Coal-based bottom ash (CBBA) waste material as adsorbent for removal of textile dyestuffs from aqueous solution

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Abstract

A locally available CBBA waste material was used as adsorbent for removal of reactive dyes from synthetic textile wastewater. This study presents the results of our investigation on color removal from synthetic wastewater containing Vertigo Blue 49 (CI Blue 49) and Orange DNA13 (CI Orange 13) by adsorption onto CBBA waste material. The effectiveness of CBBA waste material in adsorbing reactive dyes from aqueous solutions was studied as a function of contact time, initial dye concentration and pH by batch experiments. Leachability of waste material was also evaluated using standard leaching test with deionized water (DIN38414-S4).

pH 7 was more favorable for color removal from both Vertigo Blue 49 (CI Blue 49) and Orange DNA (CI Orange 13). Dyestuff adsorption capacities of CBBA for Vertigo Blue 49 and Orange DNA13 were 13.51 and 4.54 mg dye/g adsorbent, respectively. The adsorption isotherms for the CBBA can be better described by the Freundlich isotherm. The results showed that the dyestuff uptake process for both dyes followed the second-order kinetics. The bottom ash used in this study is not classified as ecotoxic/hazardous material according to the French proposal for a criterion and evaluation methods of waste ecotoxicity (CEMWE) and the German regulation on Hazardous Waste Classification (HWC).
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Keywords: Adsorption; Bottom ash; Color removal; Leaching; Wastewater treatment

1. Introduction

Textile industry wastewater is one of the major environmental problems in Çorlu district of Tekirdağ, Turkey. There are around 1000 factories around the city, situated in the western part of Turkey and their number is constantly increasing. Many industries use dyes and pigments to color their final products. Consequently, the wastewater effluents are highly colored and the disposal of these wastes into receiving waters causes damage to the environment as they may significantly affect photo-synthetic activity in aquatic life due to reduced light penetration.

Most of the dyes are resistant to biological degradation. The conventional techniques of wastewater treatment are usually based on biological oxygen demand (BOD) removal, but they are largely ineffective in removing colour from effluent. Conceptually, combination of more than one process such as adsorption and degradation of dyestuffs would probably provide a viable solution to this problem [1].

Sorption is one of the several techniques that have been successfully employed for effective removal of dyestuffs [2]. Activated carbon has been the most widely used adsorbent for this purpose. Owing to its high price and considering the great amount of wastewater normally produced by the textile factories, research has recently been directed towards alternative adsorbents. Cost effectiveness, availability and adsorption characterisics are the main criteria for selecting an adsorbent to remove colour compounds.

Orange peel [3], de-oiled soya waste [4], sawdust [5], cotton [6], apple pomace and wheat straw [7], bagasse fly ash [8], fly ash [9], bottom ash [10,11], activated sludge [12], red-mud [13], steel and fertilizer industries wastes [14], natural zeolite [15], corncob and barley husk [16], dried activated sludge [17], sugar industry mud [18], algea [19], blast furnace slag [20], starch [21], chitosan [22] and shale oil ash [23] have been used with varying success in removing color compounds.

The fly ash and bottom ash taken from coal fired thermal power plants are known to contain several toxic elements, such

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as Pb, Zn, Cd and Cu [24]. Generally, less heavy metals are released from bottom ash than from fly ash; therefore, bottom ash has been used as one of the ingredients of concrete and admixtures used in the construction of roads and bridges [25]. Some investigations have reported that alkaline fly ashes could serve as a stabilizer or a binding reagent for fixing heavy metals and nutrients present in hazardous and organic wastes [26,27]. Fly ash is one of the most abundant waste materials. Its major components make it a potential agent for the adsorption of heavy metal contaminants in water and wastewaters [28].

