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Adsorption removal of reactive dyes from aqueous solution by modified basic oxygen furnace slag: Isotherm and kinetic study

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ABSTRACT

The utilization of treated basic oxygen furnace slag (BOF slag) was successfully carried out to remove three synthetic textile dyes (Reactive Blue 19 (RB19), Reactive Black 5 (RB5) and Reactive Red 120 (RR120)) by adsorption from aqueous solutions. Batch studies were carried out to address various experimental parameters such as pH, contact time, temperature and ionic strength. In the batch system, the maximum dye uptake on acid treated BOF slag adsorbent was observed at pH 2.0, and the maximum RB5, RB19 and RR120 uptake capacities (at 500 mg l^{-1} dye concentration) were 76, 60 and 55 mg g^{-1}. The Langmuir and Redlich–Peterson models were able to describe the adsorption equilibrium. The first-order, Elovich and intra-particle diffusion models were used to describe kinetic process of dyes adsorption and adsorption kinetic process is following the first-order kinetic model.

1. Introduction

Waste effluent from the textile industry can be particularly problematic due to the presence of colour in the final effluent [1]. As a matter of fact, the discharge of such effluents in the environment is worrying for both toxicological and esthetical reasons. Various treatment methods have been developed for decontamination purposes including coagulation, chemical oxidation, membrane separation, electrochemical process, and adsorption techniques. Of the above-mentioned techniques, adsorption was recognized to be a promising and a cost-effective process to remove colours from aqueous solution. Many kinds of adsorbents have been developed for various applications [2–9]. Due to its effectiveness and versatility, activated carbon is widely employed in water and wastewater treatment. However, the operating cost of activated carbon adsorption is high. Problems of regeneration and difficulty in separation from the wastewater after use are the two major concerns of using this material. This has led to searches for unconventional adsorbents as alternative adsorbents. Utilization of industrial solid waste for the treatment of industrial wastewater is helpful not only to the environment, but also to reduce the disposal cost.

Basic oxygen furnace slag (BOF slag) is a final waste material in the basic oxygen furnace steel making process [10]. It is known that BOF slag shows strongly heterogeneous surfaces. The heterogeneity of the BOF slag surface stems from two sources, namely geometrical and chemical. Chemical heterogeneity is associated with different functional groups at a surface, and with various surface contaminants. Both the chemical and geometrical heterogeneities contribute to the unique adsorption properties of BOF slag [11]. Reactive dyes are the most widely used dyes in the textile industry. It is reported that reactive dyes are highly soluble in water [12]. It is difficult to remove reactive dyes using chemical coagulation due to the dyes' high solubility in water [13]. Adsorption appears to be the best prospect for elimination of this dye.

The characteristics of the dye adsorption behavior are mainly understood in terms of the equilibrium isotherms, kinetic models and effects of pH and ion strength from adsorption batch experiments. The modified BOF slag was prepared by being ground with a high-energy vertical planet ball mill and activated with hydrochloric acid respectively. The surface structure of the BOF slag materials was studied. The aim of the present batch adsorption work is to study the adsorption capacity of BOF slag for three kinds of reactive dyes. Langmuir, Freudlich and Redlich–Peterson models were used to describe adsorption isotherm. First-order, Elovich and intra-particle diffusion models were used to describe kinetic process. The factors such as pH of solution, temperature and ionic strength were discussed in this study.

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2. Materials and methods

2.1. Materials

BOF slag used in this study generated from the local steelmaking factory with 2 years setting time. The sieve size of BOF slag was controlled under 0.6 mm as original materials. The chemical composition of the BOF slag was measured using inductively coupled plasma-atomic emission spectrometer (ICP-AES, IRIS Advantage). The major composition of the BOF slag was 13.7% SiO_2, 6.8% Al_2O_3, 17.8% Fe_2O_3, 7.3% MgO and 45.4% CaO. The loss on ignition was found to be 6.9% by weight. There are two kinds of modified BOF slag used as adsorbents in this study: (1) sample BTM (BOF slag Treated by Milling) represented that original materials were ground for 3 h by vertical planetary ball mill, while the ratio of materials versus ball was 1:10 by mass; (2) sample BTA (BOF slag Treated by Acid) represented that original materials were pretreated in dilute hydrochloric acid, then oven-dried powders were used as adsorbents after being washed by deionised water for five times. The specific surface area was 0.75 and 0.90 $m^2\,g^{-1}$ as determined by the BET-N_2 method for both materials. The surface structure of modified BOF slag was carried out by using a scanning electron microscope (SEM, JSM-5610LV Model). An FTIR spectrum for materials was recorded on a Jasco FT/IR-300E Model Fourier transform infrared spectrometer to confirm the surface modification.

Three commercial textile dyes Reactive Blue 19 (RB19) Reactive Black 5 (RB5) and Reactive Red 120 (RR120) were provided from Shanghai, China and used in all adsorption experiments without further purification. The chemical structure of these dyes is illustrated in Fig. 1.

