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Coal Bottom Ash and Activated Carbon for Removal of Vertigo Blue Dye in Batik Textile Waste Water: Adsorbent Characteristic, Isotherms, and Kinetics Studies

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Abstract

Batik is one of the textile industries which is growing very rapidly in Indonesia. However, the large amount of waste water produced is still a major problem of this industry. Adsorption processes are still an effective technology to treat the waste, especially in removing coloring agent. However, the study of adsorption kinetics and the use of coal bottom ash as an adsorbent is still limited. The aim of this study was to evaluate the adsorption capacity of coal bottom ash (CBA) in the removal of Vertigo blue 49 dye from textile wastewater and compare it with activated carbon. The optimum conditions of adsorption were determined by investigating the effect of contact time, pH (4, 7, 9) and initial concentration of dye (25 - 100 mg/L). The equilibrium data were analyzed using Langmuir and Freundlich isotherms to obtain the characteristic parameters of each adsorption model. Experimental data were also tested using adsorption kinetic models, which included both pseudo-first-order and pseudo second-order kinetic models. The optimum conditions were found to be an initial concentration of dye of 100 mg/L giving an adsorption capacity of 3.72 mg dye/g adsorbent for the adsorption of Vertigo blue onto commercial activated carbon (CAC) at pH 4 and 2.53 mg dye/g adsorbent for CBA sorbent at pH 9, respectively.

Keywords: Coal based bottom ash (CBA), commercial activated carbon (CAC), adsorption, textile industry, bateeq

Introduction

Batik industries are growing rapidly in Central Java Indonesia since batik is used as a daily cloth. These facts lead to an increase in wastewater effluent, as result of the coloring (dyeing) and finishing processes. In proper treatment of the textile wastewater can cause damage to the environment [1]. In addition, the effluent contains dyes which are toxic and may have mutagenic or carcinogenic influences on living organisms [2-4].

Azo compounds are typical dyes found in textile wastewater. The azo dye (-N=N-) with functional groups like -SO_3,-COO-, and OH- are mostly difficult to degrade [5]. One type of azo dye that is commonly used in the batik industry is Vertigo blue 49 and its molecular formula $C_{32}H_{23}ClN_7Na_3O_{11}S_3$ and molecular weight of 882.186 g/mol are shown in **Figure 1** [6,7].

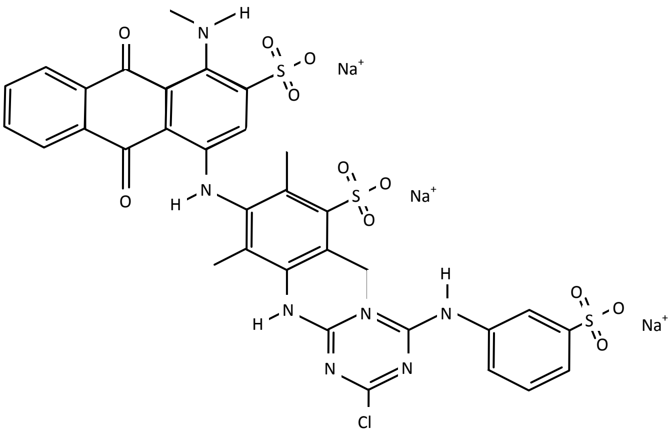


Figure 1 The chemical structure of Vertigo blue 49 [8].

Various techniques have been employed to remove dyes from wastewater, including biological treatment, adsorption, chemical oxidation, coagulation, membrane filtration and photochemical degradation [5,9,10] or a combination of these wastewater treatments [6]. Among these methods, adsorption is often used due to its effectiveness, simplicity in the operational, low cost and low energy requirements [6,7,11].

In the adsorption process, the choice of adsorbent is important. Commercial activated carbon (CAC) has been widely used for CO_2 adsorption, water vapor or other chemicals, as well as used as adsorbents in wastewater treatment processes of textile industry due to its advantages such as large surface area, large adsorption capacity and easy application. However, it requires a high cost adsorbent [1,2,5]. Another option is Coal bottom ash (CBA) derived from coal combustion for electricity generation in power plants or some industries. CBA is abundantly available in Indonesia and it is an inexpensive material. Based on the data of the Indonesian environment ministry (2006), 5.8 tons of CBA is produced per day. The main composition of CBA are SiO_2, Al_2O_3, Fe_2O_3, CaO and the residual carbon from burning coal [8]. Due to the high composition of silica and other metal oxides, it has the possibility to remove dye from wastewater.

This work studied the effectiveness of CAC and CBA to remove Vertigo blue 49 from textile wastewater. The parameters such as effect of contact time, pH and initial concentration were investigated to study kinetic and isotherm models. The physical properties of CAC and CBA were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray fluorescence (XRF) and scanning electron microscopy (SEM).

