Adsorption of Bromothymol Blue (BTB) Dye Using Four Zeolites as Adsorbent

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Abstract

This study examined adsorption of anionic dye on four zeolitic materials incorporated (VS-1, CuZSM-5) and not incorporated into metals (S-1, ZSM-5). The adsorption of the bromothymol blue (BTB) dye on the four adsorbents was analysed using isotherm models Langmuir, Freundlich, and Temkin. Two kinetic models were also applied to study the adsorption process, pseudo-first order and pseudo-second order. The isothermal data showed good correlation. The kinetics of adsorption were better described by the pseudo-second order model. The results obtained indicate that the maximum percentage removal of the BTB dye was given by a purely non-incorporated silicic zeolite (S-1).

Keywords

Zeolites, adsorption isotherm, bromothymol blue, dye degradation

1 Introduction

The environment is now an integral part of the development strategies designed and implemented in every country in the world. The most important source of pollution comes from industrial activities, where effluents from industry have an adverse impact on human health. These effluents are mainly made up of dyes.

The industrial developments of recent years have left their negative impressions the environment. Such industries include the manufacture of dyes, textile, printing, paper, leather, cosmetics, and many others that use dyes and dyeing processes to produce their finished products.[1]

The dyes used in the textile industry are classified into three classes: anionic (which include direct dyes, acid and reactive), cationic which include all basic dyes, and non-ionic which include dispersed dyes.[2]

Dyes have a synthetic origin and complex aromatic molecular structure, which makes them more stable and more difficult for biodegradation and photodegradation.[3,4]

There are several techniques that are used to remove dyes, however, adsorption is the most effective method due to its simplicity, high yield, easy recovery, and reuse of the adsorbent.[5]

The dye used in this study was a triphenylmethane dye bromothymol blue (BTB), which belongs to the family of anionic dyes. BTB is a chemical compound often used as a coloured indicator of pH, and it has halochromic properties. The acid form is yellow (pH < 7) and the basic form is blue (pH > 7). It is widely used in biomedical, biological, and chemical engineering applications.

The degradation of this dye has been studied by many researchers. *H. Ayoub et al.*[6] carried out photodegradation of the dye (BTB) using TiO$_2$ as a catalyst. In their work, *L. Cao et al.*[7] and *M. S. E. Farida et al.*[8] studied the adsorption of BTB on QCF (quaternized cellulose fibres) and on bentonite carbon composite, respectively. *M. Ghaedi et al.*[9] and *H. Tavakkoli et al.*[10] used gold nanoparticle-loaded activated carbon (Au-NP-AC) and nanoparticles of perovskite type for the elimination of BTB. *Y. Zheng et al.*[11] studied the photocatalytic performance of MgO in the degradation of BTB. *A. Ameri et al.*[12] carried out a photocatalytic bleaching of BTB using biogenic selenium nanoparticles.

In this paper, we present an adsorption study of bromothymol blue dye on four zeolitic materials. Isotherm and kinetic models were used to follow the adsorption process of the dye studied.

2 Experimental

2.1 Synthesis of materials

The synthesis of the materials was carried out according to a protocol by following the molar composition of each material. The molar composition of each zeolite is presented in Table 1.

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Table 1 – Molar composition of four materials (S-1, ZSM-5, VS-1, and CuZSM-5)

Zeolites	Molar composition
S-1	KF – 0.08 TPAOH-SiO$_2$ – 20 H$_2$O
ZSM-5	SiO$_2$ – 0.02 Al$_2$O$_3$ – 0.275 TPABr – 1.13 CH$_3$NH$_2$ – 7.5 H$_2$O
VS-1	KF – 0.08 TPAOH-SiO$_2$ – 0.01 VOSO$_4$ – 20 H$_2$O
CuZSM-5	SiO$_2$ – 0.02 Al$_2$O$_3$ – 0.275 TPABr – 0.01 Cu(NO$_3$)$_2$, 3H$_2$O – 1.13 CH$_3$NH$_2$ – 7.5 H$_2$O

Zeolites (S-1 and ZSM-5) were synthesised from mixtures containing the following reagents: for zeolite (S-1) – Ludox (a source of silica), tetrapropylammonium hydroxide (TPAOH), potassium fluoride (KF), and demineralised water; for zeolite (ZSM-5) – Ludox, tetrapropylammonium bromide (TPABr), Al$_2$O$_3$ (aluminum source), methylamine (CH$_3$NH$_2$), and demineralised water.