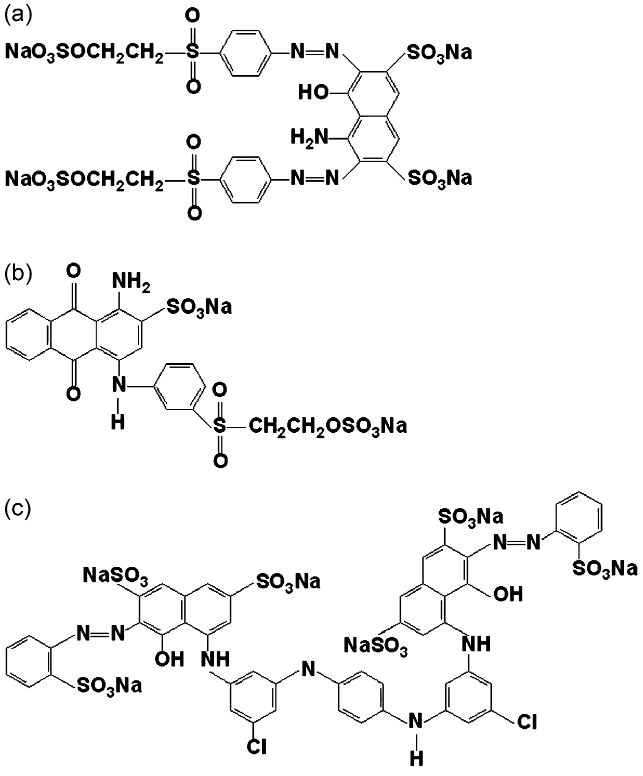

Fig. 1. The chemical structure of the reactive dyes.

2.2. Adsorption study

Adsorption experiments with modified BOF slag were performed by batch technique at room temperatures. A series of 250-mL Erlenmeyer flasks containing 100 mL of adsorbate solutions of various concentrations (25–500 mg l^{-1}) and required amount of BOF slag were employed at a desired pH by adding a small amount of HCl or NaOH solutions. These flasks were sealed to avoid evaporation and then were stirred using a mechanical magnetic stirrer for 60 min to achieve equilibration, however, stirring for extra 2 h gave practically the same uptake in each case. Once the equilibrium is through to be reached, solution was carefully filtered and concentration of the dye in the solution after equilibrium adsorption was determined by measuring the absorbance. The effects of the medium pH on the adsorption capacities of the BOF slag were investigated in the pH range 2.0–10.0. In addition, the different concentrations of NaCl (0, 0.25 and 0.5 M) were added to evaluate the competence between the Cl^- and sulfonate groups of the dye molecules for amine sites of the surface of BOF slag. In adsorption batch experiments, the pH of each solution was measured by using a laboratory scale pH meter (PHS-3C Model) and the absorbance measurements were carried out on UV–Vis spectrophotometer (Hach DR/2400) at the respective λ_{max} value (592 nm for RB19, 597 nm for RB5 and 511 nm for RR120). The experiments were performed three times, the experimental error being around 3% (mean value).

2.3. Adsorption isotherm models

Three of the most commonly used isotherm theories have been adopted to analyze data for water and wastewater treatment applications in this work, namely Langmuir, Freudlich and Redlich–Peterson equilibrium isotherm theories. The forms of these isotherms are presented by the following equations.

Langmuir model [14] form:

$$q_e = \frac{Q_m b C_e}{1 + bC_e} \tag{1}$$

For the Langmuir model (Eq. (1)), the constant b (l mg^{-1}) is related to the energy of adsorption; C_e (mg l^{-1}), the equilibrium concentration of the dyes in solution; q_e (mg g^{-1}), the amount of adsorbed dye on the adsorbent surface at equilibrium and the constant Q_m (mg g^{-1}), represents the maximum binding at the complete saturation of adsorbent binding sites.

Freudlich model [15] form:

$$q_e = K_F C_e^{1/n} \tag{2}$$

K_F and n are the Freundlich adsorption isotherm constants characteristic of the system. K_F and n are indicative of the extent of the adsorption and the degree of non-linearity between solution concentration and adsorption, respectively.

Redlich–Peterson model [16]:

$$q_e = \frac{K_R C_e}{1 + \alpha C_e^{\beta}} \tag{3}$$

K_R and α are the Redlich constants. The value of β varies from 0 to 1. This model is used to describe chemical and physical adsorption on heterogeneous surface, instead of assumption homogeneity such as equally available adsorption sites, monolayer surface coverage, and no interaction between adsorbed species.

2.4. Adsorption kinetic models

The kinetics of dye adsorption on the BOF slag preparations was determined with three different kinetic models, i.e. first-order,

Table 1
Chemical compositions of original BOF slag

Chemical composition	Content (%)
Silica (as SiO_2)	13.7
Calcium (as CaO)	45.4
Iron (as Fe_2O_3 and FeO)	17.8
Magnesium (as MgO)	7.3
Alumina (as Al_2O_3)	6.8
H_2O at 105 °C	1.1
H_2O at 950 °C	2.4

simple Elovich and intra-particle diffusion models. These typical kinetic models, as described in following equations, were used for fitting the experiment data.

First-order kinetic model [17]:

$$q_t = a(1 - \exp(-bt)) \tag{4}$$

Simple Elovich kinetic model [17]:

$$q_t = A + B \ln t \tag{5}$$

Where q_t (mg g^{-1}) is the amount of adsorption at equilibrium and at time t. The other parameters A, B, a and b are different kinetic constants, which can be determined by regression of the experimental data.