Research methodology

Adsorbent

Commercial activated carbon (CAC) was obtained from the chemical store, while the coal bottom ash (CBA) was provided by PT. Indo Acidatama, Surakarta, Central Java, Indonesia. CBA was sieved using a Sieve Shaker (AG-515 MBT) to obtain a 60 mesh size powder. The meshed coal was activated using 250 mL H_2O_2 (Merck) 0.2 N and stirred for 1 h. The CBA was repeatedly washed with distilled water and dried at 140 °C and then it was burned in the furnace (Thermolyne 48000) at 500 °C for 15 min.

Batch adsorption experiments

Aqueous solutions of Vertigo blue 49 were prepared at various concentrations and pHs. A certain gram of Vertigo blue 49 was dissolved in a 1000 mL measuring flask and then shaken in an ultrasonic bath until homogeneous and then used as the stock solution. Several concentrations of dye: 25, 50, 75 and 100 mg/L at various pHs (4, 7 and 9) were prepared from the stock solution. Batch experiments were conducted employing 10 g of adsorbent into 400 mL of dye solution. The pH of the samples was adjusted to the desired value with HCl or NaOH (Merck). The solution was stirred for 60 min at a constant agitation speed of 700 rpm. The solutions were sampled every 5, 10, 15, 20, 30, 45 and 60 min to study the effect of contact time. The sample was filtered with filter paper (Whatman 42). Furthermore the absorbance of each sample was measured using a spectrophotometer.

Dye concentration and removal capacity

The concentration of Vertigo blue 49 was determined spectrophotometrically using a UV-visible spectrophotometer (UV/VIS gamma Image 6) by taking measurements at the absorbance maximum. A calibration curve was plotted between the absorbance and the concentration of the Vertigo blue 49 solution to obtain the absorbance-concentration profile. The amount of Vertigo blue 49 uptake per unit of adsorbent (Q_e) was calculated using the following equation;

$$Q_e = (C_i - C_e) \times \frac{V}{m} \tag{1}$$

where C_i is the initial Vertigo blue 49 concentration (mg/L), C_e is the Vertigo blue 49 concentration at the adsorption equilibrium (mg/L), V is the volume of Vertigo blue 49 solution (L), and m is the weight of the activated carbon (g).

Adsorbent characteristic

The morphological features and surface characteristics of the CAC and CBA were obtained from SEM before and after activation at an accelerating voltage at 20 kV Leo 440i (UK) with a magnification 2500X and 10000X.

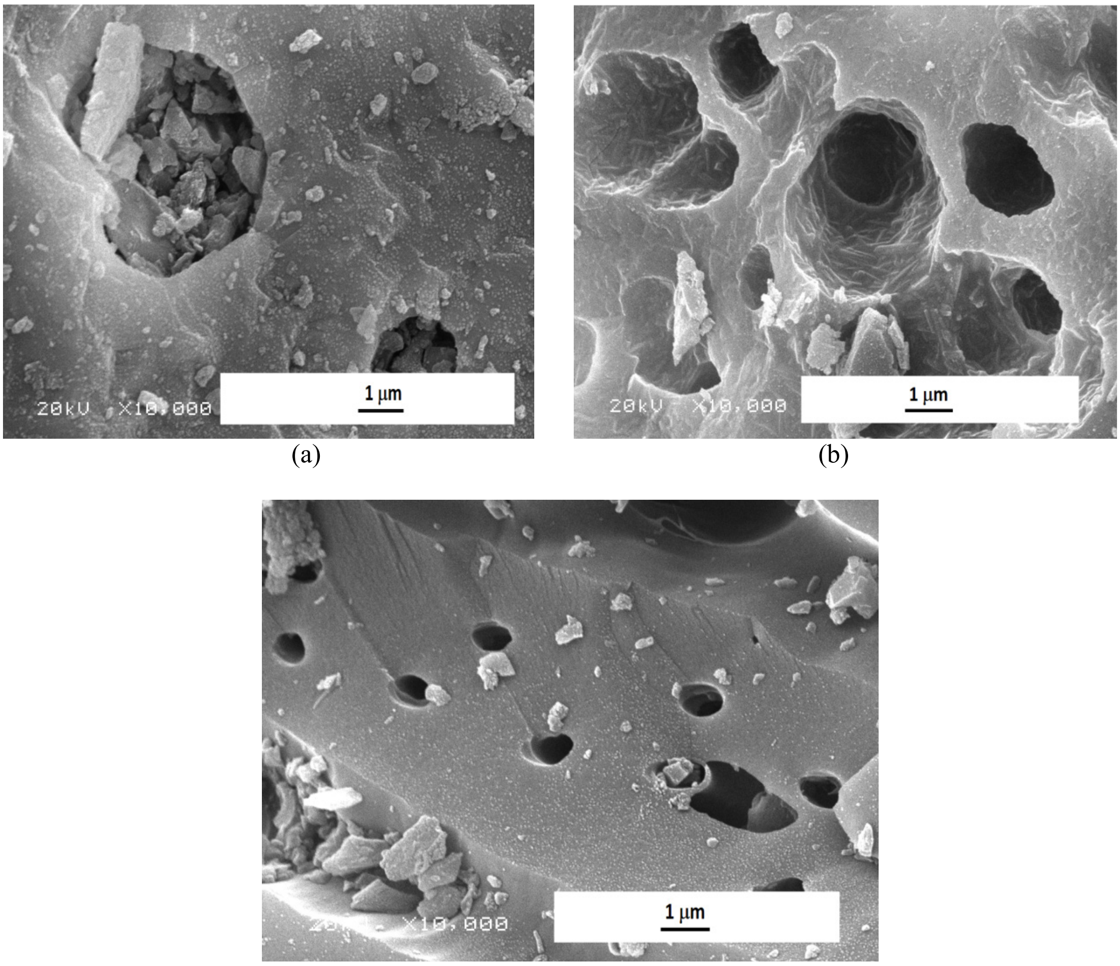
The chemical composition of CBA and CAC were determined by EDXRF (Pananlytical Minipal 4) at wavenumber 400 - 4000 cm^{-1}.

