Enhanced Removal of Brilliant Orange by Poly(4-vinylpyridine)/Acid-Activated Bentonite Composite

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The present work aimed at the adsorption of brilliant orange (BO) textile dye on treated clay (TC) and a new composite (*i.e.*, TC55) prepared by mixing TC and poly(4-vinylpyridine) (P4VP), which is a cationic polymer. The net negative structural charge of TC resulted in high adsorption capacity toward cationic dyes. The preparation of composites by alteration of minerals with polycations was used to enhance adsorption capacities for anionic dyes. Moreover, the effects of several factors, such as the contact time, the pH of dye solution, adsorbent dosage, initial dye concentrations, and temperature, on the adsorption capacity were investigated. The results showed that TC55 fixed more dye molecules than did TC. The adsorption equilibrium time for TC and TC55 was 60 min. In addition, the kinetics of dye adsorption was found to follow the pseudo-second-order model, and the adsorption isotherm was well described by the Langmuir model for all adsorbents. It is worth adding that the adsorption capacities of TC and TC55 at 295 K and pH = 4.11 were 178 and 222 mg g^{-1}, respectively. Indeed, the effect of temperature on the adsorption rate indicated that the reaction was endothermic. However, the values of the free energy showed that the adsorption was physisorption.

Keywords: Treated clay (TC), Poly(4-vinylpyridine) (P4VP), TC55 composite, Adsorption, Brilliant orange (BO) dye

INTRODUCTION

Effluents produced by chemical, pharmaceutical, textile, polymer, refinery, plastic, and leather industries contain many toxic substances, including dyes, heavy metal ions, and toxic organic compounds. The treatment of dye-contaminated wastewater is one of the most serious environmental problems faced by the above industries. Dye molecules are difficult to be biodegraded naturally because of their chemical stability [1]. Even at low concentrations, toxic dyes may pose serious threats not only to human health but also to marine life [2]. To remove the toxic compounds from colored effluents, various treatment processes, including membrane filtration [3], biological treatment [4], photocatalytic degradation [5], and adsorption [6], have been developed. Because of its low-cost, simplicity of operation,

and the availability of a wide range of adsorbents [7], adsorption is considered one of the most competitive methods adopted for removing toxic dyes from their aqueous solutions. Therefore, there has been a growing interest in renewable, economical, easily available, and highly effective adsorbents. Recently, attention has been focused on low-cost alternative materials, including bentonite [8], polymer-modified bentonite [9-10], agricultural wastes [11-12], and zeolites [13], for the removal of dyes by adsorption. Due to their high cation exchange capacity and large surface area [14], clay minerals have been studied for their potential applications as environmental remediation agents [15] in heavy metals and organic compounds adsorption [16]. However, clays such as bentonite in natural form show a low adsorption capacity for anionic dyes due to their net negative structural charge. In order to adsorb anions, the modified surface must possess positively charged exchange sites. Modification of bentonite carried out through combination

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with other materials is employed to enhance its adsorption capacity. In our earlier work, composites based on bentonite and poly(4-vinylpyridinium) salts were used to adsorb hexavalent chromium anions [17]. N-octyl quaternized poly(4-vinylpyridine) (P4VP) was also used to remove brilliant orange dye [10]. In an acidic medium, the pyridine group exists in the protonated ammonium (-NH$^+$) and is expected to form an electrostatic attraction with negatively charged dye molecules.

In this work, the removal of brilliant orange (BO) from aqueous solutions was investigated using acid-treated clay (TC), named bleaching earth, and a new composite called TC55, prepared by combining TC with (P4VP), which is a cationic polymer. The optimization of the adsorption conditions was made possible by investigating the effects of several parameters such as the pH of BO solution, contact time, adsorbent dose, initial dye concentration, and temperature. The equilibrium data were analyzed using various adsorption isotherm models. To evaluate the adsorption mechanism, the kinetic data were determined using the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models.

EXPERIMENTAL

Materials

The treatment of bentonite, preparation of TC55 composite, and their characterization are described in our earlier work [17]. The TC obtained by the industrial treatment of drilling clay with a concentrated sulfuric acid solution was supplied by a local company known as ENOF. The chemical composition of TC was determined by X-ray fluorescence (XRF) spectrometry, and the data obtained are reported in Table 1. P4VP was supplied by Aldrich, and its average molecular weight, close to 64,000 g mol^{-1}, was determined by capillary viscosity using the empirical Mark-Houwink power law [18]. All the solvents were supplied by Aldrich (analytical grade) and used without further purification.

Preparation of TC55 Composite

Five g of the TC was dispersed in 50 mL of distilled methanol and then introduced into a 100 ml flask under nitrogen. A known amount of P4VP dissolved in 7 ml of methanol, which was previously degassed with nitrogen, was added dropwise. The mixture was stirred for 24 h and then precipitated twice in ethy lether, filtered, and dried at 75 °C for 24 h.