The incorporated zeolites (VS-1 and CuZSM-5) were synthesised from gel containing the reagents: for zeolite (VS-1) – Ludox, TPAOH, VOSO$_4$ (source of the metal), KF, and demineralised water; for zeolite (CuZSM-5) – Ludox, TPABr, Al$_2$O$_3$, Cu(NO$_3$)$_2$, 3H$_2$O (source of the metal), CH$_3$NH$_2$, and demineralised water.

The incorporation of metals in these materials (VS-1, CuZSM-5) and materials not incorporated (S-1, ZSM-5) were synthesized under the temperature conditions of 175 °C and duration of crystallisation of 24 h.

The materials obtained were characterised by X-ray diffraction and UV-Vis spectroscopy. The results showed that the synthesised zeolites presented a high crystallinity with an MFI type structure.

2.2 Adsorption experiments

The procedure for adsorption of BTB dye was as follows: 100 ml of the dye solution prepared at 10 mg l^{-1} was poured into beakers, followed by the addition of 50 mg of zeolites (1, 2, 3, and 4). The mixtures were stirred for 2 h, and the pH of the solution was measured every 10 min. The mixtures were then filtered using an EBA-Hetlich centrifuge at a speed of 3500 rpm for 15 min.

The absorbance of bromothymol blue solution was measured as the pH of the solution varied.

Before starting the dye adsorption study it is necessary to determine the wavelength (λ_{max}) at which absorbance is maximum. When the dye solution is in basic form (pH > 7), the wavelength (λ_{max}) is equal to 615 nm, while the neutral form and the acid form (pH ≤ 7) of the dye solution have superimposed peaks, the wavelength (λ_{max}) is equal to 430 nm.

When the pH of the solution changes, a different peak in the UV-Vis spectrum (variation of λ_{max}) is observed, and consequently, an evolution in the colour of the BTB solution.

In our case, the solution prepared at 10 mg l^{-1} of the BBT dye chosen for the determination of the maximum wavelength (λ_{max}) of the dye, presents a visible band located at 435 nm.

2.3 Adsorption kinetics and isotherms

2.3.1. Study of the adsorption kinetics

Kinetic models were considered to analyse the experimental results obtained. Two models were studied in order to describe the adsorption phenomenon of the BTB dye on the four catalysts used: the pseudo-first-order model (Eq. (2)), and the pseudo-second-order model (Eq. (3)).[13] The kinetics of adsorption of the dye studied (BTB) were carried out for an initial dye concentration of 10 mg l^{-1}, with a concentration of 0.50 g l^{-1} for the four types of zeolites (S-1, ZSM-5) and (VS-1, CuZSM-5).

The adsorption efficiency of the dye on the four catalysts is defined by [18]:

$$R\% = \left[\frac{(c_0 - c_t)}{c_0}\right] \cdot 100 \qquad (1)$$

where c_0 is the initial concentration of the substrate (mg l^{-1}) and c_t is the concentration of the substrate at equilibrium of the adsorption process (mg l^{-1}).

The kinetic equation of pseudo-first-order is represented below by the following linear relation:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (2)$$

where q_t (mg g^{-1}) and q_e (mg g^{-1}) are the adsorption capacities at a given time t (min) and the equilibrium condition, respectively, and k_1 (min^{-1}) is the pseudo-first-order constant.

