

## THE EFFICIENCY OF NATURAL CLINOPTILOLITE FOR CIPROFLOXACIN REMOVAL FROM AQUEOUS MEDIA

Barbara Kalebić<sup>1</sup>, Jelena Pavlović<sup>2</sup>, Jelena Dikić<sup>2</sup>, Aleksander Rečnik<sup>3</sup>, Nikola Škoro<sup>4</sup>,  
Nevenka Rajić<sup>1</sup>

<sup>1</sup>Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

<sup>2</sup>Innovation Centre of Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

<sup>3</sup>Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

<sup>4</sup>Institute of Physics, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

E-mail: [bkalebic@tmf.bg.ac.rs](mailto:bkalebic@tmf.bg.ac.rs)

### ABSTRACT

Adsorption of the antibiotic ciprofloxacin (CIP) from an aqueous solution by calcium-rich clinoptilolite (CLI) was investigated. Obtained results showed that natural CLI possesses a high adsorption efficiency in the removal of CIP at 283, 288 and 293 K and at pH= 5. Adsorption kinetics studied for the initial CIP concentrations of 15–75 mg dm<sup>-3</sup> follow Lagergren's pseudo-second order equation and the adsorption is best represented by the Langmuir model. The adsorption mechanism involves strong electrostatic interactions between aluminosilicate lattice of CLI and the cationic form of CIP accompanied by an ion-exchange reaction. The CIP saturated CLI was successfully regenerated by a cold atmospheric pressure plasma treatment.

Key words: clinoptilolite, ciprofloxacin, adsorption, plasma treatment.

### INTRODUCTION

The use of antibiotics in both human and veterinary medicine is constantly increasing, while water pollution by these organics is generally poorly regulated. Antibiotics present in water media have different adverse effects on environment as well as human health. They belong to organic micropollutants (OMPs) and cannot be efficiently removed from water by conventional water treatment processes. Consequently, it is of great importance to find acceptable alternative technologies for their removal from water.

CIP is widely applied antibiotic for treatment of both human and animal bacterial infections because of its excellent activity against Gram-positive and Gram-negative bacteria. Thus, it has been found in wastewater effluents in concentrations from ng to mg dm<sup>-3</sup>, with extremely high concentration of up to 50 mg dm<sup>-3</sup> near drug manufacturing plants [1]. Moreover, due to the CIP zwitterionic nature, the charge is strongly pH dependent.

CLI is the most abundant natural zeolite. It has been extensively studied for adsorption of inorganic pollutants from water [2,3]. Reports on usability of CLI in pharmaceuticals removal are rather scarce [4]. This could be explained by the fact that adsorption of these organics has mostly been found as an irreversible process.

This study shows an excellent adsorption efficiency of CLI in CIP removal from water media. Spent adsorbent is recovered by cold atmospheric pressure plasma treatment which is novel method in regeneration of mineral adsorbents.

### EXPERIMENTAL

Clinoptilolite-rich zeolitic tuff (Z) obtained from the deposit Slanci (near Belgrade, Serbia) was used as a starting material. Rietveld analysis showed that Z contains CLI as the major mineral phase (> 80 wt.%), quartz (< 7.5 wt.%) and feldspar (< 13 wt.%). The cation exchange capacity (CEC) of the CLI determined by a standard procedure was 162 mmol M<sup>+</sup>/100

g. The particle size used in the experiments was in the range of 0.063-0.125 mm for which previous experiments showed that it is optimal one.

*Characterization:* Rigaku SmartLab diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) was used for analysis of the mineral phases present in the samples. The PXRD patterns were recorded in the  $2\theta$  range 5–65°. Elemental analysis of the CLI phase was determined by a Carl Zeiss Supra<sup>TM</sup> 3VP field-emission gun scanning electron microscope (FEG-SEM) equipped with EDS detector 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 specific surface areas and porosity characteristics were determined by N<sub>2</sub> adsorption isothermally at -196 °C, using a Micrometrics ASAP 2020, and the specific surface area of sample ( $S_{\text{BET}}$ ) was calculated according to the BET method. The zeta potential of CLI was measured by a Zetasizer NanoZS90 (Malvern Instruments Ltd., UK).

