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# Adsorption of enrofloxacin onto natural zeolite: Kinetics, thermodynamics, isotherms and error analysis

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Classical wastewater treatment processes are not efficient for removal of so-called emerging contaminants. Croatian natural zeolite - clinoptilolite has been used as alternative material for efficient removal of enrofloxacin (ENRO) from aqueous solution.

The influences of the initial ENRO concentration, contact time and temperature on adsorption performance are experimentally verified by a batch method. The kinetic data are analyzed using pseudo-first-order and pseudo-second-order kinetic models. The equilibrium data are fitted to two parameters adsorption isotherm models: Freundlich, Langmuir and Dubinin–Radushkevich. Linear and non-linear methods are used for comparing the best fitting of the isotherms. By comparing values of correlation coefficient and the error functions, it is found that Langmuire and Freundlich models best fit the enrofloxacin adsorption onto clinoptilolite. Values of thermodynamic parameters were calculated using adsorption equilibrium constant obtained from the Langmuir isotherm.

The results suggest that the ENRO adsorption on natural zeolite a non-spontaneous and endothermic process. This study shows that natural zeolite can be an important low-cost adsorbent for ENRO removal.

**Keywords:** Enrofloxacin, Natural zeolite, Isotherms, Kinetics, Thermodynamic, Error analysis

The first paper about the presence of pharmaceuticals in drinking water is published in early nineties. Since then, the presence of pharmaceuticals in different environmental compartments becomes an interesting subject of scientific research, with hundreds of investigations conducted[1]. Many studies are focusing on their removal from wastewater in order to prevent the occurrence of these compounds in the environment. Classical physico–chemical and biological processes are not efficient for removal of these organic contaminants. Therefore, alternative and more efficient methods for waste and drinking water treatment, like advanced oxidation processes, membrane technology and adsorption processes in removing contaminants from water have been investigated[2]. Adsorption processes are interesting and promising alternatives for these purposes. Many low-cost natural and easy available sorbents, such as agricultural wastes, clay materials and zeolites can be applied. In fact, of all pharmaceuticals, antibiotics are the most used, and often they are misused. Antibiotics could be obtained by natural or semi-synthetic way, but many bacteria become resistant to them. Today, more and more antibiotics, including quinolones, are produce synthetically. The quinolones, particularly nalidixic acid, as first synthetic antimicrobial agent, have been available for the urinary tract infections treatment for many years. On the other hand, recently introduced fluorinated 4-quinolones, such as enrofloxacin, represent a particularly important therapeutic advance, due to their broad antimicrobial activity and effectiveness in the treatment of a wide variety of infections. Enrofloxacin is a fluoroquinolone antibiotic, widely used in poultry production for respiratory and enteric bacterial infections treatment, so it is widely present in water[3,4].

Clinoptilolite is the most abundant natural zeolite and, as low cost sorbent, can be used for removal of different inorganic or organic contaminants[5-8]. For example, Ötker and Akmehmet-Balcioğlu[3] investigated the removal of high concentration of enrofloxacin (ranged from 50 to 200 mg/L) by adsorption on natural zeolite, as well as further decontamination of zeolite by ozone treatment. However, the amount of pharmaceuticals in waste and drinking water is well below 20 mg/L. Therefore, the main goal of this work was to investigate possible application of natural zeolite clinoptilolite for adsorption of enrofloxacin from water solution with ENRO concentration below 20 mg/L.

The specific goals are (i) to compare different adsorption models (Langmuir, Freundlich, and Dubinin–Radushkevich) that can be used to describe the adsorption of ENRO on natural zeolite using linear and non-linear regression analysis, (ii) to determine thermodynamic parameters $\Delta G°$, $\Delta H°$ *and* $\Delta S°$ and (iii) to determine the type of adsorption (physical or chemical) according to the value of mean adsorption energy obtained from the Dubinin-Radushkevich isotherm. Finally, this research will contribute to the possible application of Croatian natural zeolite clinoptilolite for removal of enrofloxacin from water.