The intra-particle diffusion model [18] (Eq. (6)) was applied to describe the dye adsorption. Assuming that the rate is controlled by pore and intra-particle diffusion, in a non-flow-agitated system, the amount adsorbed (q_t) is proportional to the square root of time ($t^{1/2}$), as per the relationship given by Weber and Moris.

$$q_t = k_d t^{1/2} \tag{6}$$

k_d (mg g^{-1} h$^{-1/2}$) is the intra-particle diffusion rate constant. The plot of q_t versus $t^{1/2}$ may present multi linearity [19], which indicates that two or more steps occur in the adsorption processes. The first sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intra-particle diffusion is rate controlled. The third portion is the final equilibrium stage, where the intra-particle diffusion starts to slow down due to the extremely low solute concentration in solution [20].

3. Results and discussion

3.1. Surface structure

3.1.1. Chemical composition and properties

The principal chemical compositions of the BOF slag are shown in Table 1. The BOF slag adsorbents consisted mainly of CaO, Fe_2O_3, SiO_2, Al_2O_3, FeO, and MgO (more than 90% by mass). It is observed in Table 2 that for BTM by milling, density, surface area, and total porosity increased. This could be regarded as effect of mechanochemistry while BOF slag was being ground. On the other hand, acid treatment led to show BTA more porous and bigger surface area than BTM, while density of materials decreased.

Table 2
Technical properties of BOF slag and adsorbents

Properties	Materials		
	Original	BTM	BTA
Density (mg cm^{-3})	3.11	3.29	2.98
Specific surface (m^2 g^{-1})	0.50	0.75	0.90
Total porosity (%)	5.76	7.18	9.22

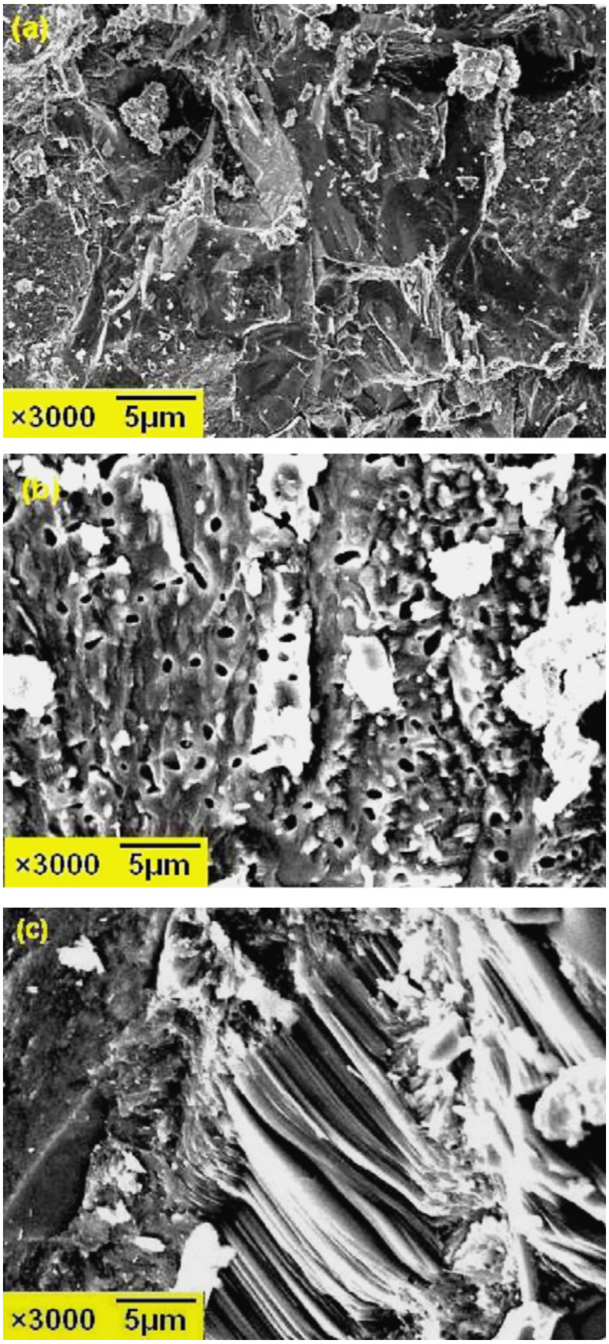

Fig. 2. SEM micrographs for BOF slag: (a) original; (b) 3 h ground by mill; (c) treated by acid.

3.1.2. Morphological structure

The morphologies of BOF slag adsorbents were examined under scanning electron microscope. Scanning photos are shown in Fig. 2. It was observed that by 3 h ground for BTM, more and more pores were exposed, and it was predicted these pores would do positive effect on adsorption. It also showed that by acid treatment, surface of BTA was coarser. Acid treatment led to an increase of porosity volume and connects the pores. In addition, these pores reduce the mass transfer resistance and facilitate the diffusion of dye molecules because of high internal surface area with low diffusional resistance in the biomass preparations (imply high adsorption capacity and rate).

