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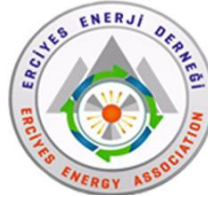
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CLINOPTILOLITE AS A PERSPECTIVE LOW-COST ADSORBENT FOR REMOVAL OF ORGANIC MICROPOLLUTANTS FROM WASTEWATER

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Abstract

Natural zeolite – clinoptilolite (CLI) from Serbian deposit Slanci (near the capital city Belgrade) was investigated as adsorbent for the adsorption of antibiotic ciprofloxacin (CIP) as a model organic micropollutant (OMP) present in wastewater. At 20 °C the adsorption capacity varies from 4.81 to 8.90 mg g⁻¹ for the initial CIP solution concentration of 15 and 50 mg CIP dm⁻³, respectively. The adsorption isotherms at 10, 15 and 20 °C are best represented by the Langmuir model and the adsorption kinetics by the Lagergren's pseudo-second-order equation. The adsorption mechanism most probably involves an ion-exchange reaction occurred at the CLI surface and according to results of Weber-Morris model does not involve intra-particle diffusion.

Keywords: Clinoptilolite, Ciprofloxacin removal, Adsorption, Water treatment

1 INTRODUCTION

Nowadays, emerging contaminants, such as organic micropollutants (OMPs), cause serious environmental problems affecting the human health as well. Since OMPs cannot be efficiently removed from wastewater by conventional wastewater treatment processes, many research efforts have been directed towards acceptable alternative technologies.

Adsorption has attracted a great attention as a simple, environmentally friendly, and cost-effective method with a wide range of available adsorbent materials. Among different adsorbents, natural zeolites are very perspective due to availability, non-toxic nature, and economic acceptability. Clinoptilolite (CLI) is the most abundant natural zeolite mostly studied for the removal of inorganic pollutants from water [1, 2]. Moreover, its unique physico-chemical properties, such as porosity and thermal stability, make CLI suitable adsorbent for use in a diverse scientific and industrial purposes [3]. This study shows that CLI can also be efficient in removal of OMPs from water media, such as the antibiotic ciprofloxacin (CIP) which is used as a model pollutant in this research.

2 EXPERIMENTAL

2.1 Starting material

Clinoptilolite-rich zeolitic tuff (Z) obtained from the deposit Slanci was used in the experiments. Rietveld analysis [4] showed that Z contains CLI as the major mineral phase (> 80 wt.%) and quartz (< 7.5 wt.%) and feldspar (< 13 wt.%) as major satellite phases.

The cation exchange capacity (CEC) of the CLI determined by a standard procedure [5] was 162 mmol M⁺/100 g. The particle size used in the experiments was in the range of 0.063-0.125 mm for which previous studies showed the best adsorptive performance [1, 2].

2.2 Characterization

Rigaku SmartLab diffractometer with CuK α radiation ($\lambda = 1.54178 \text{ \AA}$) was used for mineral analysis of the tuff. The XRD pattern was recorded in the 2θ range 5-65° in steps of 0.01° with the scan rate of 5° min⁻¹.

Elemental analysis of the CLI phase was determined by a Carl Zeiss SupraTM 3VP field-emission gun scanning electron microscope (FEG-SEM) equipped with EDS detector (Oxford Analysis) with INCA Energy system for quantification of elements.

A simultaneous thermogravimetric (TGA) and differential thermal analysis (DTA) was performed using a SDT Q-600 instrument (TA Instruments). The sample (mass approx. 10 mg) was heated in a standard alumina sample pan; the experiment being carried out under nitrogen with a flow rate of 0.1 dm³ min⁻¹.

The specific surface areas and porosity characteristics were determined by N₂ adsorption isothermally at -196 °C, using a Micrometrics ASAP 2020. Prior to the adsorption the samples were outgassed overnight at 350 °C under high vacuum. The specific surface area of sample (S_{BET}) was

calculated according to the Brunauer, Emmett, Teller (BET) method.

The zeta potential (ZP) was measured by a Zetasizer NanoZS90 (Malvern Instruments Ltd., UK).

2.3 Adsorption tests

The adsorption tests were performed by a batch method. The adsorption capacity of CLI toward CIP was studied for different initial CIP concentration (15, 25 and 50 mg dm⁻³) and temperature (283, 288 and 293 K) at pH = 5. CLI sample of about 0.2 g was suspended in 25 cm³ of the certain concentration of CIP solution and left under shaking in a thermostated water bath from 5 to 60 min. Solid was recovered by centrifugation and the CIP concentration in filtrate was measured by an UV-VIS spectrophotometer (Perkin Elmer Lambda 365) at $\lambda = 278$ nm according to a standard procedure [6].

All the experiments were carried out under controlled conditions: the temperature in the thermostated bath was maintained constant to within ± 0.1 °C, the CLI sample was weighted to four-digit accuracy, and the solution concentrations were determined also with four-digit accuracy.

