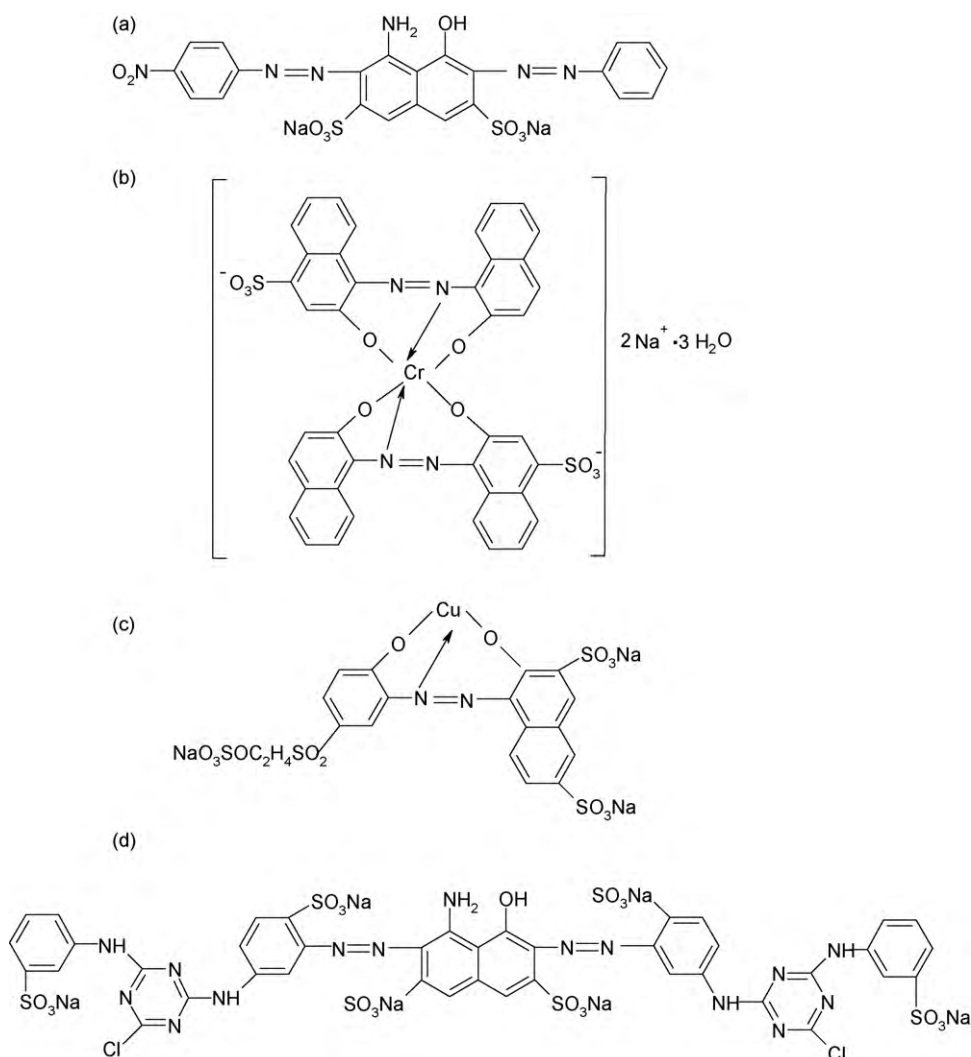


Fig. 1. Chemical structure of the anionic dyes. Acid Black 1 (a), Acid Blue193 (b), Reactive Red 23 (c) and Reactive Blue 171 (d).

2. Experiments

2.1. Adsorbents and characterization

Raw coal fly ash used in this study was provided by a full-scale power-plant in China. This material, which was collected at the electrostatic precipitator, mainly contained SiO₂ (47.2%), Al₂O₃ (24.8%), Fe₂O₃ (15.9%) and CaO (4.9%) (obtained from the plant). The loss of ignition (LOI) was measured by a standard combustion method. About 0.5 g samples were dried in an oven at 378 K for 24 h and further subjected to a furnace at 1073 K for 4 h. The difference of weight before and after combustion was used to calculate LOI, which was 3.81%.

Raw fly ash dried at 378 K overnight was separated by manually shaking stainless steel mesh screens with the opening of standard 160 μm. Fly ash particles less than 160 μm were pretreated in a furnace at 623 K for 30 min, and kept in a desiccator for further study.

The surface area and total pore volume of the FA were measured through N₂ adsorption at 77 K using a TRISTAR-3000 surface area and porosity analyzer (Micromeritics). Surface morphology of the adsorbent samples was characterized by a SM-6700F field emission scanning electron microscope (JEOL). The slurry pH of fly ashes was measured by a PHS-3C pH meter (Shanghai Precision & Scientific

Instrument Co. LTD.). pH of zero charge (pH_{pzc}) of the samples was determined using pH drift method [21].