Functional groups of CAC and CBA adsorbent were determined using FTIR. IR absorbance data were obtained for wavenumbers in the range of 4000 - 400 cm^{-1}. CBA or CAC were mixed with KBr at ratio of 1:100 and then analyzed using a FT-IR spectrometer (Mattson 1000, UK).

Results and discussion

Characteristics of the adsorbent material

Batch adsorption was conducted to determine the adsorption capacity of CBA to remove Vertigo blue 49 from aqueous solution. The effectiveness of the adsorption process was largely determined by the type of adsorbent. According to Gupta and Suhas [7,8], low cost adsorbents can be used for the removal of dye where its adsorption capacities depend on their surface area or micro/meso porosity, pore size distribution, and particle size. The surface morphology of the CAC and CBA were observed by SEM analysis (**Figure 2**).



(a) (b)

(c)

Figure 2 SEM micrographs of CBA before (a) and after activation (b) and CAC(c).

Figure 2 shows the morphology CBA before activation, **Figure 2(a)** indicating small pores sizes compared to CBA after activation due to being covered with impurities which may close the pores, while **Figure 2(b)** shows the morphology CBA after activation with no impurities, therefore it had a greater surface area. **Figure 2(c)** illustrates the morphology of CAC showing the pores. Hong *et al*. (2008) reported that coal char has a structure such as aluminum silicate which has the possibility to adsorb heavy metals from aqueous solution [12].

Functional groups and structures on the surface of the adsorbent strongly affect the adsorption capacity [7]. Functional groups in CAC and CBA were determined using FTIR spectroscopy in order to understand the functional groups which may bind with Vertigo blue 49 (**Figure 3**). The IR spectra of the samples were recorded in the range 4000 - 400 cm^{-1}. The stretching adsorption band of O–H in the crystal structure of the adsorbent is observed at 3400 to 3000 cm^{-1} which indicates the existence of-OH groups in Si-OH bond. The adsorption band on fly ash adsorbents at 3645 cm^{-1} which corresponds to the stretching vibration –OH has been also reported by Kara *et al.* [13] and Dizge *et al.* [14]. The peak at 1650 cm^{-1} indicates a cluster of water molecules that was assigned to free hydroxyl on fly ash.

