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ADSORPTION STUDY OF FLUOROQUINOLONE ANTIBIOTIC - LEVOFLOXACIN TO EVALUATE THE POSSIBILITY OF ITS REMOVAL FROM WASTEWATERS USING NATURAL ZEOLITE

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The present work is the first case where the adsorptive removal of the most commonly used fluoroquinolone antibiotic - levofloxacin (> 80 % unmetabolized in the urine) from aqueous solution as a model of wastewater treatment plant effluent by natural zeolite – clinoptilolite and its acid-modified form has been investigated under static and dynamic conditions. The effect of the inlet concentration, the flow rate and the pH value of antibiotic influent solution, also, the contact time of system zeolite/antibiotic solution on the adsorption process were examined and evaluated using the Langmuir adsorption model. The adsorption mechanism mainly composed of electrostatic interaction between the zeolite surface and adsorbate - levofloxacin. This study demonstrates and proves that natural clinoptilolite and its acid-modified form could be an efficient, eco-friendly, alternative and competitive adsorbent in terms of cheapness, selectivity and adsorption efficacy for the removal of levofloxacin from wastewaters and implemented in an industrial setting and wastewater treatment plant for purification processes.

Keywords: adsorption, natural zeolite, levofloxacin, wastewater

Antibiotic residues in the environment, even in very small trace level amounts, cause resistance in bacterial populations, which inevitably reduce therapeutic effectiveness of antibiotics against infectious diseases. Due to the extensive use of antibiotics, the occurrence of residual antibiotics in the environment is increasing day by day. They can be discharged into the environment in several different ways. The excretion of poorly metabolized antibiotics by human and animal is the primary source of antibiotic residues in the environment [1–6]. Other sources are the disposal of unused or unwanted antibiotics from pharmaceutical manufacturing processes [7, 8]. Several studies have reported that antibiotics are detected in hospital wastewater, wastewater treatment plant influents and effluents, surface waters, groundwater, sediment, and drinking water [3, 4, 9–11]. The presence of antibiotic residues in effluents is a major cause of acute and chronic toxicity, as well as the emergence of resistant bacteria. Consequently, removal of antibiotic residues from the environment is a crucial issue [12, 13].

The aim of the present paper is to describe research study regarding the investigation of adsorption process and the evaluation of the possibility of adsorptive removal of the most

commonly used FQ antibiotic - levofloxacin - $C_{18}H_{20}FN_3O_4$ (LEV) (> 80 % of daily dose can remain undegradable) from aqueous solution as a model of wastewater treatment plant effluent by natural zeolite – clinoptilolite from the local region, Georgia and its acid-modified H-form. The present study is the first case where adsorptive removal of levofloxacin has been investigated using natural zeolite as a cheap adsorbent with simple treatments and to demonstrate that natural zeolite is a potential adsorbent of antibiotic removal wastewaters. Adsorption is the widely used method for removal of a broad range of antibiotic pollutants due to its simple design, easy operation, and relatively simple regeneration with the principles of “green economy”. This approach implies a high degree of minimization of expenses during water purification from toxic and harmful components. Economic aspects of this process play a very relevant role, allowing the purification and additional treatment of wastewater, thus, reducing the anthropogenic load on water bodies. In the field of environmental protection, the most important and perspective direction of use of natural zeolites is their use for conditioning of potable water, treatment of wastewaters and domestic, industrial or agricultural wastes [11, 14, 15].

MATERIALS AND METHODS

The local natural zeolite – clinoptilolite (CL) ($(Ca,Na_2,K_2)_3Al_6Si_{30}O_{72}\cdot 24H_2O$) was obtained from Khandaki Kartli region, Georgia. In order to obtain acid-modified form of CL (H-CL), CL was treated hydrothermally using 2M HCl solution by the appropriate procedure described in papers [11, 14]. In obtained H-CL sample the Si/Al ratio was increased (Si/Al ratio > 4 and Na + K/Ca + Mg ratio < 1).