2.2. Adsorbates

The adsorbates in this study were four anionic dyes, Acid Black 1 (AB1), Acid Blue193 (AB193), Reactive Red 23 (RR23) and Reactive Blue 171 (RB171), which were obtained from a textile company. Their structures were displayed in Fig. 1. The other chemicals of analytical purity grade were purchased from Sinopharm Chemical Regent Co., Ltd. and used without any further purification. The synthetic wastewaters were prepared by dissolving dyestuffs in de-ionized water to produce a stock solution of 1 g l⁻¹. For batch study, aqueous solutions of these dyes were prepared from stock solutions in de-ionized water. The UV-visible spectrum of each dye solution was previously determined and identified the maximum absorption wavelength (λ_{max}). K_a values of anionic dyes were determined according to a standard procedure [22].

2.3. Adsorption study

Batch experiments were carried out to measure the adsorption characteristics of anionic dyes on FA. Prior to their use, the adsorbents were oven-dried at 378 K for 2 h to eliminate traces of

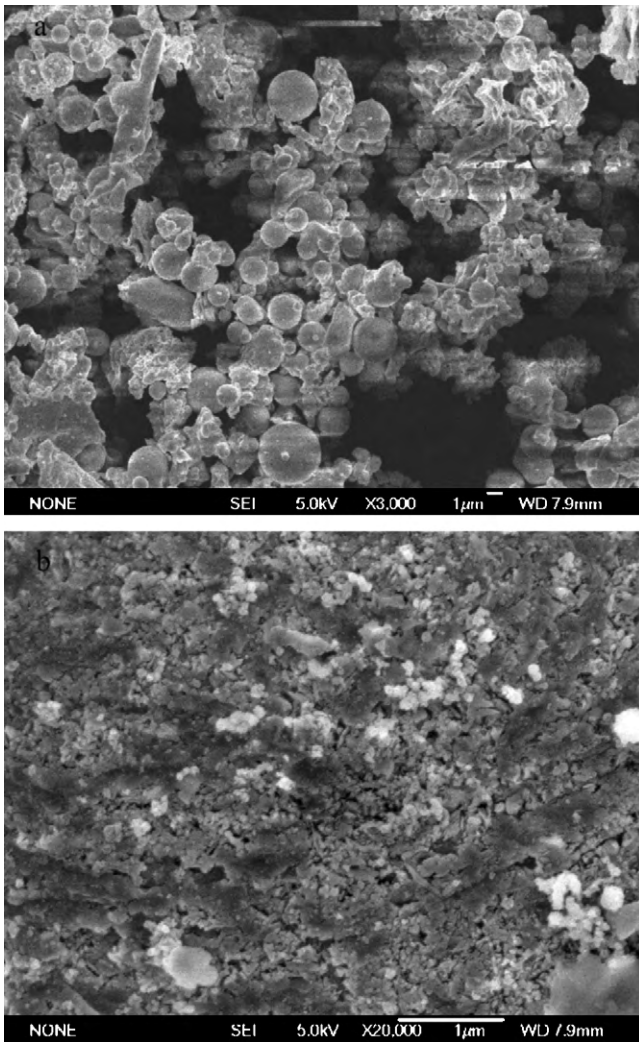


Fig. 2. SEM images of FA.

moisture. A predetermined amount of the fly ash sample was added to 50 ml of dye solution of varying concentration ($30\text{--}500\text{ mg l}^{-1}$). The mixture was stirred with mechanical agitator (150 rpm) for various times to determine the equilibrium time at 293 K. After stirring, the suspensions were separated by filtering. The residual concentration of dye solution was determined using a calibration curve prepared at the corresponding maximum wavelength using a UV-2102PC UV–visible spectrometer (Unicol Instrument Co., Ltd.). The effect of solution pH on dye removal was investigated similarly as described above by changing the initial pH (2–12) adjusting by dilute HCl or NaOH. For thermodynamic studies, the adsorption procedure of the anionic dyes was repeated at 313 K. Lagergren first-order and pseudo-second-order kinetic models were used to examine the controlling mechanism. Langmuir and Freundlich isotherm were applied to evaluate the adsorption capacity. All adsorption data reported in this paper were the average values of three runs.

3. Results and discussions

3.1. Character of dyes and fly ash

Microstructure of FA played an important role on the adsorption capacity. Fig. 2 showed the SEM images of the fly ash samples. As illustrated in Fig. 2a, the FA mainly constituted of compact or

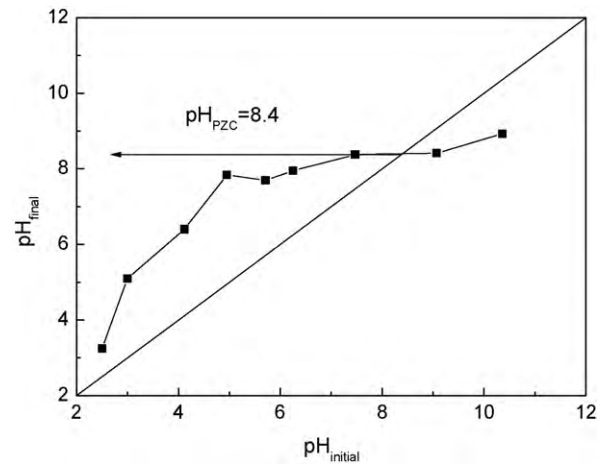


Fig. 3. Determination of pH_{pzc} of FA.