The second model is represented by the following formula:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

where q_t is the quantity of the dye adsorbed at time t (mg g^{-1}), q_e is the maximum adsorption capacity of the pseudo-second-order (mg g^{-1}), and k_2 is the kinetic constant of adsorption of the pseudo-second-order (g mg^{-1} min^{-1}).

2.3.2 Adsorption isotherms

Adsorption isotherms play an important role in determination of maximum adsorption capacities and in the design of new adsorbents. There are many theoretical models to describe the adsorption isotherms. This study included only the Langmuir Eq. (4),[14] Freundlich Eq. (5),[15] and Temkin Eq. (6)[16] models. These models are given by the following equations:

$$\frac{c_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}c_e} \tag{4}$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln c_e \tag{5}$$

$$q_e = b \ln K_T + b \ln c_e \tag{6}$$

K_L is the Langmuir adsorption equilibrium, constant q_{max} (mg g^{-1}) represents the maximum adsorption capacity, K_f

is the Freundlich constant (l kg^{-1}), $1/n$ is the heterogeneity factor, b is the variation of adsorption energy (J mol^{-1}), and K_T is Temkin constant (l mg^{-1}).

3 Results and discussion

3.1 Adsorption kinetics

Concerning pseudo-first-order kinetics, the plot of $\ln(q_e\text{-}q_t)$ as a function of time for the dye studied gives a linear form (Fig. 1), and pseudo-second-order was examined by plotting t/q_t as a function of time (Fig. 2).

All the kinetic parameters determined from these lines are presented in Table 2 on the zeolites S-1, ZSM-5, VS-1, and CuZSM-5, respectively.
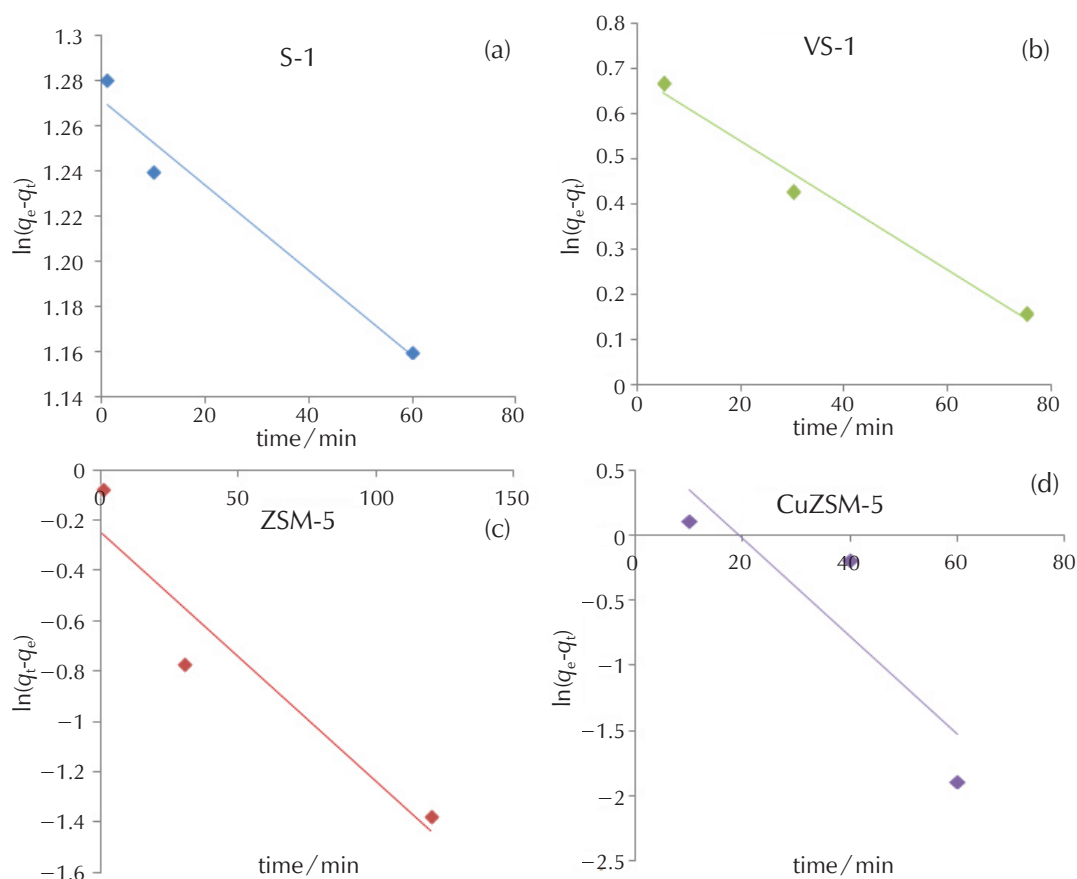