For study of adsorption dynamic process there was used the specially constructed laboratory dynamic type equipment with fixed bed adsorption glass column and high-pressure pump at constant temperature of 20 °C in the laboratory room with temperature-controlled conditions. The equipment (Fig. 1) consists of three parts: 1) a glass adsorption 1.0×8 cm column (packed with 9 g of natural zeolite); 2) influent/effluent collection tanks; 3) a high-pressure pump to control the flow rate of test solution. Under dynamic conditions through the prepared zeolite sample placed in a glass adsorption column, the antibiotic test solution at different concentration was passed. The experiment was carried out with different liquid flow rates [11, 14, 15].

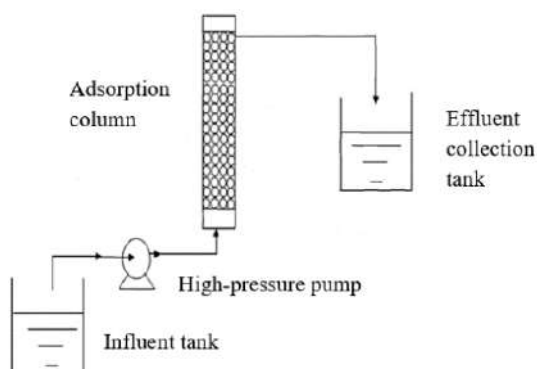


Fig. 1. The laboratory dynamic type equipment for adsorption study

The effluent samples were collected initially, at different time intervals and the end of the adsorption experiment after the saturation state occurred. The effect of working parameters such as the pH value, the flow rate and the initial concentration of test solution were investigated. The concentration of test adsorbate in influent and effluent stream was determined using an HPLC system - LC-20AD Prominence Shimadzu (Japan) with DAD detector (detection was done at

293 nm) and a column - Agilent SB-C18 4.6×250 mm, 5 μm (USA). The test stock solutions (adsorbate influent solution) with 0.2–2.0 mg/mL concentration were prepared by dissolving LEV analytical standard in purified water. The quantification was performed by the external standard method. The initial pH value of test solution was adjusted by adding 0.1 N NaOH and HCl solution.

The concentration of LEV – C_u in an effluent test solution, expressed in mg/mL was calculated by the following formula:

$$C_u = \frac{A_u \times W \times D \times P}{A_s \times 100}, \quad (1)$$

where A_u – the peak area of LEV obtained with an influent/effluent test solution; A_s – the peak area of LEV obtained with standard solution; W – the weight of LEV analytical standard, mg; D – the combined dilution factor of standard and test solutions; P – the purity of LEV standard, %.

In order to study adsorption by static method, 0.2 g of zeolitic adsorbent with 20 mL of antibiotic test stock solution at 0.2–2.0 mg/mL concentration range was used. Initially, zeolite sample with adsorbate antibiotic solution was left on an orbital shaker at 150 rpm for 15 min, then allowed to stand statically for the determined time interval and then the adsorbent samples were centrifuged at 3000 rpm for 5 min. The taken aliquots from the obtained supernatants at different time intervals during the experiment were analyzed using HPLC.

The breakthrough curve for LEV adsorption on zeolite adsorbent in terms of the effluent to influent concentrations ratio, C/C_0 , versus the contact time – τ , min was investigated by carrying out a set of fixed bed experiment at constant temperature of 20 °C. The removal efficiency – R , % and the adsorption capacity – q , mg/g were calculated by the following equations [11, 14, 15].

The removal efficiency – R , % was calculated by the following formula:

$$R, \% = \frac{(C_0 - C_e) \times 100}{C_0}, \quad (2)$$

where C_e - the equilibrium concentration of the adsorbate test solution at the fixed time (contact time with adsorbent – τ , hrs), mg/mL; C_0 – the initial concentration in the adsorbate test solution, mg/mL.

The adsorption capacity – q , mg/g was calculated by the following formula:

$$q = \frac{(C_0 - C_e) \times V}{m}, \quad (3)$$

where V – the used volume of adsorbate solution, mL; m – the mass of adsorbent, g.