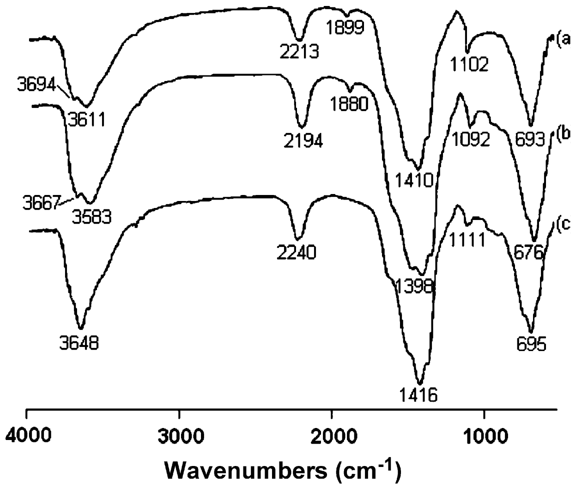

Fig. 3. FT-IR spectra for BOF slag: (a) original; (b) 3 h ground by mill; (c) treated by acid.

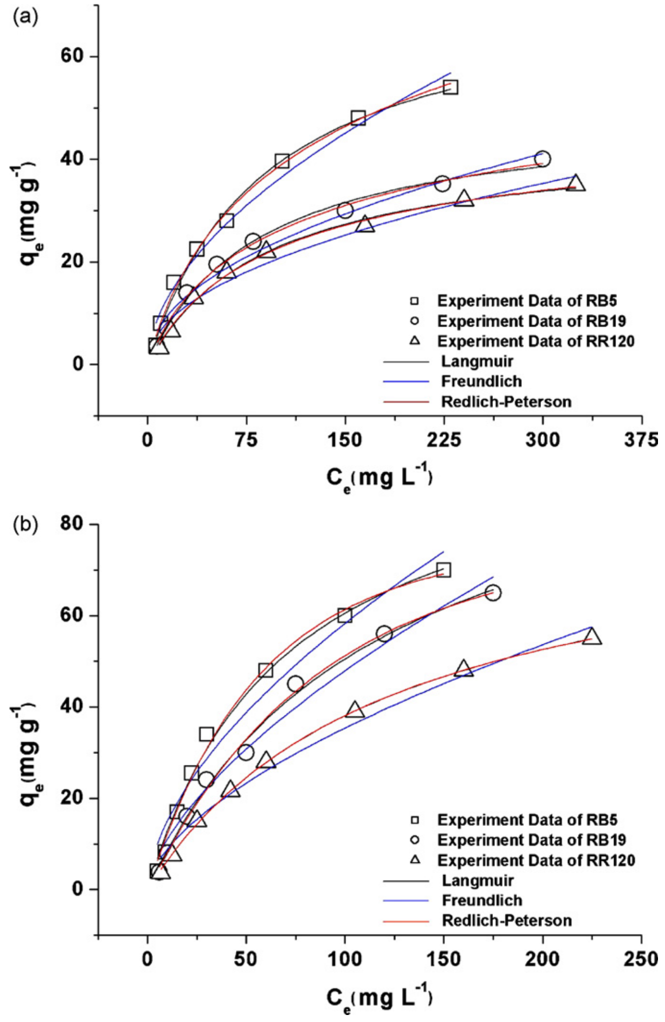

Fig. 4. Effect of initial dye concentration on the BOF slag and three different adsorption isotherm models regression for (a) BTM and (b) BTA. Initial dyes concentration: 25–500 mg l^{-1}; pH 2.0; temperature: 298 K; BOF slag dose: 5.0 mg mL^{-1}; contact time: 3 h.

3.1.3. *Infrared spectra*

In order to confirm the existence of functional adsorption groups on the BOF slag, the FT-IR spectra of BOF slag preparations were obtained and presented in Fig. 3. Fig. 3(a) shows the original slag IR spectrum, indicating that there are few peaks which almost exist at low frequency area in the spectrum. The spectrum also shows that the stretching vibration of [OH] (surface hydroxyl groups) appears at 3694 cm^{-1} which is not clear, and the stretching vibration of H_2O appears at 3611 cm^{-1}. Absorptions of higher intensity are found at 1102 and 1410 cm^{-1} due to the Si–O valence vibrations of SiO_4 and other absorption of higher intensity appear at 693 cm^{-1} due to the Si–O valence vibrations of SiO_4. The peaks appearing at 1899 cm^{-1} is an indication of the presence of calcite. It is obvious that the characteristic bands of calcite have completely disappeared in Fig. 3(b). This was attributed to the acid. The frequency of most remaining bands has changed slightly between Fig. 3(b) and (a). This indicates that ground treatment by mill had negligible effect on the structure of silicate materials present in BOF slag. After being treated by mill or acid, the intensity of the 2213 cm^{-1} band decreases, which indicates partial water lost.