There is limited number of studies on the use of CBBA for removal of textile dyestuffs from wastewaters. Therefore, the objective of this study is to investigate the possibility of using CBBA for adsorption of reactive dyes since the CBBA is an abundant and free available waste material. The effects of various operating parameters on adsorption such as initial pH, initial dye concentration and contact time were investigated in controlled batch experiments. Kinetics and equilibrium isotherms for adsorption of both vertigo blue 49 and orange DNA13 were studied. The Langmuir and Freundlich isotherm models were tested for their applicability. Since the bottom ash contains potentially hazardous heavy metals, it is necessary to evaluate the possibility of heavy metal leaching. The results indicated that CBBA can be used as an effective adsorbent for removal of reactive dyestuffs from dilute dyestuff containing wastewaters.

2. Materials and methods

The CBBA used in this study was collected as a homogenous 20 kg composit sample from the domestic heating systems in Çorlu, Tekirdağ. The CBBA was used as it was received, without any pre-treatment. The particle size distribution of bottom ash was determined by sieving the samples through stainless steel ASTM sieves with openings of standard 0.074, 0.125, 0.177, 0.25 and 0.59 mm. The particle size distribution of the adsorbent was in the range of: $D_p < 0.074$ mm, 26.9%, 0.074–0.125 mm, 17.8%, 0.125–0.177 mm, 14.1%, 0.177–0.250 mm, 14.7%, 0.25–0.59 mm, 25.9%, >0.59 mm, 0.6%.

The chemical composition of the CBBA was measured using ICP spectroscopy. Composition of the collected CBBA was 32.35% SiO_2, 12.00% Al_2O_3, 7.28% Fe_2O_3, 4.54% MgO, 9.83% CaO, 3.14% Na_2O, 1.83% K_2O, 0.55% TiO_2, 0.06% MnO, 7.53% SO_3, 0.13% Ba, <0.005% Cd, <0.02% Cu, 0.04% Cr, <0.005% Co, 0.04% Ni, <0.02% Pb, <0.02% Sb and 0.10% Zn. The loss on ignition was found to be 20.5% by weight. Bottom ash was alkaline in nature. The pH of 300 ml water + 10 g ash mixture was 9.63. The specific surface area was 1.77 m^2/g as determined by the BET-N_2 method. The surface area of bottom ash was measured by a Quantachrome Autosorb-1 surface area analyzer.

The commercially available reactive dyes, Orange DNA13 and Vertigo Blue 49, were obtained from Goteks Chemical Company. Vertigo Blue 49 has the colour index classification CI Vertigo Blue 49 (molecular weight: 882.186 g/mol, molecular formula: $C_{32}H_{23}ClN_7Na_3O_{11}S_3$). Orange DNA13 has the colour index classification CI Orange 13 (molecular weight: 696.1 g/mol, molecular formula: $C_{24}H_{18}ClN_7O_{10}S_3$). Vertigo

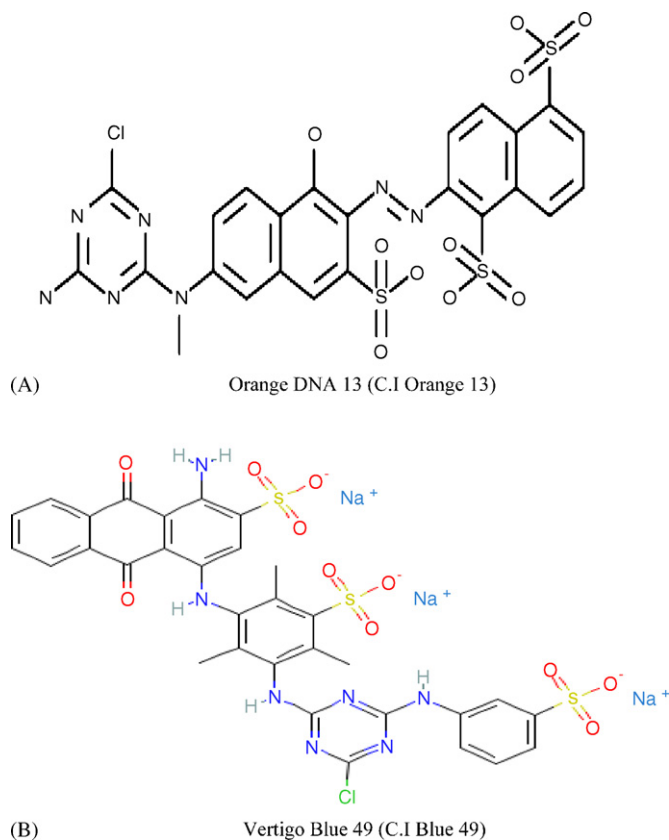(A) Orange DNA 13 (C.I Orange 13)

(B) Vertigo Blue 49 (C.I Blue 49)

Fig. 1. Structures of the reactive dyes: Orange DNA13 (A) and Vertigo Blue 49 (B).

