Adsorption Study of Textile Dye Basic Red 46 on Clinoptilolite

Amin, Goran; Konstantinovic, Sandra
Faculty of Technology, Bulevar Oslobodjenja, Leskovac, SERBIA

Jordanov, Igor
Faculty of Technology and Metallurgy, Ruger Boskovic, Skopje, NORTH MACEDONIA

Djordjevic, Dragan[*+]
Faculty of Technology, Bulevar Oslobodjenja, Leskovac, SERBIA

ABSTRACT: *The study investigates the application of clinoptilolite for the elimination of textile basic dye from water. It is about modeling the process of dye adsorption from an aqueous solution to a natural adsorbent. The natural adsorbent-clinoptilolite is originally from Serbia, it has been characterized by chemical analysis which determined that SiO_2 dominates (58.23%). The most common mineral phase in clinoptilolite is a mineral from the group of clinoptilolite with a mineral content in the tuff of about 85%. The concentration of basic dye and adsorption time were varied in the study (20–120 mg/dm^3 and 2-60 min), while the amount of clinoptilolite was constant (1 g). Two-, three-, four- and five-parameter models were used to describe the adsorption process. The two-parameter Langmuir linear model perfectly describes equilibrium adsorption, whereas the Radke-Prausnitz isotherm proved to be the best of the several parametric models ($R^2=0.999$). In kinetics, the dominance of the Pseudo-second order adsorption mechanism was confirmed. According to the results, it can be said that clinoptilolite is an effective adsorbent for removing the basic dye from an aqueous solution.*

KEYWORDS: *Clinoptilolite; Adsorption; Textile basic dye, Adsorption models; Adsorption kinetics.*

INTRODUCTION

Many industries, such as the textile, leather, food, and paper industries, are extensive consumers of dyes. Among them, the textile industry is the first to use dyes for dyeing various fibers. Dyes can pose a danger to the environment due to the presence of many contaminants, such as toxic organic residues, acids, alkalis, and inorganic substances. Some dyes are carcinogenic and mutagenic because they were previously formed from dangerous chemicals such as benzidine and metals. The release of colored liquid waste in the receiving waters not only affects their aesthetic nature but also interferes with the transmission of sunlight and thus reduces photosynthetic activity, disturbing the natural balance [1,2].

Treatment and process of industrial wastewater is necessary especially due to international regulations that increasingly prescribe a reduction in the amount of various chemicals in the water. In this regard, a clean environment and environmental requirements related to the presence of dyes in wastewater are becoming a challenge and a problem for industrial dye production and textile processing [3-5].

In the last few decades, several physical, chemical, and biological methods of decolorization have been published, some of which have been accepted by the textile industry. Among many dye removal techniques, the adsorption process gives the best results, as it can be used to remove different types of colored materials. Most commercial systems use activated carbon as an adsorbent to remove dyes from wastewater, due to its excellent adsorption ability. Although activated carbon is preferred as an adsorbent, its widespread use is limited due to its high cost. To reduce the cost of treatment, there have been attempts to find cheaper alternative adsorbents [6-11].

Clinoptilolite is a rich source of aluminosilicates and usually has a high cation exchange capacity. They act as polyfunctional adsorbents in the wastewater treatment process, however, they cannot adsorb anions due to the negative charge of their aluminosilicate network. Many products from clinoptilolite are known, such as building stone, cement pozzolan, filler for paper, drying agents, for separating gases, liquids, etc. A more significant commercial application of natural zeolites is the removal of heavy metal ions from wastewater [12].

More specifically, clinoptilolites are natural aluminosilicates with a 3D-dimensional structure, that have a large surface area, ion exchange capacity, variable porosity as well as high mechanical and thermal stability. The large surface area and porous nature make clinoptilolite an effective material for water and air purification [13]. In addition, clinoptilolites have also been used for the adsorption of various organic substances in water [14,15], and there are studies dealing with the removal of dyes from aqueous solutions using clinoptilolites [16,17].