3.2. *Adsorption isotherm study*

Adsorption of RB19, RB5 and RR120 from aqueous solutions onto BOF slag was measured at given contact times (3 h) and pH 2 for three different initial dye concentrations (25–500 mg l^{-1}) at an adsorbent dose of 5 mg mL^{-1}. The amount of adsorbed reactive dyes onto the BOF slag at equilibrium was studied and plotted as a function of the equilibrium concentration of dye in Fig. 4. The dyes adsorption capacity of the BOF slag increased with increasing of the initial concentration of dyes. The maximum RB5, RB19 and RR120 adsorption capacities are 54, 40 and 35 mg g^{-1} for the BTM; 76, 60 and 55 mg g^{-1} for the BTA adsorbent, respectively. According to the results of the dyes adsorption isotherm experiments, the BTA had higher adsorption capacity than that of the BTM. Based on the experiment results for each reactive dye, it is found that the RB5 is easy to be adsorbed by both of BOF slag adsorbents while the RR120 adsorption capacity of BOF slag is the lowest as compared to other two dyes. This may be attributed large molecular weight and complex chemical structure of RR120. It was believed that the surface structure changes of the material played the most important role in the adsorption capacity of dyes. When the slag was modified and treated with HCl, the surface structure of the BTA material was changed. For the BTA, the surface area increased, which resulted from opening of channels and enlargement of aperture diameter and the creation of micro porosity of the material as compared with the BTM. On the other side, the negative charges of the BTA surface may decrease after treated by HCl, and this would be more significantly in favor of the adsorption of anions in solution (–SO_3^- of the dyes chemical structure).

Three theoretical isotherm models were used to fit the experimental data: Langmuir, Freundlich and Redlich–Peterson models. Curves of related adsorption isotherms are regressed in Fig. 4 and parameters of equations are provided in Table 3. It is shown that the experimental data of reactive dyes adsorption onto BOF slag could be well fitted by the isotherm models used in this study. The lower maximum adsorption capacity and coefficient of Freudlich also indicates that RR 120 is not easy to be adsorbed and removed by BOF slag. In all results, correlation coefficient is higher with the Langmuir and Redlich–Peterson isotherm models than with the Freundlich isotherm model. Clearly, the Langmuir and Redlich–Peterson isotherm models provided better fitting in terms of the correlation coefficient value.

Table 3
Adsorption isotherms equations and correlation coefficient of three active dyes onto BOF slag

Dyes–adsorbent system	Langmuir equation $q_e = Q_m b C_e/(1 + bC_e)$			Freundlich equation $q_e = K_F C_e^{1/n}$			Redlich–Peterson equation $q_e = K_R C_e/(1 + \alpha C_e^{\beta})$			
	Q_m	b	R^2	K_F	$1/n$	R^2	K_R	α	β	R^2
RB5-BTM	74.4	0.011	0.9952	3.00	0.541	0.9807	1.036	0.036	0.831	0.9967
RB19-BTM	49.4	0.012	0.9943	2.57	0.486	0.9773	0.716	0.033	0.861	0.9985
RR120-BTM	44.1	0.011	0.9959	2.23	0.484	0.9704	0.520	0.017	0.941	0.9962
RB5-BTA	109.5	0.014	0.9921	3.87	0.689	0.9639	1.305	0.004	0.916	0.9934
RB19-BTA	103.4	0.008	0.9946	2.53	0.638	0.9788	0.847	0.003	0.960	0.9952
RR120-BTA	84.5	0.009	0.9995	2.24	0.600	0.9850	0.689	0.007	0.986	0.9995

3.3. Adsorption kinetic study

As has been shown the dyes with the higher adsorptive capacity were RB5, RB19 and RR120, in light of this, kinetic studies and modeling were undertaken with these particular adsorbents. The kinetic experiments were performed at pH 2 for the initial dye concentrations of 100 mg l^{-1} at an adsorbent dose of 5 mg mL^{-1} under room temperature. Three types of dyes adsorption rates were obtained by following decrease of the concentration of each dye within the adsorption medium with contact time. The time necessary to reach equilibrium for the removal of the dye molecules by BTM and BTA from aqueous solution was established about 3 h. After equilibrium, the amount of adsorbed dye did not change significantly with time in Fig. 5. The removal rate in the first 30 min varies from 65% to 85% of the maximum removal in the case of RB5, RB19 and RR120 onto BTM and BTA, respectively. The estimated parameters and kinetic equation with correlation coefficient are shown in Table 4. In this study, the dyes adsorption kinetic data were fitted with the first-order kinetic model by non-linear regression due to its higher correlation coefficient. It indicates that adsorption kinetic process is following the first-order kinetic model. This is generally in agreement with other research's result that the first-order kinetic model was able to describe properly the kinetic process of dyes adsorption onto different industrial waste adsorbents [21]. Other two kinetic equations were not well-described adsorption of the dye on all the BOF adsorbents, especially for the intra-particle diffusion model. This was attributed to the stage of dyes adsorption onto BOF slag is dominated and controlled by the external surface adsorption or the instantaneous adsorption stage.

3.4. Effects on dyes adsorption

3.4.1. Effect of pH

Solution pH affects both aqueous chemistry and surface binding sites of the adsorbents. The effect of initial pH on adsorption of reactive dyes was studied from pH of 2 to 10 at room temperature, constant initial dyes concentration of 100 mg. l^{-1}, adsorbent dose of 5 g l^{-1} and contact time of 3 h. Fig. 6 shows the effect of pH on the adsorption of three reactive dyes onto BOF slag. The maximum uptake of the reactive dyes is obtained at studied pH of 2. Fig. 6 depicts that the pH significantly affects the extent of