Fig. 1 – Pseudo-first-order kinetics of bromothymol blue on the four zeolites

Table 2 – Kinetic adsorption constants of the dye studied for the two models on the four materials (S-1, ZSM-5, VS-1, and CuZSM-5)

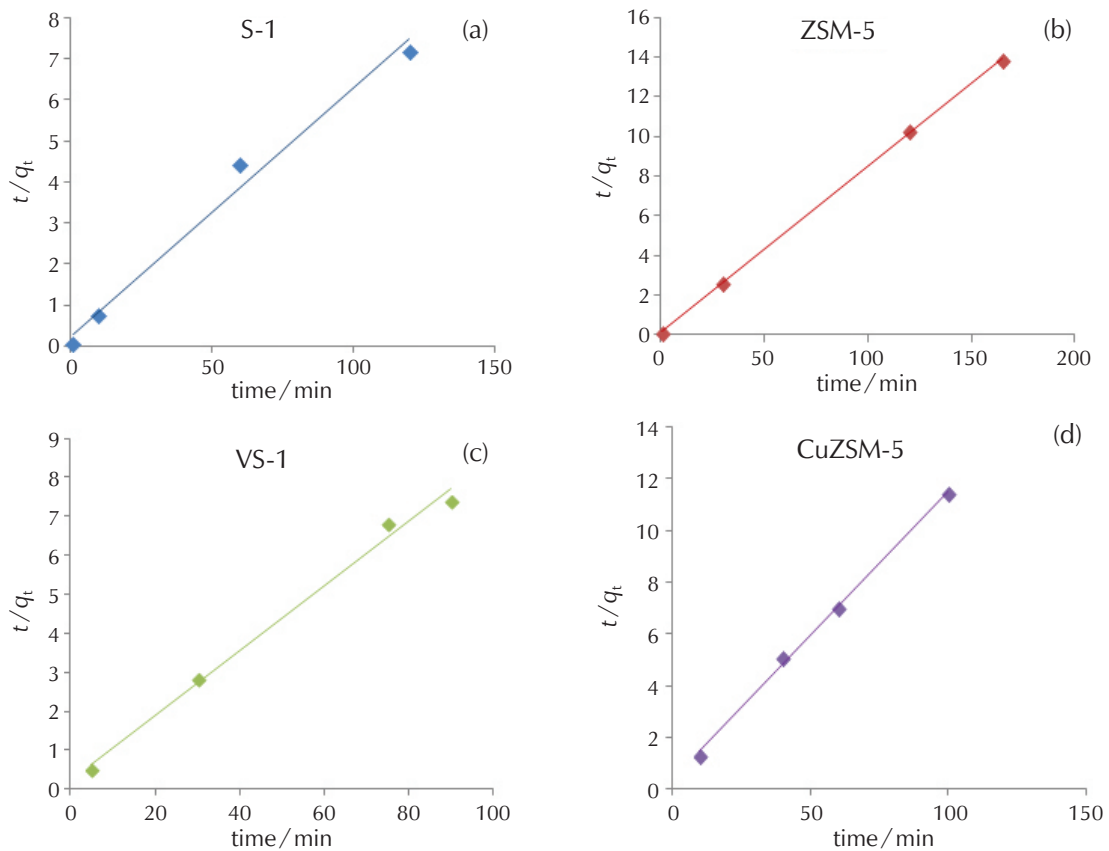| Dye	Zeolites		Pseudo-first-order			Pseudo-second-order		
		q_e(exp)/mg g^{-1}	q_e(cal)/mg g^{-1}	k_1/min^{-1}	R^2	q_e(cal)/mg g^{-1}	k_2/g mg^{-1} min^{-1}	R^2
BTB	S-1	16.70	0.477	0.0019	0.963	16.583	$1.530 \cdot 10^{-2}$	0.985
	ZSM-5	11.92	2.808	0.0099	0.899	11.890	$10.890 \cdot 10^{-2}$	0.999
	V S-1	12.21	0.935	0.0071	0.978	12.019	$3.309 \cdot 10^{-2}$	0.992
	Cu ZSM-5	8.75	3.906	0.0375	0.767	8.976	$3.655 \cdot 10^{-2}$	0.998