Blue 49 and Orange DNA13 have three anionic clusters. The commercial name and chemical structure of the dyestuffs are shown in Fig. 1. The synthetic wastewaters were prepared by dissolving dyestuffs in deionised water to produce a stock solution of 1000 mg/l (pH 7). This stock solution was diluted in desired proportions to produce solutions with different initial dyestuff concentrations.

Adsorption experiments were carried out by agitating 300 ml of dye solution of the desired concentration (25, 50, 75, 100, 150 and 300 mg/l) and 10 g of dry bottom ash in 500 ml conical flasks. Contact time studies were conducted until equilibrium was achieved. The samples were taken at pre-determined time intervals (5, 15, 30, 45, 60 and 90 min) and the concentrations of dyes were measured. A control flask with only the adsorbent in 300 ml of deionized water was used simultaneously under the same conditions. The flasks were agitated at room temperature (25 °C) at 250 rpm (model SL350 Nüve). Batch adsorption studies were carried out to obtain kinetic and equilibrium data for the decolorisation experiments. pH was measured using a pH meter (WTW 340). The pH of the wastewater was controlled at desired levels by the addition of diluted HCl or NaOH [29,30]. The effect of solution pH was studied by performing the adsorption experiments of dyes at three different pH levels: 4.0, 7.0 and 9.0. After 90 min of contact time, the equilibrium pH_{eq} was recorded and the dye concentration was determined. The experiments were conducted in duplicates and were found reproducible. Effluent samples were withdrawn at suitable time intervals and

the remaining colour in solution was monitored using a spectrophotometer at λ_{max}. The dye solution was separated from the adsorbent by centrifugation (CN180 Nüvefuge) at 2000 rpm for 60 min. The dye removal was determined spectrophotometrically by monitoring absorbance changes at the wavelength of maximum absorption for vertigo blue 49 ($\lambda_{max} = 580$ nm) and Orange DNA ($\lambda_{max} = 417$ nm) using an aquamate spectrometer. The surface area of bottom ash was determined by the BET nitrogen adsorption method. The determination of zero point charge (zpc) of CBBA was carried out using a zeta potential meter (Zetasizer 3000HSA, Malvern). Titration method [31] was applied for the determination of iso electric point (IEP) of the orange DNA13 used in the present study. Langmuir and Freundlich isotherms were employed to determine the adsorption capacity of the adsorbent.

Leaching experiments consisted of batch leaching of bottom ash using deionised water with the samples equivalent to 100 g of dry bottom ash per litre of water. Leaching experiments were performed under continuous stirring at room temperature for 24 h [32]. After recording the pH, the resulting suspension was filtered through over 0.45 μm membrane filters. The amount of metals leached was determined by measuring the concentrations in the supernatant using atomic absorption spectrometer.

3. Results and discussion

The CBBA was used as an adsorbent for removal of Vertigo Blue 49 and Orange DNA13 reactive dyes from synthetic wastewater. As shown in Table 1, the major components of bottom ash were silica, iron, alumina, magnesium and SO_3 along with other compounds present at low concentrations.