## Experimental section

### *Adsorbent*

The tested natural zeolite - clinoptilolite originates from the mine Donje Jesenje, Croatia, where it was ground and separated into fraction with particle sizes less than 150 μm. Chemical composition of natural zeolite was determined by the standard chemical analysis for alumosilicates and results in mass % are $SiO_2$-64.93; $Al_2O_3$-13.39; $Fe_2O_3$-2.07; $Na_2O$-2.40; $K_2O$-1.43; CaO-2.00; MgO-1.08; loss by ignition at 1000 °C -9.63.

X-ray diffraction (XRD) analysis was performed by PHILIPS PW 1010 diffractometric system (CuKα radiation, $2\theta = 3\text{-}60$ °) on natural sample to confirm the mineral identity of the zeolites. The tested zeolite was stated to be of 40%-50% purity on clinoptilolite, while the impurities included illite, feldspar, quartz and muscovite.

### *Adsorbate*

High purity (>98%) enrofloxacin (1-cyclopropyl-7-(4-ethyl-1-piperazinyl)-6-fluoro-1,4-dihydro-4-oxo-3-quinolonecarboxylic acid; $M$r=359.39; $C_{19}H_{22}FN_3O_3$) was supplied from Veterina (Kalinovica, Croatia). A stock solution of ENRO (100 mg/L) was prepared by dissolving a required amount of ENRO in MilliQ water. The stock solution was diluted with MilliQ water to obtain desired concentrations ranging from 1 to 20 mg/L.

### *Batch adsorption experiments*

First set of experiments were performed in order to determine the contact time required to reach adsorption equilibrium of ENRO. For this purpose, 0.150 g of zeolite has been equilibrated with 15.0 mL of 10 mg ENRO/L at 25 °C during a period of 60 min.

Second set of experiments were performed in order to investigate effect of initial concentration and temperature on adsorption process of ENRO on natural zeolite. Investigated initial ENRO concentrations were: 1, 2, 5, 10, 15 and 20 mg/L with contact time of 5 min. The temperatures examined were 298, 308 and 313 K. Suspensions were shaken in an INNOVA 4080 shaker (New Brunswick Scientific, Inc, New Jersey, USA) at rotation speed of 200 rpm. After shaking in a thermostated system, the solid phase was separated from the solution by filtration (Whatman blue ribbon filter), and ENRO concentration was determined in the liquid phase by means of UV–Vis spectrophotometer (Perkin Elmer Lambda 35, Connecticut, USA).

The difference between the initial and equilibrium mass concentration of ENRO is used for calculation of the quantity of ENRO adsorbed per unit mass of natural zeolite-clinoptilolite ($q$, mg ENRO/g of the zeolite), taking into consideration the data related to the zeolite weight, volume and mass concentration of the solution. The amount of ENRO adsorbed onto natural zeolite was calculated using the following expression:

$$q_e = \frac{(\gamma_0 - \gamma_e)}{m} \cdot V \qquad \text{... (1)}$$

where $q_e$ is the equilibrium adsorption capacity of ENRO adsorbed per unit mass of the natural zeolite (mg/g); $\gamma_0$ and $\gamma_e$ are the initial ENRO concentration and ENRO concentration at equilibrium (mg/L), respectively; $V$ is the volume of the ENRO solution (L); and $m$ is the mass of the adsorbent-natural zeolite (g). All experiments were conducted in triplicate.

### *Adsorption kinetic models*

Several kinetic models are available to describe the behavior of the adsorbents and to define the controlling mechanism of the adsorption process. In the present investigation, the adsorption data were analyzed using pseudo-first-order and pseudo-second-order kinetic models.

Lagergren's first-order rate equation is the earliest known one describing the adsorption rate based on the adsorption capacity. It is summarized as follows[9,10]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad \text{... (2)}$$

where $q_e$ and $q_t$ are the amounts of ENRO, (mg/g) adsorbed on adsorbents at equilibrium, and at time $t$, respectively and $k_1$ (min$^{-1}$) is the rate constant of the pseudo-first-order adsorption. Integrating Eq. (2) with the boundary conditions of $q_t$=0 at $t$=0 and $q_t$=$q_t$ at $t$=$t$, yields[11]:

$$\ln\left(\frac{q_e - q_t}{q_e}\right) = k_1 t \qquad \text{... (3)}$$

A plot (which is not shown here) of ln ($q_e$ – $q_t$) against $t$ gives $-k_1/2.303$ as the slope and ln ($q_e$) as the intercept.