For explanation of the mechanism of adsorptive removal of LEV and the interaction of zeolite adsorbent with antibiotic was studied by the most commonly used Langmuir isotherm model which assumes monolayer adsorption on the surface of the adsorbent. The experiment was carried out with different initial concentrations of antibiotic over a range from 0.5 to 2 mg/mL [11, 14, 15].

RESULTS AND DISCUSSION

Under static conditions to study adsorption process of the selected adsorbate - LEV with different concentrations – 0.5–2.0 and 20 mL of volume, an experiment was carried out using 0.2 g of CL and H-CL at pH 7. Based on the

experimental data, the plotted adsorption isotherms are given Fig. 2. The results show that isotherms have a good correlation ($R^2 > 0.91$) and define a monolayer adsorption.

The adsorption mechanism mainly composed of electrostatic interaction between the adsorbent surface and adsorbate. The fastest adsorption was observed at the low concentration – 0.5 mg/mL. The removal efficiency – R , % increased with a decrease of the concentration of adsorbate solution. Thus, the amount of FQ antibiotic adsorbed per unit mass of zeolite is a function of the contact time of adsorbate with adsorbent and the concentration of FQ antibiotic in test solution (Fig. 3).

The behavior of breakthrough curve at different flow rates of 1.5, 2.5 and 5.0 mL/min and inlet concentration of 0.2 and 1.0 mg/mL at constant temperature of 20 °C were observed under the dynamic adsorption conditions.

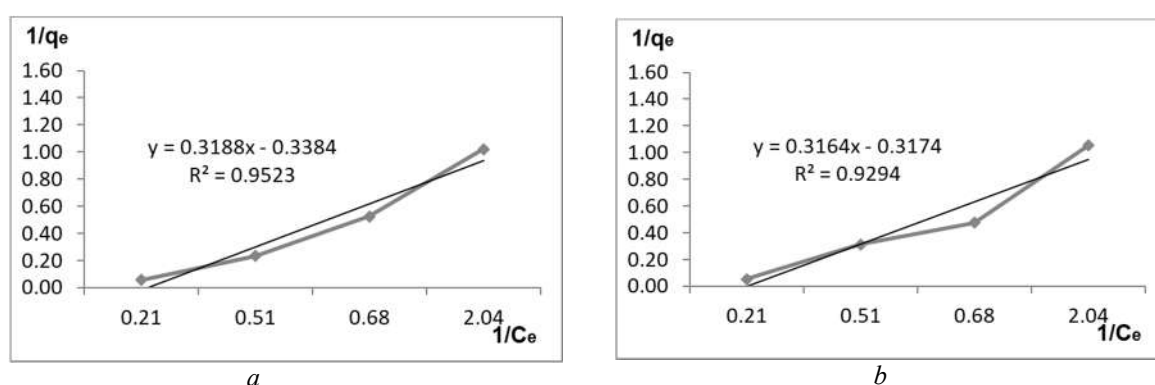


Fig. 2. The Langmuir adsorption isotherms of LEV on CL (a) and H-CL (b)

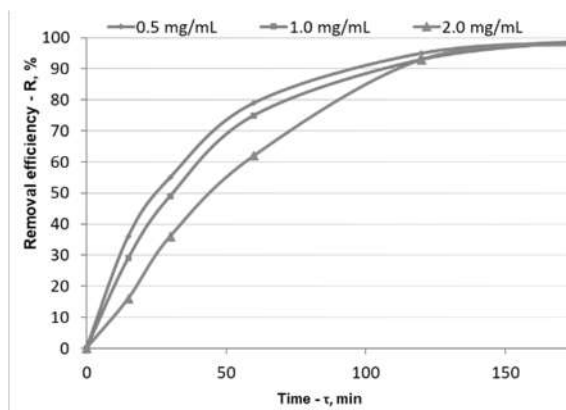


Fig. 3. The graph of the removal efficiency, % versus contact time on CL at three different concentrations of LEV test solution