The modified TC was named TC55 (5 g of treated clay and 0.5 g of P4VP) (see Table 2). TC and TC55 composite samples were characterized by Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). In addition, TGA and FTIR were used to determine weight loss percentage and confirm the adsorption of P4VP on the TC, respectively [17].

Table 1. Chemical Composition of the TC [17]

Species	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	Na$_2$O	CaO	K$_2$O	MgO	TiO$_2$	LOI
(w/w)%	65.4	14.46	1.19	2.15	2.03	0.08	1.93	0.11	12.1

Table 2. The Weight Percentage of Coated P4VP on the TC [17]

Sample	Initial amount of P4VP (g)	Weight loss % from 20-200 °C (water)	Weight loss % from 300-800 °C (P4VP)
P4VP			92.5
TC		0.5	3.9
TC55	0.5	7.2	7.3

For the TC, only a broad absorption band appeared between 1600 and 1800 cm^{-1}, with a maximum at 1650 cm^{-1}. This absorption band corresponds to adsorbed water. For pure P4VP, the spectrum was characterized by two main bands at 1600 cm^{-1} (C=N stretching vibration in the aromatic ring) and at 1420 cm^{-1} (C=C stretching vibration in the aromatic ring). In the FTIR spectrum of the TC55 composite, the characteristic bands of both the polymer and unmodified TC were represented. The presence of P4VP on the TC was clearly confirmed by two narrow bands at 1600 cm^{-1} and 1420 cm^{-1} [17].

Dye Solution

The (BO) anionic dye used industrially for polyamide fibers was considered as a model organic dye to assess the adsorption potential of the TC and TC55 composite. The BO dye was used without any purification, and its characteristics are shown in Table 3.

Once prepared, a stock solution containing 1000 mg l^{-1} of the dye was kept in a dark vessel for further experiments. This compound was absorbed at 492 nm on a UV-Vis spectrophotometer (OPTIZEN 1412 V). Intrinsic pH values of 6.2 were measured at 25 °C with a Denver instrument model 225 potentiometer for a 25 ml aqueous aliquot containing 0.5 g of BO dye. This pH value did not vary after the addition of TC or TC55 composite. Bi-distilled water was used for the preparation of all experimental solutions.

Determination of pH$_{PZC}$

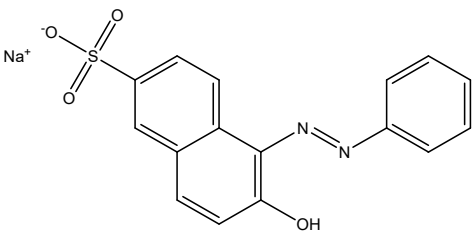The pH at which the net charge of the adsorbent can be used as an important parameter to determine the adsorption ability of the surface and the type of surface-active centers is known as the point of zero charge (pH$_{PZC}$). In the present work, the pH$_{PZC}$ of the adsorbent (*i.e.*, TC and TC55) was determined using a batch equilibrium method, following the procedures previously outlined by Monvisade *et al.* [19].

Briefly, 100 ml of NaCl solution (0.1 M) was adjusted to the appropriate pH in the range of 1-12 using HCl (0.1 M) or NaOH (0.1 M) solutions. Afterward, 30 mg of adsorbent was added, and the suspension was stirred for 24 h at room temperature before the final pH of the solution (pH$_f$) was determined. The pH$_{PZC}$ was obtained from a plot of pH$_i$-pH$_f$ *vs.* pH$_i$.

Studies of BO Adsorption by TC and TC55 Composite

To study the effect of pH value on the adsorption of BO onto the TC and TC55 composite, the initial pH values were adjusted from 2 to 9 by adding a few drops of 0.10 M HCl or 0.10 M NaOH solutions. Then, 30 mg of the samples (TC and TC55 composite) were added to 40 mL of BO solution at 50 mg l^{-1}. The samples were agitated on a thermostated shaker for 180 min at 298 K. The adsorption kinetic experiment at 50 mg l^{-1} on BO solution at pH = 4.11 was performed by the batch method, where 30 mg of the adsorbent (TC and TC55 composite) was added to 40 ml of BO solution. The samples were agitated for times varying from 2 to 300 min. The initial adsorbent mass effect was also studied. To this end, various amounts of adsorbent (10-100 mg) were added to 40 ml of BO solution at 50 mg l^{-1} and stirred for 60 min at 298 K. Adsorption isotherms were determined by adding 10 mg of adsorbent into 40 ml of dye

Table 3. Characteristics of the (BO)

C.I. name	Chemical structure	Molecular formula	M_w (g mol^{-1})	λ_{max} (nm)
Brilliant orange		$C_{16}H_{11}N_2NaO_4S$	350.32	492

solutions and agitating them in a thermostated shaker for 60 min at 298 K. The concentration of initial BO solutions varied between 10 and 350 mg l^{-1}. Furthermore, the effect of temperature on the adsorption capacity was investigated. Experiments at different temperatures (308, 318, and 328 K) were carried out by adding 10 mg of samples TC and TC55 composite to 40 ml of 50 mg l^{-1} BO solution. The samples were agitated for 60 min. At the end of each experiment, the samples were collected by centrifugation, and the concentration of the residual BO in the supernatant was determined using a UV-Vis spectrophotometer at λ_{max} = 492 nm. The adsorption capacity and removal efficiencies of the TC and TC composite were calculated based on the initial and final concentrations of dyes present in the solution using the following equation:

$$q_e = \frac{(C_0 - C_e) \, V}{m} \tag{1}$$

where C_0 and C_e are the concentrations of BO in the initial solution and at equilibrium, respectively, V is the volume of BO aqueous solution (l), and m is the mass of adsorbent (g).