The kinetic data were further analyzed using pseudo second-order kinetic model. This model is based on the assumption that the adsorption follows second order chemisorption. The pseudo-second-order equation is represented as[9]:

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

where $q_e$ and $q_t$ are the amounts of ENRO, (mg/g) adsorbed on adsorbents at equilibrium, and at time $t$, respectively and $k_2$ is the rate constant of pseudo-second-order adsorption (mg/g min). Integrating Eq. (4) for the boundary conditions $q_t = 0$ to $q_t = q_t$ and $t = 0$ to $t$=t, the following equation is obtained:

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

A plot $t/q_t$ against $t$ gives $1/q_e$ as the slope and $1/(k_2 q_e^2)$ as the intercept.

The initial adsorption rate, $h$ (mg/g min), at $t \to 0$ can be defined as (equation 6)[9,10]:

$$h = k_2 q_e^2 \quad \ldots (6)$$

***Adsorption equilibrium isotherm models***

To investigate an interaction of adsorbate molecules (ENRO) and adsorbent surface (natural zeolite - clinoptilolite) three well-known models, the Freundlich[12], Langmuir[13] and Dubinin-Radushkevich (DR)[14] isotherms, were selected to explicate ENRO – zeolite interactions in this study.

The Freundlich isotherm describes the non-ideal adsorption of a heterogeneous system and reversible adsorption in which it is characterized by the heterogeneity factor $1/n$ [12]. The model can be expressed as:

$$q_e = K_F \cdot \gamma_e^{1/n} \quad \ldots (7)$$

where $q_e$ is the amount of ENRO adsorbed per unit of adsorbent - zeolite (mg/g), $\gamma_e$ is the concentration of ENRO at adsorption equilibrium (mg/L), $K_F$ is a constant indicative of the relative adsorption capacity of the adsorbent ((mg/g)(L/mg)$^{1/n}$)) and $n$ is a constant indicative of the intensity of the adsorption. If the adsorption obeys Freundlich equation (8), $K_F$ and $n$ can be calculated from the slope and the intercept of the plot ln ($q_e$/ $\gamma_e$) versus $q_e$.

$$\log q_e = \log K_F + \frac{1}{n} \log \gamma_e \quad \ldots (8)$$

The Langmuir model is valid for monolayer adsorption. This model assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent. It is then assumed that once ENRO molecule occupies a site, no further adsorption can take place at that site. It is represented by[13]:

$$q_e = \frac{q_m K_L \gamma_e}{1 + K_L \gamma_e} \quad \ldots (9)$$

where $q_e$ is the equilibrium adsorption capacity (mg/g), $\gamma_e$ is the equilibrium liquid phase concentration (mg/L), $q_m$ is the maximum adsorption capacity (mg/g) and $K_L$ is adsorption equilibrium constant (L/mg).

The Dubinin-Radushkevich (DR) isotherm is more general than the Langmuir and Freundlich isotherms. It helps to determine the apparent energy of adsorption. The Dubinin-Radushkevich isotherm equation is given as[14]:

$$q_e = q_{\max} \exp\left(-\beta \varepsilon^2\right) \quad \ldots (10)$$

where $q_e$ is the equilibrium concentration of adsorbate in solid phase (mg/g), $q_{\max}$ is the theoretical saturation capacity (mg/g), $\beta$ is the constant of the adsorption energy (mol$^2$/kJ$^2$), and $\varepsilon$ is the Polanyi potential, which is described as:

$$\varepsilon = RT \ln\left(1 + 1/\gamma_e\right) \quad \ldots (11)$$

The value of mean adsorption energy, $E$ (kJ/mol), can be calculated from parameter $\beta$ as follows:

$$E = (2\beta)^{-1/2} \quad \ldots (12)$$

***Error analysis***

Error functions employed were as follows[15,16]:

– Residual root mean square error (RMSE):

$$\sqrt{\frac{1}{n-2}\sum_{i=1}^{N}\left(q_{e,\exp} - q_{e,\mathrm{cal}}\right)^2} \quad \ldots (13)$$

– Chi-square ($\chi^2$):

$$\chi^2 = \sum_{\mathrm{i}=1}^{N} \frac{\left(q_{e,\exp} - q_{e,\mathrm{cal}}\right)^2}{q_{e,\mathrm{cal}}} \quad \ldots (14)$$

– The sum of the squares of the errors (ERRSQ):

$$\sum_{\mathrm{i}=1}^{N}\left(q_{e,\exp} - q_{e,\mathrm{cal}}\right)_i^2 \quad \ldots (15)$$

– A composite fractional error function (HYBRD):

$$\sum_{i=1}^{N}\left[\frac{\left(q_{e,\exp} - q_{e,\mathrm{calc}}\right)^2}{q_{e,\exp}}\right] \quad \ldots (16)$$

– Marquardt's percent standard deviation (MPSD):

$$\sum_{i=1}^{N}\left[\frac{\left(q_{e,\exp}-q_{e,\mathrm{calc}}\right)}{q_{e,\exp}}\right]_i^2 \qquad \ldots (17)$$

The subscripts "exp" and "calc" indicate experimental and calculated values, $n$ is the number of experimental observations. The obtained isotherms were analyzed by non-linear curve fitting (instead of linearization), using MATLAB-7 software.

## Results and Discussion

### Adsorption kinetics

The time-dependent ENRO adsorption behavior was monitored by varying the equilibrium time between adsorbate and adsorbent in the range of 1–15 min. The adsorption capacity of ENRO as a function of contact time is shown in Fig. 1a indicating that adsorption was very fast in first 2 min and equilibrium between the ENRO and the natural zeolite was attained in 5 min. After that amount of ENRO adsorbed onto zeolite was not change significantly.

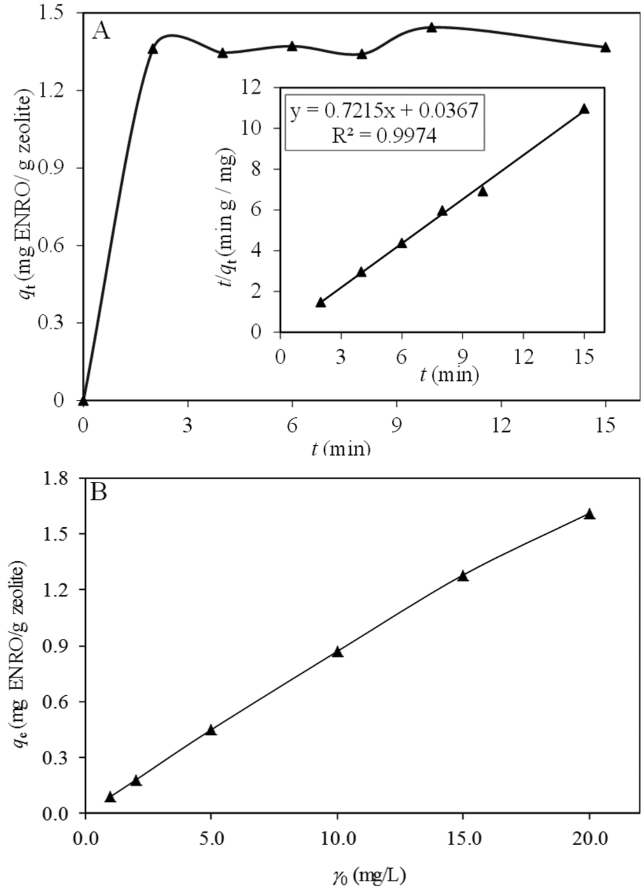

Fig. 1 — (A) Adsorption of ENRO onto natural zeolite as a function of contact time. Insert describes the liner plot of pseudo-second-order fit to the observed data (initial concentration of ENRO is 20 mg/L, $T$=298 K); (B) Adsorption of ENRO onto natural zeolite as a function of initial concentration ($m$(zeolite) = 0.150 g; $V$(solution) = 15.0 mL; $T$ = 298 K).

