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Adsorption of Basic Violet 14 from aqueous solution on bentonite

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Abstract

The adsorption of Basic Violet 14 (BV14) from aqueous solution on bentonite was studied with respect to contact time, initial concentration, and presence of selected salts. It was found that the adsorption of BV14 increases with increasing initial BV14 concentration and decreases in the presence of salt. The experimental data can be well represented by Langmuir and Freundlich models. The maximum monolayer adsorption capacities obtained from the Langmuir model are 147.9 and 100 mg g⁻¹ for Na-bentonite and Ca-bentonite, respectively. *To cite this article: Y.-X. Jiang et al., C. R. Chimie 11 (2008).*

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1. Introduction

Effluents from the textile industry are one of the major sources of water pollution. Hence, treatment of dye wastewater has become an important task for environmental managers. While there are many methods available for treating dye wastewater, adsorption has been found to be an efficient one [1,2].

Activated carbon exhibits high adsorption capacity for organic dyes. However, its relatively high cost makes it less attractive economically. Hence, there is a need for a cheaper, but comparably effective adsorbent material. Bentonite is a promising alternative adsorbent. Numerous studies have been carried out to investigate the effectiveness of bentonite in removing

pollutants [3–6]. In the current study, we report on the ability of natural bentonite (Ca-bentonite) and Na-bentonite to remove the dye Basic Violet (BV14) by adsorption from aqueous solution. Kinetics and isotherm studies were conducted to evaluate the adsorption capacity of bentonite. The aim of this work was to investigate the possibility of using bentonite, which is available in large quantities in Guangxi Autonomous Region of China, as a low-cost adsorbent for the removal of BV14.

2. Materials and methods

2.1. Materials

The natural bentonite (Ca-bentonite) of industrial grade was purchased from Ningmin County, Guangxi,

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Table 1
The chemical composition of natural bentonite

Constituents	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
Percentage (%)	64.53	17.86	0.38	3.23	1.69	3.05	1.17	1.27

China, and its chemical composition, as reported by the supplier, is shown in Table 1. Chemical-grade BV14 was purchased from Tianjin Chemicals Ltd. Co. and used without further purification. The structure of BV14 is shown in Fig. 1.

2.2. Adsorbent

Ca-bentonite was purified by a previously reported sedimentation technique [7]. Na-bentonite was obtained by treating Ca-bentonite with three successive NaCl solutions. Purified Ca-bentonite (10 g) was dispersed in 400 mL of distilled water to make a clay suspension, to which was added 100 mL of 1 M NaCl solution at 80 °C for 2 h, followed by filtration and washing in distilled water. This cation exchanging process was repeated three times, and the final sample was dried at 90 °C for 2 h.

The cation exchange capacities (CECs) of Ca-bentonite and Na-bentonite, characterized by the methylene blue method [8], were determined to be 0.65 and 1.15 mmol g⁻¹, respectively.

2.3. Sample characterization

X-ray powder diffraction patterns were recorded on a Rigaku D/MAX 2500V diffractometer with a copper tube as radiation source ($\lambda = 1.54178 \text{ \AA}$) and operating at 40 kV and 120 mA. Its profiles were recorded at 2° (2 θ) per minute.

2.4. Adsorption experiments

Adsorption experiments were carried out at 25 °C. BV14 solution (100 mL) of known initial concentration

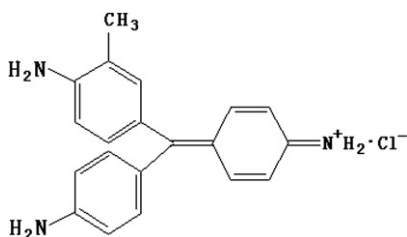


Fig. 1. The structure of BV14.

was shaken with 0.5 g adsorbent at pH 6 in a temperature-controlled shaker. At various time intervals throughout the adsorption, samples were taken, and the adsorbent was separated by centrifugation. The supernate was analyzed for residual concentration of BV14 by spectroscopic analysis at the wavelengths of 555 nm, using a UV-2501PC spectrophotometer (Shimadzu).

The amount of adsorbed dye per unit mass of adsorbent at time t , q_t , was then determined by the mass-balance equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 and C_t (mg dm⁻³) are the initial concentration and concentration at time t , respectively, m (mg) is the mass of the adsorbent, and V (dm³) is the volume of the liquid phase.