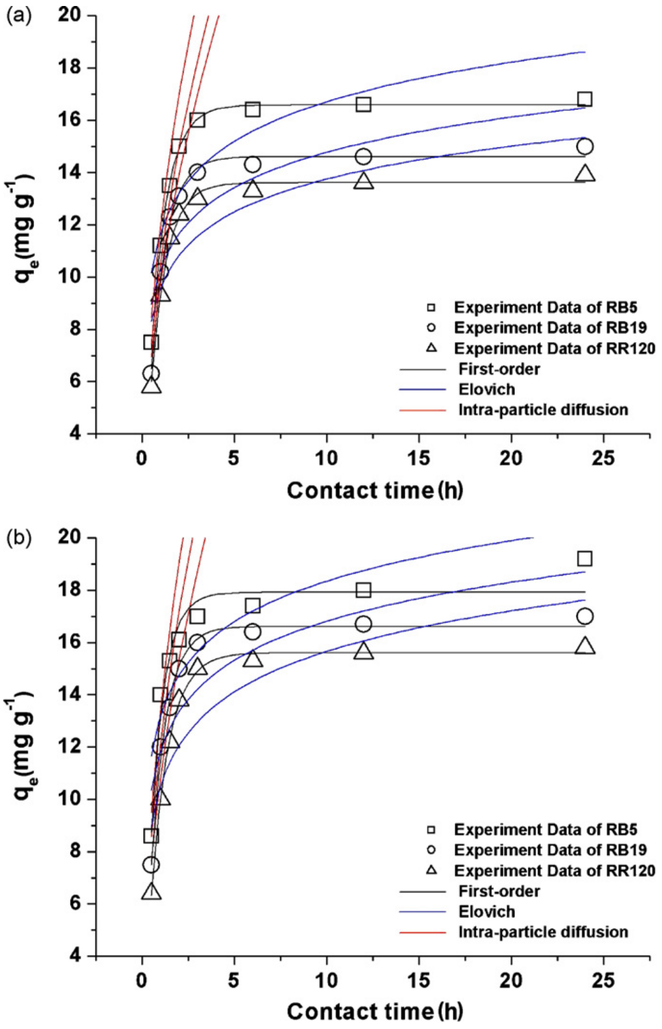

Fig. 5. Effect of contact time on the dyes adsorption and three different adsorption kinetic models regression for (a) BTM and (b) BTA. Initial dyes concentration: 100 mg l^{-1}; pH 2.0; temperature: 25 °C; BOF slag dose: 5.0 mg mL^{-1}; contact time: 3 h.

Table 4
Adsorption kinetic equations and correlation coefficient of three active dyes onto BOF slag

Dyes–adsorbent system	First-order equation $q_t = a(1 - \exp(-bt))$			Elovich equation $q_t = A + B \ln t$			Intra-particle diffusion $qt = k_d t^{1/2}$	
	a	b	R^2	A	B	R^2	k_d	R^2 [a]
RB5-BTM	16.58	1.151	0.9976	11.68	2.184	0.8435	5.23	–
RB19-BTM	14.61	1.173	0.9938	10.30	1.943	0.8379	4.63	–
RR120-BTM	13.60	1.163	0.9937	9.57	1.816	0.8232	4.31	–
RB5-BTA	17.92	1.342	0.9967	13.20	2.236	0.8778	5.80	–
RB19-BTA	16.61	1.199	0.9928	11.85	2.154	0.8491	5.28	–
RR120-BTA	15.61	1.039	0.9978	10.51	2.238	0.8592	4.88	–

[a] Correlation coefficient is too lower to be provided in this table.

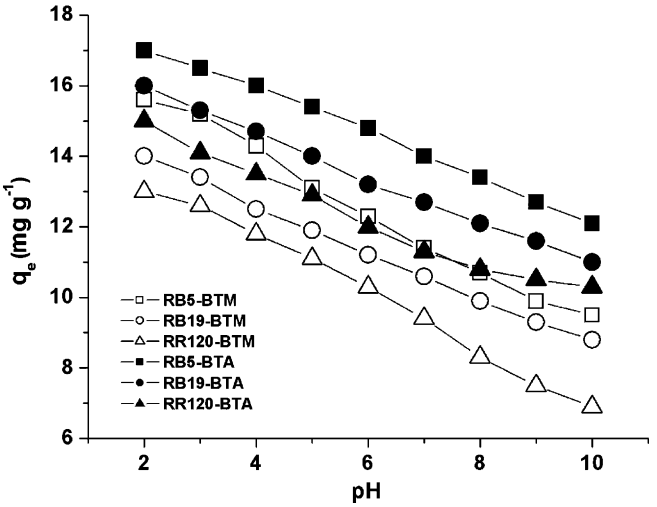

Fig. 6. Effect of initial pH of solution on the dyes adsorption onto BTM and BTA. Initial dyes concentration: 100 mg L^{-1}; pH 2.0–10.0; temperature: 298 K; BOF slag dose: 5.0 mg mL^{-1}; contact time: 3 h.

adsorption of dye over the adsorbent and a reduction in the amount adsorbed with increasing pH was observed. The hydrolysis constant value of the sulfonate groups of the dye molecule is 2.1. This functional group can be easily dissociated and thus, the dye molecule has net negative charges in the working experimental conditions. Higher uptakes of dye obtained at lower pH values may be due to the electrostatic attractions between these negatively charged dye's anions and positively charged adsorbent's surface. A lower adsorption at higher pH values may be due to the abundance of OH$^-$ ions and because of ionic repulsion between the negatively charged surface and the anionic dye molecules. There are also no more exchangeable anions on the outer surface of the adsorbent at higher pH values and consequently the adsorption decreases. At lower pH, more protons will be available, thereby increasing electrostatic attractions between negatively charged dye anions and positively charged adsorption sites and causing an increase in dye adsorption [22]. Similar results were reported for the adsorption of other reactive dyes from aqueous solutions [23].