RESULTS AND DISCUSSION

Determination of pH_PZC

The variations in the pH medium were one of the most important factors affecting the adsorption process. Bentonite TC possessed silanol groups, which resulted from broken Si-O-Si bonds at external surfaces and balanced the residual charge by accepting either hydroxyl groups or protons to form Si-OH groups [20]. The silanol groups at the external surfaces of the bentonite can be protonated and deprotonated under acid and alkaline pH conditions, respectively. While the surface is essentially uncharged at pH_{PZC}, it will be positively and negatively charged at pH values below and above the pH_{PZC}, respectively. The change in the ΔpH is greater under alkaline than under acid conditions (Fig. 1). It seems that the protonation of silanol groups is preferred over their deprotonation. The magnitude of the positive charge under acid conditions is relatively low. At around pH = 4.3, $pH_{initial}$ = $pH_{final,}$ the TC maintained its neutral character. Similar results were reported for montmorillonite, with a pH_{PZC} of 4.2 [21]. Another very similar pH_{PZC} at pH = 4.5

was observed for sodic bentonite [22]. However, electrostatically bonded and positively charged P4VP onto the TC surface caused the shift of pH_{PZC} at pH = 5.3. As a result, the coating of P4VP on the TC surface was done successfully. These results are in agreement with those reported for quaternized poly(N-vinylimidazole)/ montmorillonite poly(N-vinylimidazole)/ montmorillonitenanocomposite [23]. At pH values lower than the pH_{PZC}, the TC55 surface was positively charged and the adsorption of anions as BO dye molecules was favored while the adsorption of cations was favored for pH > pH_{PZC}.
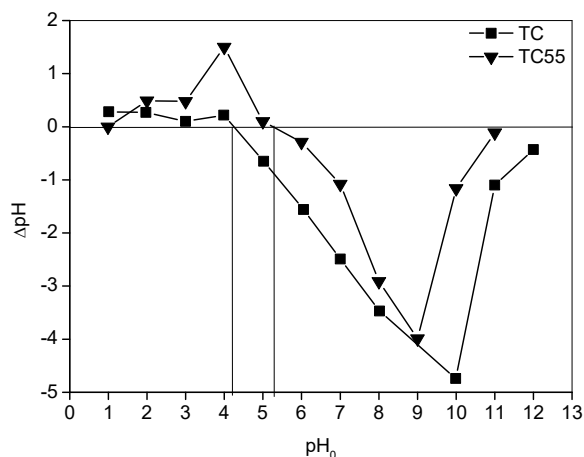

Fig. 1. The determination of pH_{PZC}.

The pH Effect of BO Solution Dye on the Adsorption Capacity

The effect of solution pH on the adsorption of BO dye onto the TC and TC55 composite was investigated at pH values from 2 to 9. It should be noted that BO dye was not altered in that pH range. Moreover, blank studies for BO dye were done in the same pH range. The solution was kept for 1 h after the pH adjustment and, thereafter, the absorbance of the solution was determined. The color was found to be stable over the pH range of 2-9. As shown in Fig. 2, the adsorption of the anionic dye was dependent on the pH medium. For the TC, the adsorption was more pronounced at lower pH values due to the high abundance of positive charges in the suspension. However, this adsorption decreased with increasing pH due to the repulsive force of negative charges.
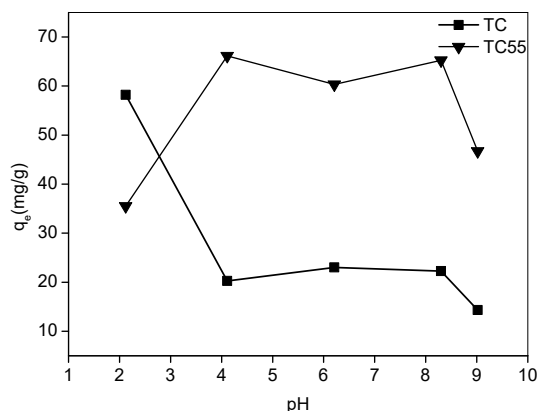
Fig. 2. The effects of pH on the adsorption of BO dye onto the TC and TC55 composite.