3 RESULTS AND DISCUSSION

The XRD pattern of Z (Figure 1) clearly showed that CLI is the main mineral phase in the Z. Presence of quartz is evident from characteristic diffraction at $2\theta = 26.6^\circ$ whereas feldspar displays diffraction at $2\theta = 27.1^\circ$ [7].

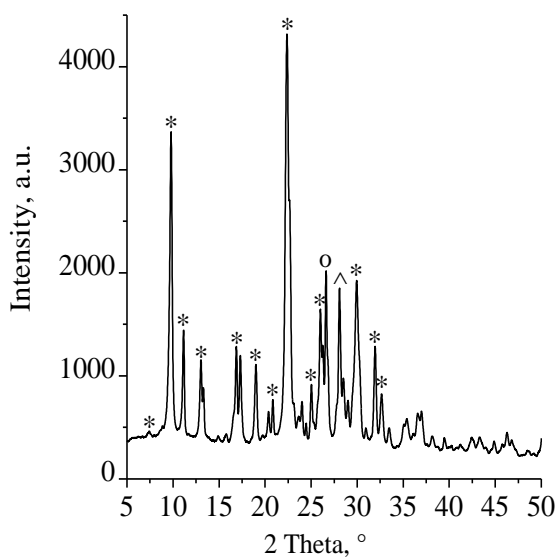


Figure 1. XRD pattern of Z (* - clinoptilolite, ° - quartz and ^ - feldspar)

Elemental analysis of CLI showed that the Si/Al molar ratio is 5.03 that is common value for natural

clinoptilolite. The specific surface area (S_{BET}) was 23.57 m² g⁻¹ that is in accordance with reported values for S_{BET} (usually in the range 15-40 m² g⁻¹). ZP measurements showed that CLI surface is negatively charged in the whole range of pH values (Figure 2).

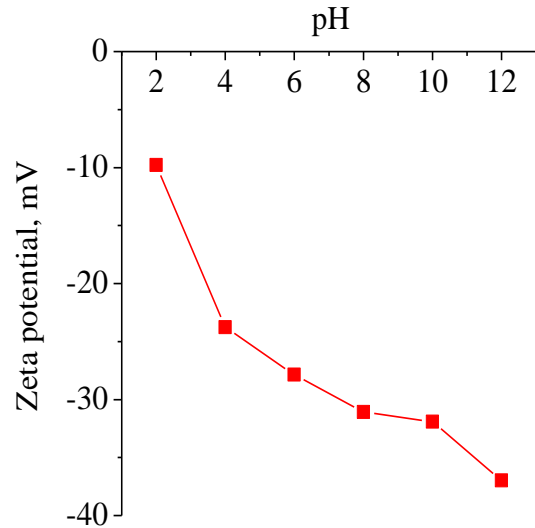


Figure 2. pH dependence of surface charging of CLI

Since CIP molecule (Figure 3) mainly exists as a zwitterion at neutral pH values, positively charged at $pH < 5.9$ and with a shift towards anionic form at $pH > 8.9$, pH of the solution strongly affects its adsorption performance.

Accordingly, the adsorption experiments were performed at pH = 5.

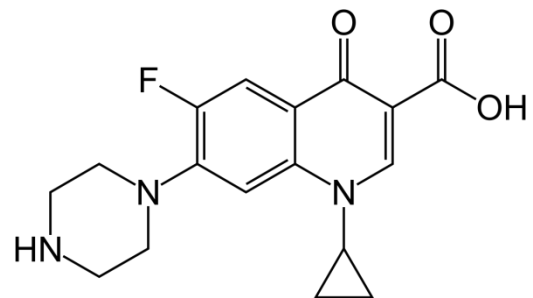


Figure 3. Structure of ciprofloxacin (CIP)

Adsorption isotherms were studied at 283, 288 and 293 K. The equilibrium data were analysed by several empirical adsorption isotherm models [8]. Among the two-parameter models the Langmuir and Freundlich models gave the best results. As judged by the values of the linear regression correlation coefficients – R^2 (Table 1), the Langmuir equation gave better description of the CIP adsorption on the CLI. The Langmuir model [9] can be represented as:

$$q_{e} = \frac{q_{\max} b_L C_e}{1 + b_L C_e} \quad (1)$$

where C_e is the equilibrium concentration of the solute (mg dm^{-3}), q_e is the equilibrium concentration of the solute adsorbed (mg g^{-1}), while q_{max} (mg g^{-1}) and b_L ($\text{dm}^3 \text{mg}^{-1}$) are Langmuir constants (q_{max} corresponding to the maximum achievable uptake by a system, and b_L is related to the affinity between the sorbate and adsorbent).

Taking into account assumptions of the Langmuir model [9], it could be concluded that one active site at the CLI surface is occupied by only one CIP molecule.