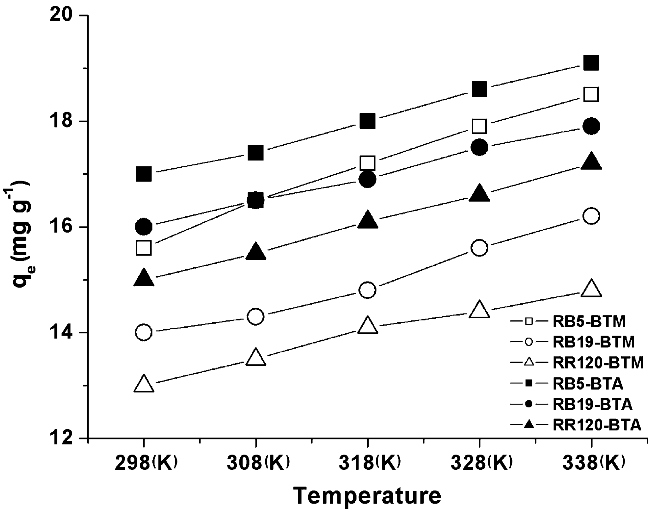

Fig. 7. Effect of temperature on the dyes adsorption onto BTM and BTA. Initial dyes concentration: 100 mg L^{-1}; pH 2.0; temperature: 298–335 K; BOF slag dose: 5.0 mg mL^{-1}; contact time: 3 h.

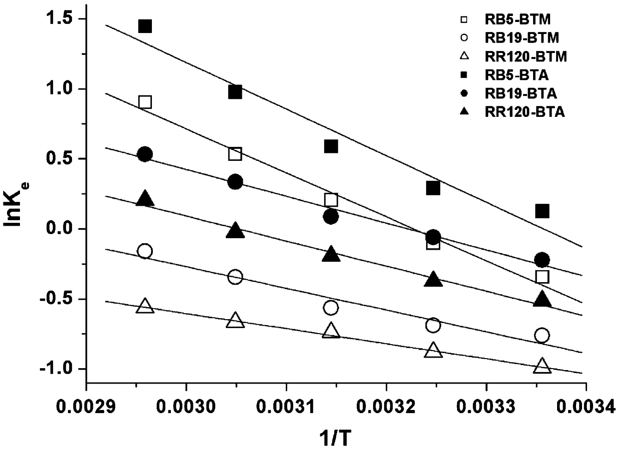

Fig. 8. Van't Hoff plots of dyes adsorption onto BOF slag for different temperature. Initial dyes concentration: 100 mg L^{-1}; pH 2.0; temperature: 298–335 K; BOF slag dose: 5.0 mg mL^{-1}; contact time: 3 h.

3.4.2. Effect of temperature

Various textile dye effluents are produced at relatively high temperature, therefore temperature can be an important factor for the real application of the BOF slag. To determine whether the ongoing adsorption process was endothermic or exothermic in nature, reactive dyes adsorption studies over BOF slag were carried out at 298, 308, 318, 328, 338 K at constant initial dyes concentration of 100 mg. l^{-1}, pH of 2, adsorbent dose of 5 g l^{-1} and contact time of 3 h. In general for both the adsorbents the adsorption of dyes increased with an increase in temperature in Fig. 7, which indicates that the process was endothermic in both cases.

In thermodynamics equation, change of Gibbs free energy was calculated by Eqs. (7) and (8), and change of entropy and heat of adsorption were calculated and estimated by Eq. (9)

$$\Delta G^0 = -RT \ln K_e \tag{7}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{8}$$

$$\ln\ K_e = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{9}$$

Where, at equilibrium for all equations, ΔG^0 is change of Gibbs free energy (kJ/mol), ΔS^0 (J/(K mol)) and ΔH^0 (kJ/mol) are change

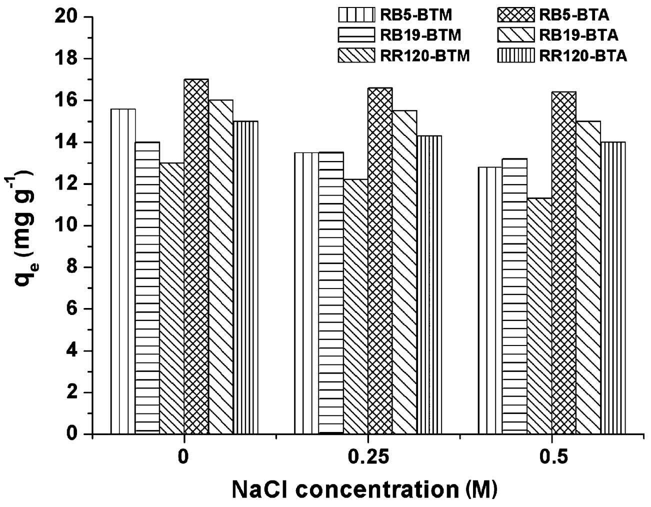

Fig. 9. Effect of ionic strength on the dyes adsorption onto BTM and BTA. Initial dyes concentration: 100 mg L^{-1}, pH 2.0; NaCl concentration: 0–0.5 M; temperature: 298 K; BOF slag dose: 5.0 mg mL^{-1}; contact time: 3 h.