Moreover, and as mentioned above, the point of zero net proton charge of TC was 4.3, which indicates that particle edges were mostly negatively charged for higher pH values. For the TC, the maximum adsorption capacity was observed at pH = 2. However, an increase in pH values caused a decrease in the adsorption capacity (Fig. 2). Similar results were observed by Vanaamudan *et al.* [24], who studied the adsorption of Reactive Blue 21 dye onto the clay. Irrespective of the pH value, the adsorption capacity of the TC55 composite was still significantly higher than that of the TC. The amount of removed dye decreased for the TC and TC55 when pH increased. The maximum adsorption was obtained in an acid medium for the TC55 composite.

In our previous work, we investigated the pH effect on the adsorption of BO by quaternized P4VP [10]. The pH effect on the adsorption capacity of TC55 composite may be attributed to the combined effect of pH on dye adsorbed species and the cationic or/and neutral character of TC55 composite. In the present study, the adsorption capacity of BO dye increased drastically at pH values between 2 and 4 and decreased with the increase in the initial pH of the solution. At pH < 4, electrostatic interactions between positive charges of protons and negative charges of sulfonic ions led to a reduction in the number of charges and, consequently, to a reduction in the adsorption capacity of dye molecules by adsorption on the adsorbent surface [25-26]. The adsorption capacity decreased significantly when the pH value exceeded 8 (basic medium). To explain this behavior,

it was necessary to examine various mechanisms such as electrostatic attraction/repulsion, chemical interaction, and ion exchange. The P4VP adsorbed on the TC55 composite exhibited a weak alkaline character. In an acidic medium, the pyridine group existed in the protonated ammonium ($-NH^+$) group and formed electrostatic interactions with sulfonic groups present on dye molecules, causing an increase in dye adsorption. However, the pyridinium group disappeared with increasing pH, and the polymer adsorbed onto the TC55 composite recovered the free pyridine. For pH < 8, the abundance of hydroxide ions resulted in lower dye adsorption. This could have been due to the ionic repulsion occurring between the anionic dye molecules and the less protonated adsorbed polymer particles. As pH increased, the surface functional group deprotonated and caused a decrease in surface charge density. Consequently, the electrostatic effect on anionic species was very weak [27].

Adsorption Kinetic Studies

Adsorption kinetics experiments of BO dye at pH = 4.11 and T = 298 K were carried out for 300 min to determine the optimal contact time. As shown in Fig. 3, the adsorption process was rapid during the first 30 min of the contact time; then, the adsorption capacity increased slowly and reached equilibrium within 60 min. There was almost no further adsorption beyond this time (60 min). Thus, it can be said that the TC and TC55 composite achieved complete adsorption equilibrium in 60 min.
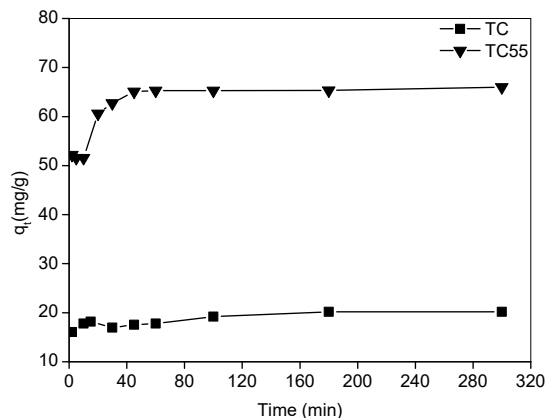

Fig. 3. The effect of contact time on the adsorption capacity of BO onto the TC and TC55 composite.

To examine the adsorption process of BO dye onto the TC and TC55 composite, the kinetic study was carried out with the pseudo-first-order, pseudo-second-order, and intra-particle kinetic models, which are presented below, respectively.

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

$$q = k_{id} t^{1/2} + C \tag{4}$$

where q_e and q are the amounts of dye adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, k_1 (min^{-1}), k_2 (g mg^{-1} min^{-1}), and k_{id} (mg g^{-1} min$^{-0.5}$) are the pseudo-first-order, pseudo-second-order, and the intra-particle diffusion rate constants of the adsorption, respectively, and C (mg g^{-1}) is the intercept. The value of C gave a good impression of the boundary layer thickness, *i.e.*, the boundary layer effect was greater at the higher values of C.

The adsorption kinetic plots are shown in Figs. 4, 5, and 6. In addition, the kinetic parameters and correlation coefficient (R^2) of the three models are given in Table 4.
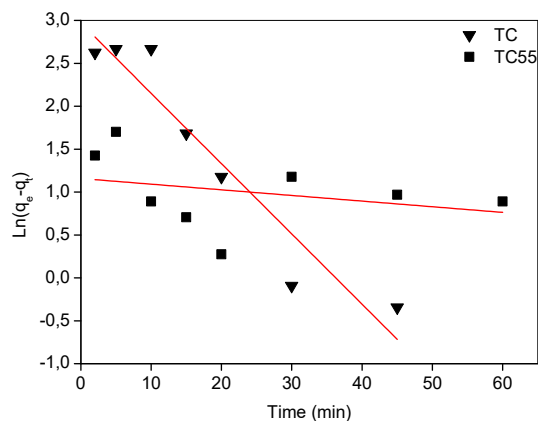

Fig. 4. Pseudo-first-order adsorption kinetics of BO onto the TC and TC55 composite.