The dye binding capacity of bottom ash is shown in Fig. 2 as a function of initial pH and initial dye concentration. In order to study the effects of pH (4, 7 and 9) on adsorption of dyes by bottom ash similar experiments were performed at 25, 50, 75, 100, 150 and 300 mg/l dye concentrations. When initial pH of the dye solutions was increased from 4 to 7 for Vertigo Blue 49 and Orange DNA13, the amounts of dye adsorbed at equilibrium increased from 6.002 to 7.219 mg/g and from 3.666 to 3.85 mg/g, respectively, for 300 mg/l initial dye concentration. Further increases in pH from 7 to 9 resulted in decreases in
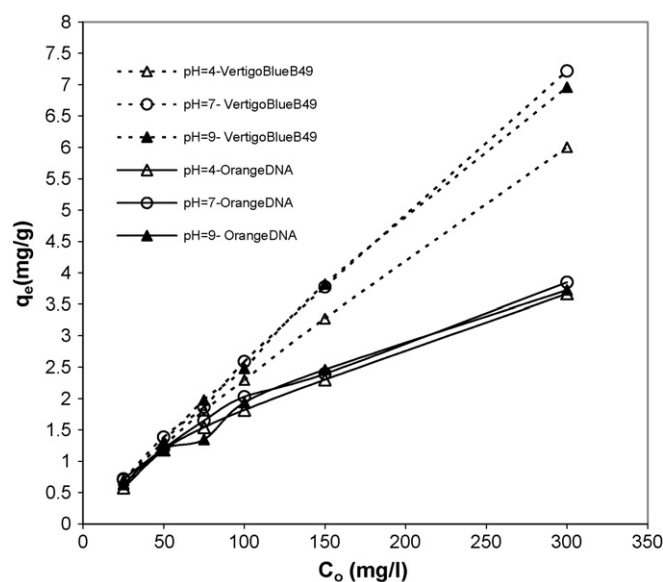

Fig. 2. Effects of initial pH and dyestuff concentrations on adsorption by coal based bottom ash (adsorbent dose 10 g/300 ml, $T = 25\,^{\circ}$C).

adsorption capacity of CBBA. The amounts of Vertigo Blue B49 and Orange DNA adsorbed at equilibrium decreased from 7.219 to 6.959 mg/g and 3.85 to 3.727 mg/g, respectively, for 300 mg/l initial dye concentration. Reactive dyes are characterized by azo bonds (N=N) and have $-SO_3$, $-COO-$, and OH^- groups. These dyes have high solubility and they are not liable for flocculation [33]. Adsorption of dyes was found to be strongly related to solution pH, zero point charge (zpc) of the CBBA and iso electric points of dyes. The pH_{zpc} of CBBA was found to be 6.0 by using zeta potential meter. Surface of the CBBA is positively charged for pH values below 6.0. pH values above 6 result in negative surface charges. The iso electric point (IEP) was observed at pH 7.0 for reactive Vertigo Blue 49 [33] and pH 6.8–7.0 for Orange DNA13. Therefore, at a pH above their IEP, the net charge on each dye becomes negative. A negatively charged surface site on the adsorbent does not favour the adsorption of dye anions due to the electrostatic repulsion. Due to high electrostatic repulsion between the positively charged surface of the adsorbent ($pH_{zpc,CBBA}$ 6.0) and positively charged dyes (pH_{IEP} 7.0 for Vertigo Blue 49 and 6.8–7 for Orange DNA13) adsorption capacity of CBBA was low for initial pH levels lower than 6.0. For pH levels between 6 and 7, high electrostatic attraction exists between the negatively charged surface of the adsorbent and positively charged dyes resulting in high adsorption capacities. As presented in Fig. 2, the adsorption of dyes increased with pH up to 7.0 and then slightly declined with further increase in pH.

The percent adsorption of dyes was found to decrease while the amount of dye adsorbed increased with increased initial concentration of dyes. An increase in the initial dye concentration leads to an increase in the adsorption capacity of the dyes on CBBA. This is due to the increase in the driving force of the concentration gradient with an increase in the initial dye concentration [34].