hollowed spheres of different size and some unshaped fragments ascribed to unburned carbon. It might also be seen in the micrograph where some of the smaller size particles were adhered on bigger size particles. Fig. 2b illustrated a number of pores on the surface of the FA, revealing the potential adsorption power. The specific surface area and pore volume of the FA obtained from the N_2 equilibrium adsorption isotherms were found to be $9.84\text{ m}^2\text{ g}^{-1}$ and $0.023\text{ cm}^3\text{ g}^{-1}$, respectively. pH_{pzc} of FA was influenced by the chemical composition, mainly composed of SiO_2 , Al_2O_3 and Fe_2O_3 . The pH_{pzc} of SiO_2 , $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ was 2, 9.1 and 6.7, respectively [10]. At $\text{pH} < \text{pH}_{\text{pzc}}$, the surface of FA had a net positive charge, while at $\text{pH} > \text{pH}_{\text{pzc}}$ the surface had a net negative charge. Fig. 3 depicted the results of “pH drift” experiment, from which the pH_{pzc} of FA studied in this test was found to be 8.4.

Anionic dyes presented various acid–base properties in solution, which could be described by acidity constants (K_a), which was analyzed by the alkali–metric titration method using suitable acid or base solution. The $\text{p}K_a$ values of anionic dyes were calculated by plotting the buffer intensity of dye versus the equilibrium pH. Fig. 4 illustrated the variation in buffer intensity of RB 171 against pH. Result revealed that dye solution had peak buffer intensity at pH 5.7. Similar curves were observed for the other anionic dyes (plot not shown). Table 1 summarized the characterization of these dyes including $\text{p}K_a$ values.

3.2. Effect of solution pH

Solution pH had a significant effect on the uptake of dyes, since it determines the surface charge of the adsorbent and the degree of

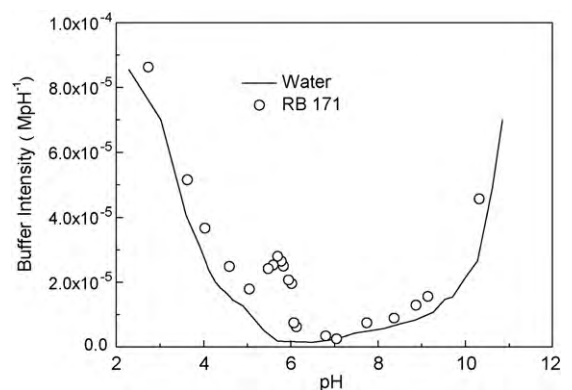


Fig. 4. Buffer intensity curve for Reactive Blue 171.

Table 1
Characterization of anionic dyes.

Name	Molecular weight	λ_{\max} (nm)	Number of ionizable group	Percent of ionizable group	pH _{pzc}
AB1	616	614	2	26.0	4.9
AB193	900	592	2	17.8	5.8
RR23	740	532	2	21.6	5.7
RB171	1388	602	6	4.5	6.3

ionization and speciation of the adsorbate. Moreover, the hydrogen ion and hydroxyl ion were adsorbed strongly and subsequently the adsorptions of other ions were affected. Fig. 5 presented the relationship between the initial solution pH and dye removal. It was clear that the removal percentages of RR23 and RB171 were maximum at basic pH (pH 7.5–8.5), and decreased with further increase or reduction in pH. Similar optimal pH rang that maximized the removal efficiency of reactive dye was reported in documents [2,10]. As comparison, removal efficiencies of both acid dyes were maximum at initial pH of 5–6 and decreased above and below this pH. Further experiments were carried out at the optimum pH of 5–6 and 7.5–8.5 for acid dyes and reactive dyes, respectively.

Generally, pH effect on the adsorption was explained by electrostatic interaction between FA and dye molecules. In the pH range of 7.5–8.5, the surface of FA was positively charged (pH_{pzc} = 8.4) and reactive dyes were negatively charged (pK_a = 5–7), revealing the strong electrostatic attraction. At acidic pH, the sulphonate groups of reactive dyes were almost protonated (SO₃H, i.e., neutral). Furthermore, the protonation of nitrogen atoms especially those not involved in aromatic systems was also probable [2]. All this may result in reactive dye molecules that were natural or positive charged, which reduced sharply the attraction between reactive dye and FA. The low dye removal at highly basic solution could be due to the repulsion interaction between negatively charged FA and deprotonated reactive dye molecules. Also, there was competition between OH⁻ (at high pH) and dye ions for positively charged adsorption sites.