The modeling of equilibrium adsorption, as well as the rate of adsorption of textile basic dye on natural clinoptilolite, was investigated in this paper. Practically, it is a process of decolorization of the colored water model, made as a wastewater model, created after the dyeing of textiles. Clinoptilolite was used as an adsorbent, whose porous particles adsorb the basic dye from the aqueous solution on its surface and inside.

EXPERIMENTAL SECTION

Clinoptilolite obtained from a site near Brus, Serbia, was used as an adsorbent. The most common mineral phase is a mineral from the group of zeolites, clinoptilolite, with a mineral content in tuff of about 85%.
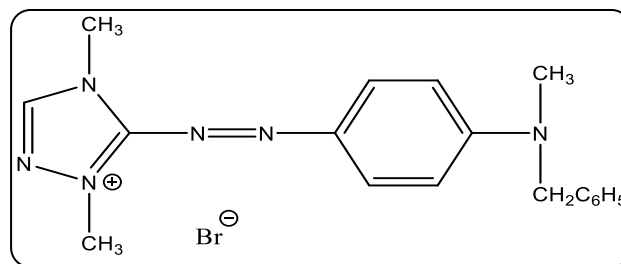

Fig. 1: The structure of the applied Basic Red 46 dye

Before the experiment, the preparation of clinoptilolite was done which included numerous rinsing with distilled water and drying. Finally, the material is ground by grinding to micrometer sizes (mechanical activation) to obtain a larger free surface area of the particles and thus better adsorption capacity.

The textile red basic dye CI Basic Red 46 was used in the research whose molecular formula is $C_{18}H_{21}BrN_6$, and the molar mass is 401.3 g/mol. The dyestuff is in the form of a dark red powder, the solubility in water is 80 g/dm^3 at 30 °C. It is mainly used for dyeing acrylic fibers, but can also be used for textile printing. The initial concentrations of this dye in the experiment were defined as the amount of dye of the same type remaining in the water after commercial textile dyeing.

For the analysis of the influence of the pH solution on adsorption, 1M solutions of NaOH and H_2SO_4 were used (for pH 2-11). According to the previous check and the achieved results, the most effective adsorption of the basic-cationic dye occurs at pH 8, and the adsorption processes were performed at this pH value of the solution.

The adsorption test itself was performed in laboratory conditions, in glass reactors, and placed on a shaker with 130 rpm, at 333 K. The amount of clinoptilolite in all cases was 1 g, whereas the solution was in a constant amount (0.1 dm^3), containing the dye of the initial concentration of 20–120 mg/dm^3. Processing time, with continuous stirring, was 2–60 min.

The following measurement methods and calculations were applied:

•   The chemical composition of the adsorbent was determined by X-Ray Fluorescence (XRF) spectrometry on an energy-dispersive spectrometer ED2000 (Oxford Instruments, UK).

•   After the deposition of a thin gold layer on the powder surface, a TESCAN MIRA 3 XMU Field Emission Scanning Electron Microscope (FE-SEM), operated at 20 keV, was used to analyze the morphology of the materials.

- UV-Vis spectrophotometry, Cary 100 Conc UV-Vis Varian apparatus (absorption maximum at 520 nm) was used to determine the dye concentration in the solution.
- The degree of basic dye exhaustion [1] was calculated using the equation:

$$Degree\ of\ exhaustion = \frac{C_0 - C_t}{C_0} \cdot 100\ (\%) \tag{1}$$

where: C_0 and C_t, (mg/dm^3), initial and dye concentration (adsorbate) at time t.

- The amount of adsorbed dye [3] was obtained *via* the equation:

$$q_{t,e} = \frac{C_0 - C_{t,e}}{w} \cdot V \tag{2}$$

Where: $q_{t,e}$ (mg/g), amount of adsorbed dye per unit mass of clinoptilolite (adsorbent) at adsorption time ($_t$) and equilibrium time ($_e$); C_0 (mg/dm^3), initial dye concentration; $C_{t,e}$ (mg/dm^3), dye concentration in solution at adsorption time ($_t$) and equilibrium time ($_e$); w (g), mass of adsorbent; V (dm^3), volume of adsorption solution.