The experimental data for the removal of ENRO where analyzed using pseudo-first- and pseudo-second-order models. The agreement between experimental data and model-calculated values was expressed by the correlation coefficient ($R^2$). The low correlation coefficient value ($R^2$ = 0.9167) obtained for linear relation between ln($q_e$ − $q_t$) and $t$ (not show here) indicates that adsorption of ENRO did not follow the pseudo-first-order kinetic model. A linear plot of $t/q_t$ against $t$ (Fig. 1b) with corresponding correlation coefficient ($R^2$=0.9974) value show good agreement between experimental data and pseudo-second-order kinetic model (Eq. (4)). Kinetic parameters for the adsorption of ENRO onto natural zeolite - clinoptilolite, as calculated from the linear plots of the pseudo-second-order kinetics models (Fig. 1A) are $k_2$=14.1843 g/mg min, $q_e$=1.3860 mg/g and $h$ =27.25 mg/g min.

### Equilibrium isotherms

Results of adsorption of ENRO onto natural zeolite as a function of initial concentration (time of contact was 5 min) are presented in Fig. 1B (for adsorption process at 298 K) and Table 1 (comparison of adsorption process at three temperatures: 298, 308 and 318 K).

Obtained results (Table 1) show that the removed amount of ENRO slightly decreases with increasing temperature.

The adsorption data for ENRO by natural zeolite at three temperatures were analyzed by a linear and non-linear regression analysis. The linear and non-linear plots of Freundlich, Langmuir and Dubinin–Radushkevich equations at 298 K are shown in Fig. 2. Isotherm parameters obtained for three temperatures are presented in Table 2 (linear regression analysis and non-linear regression analysis).

The linear plot of log $q_e$ against log $\gamma_e$ is shown in Fig. 2A and non-linear plot is show in Fig. 2D. The

Table 1 — Removed amount of ENRO at different temperatures of adsorption process.

| $\gamma_0$ (mg ENRO/L) | $q_e$ (mg ENRO/g zeolite) | | |
|---|---|---|---|
| | 298 K | 308 K | 318 K |
| 1.0 | 0.091 | 0.085 | 0.078 |
| 2.0 | 0.180 | 0.175 | 0.171 |
| 5.0 | 0.450 | 0.440 | 0.410 |
| 10.0 | 0.870 | 0.860 | 0.857 |
| 15.0 | 1.280 | 1.271 | 1.263 |
| 20.0 | 1.610 | 1.502 | 1.410 |