According to the electrostatic mechanism, the theoretical maximum removal percentages of acid dyes should appear in range pH 6–8, while the experimental value was in pH range of 5–6. This phenomenon suggested that the electrostatic interaction was not the sole mechanism of adsorption. In fact, the spatial structures of dye molecular may influence this adsorption process, which is needed to be studied further.

3.3. Effect of contact time

The effect of contact time for the adsorption of acid dyes and reactive dyes on FA was studied for a period of 6 h for initial dye concentration of 100 mg l⁻¹ at respective optimum pH, as depicted in Fig. 6a. The adsorption of anionic dyes was quite rapid in the first 20 min, then gradually increased with the prolongation of contact time. After 60 min of contact, no obvious variation in dye adsorbed was examined. Based on these results, 60 min was taken as the equilibrium time in batch adsorption experiments. It was also found from Fig. 6a that the adsorption amount of acid dyes was much higher than that of reactive dyes at any contact time. At equilibrium, the adsorption capacity of each acid dye exceeded 10 mg g⁻¹, while the maximum adsorbed amount of each reactive dye was less than 3 mg g⁻¹.

3.4. Effect of initial dye concentration

The adsorption experiments were carried out in initial dye concentration range of 30–500 mg l⁻¹. Fig. 7 showed the effect of the initial concentration on the removal efficiency and adsorption capacity. It was observed that dye removal efficiency for all

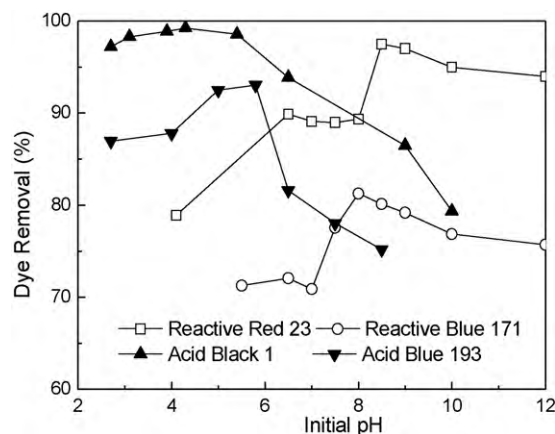


Fig. 5. Effect of initial solution pH on dye removal. Experiment condition: initial dye concentration 100 mg l⁻¹, fly ash dose 0.4 g/40 ml for acid dye and 2.0 g/40 ml for reactive dye, contact time 6 h.

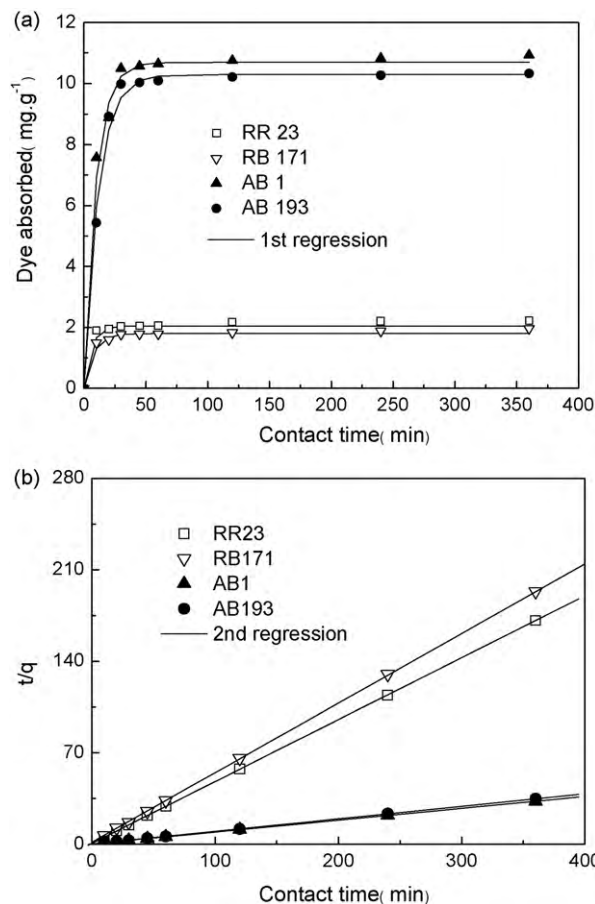


Fig. 6. Lagergren first-order (a) and pseudo-second-order (b) kinetics of dyes onto FA. Experiment condition: initial dye concentration 100 mg l⁻¹, fly ash dose 0.4 g/40 ml for acid dye and 2.0 g/40 ml for reactive dye.