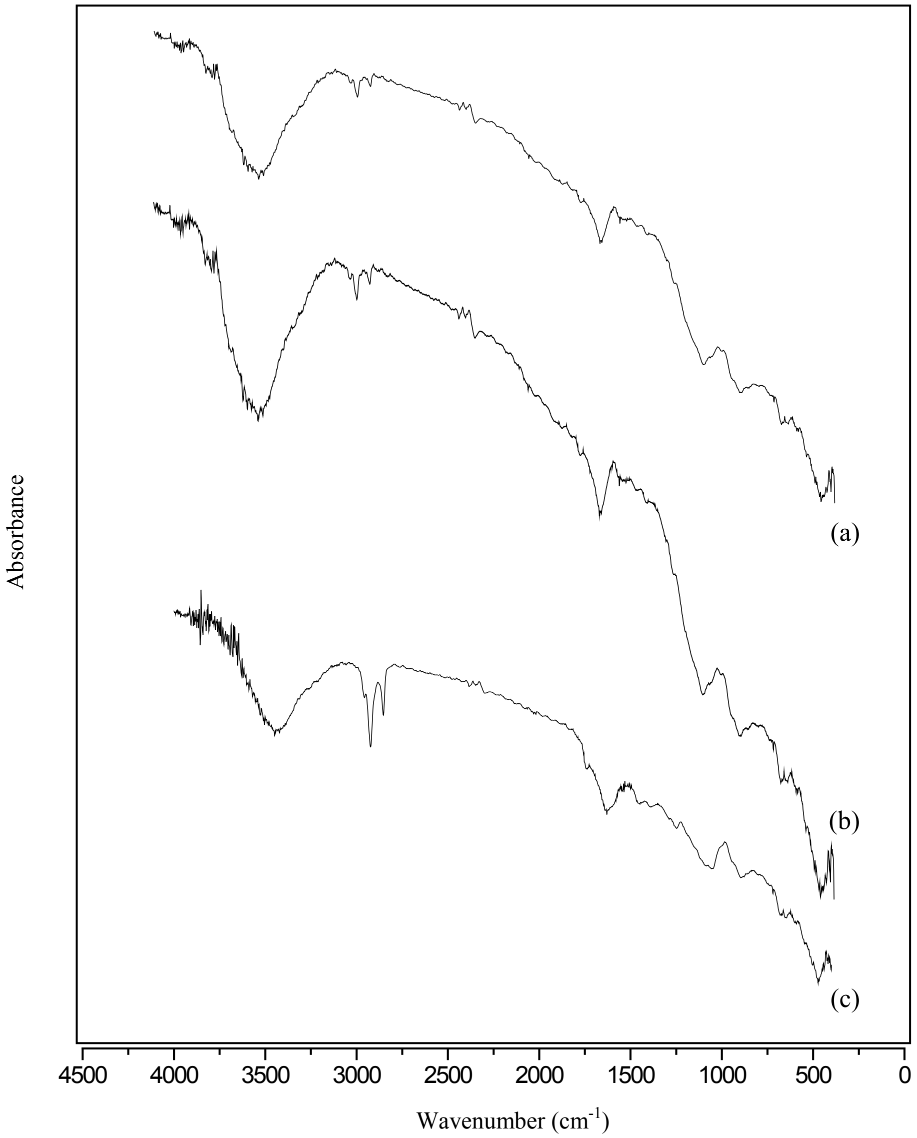


Figure 3 FT-IR spectra of CBA after activation (a), CBA before activation (b) and CAC(c).

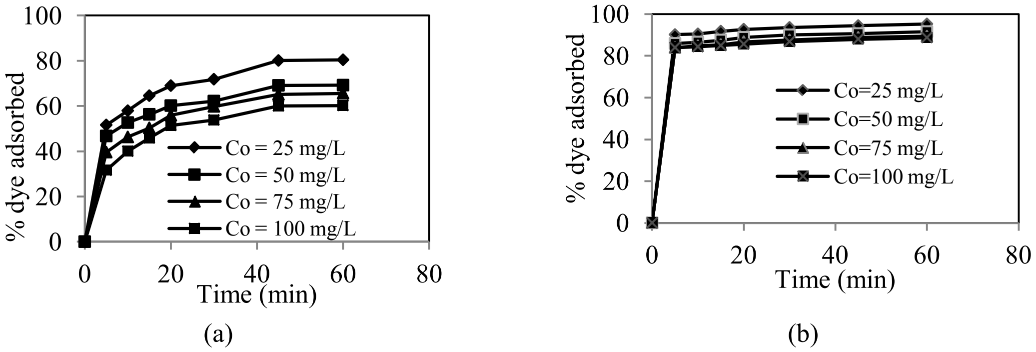
The composition of CAC and CBA were analyzed using XRF and the results are presented in **Table 1**. XRF results showed that the largest component in CAC is Fe_2O_3, SiO_2, and CaO while CBA is SiO_2, Al_2O_3, and Fe_2O_3. The composition of coal fly ash based on XRF analysis was reported by Hong *et al.* (2008) which showed that SiO_2 (53.4 %), Al_2O_3 (21.0 %), Fe_2O_3 (8.0 %) and CaO (7.4 %) was the main component of fly ash [12]. Kara *et al.* [12] reported the fly ash composition consisted of SiO_2 (15.14 %), Al_2O_3 (7.54 %), CaO (23.66 %), Fe_2O_3 (3.3 %).

Table 1 The main components contained in CAC and CBA after activation.