The results showed a bad fit between the kinetic data and the intra-particle diffusion model. However, a good fit
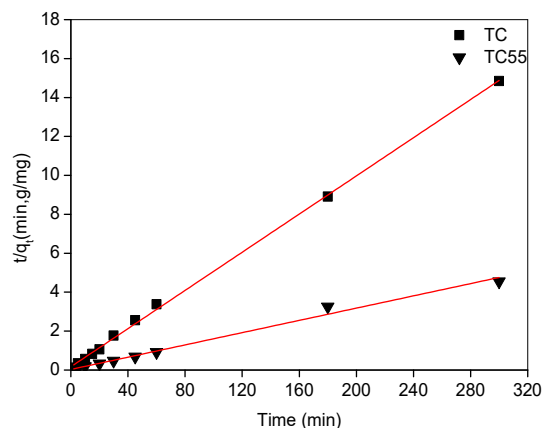

Fig. 5. Pseudo-second-order adsorption kinetics of BO onto the TC and TC55 composite.
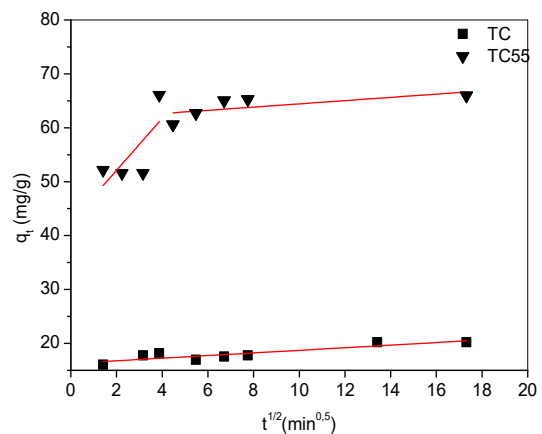

Fig. 6. Intra-particle diffusion adsorption kinetics of BO onto the TC and TC55 composite.

was obtained between the kinetic data and pseudo-second-order models, evidenced by the related high correlation coefficients. It can be seen that the $q_{e,exp}$ and the $q_{e,cal}$ values from the pseudo-second-order kinetics model were very close to each other. Also, the calculated correlation coefficients were very close to each other. These results indicated that the adsorption of BO onto the TC and TC55 composite followed the pseudo-second-order model.
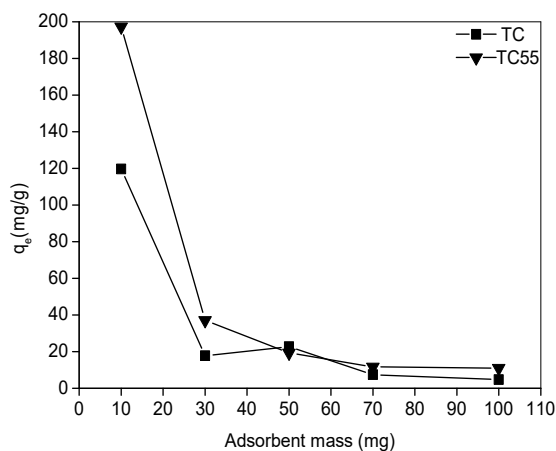
The Effect of Adsorbent Dosage

The solid/solution ratio is particularly important because

Table 4. Kinetic Constants for Pseudo-First-Order, Pseudo-Second-Order, and Intra-Particle Diffusion Models for the Adsorption of BO onto the TC and TC55 Composite

	Pseudo-first-order model				Pseudo-second-order model			Intra-particle diffusion			
	q_e,exp (mg g⁻¹)	q_e,cal (mg g⁻¹)	K_1 (min⁻¹)	R^2	q_e,cal (mg g⁻¹)	K_2 (g mg⁻¹ min⁻¹)	R^2	K_{id1} (mg g⁻¹ min⁻¹/²)	K_{id2} (mg⁻¹ g.min⁻¹/²)	l (mg g⁻¹)	R^2
TC	20.20	3.18	0.0066	-	20.40	0.0143	0.999	0.2411	-	16.30	0.799
TC55	65.99	18.61	0.0586	0.964	63.29	0.00807	0.990	4.8279	-	42.46	0.523
								-	0.3003	61.43	0.486

it determines the extent of decolorization and can also be used to predict the cost of adsorbent per the unit of the solution to be treated. The effects of adsorbent dosage on the percentage removal of BO dye by both the TC and TC55 are shown in Fig. 7. It was observed that the amount of dye adsorbed decreased from 120 to 5 mg g⁻¹ and from 198 to 11 mg g⁻¹ for the TC and TC55 composite, respectively, when their mass increased from 10 to 100 mg. This may be attributed to the overlapping or aggregation of adsorbents at high dosage, which, in turn, may reduce the total surface area available. Consequently, the diffusion path length for the dye molecules increased. These results show that a high adsorbent dosage may not effectively adsorb dye molecules and could be cost-ineffective [10].