Table 1
Typical composition of the CBBA waste material (composite sample)

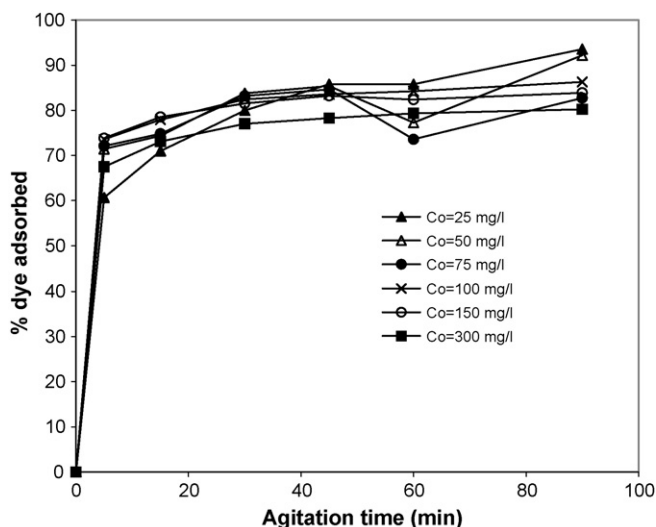| Major element	Bottom ash (wt.%)	Minor element	Bottom ash (wt.%)
SiO_2	32.35	Cd	<0.005
Fe_2O_3	7.28	Cu	<0.02
Al_2O_3	12	Cr	0.04
TiO_2	0.55	Ni	0.04
CaO	9.83	Pb	<0.02
MgO	4.54	Sb	<0.02
SO_3	7.53	Zn	0.10
Na_2O	3.14	Ba	0.13
K_2O	1.83		
Loss on ignition	20.5		

Fig. 3. Effect of agitation time and concentration of Vertigo Blue B49 on removal efficiency: adsorbent dose, 10 g/300 ml, pH 7, $T = 25\,^\circ$C.

Effect of agitation time and dye concentration on removal of dyestuffs are presented in Figs. 3 and 4 for Vertigo Blue 49 and Orange DNA13, respectively. Dyestuff removal efficiency was higher for low dyestuff concentrations because of availability of unoccupied binding sites on the adsorbent. Percent color removal decreased with increasing dyestuff concentrations because of nearly complete coverage of the binding sites at high dyestuff concentrations. As shown in Figs. 3 and 4, when the dye concentration was increased from 25 to 300 mg/l, percent dye adsorption at equilibrium decreased from 93.55% to 80.22% for Vertigo Blue 49 and from 95.68% to 42.78% for Orange DNA13. Larger amounts of dyes were removed by the bottom ash within the first 20 min of contact time and equilibrium was established in 60–90 min for all concentrations studied. The extent of dyestuff removal was found to be strongly dependent
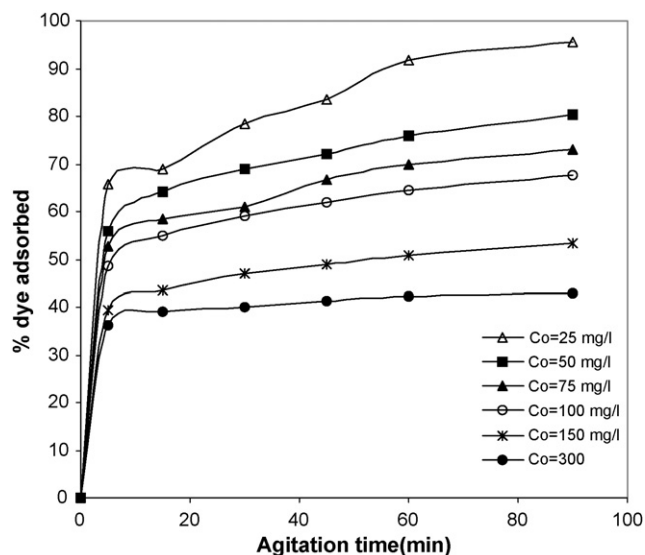
Table 2
pH and leachable contents of trace elements from bottom ash and chemical limits defined in the French (CEMWE) and in the German regulation (HWC)

Heavy metals	Bottom ash (mg/l)			CEMWE[a] (mg/l)	HWC[b] (mg/l)
	pH 4	pH 7	pH 9		
Cadmium	0.025	0.025	0.025	0.2	0.1–0.5
Copper	0.135	0.02	0.02	0.5	5–10
Nickel	0.163	0.02	0.02	0.5	1–2
Chromium	0.01	0.01	0.01	0.5	–
Manganese	0.05	0.05	0.05	–	–
Lead	0.01	0.01	0.01	0.5	1–2
Zinc	0.730	0.520	0.150	2	5–10

[a] Maximum values for non-ecotoxic residues.
[b] Interval limits/minimum values for hazardous residues.

on the concentration of dyestuffs resulting in higher removal efficiencies at low dye concentrations. As a result, time required for equilibrium adsorption of Orange DNA13 was much longer than that of Vertigo Blue 49.