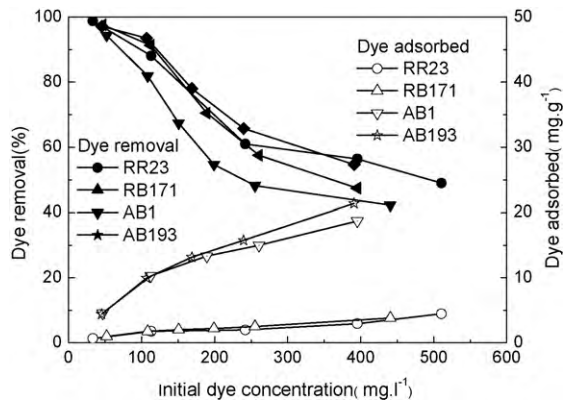


Fig. 7. Effect of initial dye concentration on dye removal and dye adsorption capacity by FA. Experiment condition: contact time 60 min, fly ash dose 0.4 g/40 ml for acid dye and 2.0 g/40 ml for reactive dye.

dyes reached up to 95% at lower concentration, then decreased to less than 55% at higher concentration. Dye removal efficiency was higher for low initial concentration because of availability of unoccupied binding sites on the adsorbents. Percent color removal decreased with increasing dye concentration because of nearly complete coverage of the binding sites at high dye concentration.

In contrast, the amount of dye adsorbed was found to increase with increasing initial concentration of dyes. When the dye concentration was increased, acid dye adsorption capacities rapidly increased from 4.46 to 18.73 mg g^{-1} for AB1 and from 4.40 to 21.37 mg g^{-1} for AB 193. In the case of reactive dyes, the dye uptake was slow and gradually increased to the maximum adsorption values of 4.45 and 3.82 mg g^{-1} for RR23 and RB171, respectively. The effect of initial dye concentration on dye adsorption could be attributed to the increase in the driving force of the concentration gradient with an increase in the initial dye concentration [23].

3.5. Adsorption dynamic

Both the first and the second-order rate equations were used to determine the most suitable rate expression for adsorption of the tested dyes on FA. The optimal modal was considered based on two indicators: correlation coefficient (r^2) and root mean square error (RMSE). The correlation coefficient was frequently used to decide whether the model represents correctly the experimental data. RMSE was defined as:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^N (q_{\text{exp}} - q_{\text{cal}})^2}{N}} \quad (1)$$

Table 2

Comparison of the first and second-order adsorption rate constants, and calculated q_{cal} and experimental q_{exp} value at initial dye concentration of 100 mg l^{-1} .

		AB1	AB193	RR23	RB171
First-order kinetic modal	q_{exp} (mg g^{-1})	10.331	10.937	2.102	1.860
	q_{cal} (mg g^{-1})	10.937	10.722	2.047	1.800
	k_1 (min^{-1})	0.075	0.104	0.168	0.131
	r^2	0.972	0.972	0.980	0.974
	RMSE	0.838	0.434	0.019	0.048
Second-order kinetic modal	q_{cal} (mg g^{-1})	10.417	11.013	2.110	1.871
	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.027	0.029	0.344	0.202
	r^2	0.999	0.999	0.999	0.999
	RMSE	0.293	0.306	0.090	0.079

where q_{exp} and q_{cal} are the experimentally measured and the modal prediction for the amount of dyes adsorbed, respectively. Smaller RMSE represents that the equation can predict the experiment results more accurately.

The Lagergren first-order model was given by the Eq. (2) [10].

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (2)$$

where q (mg g^{-1}) is the amount of material adsorbed at time t , q_e (mg g^{-1}) is the adsorption capacity at equilibrium, k_1 (min^{-1}) represents the rate constant of the first-order model. For this rate equation, it is better to apply the following equation to avoid the unknown q_e .

$$q = q_e(1 - \exp(-k_1 t)) \quad (3)$$

The pseudo-second-order [8] equation was defined as follows:

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

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of the second-order model.

Batch dynamic parameters were obtained using linear or non-linear regression analysis (MATLAB 7.5). The single-component experiment data and modal prediction were plotted in Fig. 6. Table 2 showed the adsorption parameters and the two indicators using each of the modal. The performances of kinetic models tested were comparable based on the correlation coefficients and RMSEs for each dye. For the four anionic dyes, r^2 ($r^2 < 0.99$) for the first rate modal were observed to be relatively lower than those values for the pseudo-second-order kinetics. Also higher RMSE values for acid dyes and similar RMSE values for reactive dyes were obtained with the first-order kinetics. These results suggested that pseudo-second-order modal was applicable to the adsorption kinetics. Based on the pseudo-second-order model, these observations indicated that the rate of dye adsorption process was controlled by the chemisorption process, which depended on the chemical character of FA and dyes [10,22].

Similar kinetic results were also found in the adsorption of Reactive Black 5 and Reactive Yellow 176 on biomass fly ash [10], in the sorption of Acid Red 1 on fly ash [8] and in the adsorption of Reactive Black 5 on high lime coal fly ash [24]. While Khare et al. [25] found that the process of Victoria Blue adsorption on fly ash followed the first-order adsorption rate expression. Azizian [26] explored the kinetics of adsorption from a solution onto an adsorbent theoretically, and found that the adsorption process obeyed first-order kinetics at high initial concentration of solution while it obeyed pseudo-second-order kinetics at lower initial concentration of solution.