Fig. 7. The effect of adsorbent dosage on the adsorption capacity of BO onto the TC and TC55 composite.

Adsorption Equilibrium Models

The experimental adsorption isotherm data of BO on the TC and TC55 composite are shown in Fig. 8. The plots indicate that an increase in the initial dye concentration caused an increase in the adsorption capacity. The obtained plot is the Langmuir (L)-type adsorption isotherm.
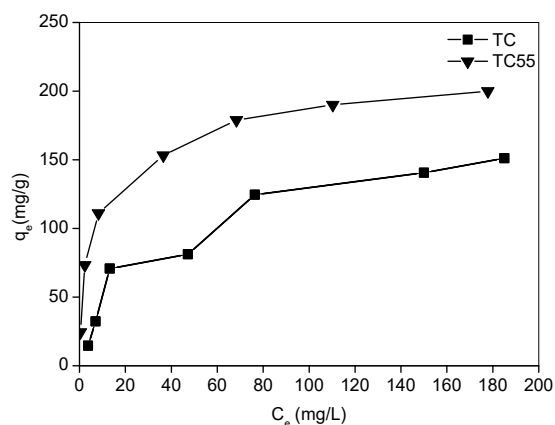
Fig. 8. The effect of initial dye concentration on the adsorption capacity of BO onto the TC and TC55 composite.

The above type of isotherm usually indicates chemical adsorption (chemisorption) and reflects a relatively high affinity between the adsorbate and the adsorbent. The isotherm plot can be further classified as an L_2-type isotherm. An adsorption isotherm is very useful in providing information on adsorption mechanisms, surface properties,

and affinity of an adsorbent toward an adsorbate. In this study, the adsorption isotherm indicated how BO dye molecules interacted with the TC and TC55 composite and attained equilibrium. Adsorption data fitted the Langmuir, Freundlich, and Dubinin-Radushkevich isotherms, which are presented in Figs. 9, 10, and 11, respectively.

The Langmuir isotherm is valid for monolayer sorption and is based on the assumption that adsorption takes place at specific equal sites within the adsorbent. Theoretically, the adsorbent has a finite capacity to adsorb adsorbates. The monolayer adsorption capacity can be expressed in a linear form as in Eq. (5):
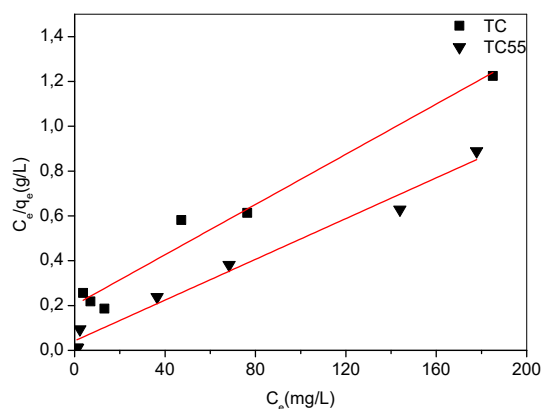

Fig. 11. The Dubinin-Radushkevich (D-R) isotherm for the adsorption of BO onto the TC and TC55 composite.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m \, b} \frac{1}{C_e} \tag{5}$$

where C_e is the equilibrium concentration (mg l^{-1}), q_e is the amount adsorbed at equilibrium (mg g^{-1}), the Langmuir constant q_{max} (mg g^{-1}) represents the monolayer adsorption capacity, and b (l mg^{-1}) is the heat of adsorption. The Langmuir isotherm adsorption equation can also be expressed by means of R_L, a dimensionless constant referred to as the separation factor or equilibrium parameter. R_L can be calculated using the following equation:

$$R_L = \frac{1}{(1 + b \times C_0)} \tag{6}$$

where C_0 is the initial dye concentration (mg l^{-1}).

The shape of the isotherm curve is determined by the R_L parameter; accordingly, if:

$R_L > 1$, unfavorable adsorption,

$0 < R_L < 1$, favorable adsorption,

$R_L = 0$, irreversible adsorption,

$R_L = 1$, linear adsorption.

The calculated R_L values were 0.187 and 0.057 for the adsorption of BO dye on the TC and TC55 composite, respectively (Table 5), indicating that the adsorption was favorable at the studied temperature.