Fig. 2 – Pseudo-second-order kinetics of bromothymol blue on the four zeolites

The results showed that the pseudo-second-order model was more reliable for determining the order of the adsorption kinetics of BTB on the S-1, ZSM-5, VS-1, and CuZSM-5 zeolites, because the correlation coefficients were closer to one ($R^2 > 0.99$) compared to those of the pseudo-first-order model.

3.2 Adsorption isotherms

The experimental results of the BTB adsorption isotherms on zeolites modelled by the Langmuir, Freundlich, and Temkin equations are shown in Figs. 3, 4, and 5.

The Langmuir, Freundlich and Temkin parameters for the BTB on the four zeolites are presented in Table 3.

The correlation coefficient R^2 of the Langmuir model is very close to one for the dye on the four zeolites. According to the constants q_{max} calculated from this model, it was observed that the adsorption capacity of BTB on (S-1) ($q_{max} = 11.025$ mg g^{-1}) was higher compared to the other zeolites ZSM-5, CuZSM-5, and VS-1 (6.587, 3.345, and 6.317 mg g^{-1}), respectively.

Langmuir isotherm is characterized by the separation factor or equilibrium parameter, R_L, which is used to predict whether an adsorption system is "favourable" or "unfa-

Table 3 – Adsorption isotherm constant of the dye studied on the four zeolites (S-1, ZSM-5, VS-1, and CuZSM-5)