3.6. Adsorption isotherm

For solid-liquid system, adsorption isotherm is important in description of adsorption behavior. In this work, two well-known models of Langmuir and Freundlich isotherm would be evaluated.

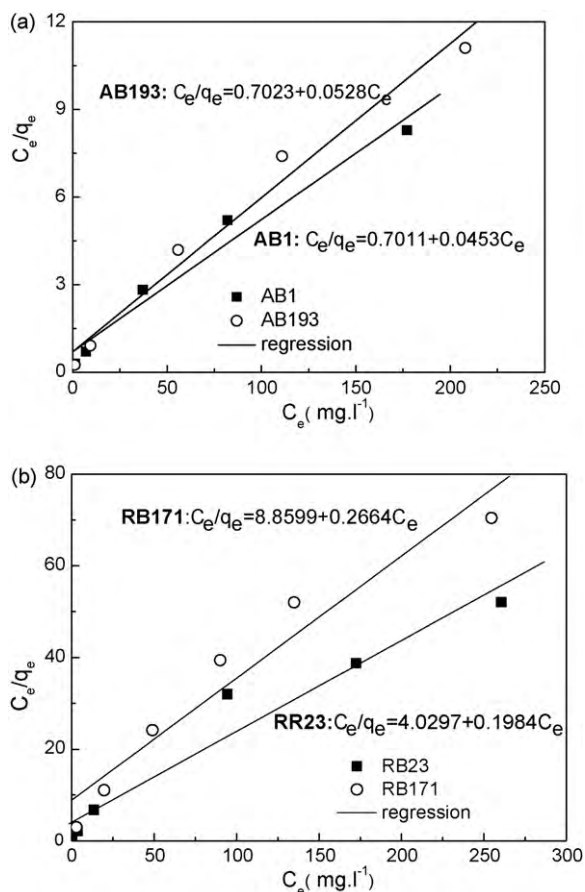


Fig. 8. Langmuir isotherm of acid dyes (a) and reactive dyes (b) onto FA. Experiment condition: initial dye concentration range, 30–500 mg l⁻¹, contact time 60 min, fly ash dose 0.4 g/40 ml for acid dye and 2.0 g/40 ml for reactive dye.

As depicted above, correlation coefficient (r^2) and root mean square error (RMSE) were calculated to evaluate the fit of the two models.

3.6.1. Langmuir isotherm

The Langmuir isotherm assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface. This model is the most widely used two-parameter equation, generally expressed in the form by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \quad (5)$$

where q_e (mg g⁻¹) and C_e (mg l⁻¹) are defined as the amount of dye adsorbed per unit weight of adsorbent and equilibrium liquid-phase concentration, respectively. Q_0 (mg g⁻¹) is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity. K_L (l mg⁻¹) is a direct measure of the intensity of the sorption. C_e/q_e was plotted against C_e using linear regression analysis (MATLAB 7.5), as shown in Fig. 8. The constants Q_0 and K_L were determined from the intercept and slope of the linear plots, respectively. As shown in Table 3, the Q_0 from the Langmuir isotherm were 18.393 and 22.075 mg g⁻¹ for AB1 and AB193, respectively, while the maximum values were only 5.042 and 3.754 mg g⁻¹ for RR23 and RB 171, respectively. By comparing the values of K_L it could be concluded that adsorptions of acid dyes ($K_L = 0.0751$ and 0.0646 l mg⁻¹) were more favorable than that of reactive dyes ($K_L = 0.0492$ and 0.0301 l mg⁻¹).

The essential characteristic of Langmuir equation can be expressed in terms of a dimensionless separation factor R_L [10],

Table 3
Isotherm constant for the Langmuir and Freundlich isotherm.

		AB1	AB193	RR23	RB171
Langmuir	Q_0 (mg g ⁻¹)	18.939	22.075	5.041	3.754
	K_L (l mg ⁻¹)	0.0751	0.0646	0.0492	0.0301
	r^2	0.987	0.985	0.975	0.970
	RMSE	2.525	2.196	0.310	0.305
Freundlich	K_f (mg g ⁻¹)	1.989	1.936	0.980	0.879
	n	3.952	3.367	3.454	3.806
	r^2	0.998	0.983	0.980	0.977
	RMSE	1.736	1.756	1.138	1.072

which is defined as

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

where C_0 (mg l⁻¹) is the initial dye concentration. R_L indicates the nature of the adsorption process. The calculated R_L values of acid dyes and reactive dyes were found to be between 0.03 to 0.25 and 0.07 to 0.39 for dye concentrations of 30–500 mg l⁻¹, respectively (data not shown). The magnitude of the R_L values, i.e., $0 < R_L < 1$, indicated the favorable adsorption of each of the dyes under consideration.