Composition	XRF	
	CAC (%)	CBA after activation (%)
Al_2O_3	5.4	24.64
SiO_2	11.2	45.8
Fe_2O_3	40.8	16.6
CaO	9.84	4.036
K_2O	21	2.05
MnO	2.9	0.12
BaO	0.2	0
CuO	0.92	0.2
Cr_2O_3	0	0.03
TiO_2	2.2	6.16

Effect of initial concentration

Figures 4(a) and **4(b)** show the percentage removal of Vertigo blue 49 dye adsorption at different initial concentration and time using CBA and CAC, respectively. The results show that for both CBA and CAC, the percentage removal of dye adsorption increased with decreasing initial dye concentration and increasing contact time. For CBA, the maximum dye adsorption was found at 60 min and 25 mg/L initial dye concentration which resulted in a percentage of dye adsorbed of 80.37 %. From **Figure 4(a)**, it can be seen that the increasing dye concentration from 25 to 100 mg/L led to a decrease in the removal of dye from 80.37 to 60.21 %. CBA shows a gradual increase of dye adsorption until it reach equilibrium at 60 min contact time. At initial concentrations (25 - 100 mg/L), equilibrium was achieved at 60 min contact time. This result is in accordance with the results reported by Dizge *et al.* [14] which found that the removal of dyes was dependent on the concentration uptake of dye. Singh *et al.* [15] reported that a high initial concentration resulted in a high driving force between the dye and adsorbent hence increased the percentage removal dye but after the maximum initial dye concentration, the adsorption of dye declined. A higher dye uptake was observed at lower initial concentration due to the interaction between all sorbate ions in the solution with the binding sites of the adsorbent. Moreover, a decreasing trend in the % uptake of dye by the adsorbent at higher initial concentration was due to the saturation of adsorbent sites.



(a) (b)

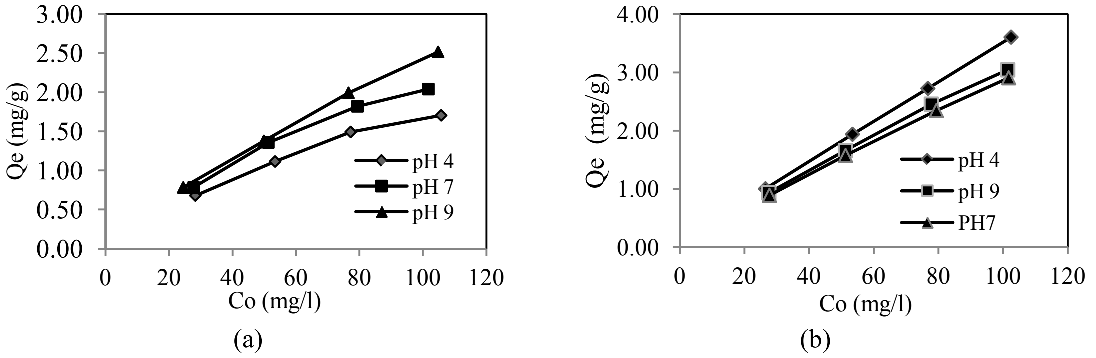
Figure 4 (a) Effect of contact time on the percentage of dye absorbed using CBA at various initial concentrations (adsorbent dosage = 10 g, V = 400 mL at pH 9) and (b) Effect of time on the percentage of dye absorbed using CAC at various initial concentrations (adsorbent dosage = 10 g, V = 400 mL at pH 4).

Figure 4(b) illustrates the effect of initial dye concentration and contact time on the percentage of dye removal using CAC. As can be seen, the percentage of dye removal decreased with increasing initial concentration from 25 to 100 mg/L which resulted in a decreasing percentage of dye adsorbed from 95.21 to 88.71 %. It also shows that increasing the contact time, leads to a considerable increase in dye adsorbed until it reaches equilibrium (5 min contact time) for all initial concentrations from 25 to 100 mg/L. It has been reported that when the equilibrium time is reached increasing contact time will not give a change in the mass uptake and the percentage removal adsorption constant [3]. It shows a faster contact time to reach equilibrium was observed for CAC than that of bottom ash due to the coal- bottom ash not having much micro and macroporous structure and possessing a low BET surface area, which is responsible for its low adsorption capacity [16]. Furthermore, a large amount of vacant sides available in active carbon at initial time resulted in an increase in the amount of dye adsorbed to the surface of the adsorbent until reaching equilibrium [6].

The results also indicated that CBA has the potential to be used as an adsorbent for removal of azo dyes from wastewater, especially Vertigo blue 49. However, % removal of Vertigo blue dye on CBA was lower than that on CAC, this is due to the greater of surface area of CAC. The adsorbent surface area is very important in the adsorption process. The effective surface area increased as the particle size decreased and as a consequence, the saturation capacity per unit mass of the adsorbent increased [4].