Langmuir two-parameter isotherm [7] is represented by the following expression:

$$\frac{1}{q_e} = \left[\frac{1}{b \cdot Q_0}\right] \cdot \frac{1}{C_e} + \frac{1}{Q_0} \tag{3}$$

Where: q_e (mg/g), amount of adsorbate adsorbed per unit mass of adsorbent; C_e (mg/dm), equilibrium adsorbate concentration; Q_0 (mg/g), the maximum amount of adsorbate that can bind to the adsorbent; b (dm^3/mg), the ratio of the adsorption rate constant and the adsorbate desorption rate constant.

The Radke-Prausnitz three-parameter isothermal model has several important properties which is why it is more desirable in most adsorption systems at low adsorbate concentrations. The model of this isotherm is reduced to a linear isotherm (Henry's model) when the adsorbate concentration is low, and it becomes a *Freundlich* isotherm when the adsorbate concentration is high. If the value of m_{RP} is equal to 1, the Radke-Prausnitz model is reduced to the Langmuir model [18].

The Radke-Prausnitz isothermal model [18] is given by the equation:

$$q_e = \frac{q_{max} \cdot K_{RP} \cdot C_e}{1 + K_{RP} \cdot C_e^{m_{RP}}} \tag{4}$$

Where: q_{max} (mg/g), Radke-Prausnitz maximum adsorption capacity; K_{RP}, Radke-Prausnitz equilibrium constant; m_{RP}, Radke-Prausnitz exponent of the model.

The Marczewski-Jaroniec isotherm is also known as the general four-parameter Langmuir equation. It is recommended based on the assumption of the local Langmuir isotherm and the distribution of adsorption energies in the active sites on the sorbent [19].

The Marczewski-Jaroniec isotherm equation [19] is expressed as follows:

$$q_e = q_{m_{MJ}} \cdot \left(\frac{(K_{MJ} \cdot C_e)^{n_{MJ}}}{1 + (K_{MJ} \cdot C_e)^{n_{MJ}}}\right)^{\frac{m_{MJ}}{n_{MJ}}} \tag{5}$$

Where: q_{mMJ} (mg/g), maximum single layer adsorption capacity; K_{MJ} (dm^3/mg), Marczewski-Jaroniec equilibrium constant; n_{MJ} and m_{MJ}, exponents of the Marczewski-Jaroniec model.

n_{MJ} and m_{MJ} parameters characterize the heterogeneity of the sorbent surface (which varies between 0 and 1), m_{MJ} describes the expansion of the distribution towards higher adsorption energy, and n_{MJ} describes the expansion towards lower adsorption energies. The isotherm is reduced to the *Langmuir* isotherm when n_{MJ} and m_{MJ}=1; when n_{MJ}=m, it reduces to the Langmuir-Freundlich model.

The Fritz-Schlunder *V* empirical expression [19] has five parameters that give a wide field of equilibrium data:

$$q_e = \frac{q_{mFS} \cdot K_1 \cdot C_e^{m_1}}{1 + K_2 \cdot C_e^{m_2}} \tag{6}$$

Where: q_e (mg/g), amount of adsorbate adsorbed at equilibrium; q_{mFS} (mg/g), maximum Fritz-Schlunder adsorption capacity; K_1, K_2, m_1 and m_2, Fritz-Schlunder parameters (exponents m_1 and m_2 are less than or equal to 1).

The five-parameter *Fritz-Schlunder* model reduces to the *Langmuir* model when the exponents m_1 and m_2 are equal to one. For higher concentrations in the liquid phase, the Fritz-Schlunder model is converted to the Freundlich model.

The Pseudo-second order model [20] describes the adsorption kinetics as follows:

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot (t) \tag{7}$$

Where: k_2 (g/mg·min), second order adsorption rate constant; q_e and q_t (mg/g), adsorption capacity in equilibrium and after time t, respectively.

RESULTS AND DISCUSSION

The used adsorbent-clinoptilolite is a relatively fine bulk material with heterogeneous porous particles, of dispersed shape and form, generally below 15 μm in size.