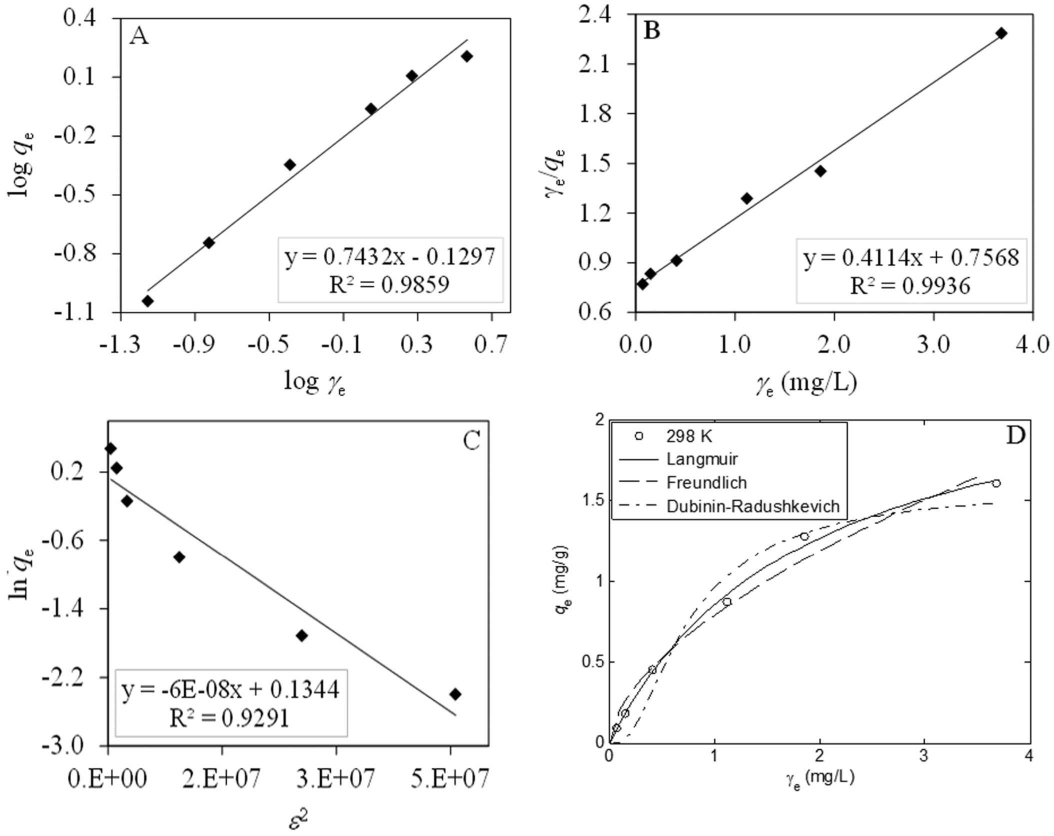

Fig. 2 — The linearized (A) Freundlich (B) Langmuir and (C) Dubinin–Radushkevich isotherms and (D) non-linearized isotherms for the adsorption of ENRO onto natural zeolite ($T$ = 298 K).

Table 2 — Isotherms parameters obtained using linear and non-linear regression method for the adsorption of enrofloxacin onto natural zeolite

| | | **Linear regression method** | | |
|---|---|---|---|---|
| Isotherm | Parameter | Temperature (K) | | |
| | | 298 | 308 | 318 |
| | $n$ | 1.3455 | 0.7357 | 0.7146 |
| Freundlich | $K_F$ ((mg/g)(L/mg)$^{1/n}$)) | 0.7418 | 1.3549 | 1.3954 |
| | $R^2$ | 0.9859 | 0.9999 | 0.9999 |
| | $q_m$ (mg/g) | 2.4307 | 2.386 | 2.263 |
| Langmuir | $K_L$ (L/mg) | 0.5436 | 0.5584 | 0.6014 |
| | $R^2$ | 0.9936 | 0.9537 | 0.9365 |
| | $\beta$, (mol$^2$/kJ$^2$) | $6.08 \times 10^{-8}$ | $8.32 \times 10^{-8}$ | $5.59 \times 10^{-8}$ |
| Dubinin–Radushkevich | $q_m$ (mg/g) | 1.144 | 1.4667 | 1.0391 |
| | $E$ (kJ/mol) | 2.868 | 2.450 | 2.990 |
| | $R^2$ | 0.9291 | 0.9195 | 0.9215 |
| | | **Non-linear regression method** | | |
| | $n$ | 1.7094 | 0.7984 | 0.7874 |
| Freundlich | $K_F$ ((mg/g)(L/mg)$^{1/n}$)) | 0.7904 | 0.7244 | 0.7195 |
| | $R^2$ | 0.9783 | 0.9994 | 0.9998 |
| | $q_m$ (mg/g) | 2.4526 | 2.9409 | 2.9125 |
| Langmuir | $K_L$ (L/mg) | 0.5353 | 0.3921 | 0.3892 |
| | $R^2$ | 0.9968 | 0.9945 | 0.9944 |
| | $\beta$, (mol$^2$/kJ$^2$) | $1.68\times10^{-7}$ | $1.29\times10^{-7}$ | $1.36\times10^{-7}$ |
| Dubinin–Radushkevich | $q_m$ (mg/g) | 1.5742 | 1.344 | 1.3493 |
| | $E$ (kJ/mol) | 1.725 | 1.969 | 1.917 |
| | $R^2$ | 0.9512 | 0.9299 | 0.9209 |