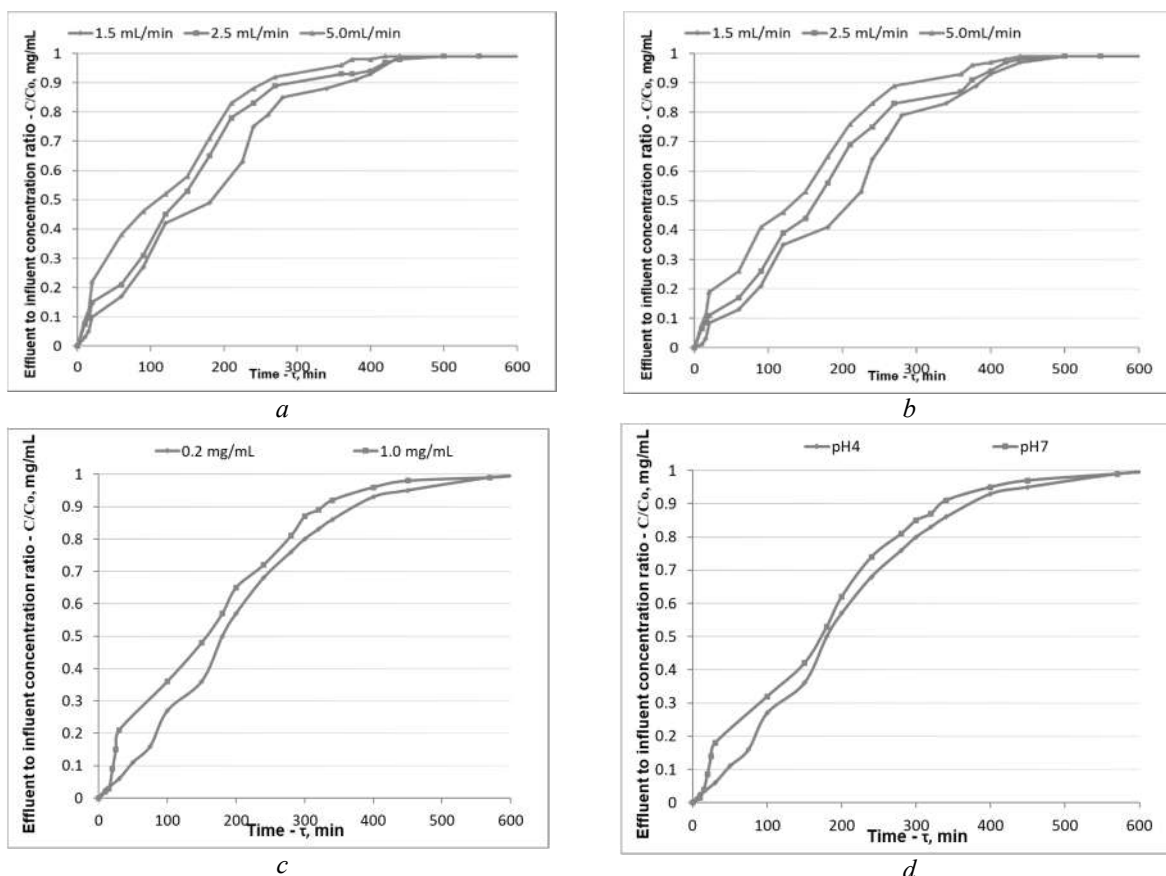


Fig. 4. The breakthrough curves for LEV adsorption on CL (a), H-CL (b) at various flow rates (0.2 mg/mL test solution), on CL (c) at two different concentrations (0.2 and 1.0 mg/mL) and on CL (d) at two different pH values of the influent test solutions (0.2 mg/mL)