Table 1: Chemical analysis (%) of native clinoptilolite sample

SiO$_2$	Al$_2$O$_3$	CaO	Fe$_2$O$_3$	K$_2$O	MgO	TiO$_2$	Na$_2$O	MnO	P$_2$O$_5$	SO$_3$	Cl
58.23	10.62	8.48	3.50	2.00	0.90	0.52	0.13	0.11	0.11	0.03	0.008
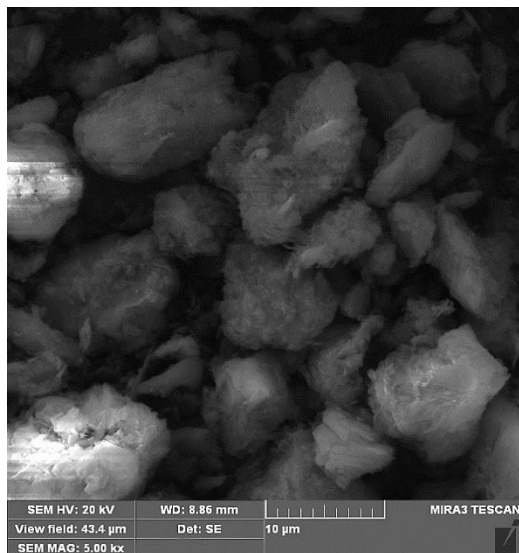
Fig. 2: Micrograph of the surface of the applied adsorbent (natural clinoptilolite)

Fig. 3: Langmuir linear adsorption isotherm for the basic dye-native clinoptilolite system (C_e=20–120 mg/dm^3; t=60 min; w=1 g; T=333 K)

The micrograph from Fig. 2 gives a view with a magnification of 5.000×. Clinoptilolite is known as a porous material, with the indication that it is mostly macroporous with a relatively small inner surface, according to the results of similar research [21,22]. The surface morphology of this adsorbent appears to depend on the method and conditions of the production process. The particles of clinoptilolite used are very spherical and glassy smooth. The presence of spherical particles confirms the higher proportions of Si and Al. It is the availability of the adsorbent surface that leads to the rapid electrostatic adsorption of the cationic dye from the solution [21].

The complete chemical analysis of the adsorbent is shown in Table 1. It is noticeable that silicon oxide dominates, as expected, followed by oxides of aluminum, calcium, iron, potassium, etc.

The mechanism of basic dye adsorption on clinoptilolite is related to the charge carried by these active species. It is known that negatively charged groups on the adsorbent are necessary for the adsorption of the basic dye. Adsorption, in this particular case, was performed at pH=8. In an acidic environment, excess H$^+$ ions in solution will compete for available adsorption sites with cationic basic dye molecules. In addition, the presence of H$^+$ ions will protonate

the clinoptilolite surface leading to an electrostatic repulsion between the positively charged surface of the adsorbent and the basic-cationic dye molecules [23].

Equilibrium adsorption is essential for research into the process of removing the basic dye of an aqueous solution with the help of clinoptilolite. Analysis of isothermal data by fitting them through different isothermal equations is an important step toward finding a suitable model that can be used to control and monitor the adsorption process. In this study, two-, three-, four- and five-parameter isothermal models of Langmuir, Radke-Prausnitz, Marczewski-Jaroniec, and Fritz-Schlunder V were used, respectively, for fitting according to experimental points with the help of OriginPro software.

Linear modeling was applied to the two-parameter model, while nonlinear modeling concerning the number of variables was used for all other isotherms.

The graph in Fig. 3 presents a linear interpretation of the Langmuir adsorption isotherm, showing the dependence of the parameter *($1/q_e$)* on the equilibrium dye concentration *($1/C_e$)*. The values of the *Langmuir* constants are determined from this graph, i.e., the slope and the segment of the functional line.