3. Results and discussion

3.1. Effect of experimental conditions on adsorption processes

3.1.1. Influence of the initial concentration of BV14

The effect of the initial concentration of BV14 in the solutions on the amount of adsorbed dye was studied and the results are shown in Figs. 2 and 3.

The results show that the Na-bentonite is a more effective adsorbent than Ca-bentonite. In addition, the amount of adsorbed dye increased with the increase of initial concentration of the dye. Increasing the initial BV14 concentration increases the mass gradient

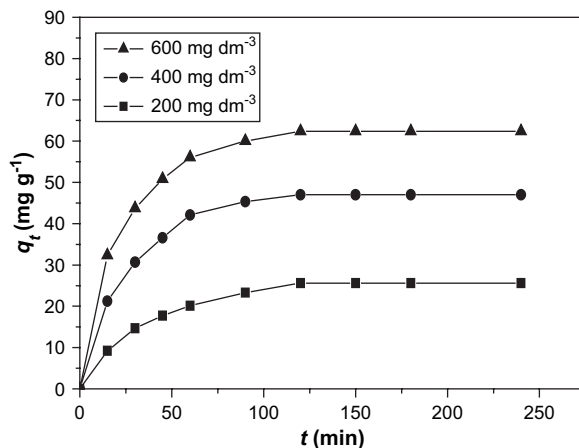


Fig. 2. Effect of initial concentration on adsorption of BV14 on Ca-bentonite.

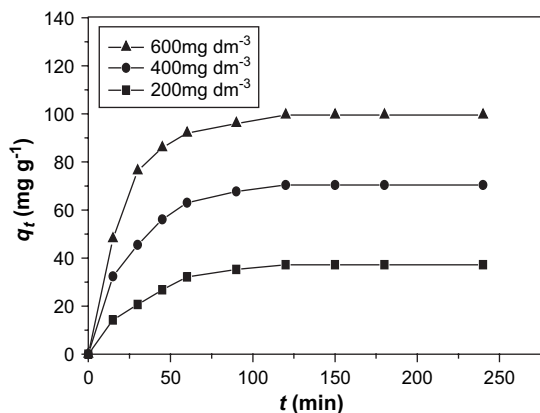


Fig. 3. Effect of initial concentration on adsorption of BV14 on Na-bentonite.

between the solution and the adsorbent, and therefore, the rate at which BV14 molecules pass from the bulk solution to the particle surface and the amount of transfer at equilibrium.

3.1.2. Influence of contact time

Figs. 2 and 3 show that equilibrium is reached within roughly 90 min, independently of the adsorbent or the initial concentration of the dye, which indicates a relatively fast process.

3.1.3. Effect of salt addition

It is well known that salts have an effect on these types of adsorption processes [9]. In this work, BaCl₂ and KCl were selected as model salts to investigate their influence on the adsorption of BV14 on bentonite. The results are presented in Figs. 4 and 5.

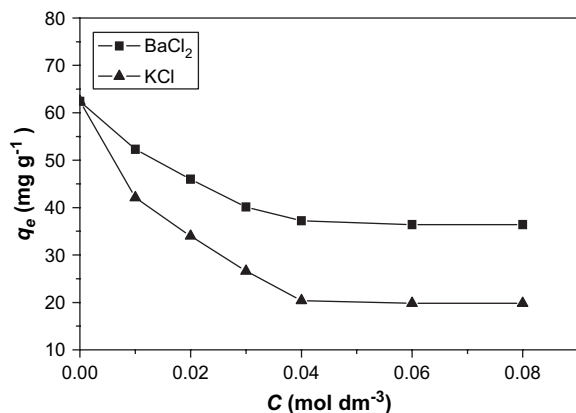


Fig. 4. Effect of salt concentrations on the adsorption of BV14 on Ca-bentonite.