In case of CL, it can be observed that at volumetric flow rates of 1.5 and 5.0 mL/min, the breakthrough times at $C/C_0 = 0.42$ are reported as 120 and 97 min, respectively. This can be related to low interaction between adsorbate and adsorbent at higher flow rate which accelerates breakthrough and saturation (Fig. 4 a). The breakthrough curve is shifted toward the origin and become steeper and rapidly reached saturation. At time of 60 min, the value of C/C_0 at the flow rate of 1.5 mL/min is 2.2 times lower than its value at 5.0 mL/min. As the flow rate drops, the adsorbate has sufficient time to diffuse through pores and produces a higher adsorption capacity. Also, high flow rate reduces the thickness of liquid film around adsorbent particles leading to low mass transfer resistance and high rate of mass transfer [11, 14]. So, according to the breakthrough curve (Fig. 4 a, b), it can be observed that at the same volumetric flow rate of 1.5 mL/min and at the same breakthrough time of 120 min, the value of ratios C/C_0 are

approximately 0.42 and 0.35 for CL and H-CL, respectively. This can be related to low interaction between adsorbates and CL which accelerates breakthrough and saturation. Also, the early breakthrough of adsorbate compared to H-CL is due to relatively low adsorption. The mechanism of interaction between adsorbate and adsorbent can be explained that CL has a frame, open and stable three-dimensional structure with negative charge, and FQ antibiotic molecules have positive charge in aqueous solutions [11, 16]. Therefore, natural CL would be able to retain antibiotic via electrostatic interaction mechanism. In addition, it is hypothesized that antibiotic is uptake by zeolite in connection with π - π electron-donor-acceptor interaction on LEV as the additional mechanism of adsorption. π - π electron-donor-acceptor interaction between the benzene ring, carboxyl of FQ and hydroxyl groups on zeolite adsorbent surface may be second major factor with electrostatic repulsion [11, 17]. Increasing adsorption capacity in case of H-CL is connected

with the effect of modification including pore sizes. The acid treatment caused a removal of cations and aluminum from initial CL, an increase in crystallinity and the relative content of Si/Al ratio in H-CL framework and pore opening as well. The Fig. 4 c shows that at higher inlet concentration, the breakthrough curve is shifted towards the origin. This behavior may be related to enhancement of driving force for mass transfer across the liquid film along with acceleration of adsorption rate which leads to an early saturation of the fixed-bed column. More precisely, the inlet concentration of 0.2 and 1.0 mg/mL, the values of C/C_0 at contact time of 100 min are reported as 0.27, and 0.36, respectively. These results for inlet concentration effect on the breakthrough curve show that the fixed bed adsorption conditions affect the value of ratio C/C_0 according to the order: inlet concentration > volumetric flow rate.

The effect of pH value of LEV solution (0.2 mg/mL) on adsorption process was investigated under acidic and neutral conditions at the values of pH 4 and 7, respectively. The results show that the breakthrough curve at the value of pH 4.0 is similar to the experimental data achieved at pH 7. As shown in Fig. 4 d, along with the pH-dependent speciation, LEV can be more positively charged (cationic).

Cationic LEV is the dominant species at the value of pH below 7. At pH 4 the cationic LEV molecule has carboxylic acid which may be the major mechanism of this adsorption. In acidic solution, carboxyl and amino groups are more protonated. At the value of pH 7, zeolite adsorbent surface would be negatively charged and hence, is the possibility of stronger electrostatic interaction. The carboxyl group LEV molecule become anionic with increasing the value of pH which cannot combine with adsorbent surface. The results confirm that the effect of electric charge is a little impact role in the process because LEV molecules and adsorbent surface are same charge at pH 4 and pH 7. The π - π electron-donor-acceptor interaction of the adsorption was the most effective at pH 4. Therefore, the observation of the removal efficiency with increasing the value of pH can be explained by lower electrostatic interaction between FQ antibiotic and zeolite adsorbent [11, 17].

The typical chromatogram obtained with the effluent test solution during adsorption experiment under dynamic conditions is given in Fig. 5.

Based on the adsorption experiment the dynamic adsorption capacities of both studied adsorbent – natural CL and H-CL were calculated and the results are given in Table.