Under the given experimental conditions, this graph reflects the significant functionality of the parameters,

Table 2: Determination coefficient with constants for nonlinear models for equilibrium adsorption of basic dye on clinoptilolite (C_e=20–120 mg/dm^3; t=60 min; w=1 g; T=333 K)

Isotherms	Constants				R^2
Radke-Prausnitz	q_{max} (mg/g)	K_{RP2}		m_{RP2}	0.999
	395.55	0.0012		1.91	
Marczewski-Jaroniec	$q_{m_{MJ}}$ (mg/g)	K_{MJ}	n_{MJ}	m_{MJ}	0.974
	11.97	0.06	1	1	
Fritz-Schlunder V	q_{mFS}	K_1	K_2	m_1 m_2	0.918
	1.14	1.14	$7.3\cdot10^{-5}$	0.51 $-2.3\cdot10^2$	

which indicates the fact that the Langmuir adsorption isotherm can be used in the explanations for the specific case of adsorption of the basic dye to natural clinoptilolite. In this particular case, the Langmuir model has a very high value of R^2, which is 0.996.

The Langmuir constants, Q_0 (15.9 mg/g) and b (0.035 dm^3/mg) refer to the maximum amount of adsorbate that can bind to the adsorbent and the free adsorption energy, respectively. Features of Langmuir isotherms can be expressed in dimensionless constant, equilibrium parameter R_L. In the specific case, R_L = 0.19, which confirms that the applied Langmuir isotherm is suitable since the equilibrium parameter is between 0 and 1.

Fig. 4 gives a comparative graphic representation of the isotherm models of Radke-Prausnitz, Marczewski-Jaroniec, and Fritz-Schlunder V through the nonlinear fitting of experimental data. The statistical parameters and the model constants obtained from the nonlinear regression as well are also listed in Table 2.

To evaluate the success of these models, a coefficient of determination (R^2) was used, which represents a relative measure of the representativeness of the regression line or a measure of the utility of the model.

The coefficient of determination (R^2=0.999) of the Radke-Prausnitz model has the highest value, which confirms that this model is the most efficient in the nonlinear simulation of isothermal adsorption of basic dye on native clinoptilolite, which can be seen in visual inspection of curves from the graph in Fig. 3. The Marczewski-Jaroniec model has a slightly lower value of R^2 (0.974), while the Fritz-Schlunder V model (0.918) has the weakest result. Since the exponents n_{MJ} and m_{MJ} = 1, the Marczewski-Jaroniec isotherm reduces to the Langmuir isotherm.
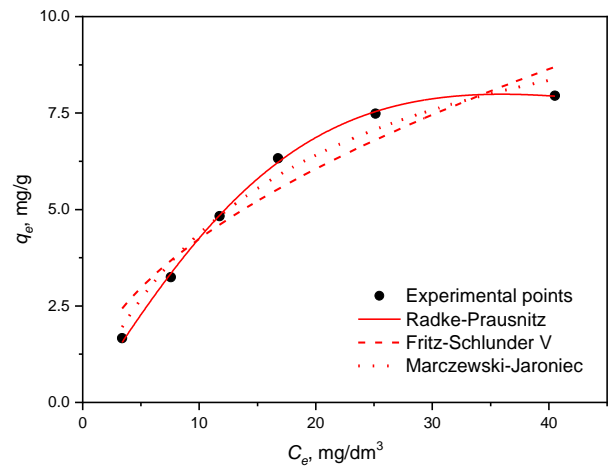

Fig. 4: Nonlinear isotherms for equilibrium adsorption of basic dye to native clinoptilolite (C_e=20–120 mg/dm^3; t=60 min; w=1 g; T=333 K)

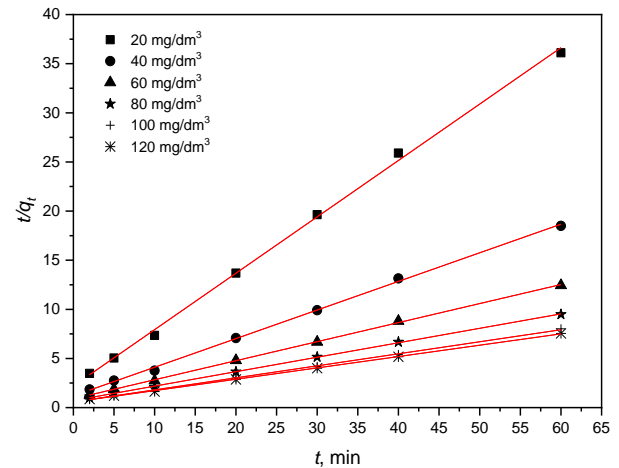*Fig. 5: Basic dye sorption rate on native clinoptilolite according to Pseudo-second order model (C_e=20–120 mg/dm^3; t=2-60 min; w=1 g; T=333 K)*

Thus, in the specific case, the Radke-Prausnitz model is the most suitable with the best fit of the model and experimental data about all other used linear or nonlinear parametric isotherms. The advantage of this model is that it is not based on a certain pure isothermal model but on a thermodynamic basis. Accordingly, all pure isothermal models (e.g., Freundlich and Langmuir) can be integrated into it.