obtained values for Freundlich parameters are presented in Table 2. The magnitude of the exponent *n* gives an indication of the favorability of adsorption. It is generally stated that values of *n* in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics[17-19]. According to obtained *n* values ($0.7146 < n < 1.7094$) the studied natural zeolite is not good sorbent for ENRO. Similar results were reported for sulfonamide and tetracyclines adsorption on montmorillonite clay[16] and for adsorption of enrofloxacin on Turchis natural zeolite[3]. Langmuir parameters $q_e$ and $K_L$ were determined from the linear plot of $1/q_e$ against $1/\gamma_e$ (Fig. 2B). The resulting straight line confirms that the Langmuir isotherm is followed (Fig. 2B) and that monolayer adsorbtion of ENRO onto zeolite occures. The values of calculated Langmuir parameters are presented in Table 2.

Calculated data for the Dubinin-Radushkevich isotherm are reported in Table 2. The magnitude of *E* could be used to predict reaction mechanism. The *E* values smaller than 8 kJ/mol indicate physical adsorption while *E* values higher than 8 kJ/mol indicate chemical adsorption (ion exchange)[20,21]. Obtained values of mean adsorption energy was found to be in the range of 2.450-2.990 kJ/mol (using linear regression method – Table 2) and in the range of 1.725-1.969 kJ/note (using non-linear regression method – Table 2), which are in the energy range characteristic for physical adsorption mechanism.

Hence, according to Table 2, it seems that both models, Langmuir and Freundlich, satisfactorily describe the studied adsorption of ENRO onto natural zeolite at 298 K. The highest $R^2$ value and the lowest RMSE, $\chi^2$, ERRSQ, HYBRID and MPSD values (Table 3) were found when modelling the equilibrium data using the Langmuir and Freundlich models.

**Thermodynamic parameters**

The amounts of ENRO adsorbed onto zeolite at different temperatures (298, 308 and 318 K) were determined in order to obtain thermodynamic parameters: change in the Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$). Gibbs free energy of adsorption ($\Delta G°$) was calculated using following equation[3,22]:

$$\Delta G° = -\mathrm{RT} \ln K_L \qquad \text{... (18)}$$

where *R* is the universal gas constant (8.314 J/mol K), *T* is the temperature (K), $K_L$ is equilibrium constant obtained for each temperature from Langmuir model through the linear regression (Table 2).

The standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were estimated from the van't Hoff equation (19) via linear regression:

$$\log K_L = \frac{\Delta S°}{2.303 \cdot \mathrm{R}} - \frac{\Delta H°}{2.303 \cdot \mathrm{R}} \cdot \frac{1}{T} \qquad \text{... (19)}$$

Values of $\Delta H°$ and $\Delta S°$ were determined from the slope and intercept of linear van't Hoff plot of log $K_L$ *vs*. $1/T$ (Figure 3). Then, the slope and intercept are

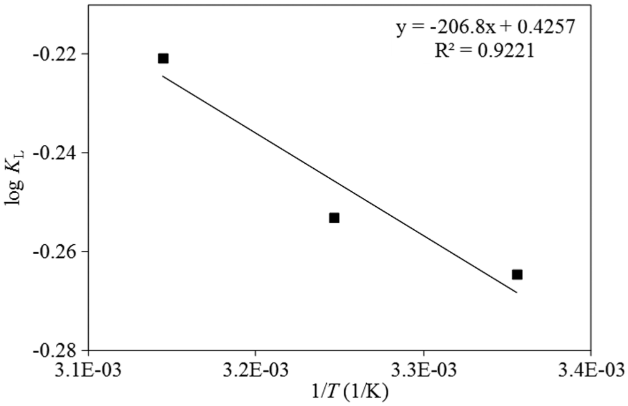

Fig. 3 — Plot of log $K_L$ *vs*. $1/T$ for the estimation of thermodynamic parameters for adsorption of ENRO onto natural zeolite.