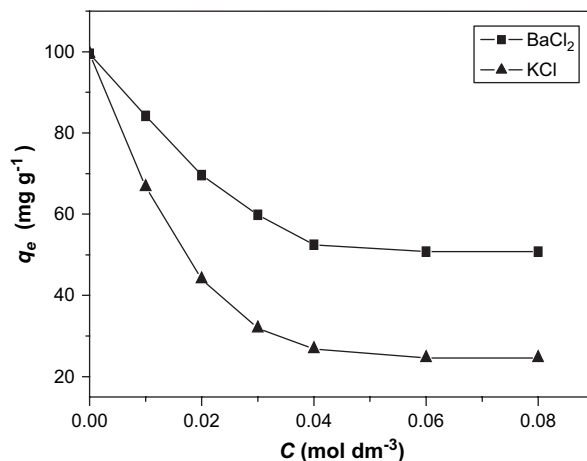


Fig. 5. Effect of salt concentrations on the adsorption of BV14 on Na-bentonite.

It was observed that the presence of salts decreased the amount of dye adsorbed on bentonite at equilibrium (q_e). Because the adsorption of basic dyes on bentonite is likely to be dominated by ion-exchange processes [10], the results may be explained in terms of the competition between BV14 and the cations in the added salt for the binding sites in the adsorbent.

3.2. Adsorption isotherm

In this work, the Langmuir model and the Freundlich model were used to describe the adsorption of BV14 on bentonite. The linear form of the Langmuir model can be represented by the following relation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (2)$$

where q_e (mg g⁻¹) is the amount adsorbed at equilibrium time, C_e (mg dm⁻³) is the equilibrium concentration of the adsorbate, Q_0 (mg g⁻¹) and b (dm³ mg⁻¹) are the Langmuir constants related to the monolayer adsorption capacity and the energy of adsorption, respectively.

The linear form of the Freundlich isotherm model is given by the following equation:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (3)$$

where K and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity of the sorbent, respectively.

The Langmuir and Freundlich constants were determined after fitting the data to the respective equations through linear regression analysis.

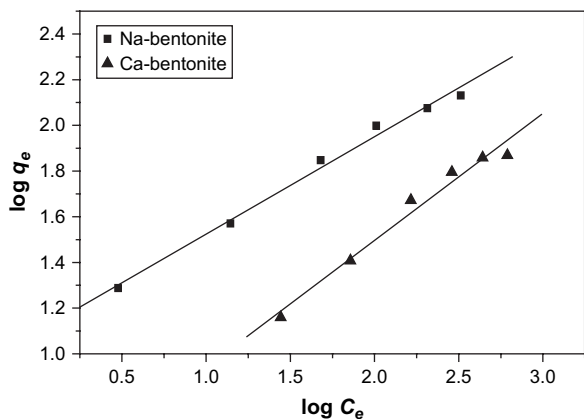


Fig. 6. Freundlich isotherms for adsorption of BV14 on bentonite.

The Freundlich adsorption isotherms of BV14 on bentonite are shown in Fig. 6. The calculated values of the constants in Langmuir and Freundlich equations and the regression correlation coefficients (r^2) are given in Table 2. It can be seen that both the Langmuir and Freundlich adsorption models were suitable for modeling the adsorption of BV14 on bentonite.

3.3. Kinetics of adsorption

Pseudo-first-order and pseudo-second-order kinetic model [11,12] were used to investigate the adsorption processes of BV14 on bentonite. The linear form of pseudo-first-order model is given by:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where k_1 (min^{-1}) is the rate constant of pseudo-first-order model and q_t (mg g^{-1}) and q_e (mg g^{-1}) are the amounts of dye adsorbed per unit mass of adsorbent at time t , and at equilibrium, respectively.

The linear form of pseudo-second-order model can be represented in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second-order rate constant and q_e is as defined above.

Table 2
Values of the constants in Langmuir and Freundlich models

Adsorbent	Langmuir			Freundlich		
	Q_0 (mg g^{-1})	b ($\text{dm}^3 \text{mg}^{-1}$)	r^2	n	K	r^2
Na-bentonite	147.49	0.0244	0.994	2.345	12.519	0.995
Ca-bentonite	100	0.00562	0.996	1.799	2.427	0.987

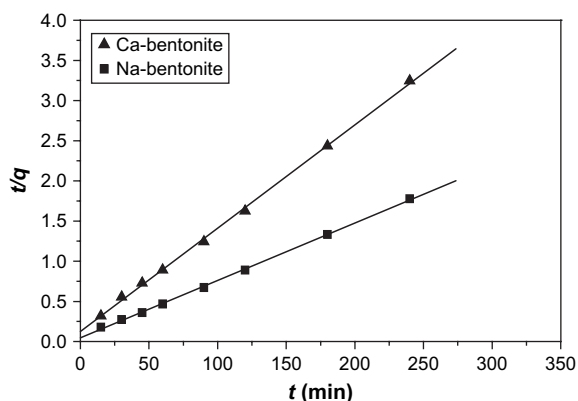


Fig. 7. Second-order kinetic plots for the adsorption of BV14 onto bentonite.