Typical values of BET (N$_2$, 77 K) surface areas for commercial activated carbons are usually between 400 and 1500 m^2/g [35]. Low surface area (1.77 m^2/g) of the adsorbent tested shows that bottom ash particles do not have many micropores.

3.1. Leaching test

The German DIN 38414-S4 leaching test procedure was used to evaluate the release of heavy metals from the bottom ash since this method is a required one by some industries in Turkey. The pH and the concentration of heavy metals in the leachate are presented in Table 2. The solubility of Cd, Cr, Mn and Pb seemed to be pH independent. The solubility of Zn, Cu and Ni decreased with increasing pH from 4 to 9. The leached concentrations of heavy metals decreased in the order of Zn, Ni, Cu, Mn, Cd, Pb and Cr in bottom ash.

The French proposal for a Criterion and Evaluation Methods of Waste Ecotoxicity (CEMWE)[36] points out limit values for chemical parameters which are presented in Table 2. All residues with chemical substances in the leachates with concentrations above these limit values are classified as ecotoxic. The German regulation on Hazardous Waste Classification (HWC) [37] defines the limit values for hazardous residues as presented in Table 2. From the chemical point of view, both CEMWE French proposal and the German regulation HWC led to a similar classification of the bottom ash.

In the batch leaching experiments, the highest leachate concentrations of metals were 0.025 mg/l Cd, 0.135 mg/l Cu, 0.163 mg/l Ni, 0.01 mg/l Cr, 0.05 mg/l Mn, 0.01 mg/l Pb and 0.730 mg/l Zn, which suggests that all these results were much lower than both the German and French criteria as shown in Table 2.

3.2. Adsorption dynamics

Both the first and the second order adsorption kinetics were tested to determine the most suitable rate expression for adsorption of the tested dyestuffs onto the CBBA waste material.
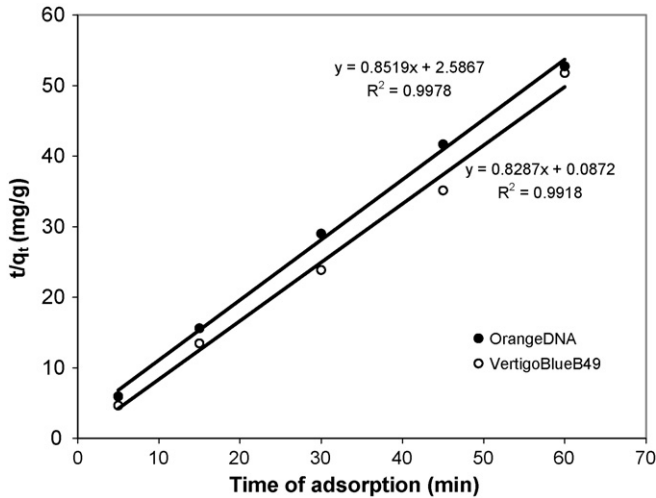

Fig. 4. Effect of agitation time and concentration of Orange DNA on removal efficiency: adsorbent dose, 10 g/300 ml, pH 7, $T = 25\,^\circ$C.

Fig. 5. Plot of second-order model for adsorption of reactive dyes on coal based bottom ash ($C_0 = 50$ mg/l).

Fig. 6. Langmuir isotherm plots for the adsorption of dyestuffs (Vertigo Blue 49 and Orange DNA13.