Effect of pH

The degree of acidity or pH and initial concentration of dyes (Co) are important factors in the adsorption process. The effect of various pH (4, 7 and 9) and the initial concentration of Vertigo blue 49 (25 - 100 mg/L) were studied and the results are shown in **Figures 5(a)** and **5(b)** for CBA and CAC, respectively. It can be seen in **Figure 5(a)** that an increasing pH from 4 to 9 led to an increased in the adsorption capacities (1.51 to 2.53 mg/g). The maximum Vertigo blue dye removal was observed at pH 9. The results are due to the number of negatively charged sites increasing and the number of positively charged sites of CBA adsorbent decreasing when the pH of the system is increased. The negatively charged surface sites on the adsorbent can enhance the adsorption of the cationic dye due to electrostatic forces [8]. The results for dye adsorption on CAC are shown in **Figure 5(b)**, maximum Vertigo blue 49 dye adsorption using CAC was observed at pH 4, while adsorption decreased for alkaline and neutral pH. **Figure 5(b)** shows that when the pH increased from 4 to 9, the adsorption capacity (Qe) decreased from 3.72 to 2.78 mg/g. In acidic pH, CAC has a higher adsorption capacity compared to alkaline or neutral pH. These results may be attributed to an increase in negative charge on carbon which will led to higher dye adsorption on the surface of the carbon while at neutral pH, the adsorption capacity was lower than at alkaline pH, due to the surface oxidation that occurs at neutral pH which led to activity of granular carbon at the surface [8]. It had been previously reported that dye adsorption is highly pH dependent that affected between the surface charge of the fly ash adsorbent [14], coal-carbon active [16] and the degree ionization of dye in solution.



(a) (b)

Figure 5 (a) Effect of initial concentration of dye Vertigo blue 49 at various pH, using activated CBA (adsorbent dosage = 10 g, V = 400 mL for 60 min) and (b) Effect of initial concentration of dye Vertigo blue 49 at various pH, using CAC (adsorbent dosage = 10 g, V = 400 mL for 60 min).

Isotherm adsorption

The adsorption mechanisms of CAC and CBA in the removal of Vertigo blue 49 dye solutions were analyzed using Langmuir and Freundlich adsorption isotherm models. The equilibrium adsorption of Vertigo blue 49 dye solutions by CAC (pH 4) and CBA (pH 9) were used to determined Langmuir and Freundlich isotherm models.

The Langmuir adsorption isotherm can be written as follows;

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 \cdot B} + \frac{C_e}{Q_0} \tag{2}$$

where, C_e and Q_e are the concentration of dye adsorbate in solution (mg/L) and the amount of dye on the adsorbent at equilibrium (mg dye/$g_{adsorbent}$), respectively [17]. Q_o and B are the Langmuir constants indicating the maximum monolayer adsorption capacity and adsorption energy [18,19]. The Langmuir constant, B and Q_0, can be determined from the intercept and slope of the linear plot between C_e versus C_e/Q_e as shown in **Figure 6** and the results are presented in **Table 2**.

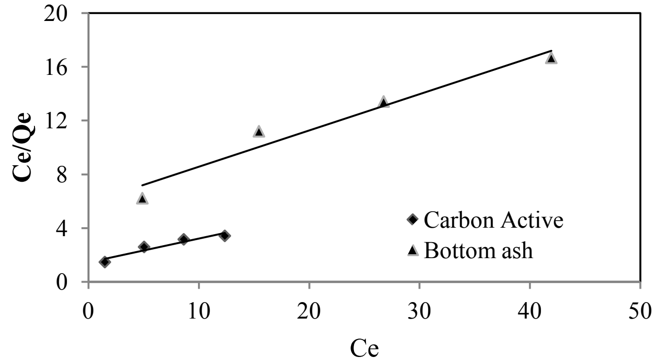


Figure 6 Langmuir adsorption isotherms of Vertigo blue 46 dye removal using CBA (pH 9) and CAC (pH 4).

The Freundlich isotherm is based on an interaction between the molecule adsorbate in a multilayer adsorption model [9]. The Freundlich isotherm is expressed by the following empirical equation;

$$Q_e = K_f \cdot C_e^{\frac{1}{n}} \tag{3}$$

The equation above can be written;

$$\log Q_e = \log K_f + \left(\frac{1}{n}\right) \cdot \log C_e \tag{4}$$

where C_e and Q_e are the concentration of dye solution at equilibrium (mg/L) and the concentration of dye adsorbed on adsorbent (mg/g) at equilibrium, respectively. K_f is the Freundlich constant that describes the adsorption capacity (mg/g) [15]. While *1/n* is the value of adsorption intensity or surface heterogeneity [9,20]. The values of K_f and *n* can be calculated from the intercept and slope of the linear plot between *log C_e* and *log Q_e* as shown in **Figure 7** with the results presented in **Table 2**.