A comparison of the maximum adsorption capacity, Q_0 , for anionic dyes on various FA was presented in Table 4. The Q_0 of acid dyes obtained from this study was similar to that obtained in the other investigations, while the values of reactive dyes were relatively low compared to other studies. Despite relatively low adsorption capacity of the studied fly ash, the use of this adsorbent for dye removal is of interest since it is low-cost and readily available waste.

3.6.2. Freundlich isotherm

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is linearized as follows:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (7)$$

where K_f (mg g⁻¹) and n are Freundlich constants. K_f can be defined as an adsorption or distribution coefficient and represents the amount of adsorbate adsorbed on an adsorbent for a unit equilibrium concentration. The slope $1/n$ is a measure of the adsorption intensity or surface heterogeneity. Fig. 9 presented the Freundlich isotherm plots for anionic dye adsorption on FA. The model parameters calculated from linear plots and correlation coefficients were shown in Table 3. The n values were in range of 3–4 for all anionic dyes, revealing the favorable adsorption.

Applicability of these isotherm equations was compared by r^2 and RMSE values. The correlation coefficients for the Freundlich model and the Langmuir model were much similar for both acid dyes and reactive dyes. However, relatively lower errors (RMSE = 1.736 and 1.756) were obtained with Freundlich model compared to Langmuir isotherms used for the two acid dyes. On the contrary, the Langmuir had the lowest values of RMSE (RMSE = 0.310 and 0.305) for reactive dyes.

3.7. Thermodynamic studies

The adsorption of four anionic dyes on the FA was studied at 293 and 313 K to determine the thermodynamic parameters, and the results were shown in Fig. 10. It was found that the adsorption capacity of four dyes increased at higher temperatures. For the acid dyes, the adsorption capacities exceeded 35 mg g⁻¹, and the values were 7.74 and 5.64 mg g⁻¹ for RR23 and RB171. This increase in adsorption could be attributed to the enlargement of the pore sizes

Table 4
Comparison of dye adsorption on fly ash.

Dye	Fly ash type	Temperature (K)	Q ₀ (mg g ⁻¹)	References
Acid red 1	Coal FA	303	92.59	[9]
Acid red 1	Coal FA-NaOH	303	12.66	[9]
Acid red 91	FA	–	1.46	[20]
Acid Blue 9	FA	–	4.31	[20]
Acid Blue193	FA	293	22.08	This work
Acid Black 1	FA	293	18.94	This work
Reactive Black 5	FA (high lime)	–	7.94	[24]
Reactive Red 198	Coal FA	293	47.26	[18]
Reactive Red 23	FA	293	5.04	This work
Reactive Yellow 84	Coal FA	293	37.26	[18]
Reactive Blue 171	FA	293	3.75	This work
Reactive Blue 19	Coal FA	293	133.69	[18]

of adsorbent particles at elevated temperatures [18]. Similar results were also observed by other researchers for the adsorption of dyes on FA [3,9,18].

The thermodynamic parameters, i.e., free energy (ΔG^0), enthalpy (ΔH^0); and entropy (ΔS^0), were calculated using the following equations:

$$\Delta G^0 = -RT \ln(K) \tag{8}$$

$$\Delta H^0 = -R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \frac{K_2}{K_1} \tag{9}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{10}$$

where K (l mg⁻¹), R (J mol⁻¹ K⁻¹) and T (K) are the equilibrium constant of the adsorption process, gas constant and absolute temperature, respectively. The thermodynamic parameters for the adsorption of anionic dyes on FA were at various temperatures summarized in Table 5. The negative values of ΔG^0 at 293 and 313K indicated the favorable and spontaneous adsorption process of anionic dyes on FA. The positive values of ΔH^0 for each dye suggested that the process is endothermic in nature. The positive values of ΔS^0 revealed the increased randomness at the solid/solution interface during the adsorption of dyes in aqueous solution on FA.