The first order adsorption rate constant was determined using the Lagergren equation as follows [38]:

$$\log(q_e - q) = \log q_e - \frac{k_{ad}t}{2.303} \tag{1}$$

where q_e and q are the amounts of dye adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_{ad} is the first-order rate constant. The plots of $\log(q_e - q)$ versus time indicated that the data did not fit well to the first-order rate expression for the whole range of incubation time since the correlation coefficients were $R^2 \leq 0.94$ and 0.98 for Orange DNA13 and Vertigo Blue 49, respectively (figures are not shown). As presented in Table 3, the experimental $q_{e,exp}$ values are not in agreement with the calculated $q_{e,cal}$, values indicating that the dye adsorption onto the coal-based bottom ash cannot be represented by a first-order kinetics.

The second-order kinetic model (linear form) can be expressed as [39]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \tag{2}$$

where k_2 (g/mg min) is the rate constant of second-order adsorption. If second-order kinetics is applicable, a plot of t/q_t versus t should show a linear relationship. q_e and k_2 can be determined from the slope and intercept of the plot. The linear plots of t/q_t versus time indicated a good agreement between the experimental data and the second order kinetic model for different initial dyestuff concentrations (Fig. 5). The correlation coefficients for the second-order kinetic model were greater than 0.99 (Table 3).
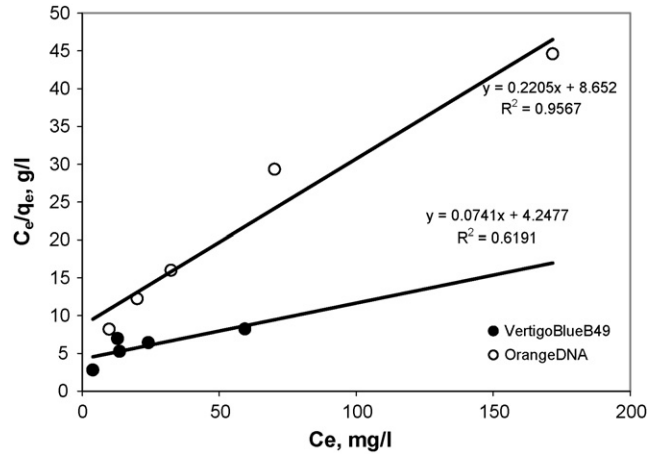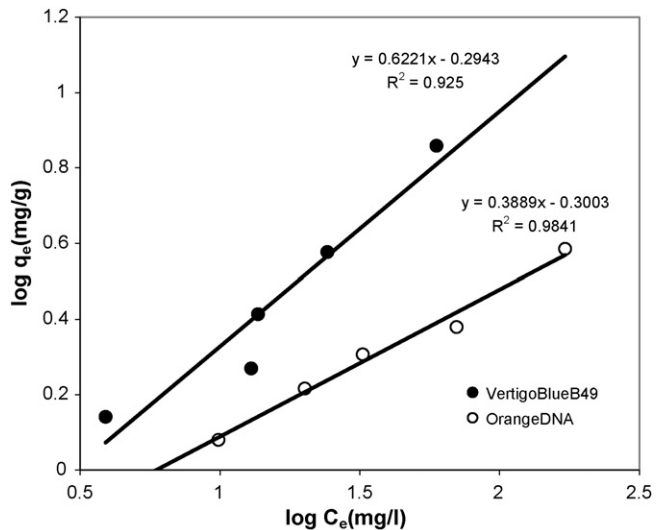

Fig. 7. Freundlich isotherm plots for the adsorption of dyestuffs (Vertigo Blue 49 and Orange DNA13).

Also, the calculated $q_{e,cal}$ values agreed well with the experimental data. The results indicated that the adsorption fits to the second-order kinetic model better than the first order.