Table 1. Parameters obtained by the adsorption isotherms for the CIP adsorption on CLI

T, K	Langmuir isotherm		
	Q_0	b	R^2
283	17.97	12.24	0.9823
288	10.09	3.62	0.9836
293	11.93	5.75	0.9844
T, K	Freudlich isotherm		
	K_f	n	R^2
283	1.87	1.61	0.9972
288	3.43	3.35	0.9659
293	2.91	2.55	0.9763

Q_0 – maximum adsorption capacity (mg g^{-1}); b – Langmuir constant ($\text{dm}^3 \text{mg}^{-1}$); K_f – Freundlich isotherm constant ($\text{dm}^3 \text{g}^{-1}$); n – Freundlich exponent ($\text{dm}^3 \text{mg}^{-1}$); R^2 – correlation coefficient.

Two reaction-based kinetic models were applied in order to describe the adsorption experimental data (Figure 4). The first model is given by the Lagergren's first-order rate equation [9]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

where q_e (mg g^{-1}) is the adsorption capacity at equilibrium and k_1 (min^{-1}) is the rate constant of the first-order adsorption. Integrating the expression (2) between the limits $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$, one obtains:

The plot of $\log(q_e - q_t)$ vs t should yield a straight line if the experimental data conform to this kinetic model.

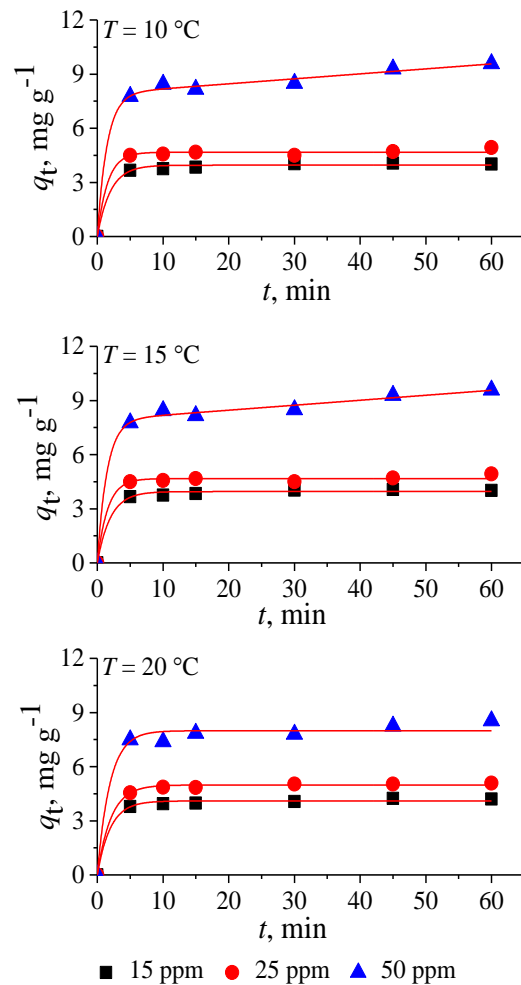


Figure 4. Adsorption kinetics for CIP on CLI for different initial CIP concentrations; q_t is the amount of the adsorbed CIP (mg per 1 g of CLI) after time t

The second reaction-based model that was applied is described by the pseudo-second-order rate equation [9] which can be written as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of the pseudo-second-order adsorption. Integration between the same limits as above yields the following expression:

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

The plot of t/q_t vs t will give a straight line if the experimental data conform to this kinetic model, and the values of q_e and k_2 are obtained respectively from the slope and intercept of such a plot.

Application of the two models on the experimental data for the adsorption of CIP showed that Lagergren's first-order model gives a rather poor agreement, the square of the linear regression

correlation coefficient being lower than 0.80. Satisfactory fits were obtained only by the pseudo-second-order kinetic model; the obtaining parameters are given in Table 2.

Moreover, in order to examine the extent to which diffusion participates in the CIP adsorption, the data were further processed by the Weber–Morris mass transfer model [10]. This did not result in agreement with experimental data suggesting that the intra-particle diffusion is not present in the adsorption of CIP on CLI.

Table 2. Kinetic parameters for the adsorption of CIP on CLI obtained for Lagergren's pseudo-second-order model

C_0	T	k_2	$q_{e,t}$	R^2
15	283	0.3394	4.09	0.9999
	288	0.2490	4.28	0.9998
	293	0.2275	4.82	0.9996
25	283	0.1896	4.90	0.9988
	288	0.2900	5.13	0.9999
	293	1.5606	5.24	0.9995
50	283	0.0436	9.78	0.9983
	288	0.0703	8.63	0.9991
	293	0.0714	8.94	0.9989

C_0 – initial CIP solution concentration (mg dm^{-3}); $q_{e,t}$ – equilibrium adsorption capacity (mg g^{-1}); k_2 – rate constant ($\text{g mg}^{-1} \text{min}^{-1}$)

4 CONCLUSION

This study shows that cost effective and environmentally friendly natural zeolite – clinoptilolite could be a promising adsorbent for the removal of antibiotic ciprofloxacin from aqueous solution. This results suggest that natural clinoptilolite can be also used as an efficient adsorbent for other organic micropollutants.

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