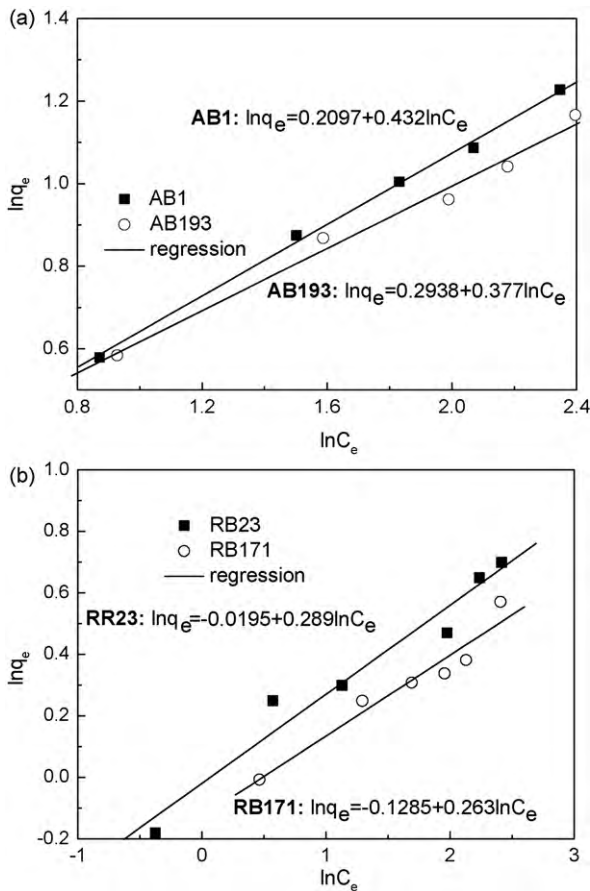


Fig. 9. Freundlich isotherm of acid dyes (a) and reactive dyes (b) onto FA. Experiment condition: initial dye concentration range, 30–500 mg l⁻¹, contact time 60 min, fly ash dose 0.4 g/40 ml for acid dye and 2.0 g/40 ml for reactive dye.

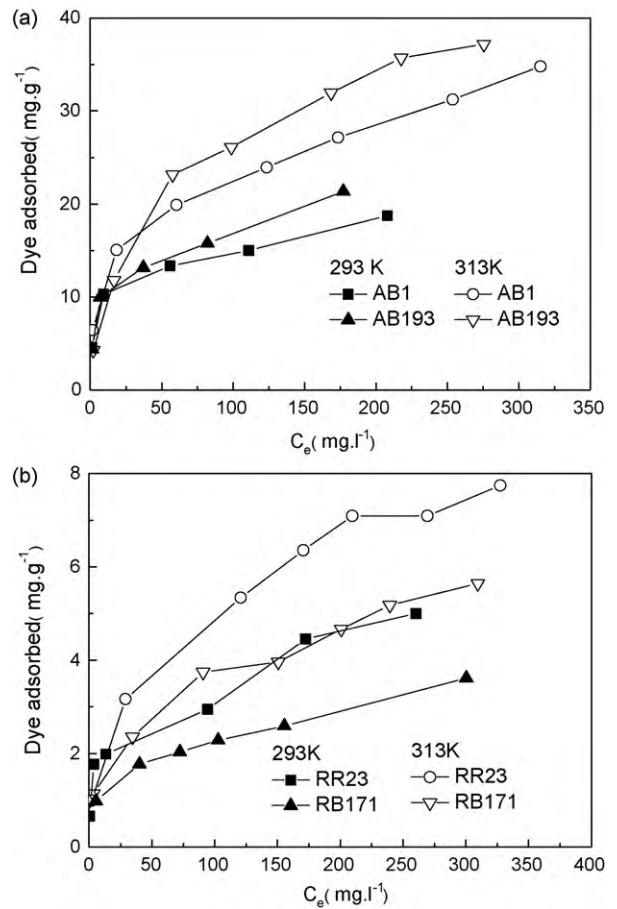


Fig. 10. Effect of temperature on adsorption of acid dyes (a) and reactive dyes (b) onto FA. Experiment condition: initial dye concentration range, 30–500 mg l⁻¹, contact time 60 min, fly ash dose 0.4 g/40 ml for acid dye and 2.0 g/40 ml for reactive dye.

Table 5
Thermodynamic parameters for the adsorption of anionic dyes on fly ash.

Dye	$-\Delta G^0$ (kJ mol ⁻¹)		ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)
	293 K	313 K		
AB1	26.2	25.4	35.7	195.7
AB193	26.6	26.9	23.6	161.4
RR23	25.6	25.4	27.1	179.6
RB171	25.6	26.7	13.7	129.3

4. Conclusions

Fly ash was investigated for the removal of RR23, RB171, AB1 and AB193 from aqueous solutions. The following conclusions could be derived from the present study.

1. Adsorption of four anionic dyes on the fly ash was found to be dependent on the initial pH of solution. The optimal pH of reactive dyes was in range of 7.5–8.5, while the optimum values of acid dyes were in range of 5–6. Adsorption equilibriums were reached within 60 min for all anionic dyes used in this test. An increase in the initial dye concentration enhanced the adsorption capacity, but decreased the dye removal efficiency.
2. Adsorption processes for the four anionic dyes were found to follow the pseudo-second-order kinetics rate expression. Freundlich isotherm described the equilibrium data of acid dyes on FA better than Langmuir isotherm, while Langmuir isotherm fitted better to the equilibrium data of reactive dyes. The values of Langmuir and Freundlich constants were found to be 18.939 and 0.989 mg g⁻¹ for AB1, 22.075 and 1.936 mg g⁻¹ for AB193, 5.041 and 0.980 mg g⁻¹ for RR23, and 3.754 and 0.879 mg g⁻¹ for RB171, respectively. Thermodynamic parameters were calculated and indicated that each of these adsorption processes was spontaneous and endothermic in nature.

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