3.3. Adsorption isotherms

The equilibrium data presented in Figs. 6 and 7 were correlated with Langmuir and Freundlich isotherms. The Langmuir isotherm is the most widely used two-parameter equation, com-

Table 3
Comparison of the first and second-order adsorption rate constants, and calculated $q_{e,cal}$ and experimental $q_{e,exp}$ values for the two reactive dyes ($C_0 = 50$ mg/l dye concentration)

Dyestuff	$q_{e,exp}$ (mg/g)	k_1 (l/min)	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e,cal}$ (mg/g)	R^2
Vertigo Blue 49 (CI Blue 49) ($\lambda_{max} = 580$ nm)	1.383	0.031	0.37	0.98	0.39	1.331	0.99
Orange DNA13 (C.I Orange 13) ($\lambda_{max} = 417$ nm)	1.204	0.030	0.41	0.94	0.28	1.174	0.99

Table 4
Isotherm constants for the Langmuir and Freundlich isotherms

Reactive dye	Freundlich adsorption isotherm			Langmuir adsorption isotherm		
	K_f (mg/g)	n	R^2	Q_0 (mg/g)	K_L (l/mg)	R^2
Vertigo Blue 49 (CI Blue 49)	0.508	1.61	0.93	13.51	0.0174	0.62
Orange DNA13 (CI Orange 13)	0.501	2.57	0.98	4.54	0.026	0.96

monly expressed as [10]

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0 C_e}, \tag{3}$$

where q_e and C_e are defined as the amount of dye adsorbed (mg/g) and equilibrium liquid-phase concentration (mg/l), respectively. K_L is a direct measure of the intensity of the sorption (l/mg), and Q_0 is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity (mg/g). The constants Q_0 and K_L were determined from the intercept and slope of the linear plots of the experimental data of C_e/q_e versus C_e, respectively. The Langmuir theory assumes that adsorption takes place at specific homogenous sites within the adsorbent and that once a dyestuff molecule occupies a site, no further adsorption can take place at that site [40].

The Freundlich isotherm was also applied for the adsorption of dyes. The Freundlich isotherm model is given by the following equation [29,41]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g), C_e the equilibrium concentration of dye in solution (mg/l) and K_f and n are Freundlich constant. 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 $1/n$, ranging between 0 and 1, is a measure of the adsorption intensity or surface heterogenity. A plot of $\log q_e$ versus $\log C_e$ enables the empirical constants K_f and $1/n$ to be determined from the intercept and slope of the linear regression. Table 4 summarizes the Q_0 and K_L values for the Langmuir isotherm, the K_f and n values for the Freundlich isotherm and the correlation coefficients for the two isotherms. The Freundlich and the Langmuir model parameters determined from Figs. 6 and 7 are listed in Table 4. It can be seen that the Freundlich model yields a much better fit than the Langmuir model because of larger correlation coefficients (R^2) as prsented in Table 4. The n values between 1 and 10 show beneficial adsorption [42]. The maximum adsorption capacities (Q_0) were 13.51 and 4.54 mg dye/g of the adsorbent for Vertigo Blue 49 and Orange DNA13, respectively. The low adsorption can be attributed to the chemical structures of dyes. Low uptake of dyes could be due to presence of both the sulfonic and azo groups which might lead to the formation of large aggregated molecules hindering free diffusion to the internal porosity [43].

4. Conclusion

The present study showed that the CBBA can be used as an adsorbent for the removal of reactive dyes from aqueous solutions. The employed adsorbent 'coal based bottom ash' is quite economic than commercially available adsorbents. The CBBA is freely available waste material with no additional cost which is usually dumped to landfill areas. The use of CBBA as an adsorbent would provide an effective treatment of dilute dyestuff containing wastewaters. Due to acid neutralizing capacity, bottom ash can also be used in the treatment of acidic industrial wastewaters.

The most suitable pH was found to be 7 maximizing the extent of adsorption of the dyestuffs tested. The CBBA exhibited a higher affinity for Vertigo Blue 49, since adsorption of Vertigo Blue occured faster and reached higher equilibrium levels as compared to the Orange DNA13. The low adsorption can be attributed in part to the lower specific surface area of the CBBA and chemical structures of dyes.

The Langmuir model, based on monolayer, uniform and finite adsorption site assumptions, did not represent the experimental data well. The Freundlich isotherm, an empirical equation for heterogeneous surfaces represented the experimental data better than the Langmuir isotherm. The adsorption process was found to fit to the second order kinetics rather than the first-order.

The results showed that the leached amounts of heavy metals from bottom ash were in the following order $Zn > Ni > Cu > Mn > Cd > Cr \approx Pb$.

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