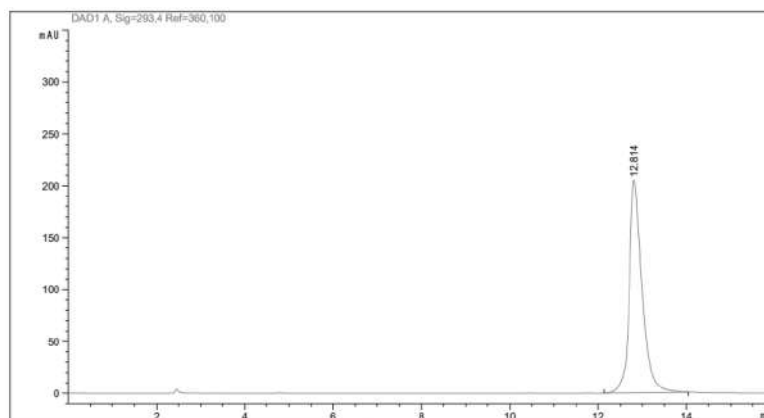


Fig. 5. The chromatogram obtained with the LEV test solution

Table. The dynamic adsorption capacities (q_d , mg/g) for CL/LEV and H-CL/LEV systems with different flow rates of LEV solutions with various concentrations - 0.2–1.0 mg/mL at the neutral pH value and constant temperature of 20 °C

Adsorbent	Levofloxacin			
	1.5 mL/min (Minimal flow rate)		5.0 mL/min (Maximal flow rate)	
	0.2 mg/mL	1.0 mg/mL	0.2 mg/mL	1.0 mg/mL
Natural Clinoptilolite	2.3	1.9	1.1	0.9
Clinoptilolite H-Form	4.3	3.5	3.2	2.1

CONCLUSION

The results show that the decrease in dynamic adsorption capacity of the test antibiotic was caused by increasing the flow rate of inlet solution of adsorbate. The decrease in dynamic adsorption capacity was observed by increasing the inlet concentration of adsorbate. The acid-modified clinoptilolite is characterized with high dynamic adsorption capacity caused by increasing the Si/Al ratio in zeolite framework and pore opening in comparison with natural clinoptilolite. The studied natural zeolites with hydrophilic pores

have a greater affinity for adsorbing antibiotic pollutants in aqueous solution. The high volumetric flow rate, the inlet concentration of antibiotic solution and the pH value accelerates breakthrough of adsorbate and correspondingly reduced adsorption capacities. Additionally, this research provides useful information for design of fixed bed adsorption column for removal studies of other antibiotics of different classes or contaminants. Hence, this research confirms that natural zeolites are competitive, eco-friendly and efficient adsorbents in terms of cheapness, shape selectivity and adsorption efficacy.

Дослідження адсорбції фторхінолонового антибіотика - левофлоксацину для оцінки можливості його видалення зі стічних вод за допомогою природного цеоліту

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Ця робота є першим випадком адсорбційного видалення найбільш часто використовуваного фторхінолонового антибіотика – левофлоксацину (> 80 % неметаболізованого в сечі) з водного розчину як моделі стічних вод очисних споруд природним цеолітом – кліноптилолітом та його кислотньо-модифікованою формою досліджено в статичних і динамічних умовах. Вплив концентрації на вході, швидкості потоку та значення рН розчину антибіотика, що надходить, а також часу контакту системи цеоліт/розчин антибіотика на процес адсорбції досліджували та оцінювали за допомогою моделі адсорбції Ленгмюра. Механізм адсорбції в основному складається з електростатичної взаємодії між поверхнею цеоліту та адсорбатом - левофлоксацином. Це дослідження демонструє та доводить, що природний кліноптилоліт та його кислотньо-модифікована форма можуть бути ефективним, екологічно чистим, альтернативним та конкурентоспроможним адсорбентом з точки зору дешевизни, селективності та адсорбційної ефективності для видалення левофлоксацину зі стічних вод і використовуватися в промислових умовах та очисних спорудах для процесів очищення.

Ключові слова: адсорбція, природний цеоліт, левофлоксацин, стічні води

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