*Adsorption tests:* The adsorption tests were performed by a batch method. The adsorption capacity was studied for different initial CIP concentration (15, 25 50 and 75 mg dm<sup>-3</sup>) and temperatures (283, 288 and 293 K) at pH= 5. About 0.2 g of the zeolite was suspended in 50,0 cm<sup>3</sup> of the certain concentration of CIP solution and left under shaking in a thermostated water bath from 5 to 60 min. Solid phase was recovered by centrifugation and the CIP concentration in filtrate was measured by an UV-VIS spectrophotometer (Perkin Elmer Lambda 365) at  $\lambda = 278 \text{ nm}$  according to a standard procedure [5].

*Adsorbent regeneration:* A surface dielectric barrier discharge (SDBD) source with a segmented electrode operating in air for 20 min was used for plasma treatment of the spent CLI.

## RESULTS AND DISCUSSION

The PXRD pattern (Figure 1) showed that CLI was the main mineral phase. Diffractions at  $2\theta = 26.6^\circ$  and  $27.1^\circ$  correspond to the presence of quartz and feldspar, respectively, which are major satellite phase [6].

Elemental analysis of CLI showed that the Si/Al molar ratio is 5.03 which is the common value for natural clinoptilolite. Furthermore, the specific surface area ( $S_{\text{BET}}$ ) was 23.57 m<sup>2</sup> g<sup>-1</sup> which is in accordance with reported values for  $S_{\text{BET}}$  (usually in the range 15–40 m<sup>2</sup> g<sup>-1</sup>).

Zeta potential measurements showed that CLI has a negatively charged surface in the whole range of pH values (Figure 2).

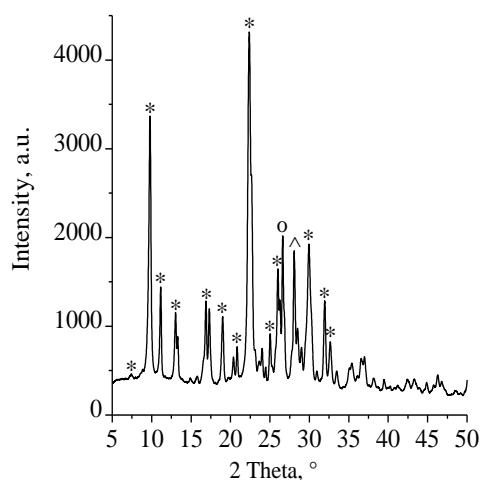


Figure 1. PXRD patterns of CLI (\* – clinoptilolite, o – quartz and ^ – feldspar).

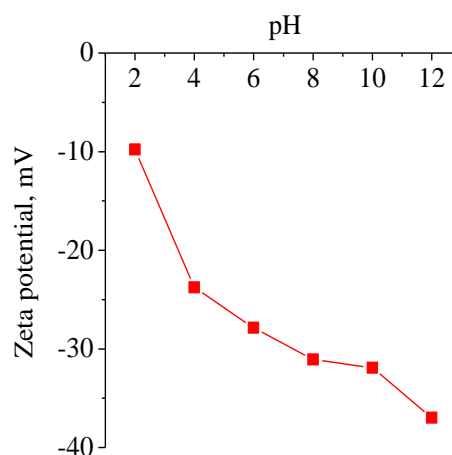


Figure 2. pH dependence of surface charging of CLI.

Since CIP molecule mainly exists as a zwitterion at neutral pH with a shift towards positively charged species at pH < 5.9 and towards anionic form at pH > 8.9, the pH of the solution strongly affects its adsorption performance [7]. Study of dependence of the adsorption capacity with pH showed that the best results can be obtained at pH= 5 (not shown). Accordingly, all experiments were done at pH= 5. 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 model gave the best results. The CIP uptake onto CLI increases rather sharply in the first 10 min for all studied temperatures and initial CIP concentrations. More than 80% of the maximum adsorption capacity was achieved in this 10 min period, indicating fast adsorption kinetics.