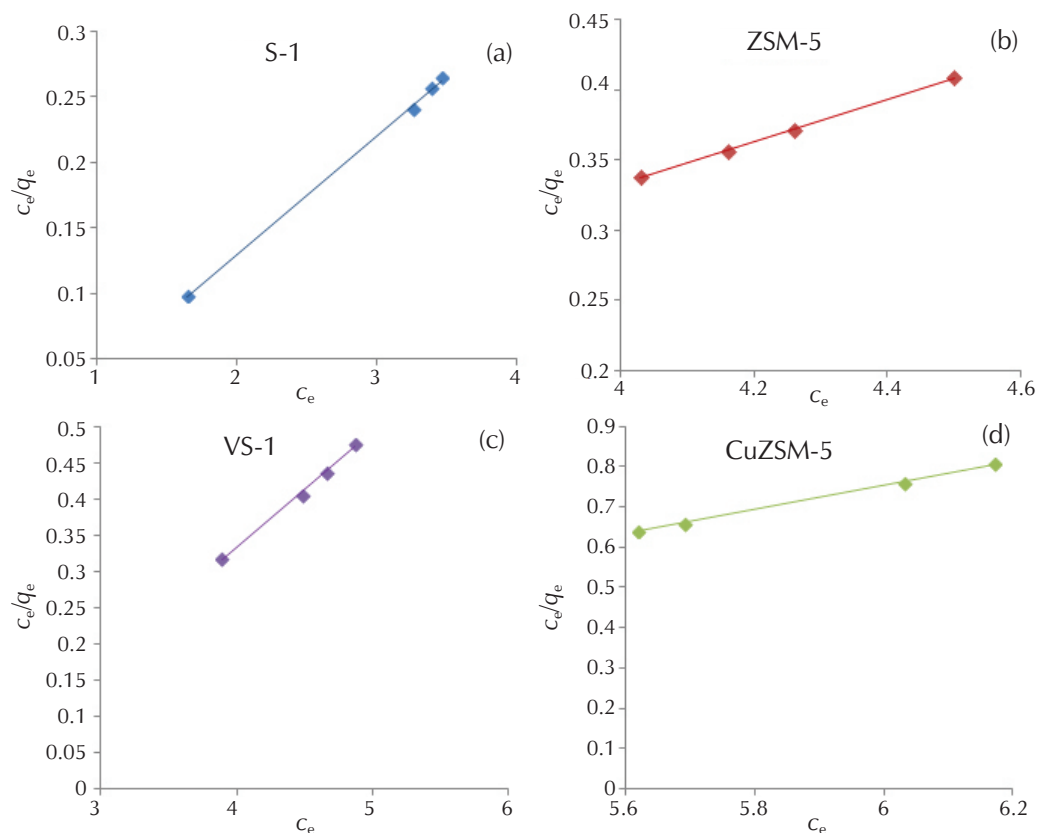| Langmuir				
zeolites	K_L	q_{max}/mg g^{-1}	R^2	R_L
S-1	1.744	11.025	0.9993	0.0542
ZSM-5	0.552	6.587	0.9990	0.1533
CuZSM-5	0.287	3.345	0.9994	0.2583
VS-1	0.528	6.317	0.9992	0.1592
Freundlich				
zeolites	K_F	$1/n$	R^2	
S-1	19.488	0.3186	0.9984	
ZSM-5	32.769	0.7336	0.9956	
CuZSM-5	35.022	0.7805	0.9964	
VS-1	107.77	1.4638	0.9960	
Temkin				
zeolites	b/KJ mol^{-1}	K_T	R^2	
S-1	−4.83	0.0191	0.9991	
ZSM-5	−8.38	0.0601	0.9971	
CuZSM-5	−12.03	0.0866	0.9985	
VS-1	−8.52	0.0619	0.9975	