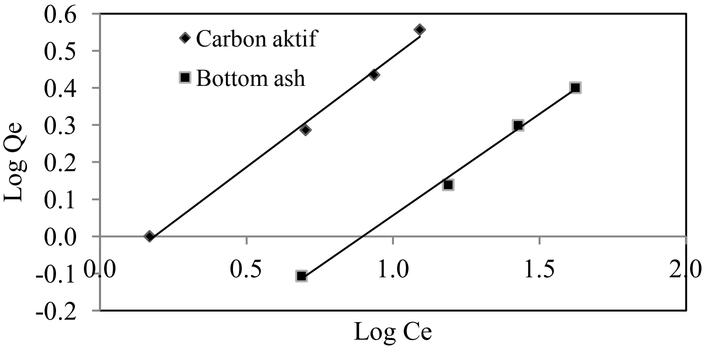


Figure 7 Freundlich adsorption isotherm of Vertigo blue 46 dye removal using CBA and CAC.

Table 2 shows the parameters obtained from plotting Langmuir and Freundlich isotherm models of Vertigo blue 49 dye adsorption on CBA and CAC. From **Table 2**, high values of correlation coefficient (R^2 > 0.967) were obtained from Freundlich models for CBA and CAC adsorbents. According to the regression coefficient, each adsorption isotherm appropriately described the adsorption of Vertigo blue 49 dye on CBA and CAC adsorbents but the Freundlich model was more suitable compared to the Langmuir isotherm model [20]. This indicates that the adsorption of Vertigo blue 49 onto CBA and CAC takes place as multilayer adsorption occurs and all the molecules outside the first layer have the same energy for adsorption [14]. The value of Q_m for CAC shows a higher value (6.29 mg/g) than that for CBA (3.72 mg/g) indicating that CAC has a higher adsorption capacity compared to CBA. The maximum adsorption capacity of CBA and CAC was occurred at pH 9 and pH 4, respectively which indicated the effect of pH on the different charges of adsorbent sites. The value of *n* represents sorption intensity where it shows *n* > 1 indicating favorable adsorption of dye on the adsorbent [14,20,21].

Table 2 Constants of Langmuir and Freundlich adsorption isotherm for adsorption of Vertigo blue 49 onto CBA and CAC.

Adsorbent	pH	Langmuir			Freundlich		
		Q_o(mg/g)	B	R^2	n	K_f	R^2
CBA	4	2.60	0.03	0.992	1.90	0.28	0.967
	7	2.92	0.05	0.996	1.83	0.32	0.996
	9	3.72	0.05	0.953	1.83	0.32	0.996
CAC	4	6.29	0.03	0.976	1.69	0.78	0.991
	7	5.68	0.12	0.883	1.40	0.27	0.996
	9	5.81	0.04	0.998	1.48	0.36	0.995

Adsorption kinetics

Kinetics of adsorption were used to determine the rate of adsorption [1,17]. Two kinetic models, pseudo-first-order rate model and pseudo-second-order rate, were used to describe the adsorption rate in this study. The equation of the model pseudo-first-order rate is as follows;

$$\frac{dQ}{dt} = k_1(Q_e - Q) \tag{5}$$

$$\log(Q_e - Q) = \log Q_e - \frac{k_1 \cdot t}{2.303} \tag{6}$$

where Q and Qe are the amount of dye adsorbed per unit mass of adsorbent (mmol/kg) at time t and at equilibrium, respectively. k_1 is the first order adsorption rate constant. The first order kinetic model indicated the rate of the adsorption process is proportional to the dye concentration [18] .

The equation of the pseudo-second model-order rate is as follows;

$$\frac{dQ}{dt} = k_2(Q_e - Q) \tag{7}$$

$$\frac{1}{(Q_e - Q)} = \frac{1}{Q_e} + k_2 \cdot t \tag{8}$$

$$\frac{t}{Q} = \frac{1}{Q_e} \cdot t + \frac{1}{k_2 Q_e^2} \tag{9}$$

where k_2 is a second order adsorption rate constant [8].

The kinetics of pseudo-first-order rate and pseudo-second-order rate models are shown in **Figures 8 (a)** and (**b**), respectively. **Table 3** shows the rate constants (k_1 and k_2), the equilibrium adsorption capacities (Q_e) and the corresponding linear regression correlation coefficient values (R^2) for both models. The higher values of R^2 were observed for the pseudo-second order model (R^2~1). The theoretical Q_e values obtained from the pseudo-second order model were also closer to the experimental $Q_{e,exp}$ values compared to the values from the pseudo-first order model. These results indicate that the pseudo-second order kinetic model gave a better correlation for the adsorption of Vertigo blue 49 on CBA as well as CAC compared to the pseudo-first order model. The second order rate constants were found to decrease with initial concentration of Vertigo blue dye in the range of 25 - 100 mg/L for both sorbents. Previous studies also reported the pseudo second-order kinetic model fitted better as compared to first-order kinetics for removal of dyes on sorbents [1,17,22-24]. Tunc *et al.* [21] also observed that the value of the second-order rate constants were diminished with increasing initial concentration of remazol black B reactive dye on cotton plant waste sorbent. The second order kinetic model is derived from adsorption processes in which the rate-controlling step is an exchange reaction [18].