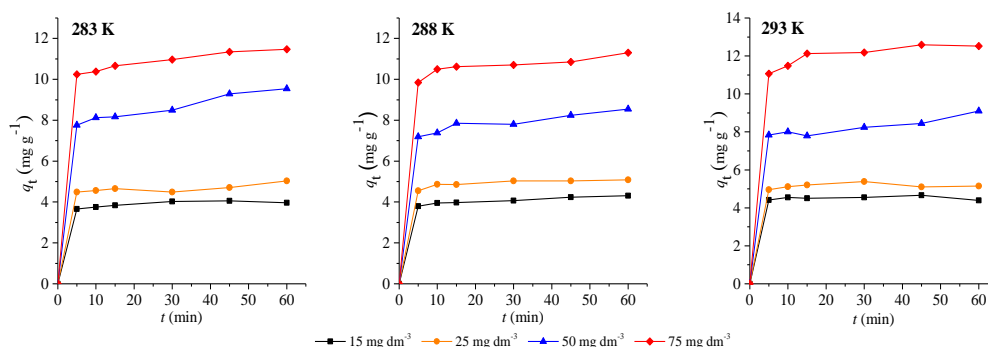


Figure 4. Adsorption kinetics for CIP on CLI for different temperatures;  $q_t$  is the amount of the adsorbed CIP (mg per 1 g of adsorbent) after time  $t$ .

Two reaction-based kinetic models were applied in order to describe the adsorption experimental data (Figure 4). Satisfactory fits were obtained only by the Lagergren's pseudo-second-order kinetic model (Table 1). Moreover, to investigate the influence of intra-particle diffusion on the CIP adsorption, the data were further processed by the Weber–Morris mass transfer model [9]. This did not result in agreement with experimental data suggesting that the intra-particle diffusion is not present in the adsorption.

Table 1. Rate constants for Lagergren's pseudo-second order kinetic model for the CIP adsorption on CLI ( $R^2$  is the correlation coefficient of the linear regression).

$C_0$ , mg CIP $\text{dm}^{-3}$	CLI			
	$T$ , K	$k_2$ , $\text{g mg}^{-1} \text{min}^{-1}$	$q_e$ , $\text{mg g}^{-1}$	$R^2$
15	283	0.3393	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	0.4011	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
75	283	0.0868	11.58	0.9997
	288	0.0886	11.28	0.9991
	293	0.0443	13.27	0.9982

$C_0$  – initial CIP solution concentration ( $\text{mg dm}^{-3}$ );  $k_2$  – pseudo-second-order rate constant,  $\text{g mg}^{-1} \text{min}^{-1}$ ;  $q_e$  – adsorption capacity,  $\text{mg g}^{-1}$ .

*Regeneration of the adsorbent.* The CIP adsorption onto CLI includes an ion exchange reaction at the CLI surface (results are not shown) which is irreversible (results are not shown). Since the adsorbent reusability is the most important issue for the operational cost of wastewater treatment based on the adsorption, we tested cold atmospheric pressure plasma for regeneration of the spent CLI. The results showed that more than 90% of the initial adsorbent capacity can be recovered in five cycles by the plasma treatment (Figure 5). This recommends cold plasma treatment as an environmentally friendly method suitable for the recycling of CIP saturated CLI.

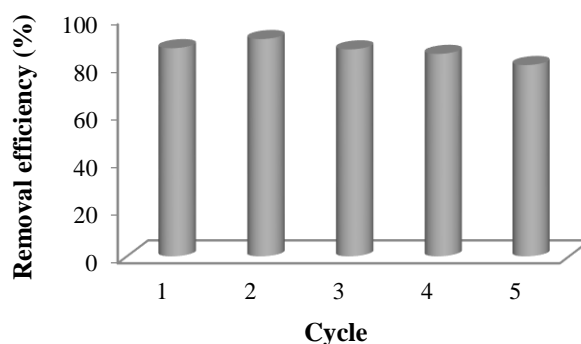


Figure 5. CLI removal efficiency through 5 adsorption cycles ( $C_0 = 25 \text{ mg dm}^{-3}$ ; solid:liquid= 1:100; pH= 5;  $T = 21 \text{ }^\circ\text{C}$ ).

## CONCLUSION

The study shows that cost effective and environmentally friendly natural clinoptilolite can be a promising adsorbent for the removal of antibiotic ciprofloxacin from water media. The spent clinoptilolite can be successfully regenerated by cold atmospheric pressure plasma treatment.

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