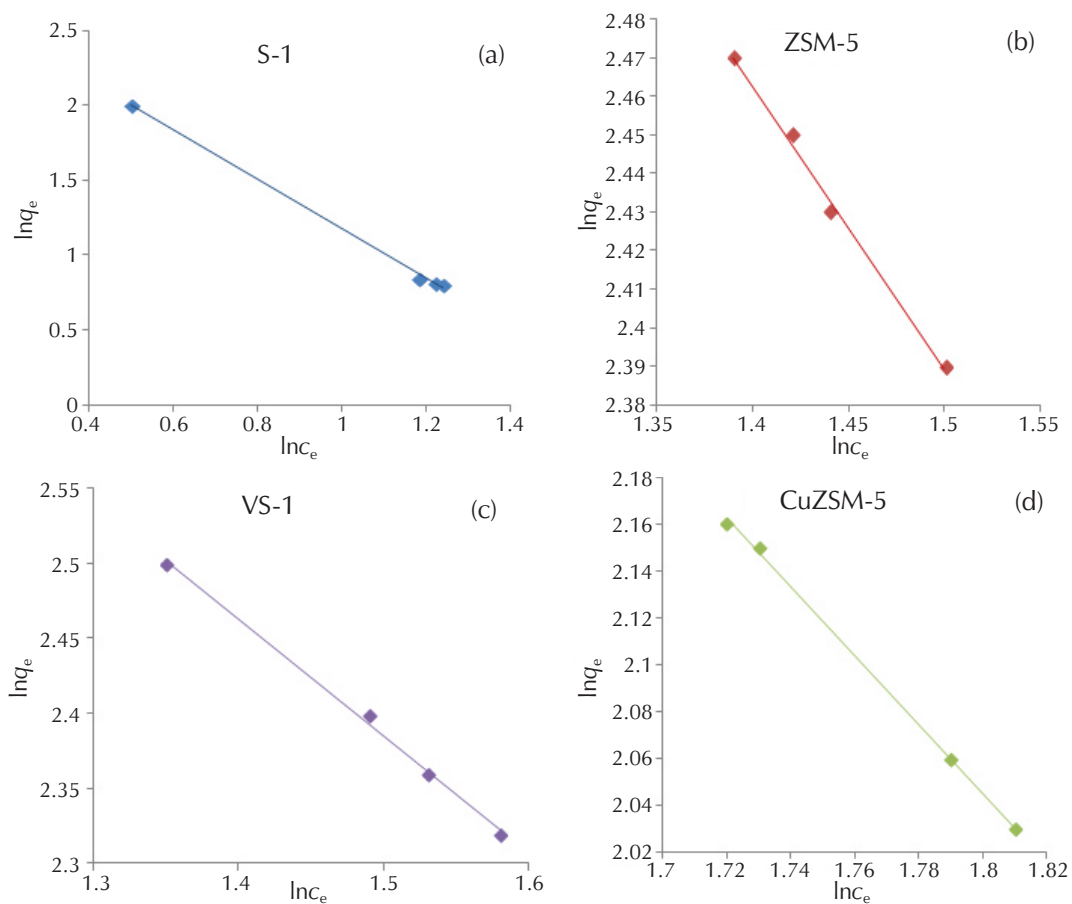Fig. 3 – Langmuir adsorption isotherm of BTB on the four zeolites

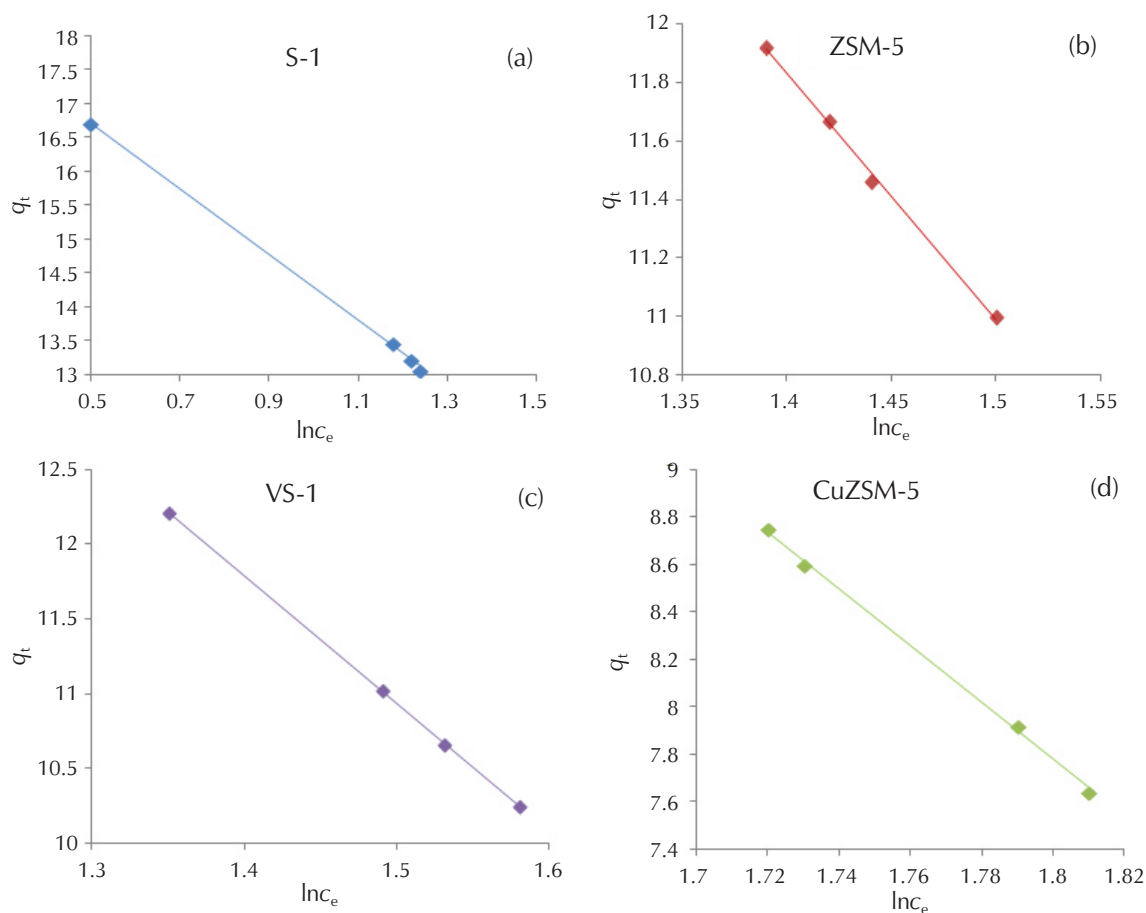Fig. 4 – Freundlich adsorption isotherm of BTB on the four zeolites