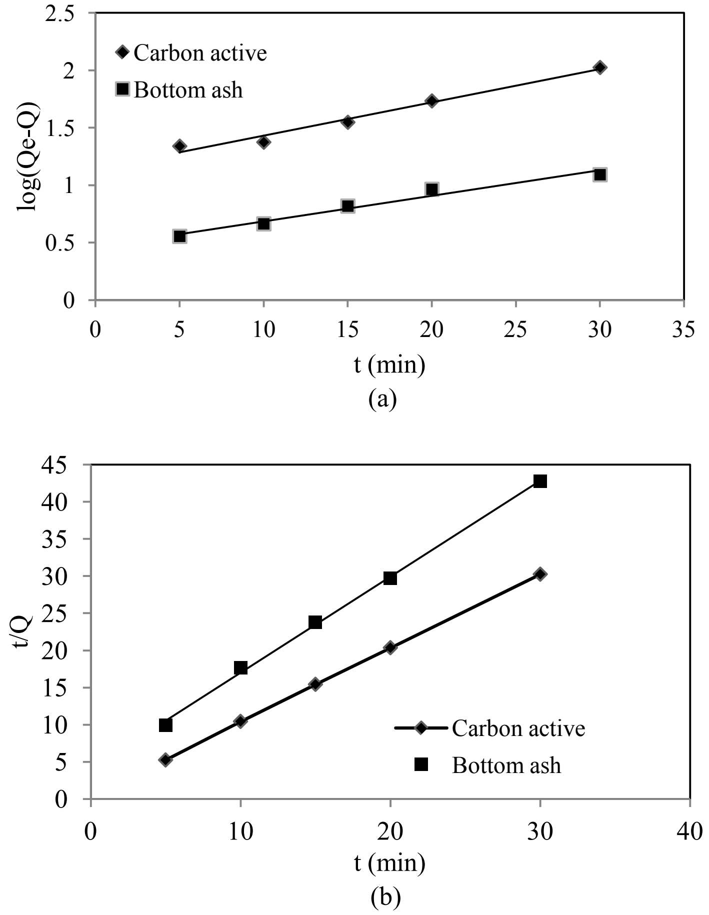


Figure 8 (a) Pseudo-first-order kinetic curves of Vertigo blue 49 dye removal on CBA (pH 9) and CAC (pH 4) sorbents and (b) Pseudo-second-order kinetic curves of Vertigo blue 49 dye removal on CBA (pH 9) and CAC (pH 4) sorbents.

Table 3 The constant of dye adsorption kinetics Vertigo blue 49 onto CBA and CAC at various concentrations.

Adsorbent	Initial Concentrations (mg/L)	$Q_{e,exp}$	Pseudo-first-order rate			Pseudo-second-order rate		
			$Q_{e,calc}$	k_1	R^2	$Q_{e,calc}$	k_2	R^2
CBA	25	0.790	0.51	0.139	0.976	0.66	0.235	0.99
	50	1.380	0.95	0.157	0.958	1.15	0.146	0.99
	75	2.010	1.27	0.124	0.965	1.71	0.085	0.99
	100	2.520	2.16	0.152	0.955	2.19	0.059	0.99
CAC	25	1.006	0.06	0.08	0.937	1.02	1.690	1.000
	50	1.943	0.13	0.10	0.980	1.97	0.767	1.000
	75	2.720	0.17	0.07	0.947	2.77	0.538	1.000
	100	3.600	0.19	0.06	0.884	3.66	0.411	1.000

Conclusions

The adsorption of Vertigo blue 49 onto CBA and CAC sorbents from wastewater was conducted in several experimental parameters such as contact time, pH solution, and initial metal concentration. The adsorbents were characterized using SEM, FTIR, and XRF. The SEM image shows that both adsorbents consists of porous particles. The IR spectra of the samples show an OH stretching vibration band at 3645 cm^{-1}. The XRF results show that the adsorbent consists mainly of Fe_2O_3, SiO_2, and CaO for CAC while SiO_2, Al_2O_3, and Fe_2O_3 for CBA. The effect of pH (4 - 9) and initial concentration (25 - 100 mg/L) shows that the Q_e of Vertigo blue 49 was observed at 2.53 and 3.72 mg/g for CBA (pH 9) and CAC (pH 4), respectively at an initial concentration of 100 mg/L. While, the percentage of adsorption decreased with increasing initial dye concentration due to the saturation of binding sites in the adsorbent at higher initial dye concentration. Equilibrium studies showed that adsorption of Vertigo blue 49 on CBA and CAC fitted better to a Freundlich isotherm model compare to a Langmuir model. Kinetic studies of Vertigo blue 49 was found to obey a pseudo-second-order model.

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