Table 5
Thermodynamic parameters of three active dyes adsorption onto BOF slag

Dyes–adsorbent system	ΔG^0 (kJ mol^{-1})					ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
	298 K	308 K	318 K	328 K	338 K		
RB5-BTM	1.00	−0.16	−0.68	−1.52	−2.37	26.10	84.22
RB19-BTM	2.05	1.68	1.32	0.95	0.59	12.90	36.42
RR120-BTM	2.44	2.22	2.01	1.79	1.57	8.96	21.87
RB5-BTA	−0.03	−0.95	−1.88	−2.81	−3.74	27.65	92.87
RB19-BTA	0.63	0.12	−0.39	−0.91	−1.42	15.92	51.30
RR120-BTA	1.34	0.89	0.44	−0.02	−0.47	14.87	45.39

of entropy and heat of reaction. K_e represents equilibrium distribution constant and R (8.314 J/(K mol)) is universal gas constant. Thus, if the equilibrium constants for an adsorption reaction at different temperatures are known, the standard enthalpic changes for adsorption can be also estimated from the slope of a linear plot of $\ln K_e$ versus $1/T$ in Fig. 8.Then the slope was used to determine the values of ΔH^0 and the Eqs. (8) and (9) were used to calculate the free Gibbs energy ΔG^0 and standard entropy ΔS^0 in Table 5.

The free energy of the process at all temperatures for RB5 adsorption onto BTA adsorbent was negative indicating the feasibility of the process and the spontaneous nature of the adsorption. The negative ΔG^0 value increased with increased temperature, indicating that the spontaneity adsorption is proportional to the temperature. The positive ΔG^0 value decreased with the increase of temperature, indicating that it is hard for RB19 and RR120 adsorbed by BTM. The free energy of the process at the higher temperatures for RB19 and RR120 adsorption onto BTA was negative. The positive value of ΔH^0 indicates that reactive dyes–BOF slag reaction is endothermic. The same behavior of the studied samples was observed for the study on the effect of the contact time at different temperatures. The positive value of ΔS^0 indicates the lower order of reaction during the adsorption of dyes onto BOF slag. The positive value of entropy reflects. The origin of these changes in the ΔS^0 for the process could be due to a combination of the affinity of the BOF slag for dye, solvent dissociation events [24,25].

3.4.3. *Effect of ionic strength*

The ionic strength of the solution is one of the factors that control both electrostatic and non-electrostatic interactions between the adsorbate and the adsorbent surface. To determine whether the on-going adsorption process was affected by salt (ionic strength), reactive dyes adsorption studies over BOF slag were carried out at sodium chloride concentrations of 0, 0.25 and 0.5 M with the constant initial dyes concentration of 100 mg l^{-1}, pH of 2, adsorbent dose of 5 g l^{-1} and contact time of 3 h. The dyes adsorption would be affected not only by the pH value on the electron donating capability, temperature on the change of entropy and heat of reaction, but also by the salt concentration on the hydrophobic and electrostatic interaction between dye and surface functional adsorptive sites of the BOF slag. The adsorption capacities of BOF slag for RB5, RB19 and RR120 were not significantly affected with increasing NaCl concentration from 0 M to 0.5 M in Fig. 9. This indicates that Cl$^-$ ions do not compete with sulfonate groups of the dye molecules for amine sites of BOF slag. Dyeing processes consume large amounts of salt. Therefore, the concentration of salt in dye wastewaters can be normally high. From this point of view, this result indicates that the BOF slag can be used for removal of acidic reactive dyes from salt containing water.

4. Conclusions

In this work, two kinds of modified basic oxygen furnace slag (BTM and BTA) have been used successfully as adsorbents for the removal of the Reactive Black 5, Reactive Blue 19 and Reactive Red 120 from synthetic textile dyes solution. Batch adsorption experiments were investigated by various parameters such as initial dye concentration, contact time, pH, temperature, and background ionic strength. The results of the study clearly showed that physical and chemical surface modification methods can be used to activate BOF slag for maximizing the dyes adsorption removal efficiency. In the batch system, the maximum dye uptake on all BOF slag adsorbents was observed at pH 2.0, and the maximum RB5, RB19 and RR120 uptake capacities (at 500 mg l^{-1} of dye concentration) were 54, 40 and 35 mg g^{-1} for the BTM; 76, 60 and 55 mg g^{-1} for the BTA adsorbent, respectively. Adsorption reaction reached equilibrium during 3 h of contact time. The medium pH and temperature played the significant role in affecting the dyes adsorption capacity of BOF slag. The adsorption capacity of BOF slag decreased with increasing solution pH value and increased with increasing temperatures under given experimental conditions. Adsorption isotherm experiments data indicated that the Langmuir and Redlich–Peterson models were able to describe the adsorption equilibrium. It could be observed that adsorption kinetic process is following the first-order kinetic model.

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