Fig. 5 – Temkin adsorption isotherm of BTB on the four zeolites

vourable". The separation factor, R_L, is defined by the following equation:[17]

$$R_L = \frac{1}{1} + (K_L c_0) \qquad (6)$$

The R_L values of the dye studied on the four zeolites were in the range of $0 < R_L < 1$, and are shown in Table 3, which indicates that the adsorption is favourable.

In the case of the Freundlich isotherm, the results showed that the correlation coefficients R^2 were good in all cases. The values $1/n$ found suggest better adsorption of the dye on (S-1), easy adsorption of the dye on (ZSM-5 and CuZSM-5), and difficult adsorption in the presence of VS-1. Therefore, the adsorption is favourable in the presence of (S-1, ZSM-5, and CuZSM-5).[19]

Regarding the Temkin isotherm, the values of the correlation coefficient R^2 were also high.

4 Conclusion

The results of this study revealed that adsorbent (S-1) highly efficient in the elimination of bromothymol blue, with a percentage of 83.44 % compared to the other adsorbents (ZSM-5, MS-1, and MZSM -5) with elimination percentages of 59.64, 61.07, and 43.75 %, respectively. The results of the adsorption isotherms suggest that the Langmuir isotherm presents higher values of the correlation coefficient R^2 compared to the other isotherm models. The kinetic study showed that the pseudo-second-order model offered a better description of the kinetics of the adsorption reaction for the dye on the four types of zeolites compared to the pseudo-first-order model, indicating a chemical reaction (chemisorption).

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SAŽETAK

Adsorpcija indikatora bromtimol modro (BTB) upotrebom četiri zeolita kao adsorbenata

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U ovoj je studiji ispitivana adsorpcija anionskih bojila na četiri zeolitska materijala inkorporirana (VS-1, CuZSM-5) i neinkorporirana (S-1, ZSM-5) u metale. Adsorpcija indikatora bromtimol modro (BTB) na četiri adsorbenta analizirana je izotermnim modelima Langmuir, Freundlich i Temkin. Također su primijenjena dva kinetička modela za proučavanje procesa adsorpcije, pseudo-prvog i pseudo-drugog reda. Izotermni podatci pokazali su dobru korelaciju. Kinetiku adsorpcije bolje je opisao model pseudo-drugog reda. Dobiveni rezultati pokazali su da je maksimalni postotak uklanjanja indikatora BTB dobiven čisto neinkorporiranim silicijskim zeolitom (S-1).

Ključne riječi
Zeoliti, adsorpcijska izoterma, bromtimol modro, razgradnja bojila

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