Fig. 5 shows the results of testing the kinetics of basic dye sorption on a clinoptilolite adsorbent for different initial adsorbate concentrations, according to a Pseudo-second order model. This model includes all phases of adsorption, such as external diffusion, adsorption, and internal diffusion in particles since it is a pseudo model.

Table 3: Kinetic parameters of the Pseudo-second order model for adsorption of basic dye on native clinoptilolite (C_e=20–120 mg/dm^3; t=2-60 min; w=1 g; T=333 K)

Dye concentration, mg/dm^3	$q_{e,exp}$ mg/g	Pseudo-second order		
		k_2, g/mg·min	$q_{e,cal}$ mg/g	R^2
20	1.66	0.150	1.74	0.998
40	3.24	0.070	3.43	0.999
60	4.82	0.040	5.16	0.999
80	6.32	0.030	6.79	0.999
100	7.49	0.025	8.16	0.999
120	7.95	0.023	8.65	0.999

Since the reaction occurs in the adsorbed layer on the sorbent surface, its rate (reaction rate) depends on the concentration of reactants in the layer on the adsorbent surface.

Table 3 shows the results of the kinetic parameters of the basic dye adsorption for clinoptilolite. The applicability or validity of the Pseudo-second order kinetic model was valorized by the coefficient of determination. Since this parameter has a very high value (R^2 = 0.999), it is concluded that full functionality has been achieved when the model can be fully used to describe a specific adsorption process. This is supported by small differences between the calculated and experimental parameters, $q_{e,cal}$, and $q_{e,exp}$, for this kinetic model.

Thus, the results confirm the dominance of the *Pseudo-second order* adsorption mechanism; the rate-limiting step may be chemisorption involving valence forces through fission or electron exchange between active sites (clinoptilolite ions and dye cations). It often happens that physical adsorption and chemisorption cannot be distinguished in certain situations, in some cases both types of bonds may be present, as in covalent bonds between two atoms that have a certain degree of ionic character and vice versa.

Also, according to the data in Table 3, the rate constant of the *Pseudo-second order* depends on the initial dye concentration in the solution and decreases with increasing of initial dye concentration, which was determined for many other systems with basic dye [24,25]. At low initial concentrations, the adsorbate will primarily bind to high-energy sites while the lower-energy sites are gradually filled as the adsorbate accumulates on the surface.

CONCLUSIONS

In laboratory conditions, native clinoptilolite showed excellent ability to adsorb textile basic red dye from an aqueous solution. Natural adsorbent-clinoptilolite is a relatively fine bulk material with heterogeneous porous particles, with dimensions, generally, below 40 µm. The composition of clinoptilolite is dominated by silicon oxide, which is expected, followed by oxides of aluminum, calcium, iron, potassium, etc. The two-parameter *Langmuir* linear model perfectly describes the equilibrium adsorption in this case. Of the several parametric models, the Radke-Prausnitz isotherm proved to be the most useful compared to all models, regardless of the form of regression, linear or nonlinear. In kinetics, the dominance of the Pseudo-second order adsorption mechanism in the explanation of the rate of depletion of the basic dye to clinoptilolite was confirmed. Based on the obtained results, it can be said that clinoptilolite is a sufficiently efficient adsorbent for the removal of basic dye from aqueous solutions with a justified tendency to apply in industrial conditions as well. After the adsorption of the dye, the clinoptilolite can be recycled, through the desorption process. Namely, after removing the adsorbate, the clinoptilolite particles are reused for new adsorption. Also, the removed adsorbate after desorption is concentrated, reused, or incinerated.

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