The Freundlich isotherm is an empirical equation suitable to describe heterogeneous systems with only a restricted

Fig. 9. The Langmuir isotherm for adsorption of BO onto the TC and TC55 composite.
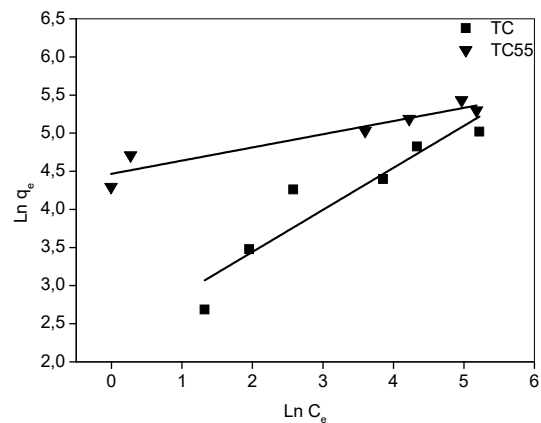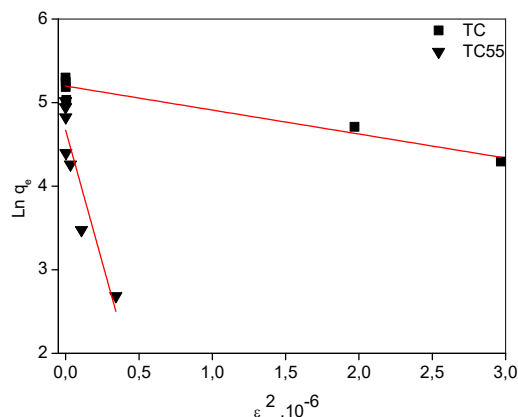

Fig. 10. The Freundlich isotherm for the adsorption of BO onto the TC and TC55 composite.

Table 5. Parameters of the Isotherm Models for the Adsorption of BO onto the TC and TC55 Composite

Model	Parameter	TC	TC55
Langmuir equation	q_m (mg g^{-1})	178.57	222.22
	K_L (l mg^{-1})	0.027	0.106
	R_L	0.187	0.057
	R^2	0.970	0.982
Freundlich equation	K_F (l g^{-1})	87.06	87.64
	n	5.78	4.738
	R^2	0.883	0.902
Dubinin-Radushkevich equation	q_m (mg g^{-1})	120.41	180.97
	β (mol^2 J^{-2}) 10^7	100	3
	E (kJ mol^{-1})	0.223	1.29
	R^2	0.886	0.936

range. In this study, it was applied to describe BO adsorption on the TC and TC55 composite. The Freundlich isotherm can be expressed in a linear form as in Eq. (7):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (7)$$

where the constant K_F represents the adsorption capacity and n is adsorption intensity. The values of K_F and n were calculated from the slope and intercept of the plot between the $\ln q_e$ and $\ln C_e$ (Fig. 10).

Dubinin-Radushkevich (D-R) isotherm is generally applied to express the adsorption mechanism on a heterogeneous surface with a Gaussian energy distribution. This model successfully fitted high solute activities at different concentration ranges. This approach was used to distinguish the chemical and physical adsorption of BO molecules. This isotherm, which is temperature-dependent, assumes that there is no homogenous surface on the adsorbent and can be expressed as follows:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \qquad (8)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \qquad (9)$$

where β and ε are D-R constant (mol^2 J^{-2}) and D-R isotherm constant, respectively, R and T are the gas constant

(8.314 J mol^{-1} K^{-1}) and temperature (K), respectively, and q_m is D-R monolayer capacity (mg g^{-1}). The parameter was obtained by the linear plots of $\ln q_e$ *vs.* ε^2.

The mean free energy, E (kJ mol^{-1}), was obtained from β and is expressed as follows:

$$E = \frac{1}{\sqrt{2\beta}} \qquad (10)$$

The isotherm parameters obtained from these models are presented in Table 5. The obtained equilibrium data fitted the Langmuir model (Fig. 9) more than the Freundlich and D-R models (Figs. 10 and 11). The Langmuir model indicated that the homogenous distribution of adsorption sites on the adsorption surface formed a single layer of dye molecules on the surface. Langmuir isotherm curves were used to calculate q_{max}, and it was found to be 178 mg g^{-1} and 222 mg g^{-1} for BO dye molecules adsorption onto the TC and TC55 composite, respectively. This result indicates that the adsorbent had a high capacity to remove BO dye from the solution. A comparison of the maximum adsorption capacity of BO dye onto the TC and TC55 composite at optimum conditions showed that the TC55 composite had a much higher affinity toward BO dye molecules adsorption than did the TC. This clearly shows that adsorption was positively influenced by the presence of pyridinium groups in solution. Thus, it can be said that polycation-modified clay as TC55 composite is a promising material for the treatment of anionic dyes from

aqueous solutions.

Thermodynamic Study

The effect of temperature on the adsorption behavior of BO onto the TC and TC55 composite was also studied using 40 mL of BO solution at 50 mg l^{-1} under optimized conditions, which included shaking time = 60 min, pH = 4.11, and adsorbent mass (10 mg) at 308, 318, and 328 K. In common practice, the thermodynamic parameters, namely, standard Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$), of an adsorption process are calculated using Eqs. (11), (12), and (13), respectively [28].

$$K_d = \frac{q_e}{C_e} \qquad (11)$$

$$\Delta G^0 = -RTLnK_d \qquad (12)$$

$$lnK_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (13)$$

where K_d is the distribution coefficient (l g^{-1}), T is the temperature (K), and R is the gas constant (8.314 J mol^{-1} K^{-1}). $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of the plot of lnK_d *vs.* 1000/T (Fig. 12).