The results of fitting experimental data with the pseudo-first-order and pseudo-second-order models (Fig. 7) for adsorption of dye onto bentonite are presented in Table 3. As can be seen, the correlation coefficients (r^2) is 0.999 for pseudo-second-order kinetic model and 0.956–0.963 for the pseudo-first-order model, indicating a better fit with the pseudo-second-order model. The better fit of this model to the experimental data is also seen in the much closer agreement between the experimental values for q_e and those from the second-order model, when compared to the q_e values generated from the first-order model.

3.4. The changes of crystalline structure of bentonite during adsorption

X-ray diffraction analysis was performed to investigate the effects of BV14 adsorption on the basal spacing

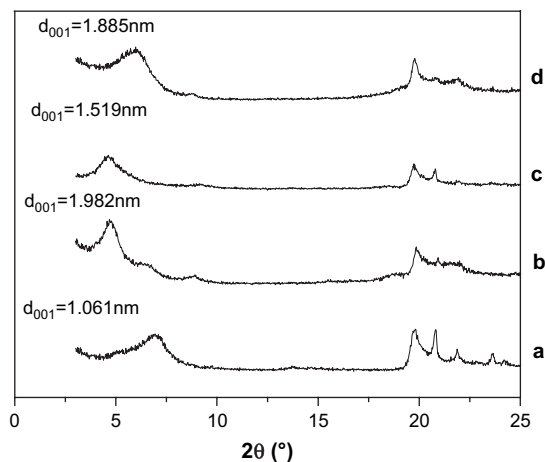


Fig. 8. XRD patterns of various samples: (a) Na-bentonite; (b) Na-bentonite after adsorption of BV14; (c) Ca-bentonite; (d) Ca-bentonite after adsorption of BV14.

Table 3
Kinetic parameters for the adsorption BV14 onto bentonite

Adsorbent	k_1 (min ⁻¹)	q_e (cal) (mg g ⁻¹)	r^2	k_2 (g g ⁻¹ min ⁻¹)	q_e (cal) (dm ³ mg ⁻¹)	r^2	q_e (exp)
Na-bentonite	7.57×10^{-2}	300.4	0.956	1.08×10^{-3}	139.9	0.999	135.0
Ca-bentonite	5.64×10^{-2}	117.1	0.963	1.29×10^{-3}	77.82	0.999	73.96

of bentonite. XRD patterns of Ca-bentonite and Na-bentonite before and after adsorption of BV14 are displayed in Fig. 8. It is noticeable that the adsorption of dye causes an increase in the basal spacing of bentonite. The results were likely due to the fact that organic cations insert themselves into the aluminosilicate sheets and expand the interlamellar spacing [13–15]. The change in the basal spacing of the bentonite structure resulting from the adsorption process is an indication of the extent to which the sorbate is reaching the interlamellar sorption sites [16]. The larger increase in basal spacing was found in Na-bentonite, implying a greater uptake on Na-bentonite than that on Ca-bentonite, which is consistent with the results in Figs. 2 and 3.

4. Conclusion

The adsorption isotherm and kinetics of BV14 from aqueous solutions on Ca-bentonite and Na-bentonite were studied in a batch experimental system. The results showed that the equilibrium adsorption is achieved in 90 min. The adsorption of BV14 increases with increasing initial BV14 concentration, and the adsorption process was influenced by the presence of salt, with a decrease in the adsorption of BV14 observed with increasing concentrations of BaCl₂ or KCl. The greater adsorption capacity of Na-bentonite may be ascribed to its larger cation exchange capacity. The Langmuir and Freundlich isotherm adsorption models were found to be applicable for the experimental data. The pseudo-first-order and pseudo-second-order kinetic models were used to describe the kinetic data, with the latter model showing a better fit to the experimental data. X-ray diffraction of the crystalline structures of two kinds of bentonite before and after adsorption of

BV14 showed evidence of an increase in the basal spacing of bentonite as a result of adsorption.

Acknowledgements

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