Table 3 — Values of five different error functions for isotherm equations.

| Isotherm | Temperature (K) | Error function | | | | |
|---|---|---|---|---|---|---|
| | | RMSE | $\chi^2$ | ERRSQ | HYBRD | MPSD |
| | 298 | 0.2284 | 0.0285 | 0.2087 | 0.3686 | 2.0937 |
| Freundlich | 308 | 0.0266 | 0.0028 | 0.0014 | 0.0027 | 0.0073 |
| | 318 | 0.0145 | 0.0006 | 0.0004 | 0.0006 | 0.0010 |
| | 298 | 0.0915 | 0.0309 | 0.0335 | 0.0309 | 0.0318 |
| Langmuir | 308 | 0.0809 | 0.0286 | 0.0131 | 0.0260 | 0.0886 |
| | 318 | 0.0770 | 0.0382 | 0.0119 | 0.0313 | 0.1371 |
| | 298 | 0.3174 | 26.1527 | 0.4029 | 0.9600 | 4.8138 |
| Dubinin–Radushkevich | 308 | 0.2832 | 1.8596 | 0.1604 | 0.3745 | 1.5995 |
| | 318 | 0.2934 | 4.6614 | 0.1721 | 0.4453 | 1.9612 |

Table 4 — Thermodynamic parameters for ENRO adsorption onto natural zeolite.

| Temperature (K) | $\Delta G°$, kJ/mol | Regression results | |
|---|---|---|---|
| | | $\Delta H°$, kJ/mol | $\Delta S°$, kJ/mol K |
| 298 | 1.51 | | |
| 308 | 1.42 | 3.96 | 0.0082 |
| 318 | 1.34 | | |

used to determine the values of enthalpy ($\Delta H°$) and entropy ($\Delta S°$). The values of the thermodynamic parameters for the adsorption of ENRO onto natural zeolite are given in Table 4.

In general, these parameters indicate that the adsorption process is spontaneous or not and exothermic or endothermic. The Gibbs free energy change ($\Delta G°$) is an important criterion for spontaneity. Reactions occur spontaneously at a given temperature if $\Delta G°$ has a negative value. If $\Delta G°$ is positive, the reaction will not proceed spontaneously. The positive values of $\Delta H°$ confirm the endothermic nature of adsorption.

The obtained positive values of $\Delta G°$ and $\Delta H°$ indicate that the adsorption of ENRO onto natural zeolite is non-spontaneous endothermic process[23]. The endothermic adsorption has also been reported for the adsorption of ENRO onto natural zeolite from Manisa, Turkey[3].

Entropy change ($\Delta S°$) is a measure of the disorder present in a system. The positive value of $\Delta S°$ reflects the affinity of the zeolite for the ENRO and suggests some structural changes in adsorbate and adsorbent[24-26].

## Conclusion

Obtained results indicate that adsorption of ENRO onto natural zeolite is very fast, equilibrium adsorption was achieved in 5 min and followed pseudo-second-order kinetic model.

Langmuire, Freundlich and Dubinin–Radushkevich isotherms were used to describe adsorption of enrofloxacin onto zeolite. Langmuir and Freundlich isotherm models gave a higher value of correlation coefficient ($R^2$) and the lowest RMSE, $\chi^2$, ERRSQ, HYBRID, MPSD values (for non-linear regression) in comparison to Dubinin–Radushkevich isotherm.

The positive value of $\Delta G°$ indicates the non-spontaneity of the process, positive value of $\Delta H°$ indicate that the adsorption of ENRO onto natural zeolite is endothermic process and positive value of $\Delta S°$ implies affinity of the natural zeolite toward ENRO.

The results of this study indicate that natural zeolite-clinoptilolite from Donje Jesenje, Croatia is an efficient, environmental-friendly, low-cost and alternative material for the removal of antibiotic enrofloxacin from aqueous solutions.

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