The values of thermodynamic parameters obtained using the above Eqs. ((11)-(13)) are given in Table 6. For both adsorbents, the negative $\Delta G°$ values indicated the spontaneity of the process. The numerical values of $\Delta G°$ were very close to the characteristic range of physisorption, which is reported to be -20 to 0 kJ mol^{-1} [29-30], but significantly lower than that of chemisorptions, which is reported to be -400 to -80 kJ mol^{-1} [29].

Table 6 shows that as temperature increased, the $\Delta G°$ value became more negative, indicating the spontaneity of
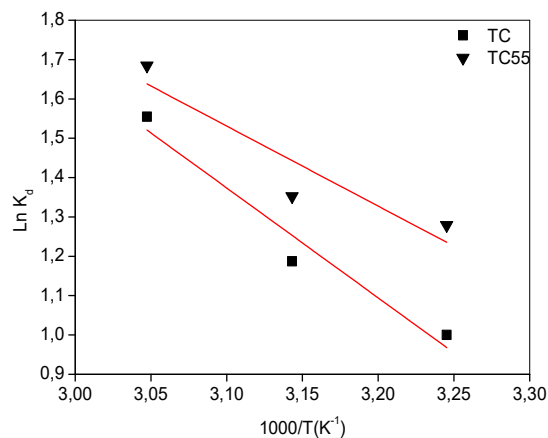

Fig. 12. Van't Hoff plot for the adsorption of BO onto the TC and TC55 composite.

the process. The positive value of $\Delta H°$ indicates the endothermic nature of the adsorption process. Also, the $\Delta H°$ values were in the range of the physisorption process, which is reported to be 1-93 kJ mol^{-1} [30]. The good affinity of dye molecules toward the TC and TC55 composite is evidenced by the positive $\Delta S°$ values [28]. The thermodynamic parameters of the present adsorption process were similar to those obtained using different adsorbents in previous studies [32-33].

A Comparison of Anionic Dyes Adsorption with Different Adsorbents Reported in the Literature

The maximum adsorption capacities q_m (mg g^{-1}) obtained for the TC and TC55 composite compared to other adsorbents are shown in Table 7.

The TC55 composite prepared in this study can be used as a potential adsorbent in the removal of various dyes because it was found to have a higher adsorption capacity compared to other adsorbents reported in the literature.

Table 6. Thermodynamic Data for the Adsorption of BO onto the TC and TC55 Composite

Adsorbent	-ΔG (kJ mol^{-1})			ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
	308 K	318 K	328 K		
TC	2,478	3,313	4,147	23,23	83,43
TC55	0,5444	1,196	1,848	19,54	65,179

Table 7. Adsorption Capacities of Various Composites for the Adsorption of Anionic Dyes

Adsorbent	Dye	q_m (mg g^{-1})	Ref.
BAS 1.5	Telon blue	500	[9]
Mesoporous silicate/polypyrrole	Telon blue	55.55	[34]
Na-Bt	Telon blue	32.25	
P-MBIM-Bt	Telon orange	128.23	[35]
	Telon red	102.57	
TC	Brilliant orange	178.57	Present study
TC55	Brilliant orange	222.22	Present study

CONCLUSIONS

In this work, the TC and TC55 composite were used as adsorbents for the removal of BO textile dye. The FTIR and TGA analysis of the TC55 composite revealed that the P4VP was successfully grafted on the surface of the TC and that the charge on the surface of the adsorbent was positive. The adsorption process was hardly affected by pH because there were many pyridinium groups on the surface of the adsorbent. At the same adsorption conditions, the maximum adsorption capacity of the TC was 178 mg g^{-1} while the equilibrium adsorption capacity of the TC55 composite was 222 mg g^{-1}. The results of the kinetic study demonstrated that the adsorption of BO onto the TC and TC55 was rapid and that the kinetics could be better described by the pseudo-second-order model in all cases. The equilibrium adsorption data for the TC and TC55 were more consistent with the Langmuir and Freundlich isotherm models, respectively. Therefore, it can be stated that the adsorption isotherm was very well described by the Langmuir model for all adsorbents.

Thermodynamically, ΔH and ΔG values revealed that the sorption process for both adsorbents was endothermic and spontaneous. The maximum adsorption capacity for the studied materials was much higher than that of most other materials. Consequently, it can be concluded that the adsorbents studied in this work are promising absorbents that can be applied in the adsorption of anionic dyes from aqueous solutions due to their low cost, high adsorption ability, and simple adsorption conditions. Finally, the results indicate that these two materials, together with other tested materials, can be used to clean liquids containing dyes.

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