

Kinetic and static parameters of a new sorbent based on clays and ways of its determination

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Abstract. The paper demonstrates experimental research results obtained while studying heavy metal ions sorption ability. These ions were extracted from a multicomponent model solution. The research was conducted for a new sorption sample based on clays under static conditions and carried out in the range of low concentrations of heavy metal ions in the solution. For the development of sorption isotherms, the method of non-variant test portions and variable concentrations of heavy metal ions was used. As a result, the researchers constructed sorption isotherms for copper, zinc, manganese, iron and lead. The experimental data was approximated by the Freundlich, Langmuir, Langmuir-Freundlich, Toch and Redlich-Peterson equations. *MathCAD* and *SciDAVis* software programs were used for mathematical processing. The authors came to the conclusion that the Langmuir equation most adequately described the sorption isotherms for copper, lead and zinc, the Toch model was preferable for iron and manganese isotherms. During the experiment, sorption constants and determination coefficient were also determined for each metal.

1. Introduction

The most difficult task in the field of wastewater treatment is to achieve MAC standards for heavy metal ions that exist in water at low concentrations in conditions than these ions at the same time exceed MAC standards by several times. Sorbents based clay demonstrate high capacity relative to ions of heavy metals [1-5]. Clay, the main sorbent component, is widespread and inexpensive in comparison with activated coals. When clays are modified, their sorption capacity considerably increases [6]. Many studies confirm the existence of high content of exchange cations and anions retained on the surface of the material. For these reasons, the attention of many scientists has been focused on the use of clay materials as an adsorbent for water treatment. Montmorillonite and its modified forms have a higher adsorption capacity to metals than kaolinite [7]. The absorption of heavy metals by clay minerals involves a number of complex adsorption mechanisms, such as direct binding of metal cations to the surface of clay minerals, surface complexion formation, ion exchange, etc. [8-10].

The objectives of this research are to study sorption properties of a new sample of sorbent intended for wastewater final treatment from heavy metals, to construct a series of selectivity, to empirically identify mathematical equations that best describe experimental data, to calculate determination coefficients and the sorbent total capacity.

The composition of the new sample included montmorillonite, kaolin, peat and dolomite, with polyvinyl acetate used as a binder. In order to change the chemical structure and morphology of the surface and to obtain porosity, the authors applied thermal modification [1].



2. Methods

The sorbent, which properties are studied in this work, was previously collected from ten samples, also obtained on the basis of clays. It was chosen because this sorbent was characterised by the best kinetics and the highest sorption capacity for heavy metal ions [12]. The main parameters obtained during the experiment are presented in Table 1.

To build sorption isotherms the researchers used the method of constant weighed portions and variable concentrations of heavy metal ions (from 27 to 0.05 mg/l). The volume of the solution (V) was taken as 200 ml, the mass of the sorbent (m) – 1 g, the temperature equalled 20°C. Each experiment was carried out twice. The initial solutions were prepared in the volume enough for two parallel samples. Their concentrations were tested analytically. The results of the experiment are shown in Figure 1. Adsorption capacity (A) was figured out for decrease of concentration, mg/g:

$$A = \frac{C_{en} - C_{ex}}{m} \times V, \quad (1)$$

3. Results and discussion

The high rate of sorption in the initial period of interaction is associated with the attraction of metal cations from the solution to the negatively charged surface of clay minerals [13]. The ions of iron, copper and zinc sorption flowed at a high speed during the first 5-20 minutes, then the speed decreased and the curves smoothed out [14].

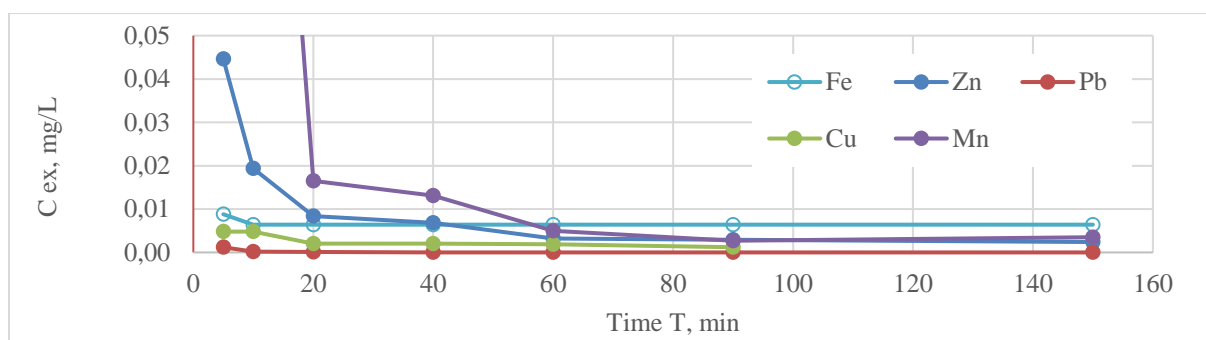


Figure 1. Sorption kinetics of heavy metal ions.

The results obtained under static conditions with a stirring duration of 150 minutes are presented in Table 1.

Sorption isotherms are built while taking average concentrations, defined from two parallel experiments (see Fig. 2). The values of the exchange capacity corresponding to MAC for metal ions are, mg/g: for iron – more than 1.95; for copper – more than 0.75; for zinc – more than 0.464; for manganese – more than 0.011, for lead – more than 0.77. Figure 2 testifies that achieved equilibrium concentration for the ions of iron and manganese corresponded to the maximum capacity of the sorbent, that is 3.17 and 1.14 mg/g. For the ions of copper, zinc, manganese saturation at the given concentrations was not reached and the greatest values of capacity were 2.33, 1.75 and 1.14 mg/g respectively.

In the area of low concentrations, the isotherms are almost parallel to the ordinate axis, which proves the chemical nature of sorption. This is especially evident on Fe^{3+} , Cu^{2+} and Zn^{2+} sorption isotherms.

Table 1. Results of ions of heavy metals sorption by modified clay sorbent in statics.

| Fe ³⁺ , mg/l | | Zn ²⁺ , mg/l | | Pb ²⁺ , mg/l | | Cu ²⁺ , mg/l | | Mn ²⁺ , mg/l | | pH _{en} | pH _{ex} |
|-------------------------|-----------------|-------------------------|-----------------|-------------------------|-----------------|-------------------------|-----------------|-------------------------|-----------------|------------------|------------------|
| C _{en} | C _{ex} | C _{ex} | C _{ex} | C _{en} | C _{ex} | C _{en} | C _{ex} | C _{en} | C _{ex} | | |
| 0.124 | 0.010 | 0.217 | 0.004 | 0.050 | 0.000 | 0.086 | 0.000 | 0.066 | 0.010 | 5.07 | 9.90 |
| 0.268 | 0.006 | 0.823 | 0.003 | 1.054 | 0.001 | 0.588 | 0.000 | 0.361 | 0.038 | 4.53 | 9.66 |
| 4.865 | 0.004 | 2.355 | 0.008 | 1.062 | 0.001 | 1.567 | 0.000 | 1.112 | 0.240 | 4.08 | 7.70 |
| 6.886 | 0.004 | 4.420 | 0.157 | 2.237 | 0.001 | 3.800 | 0.000 | 2.389 | 0.896 | 3.87 | 7.40 |
| 9.872 | 0.006 | 9.840 | 4.138 | 3.893 | 0.001 | 6.819 | 0.337 | 5.345 | 1.948 | 3.62 | 5.90 |
| 16.958 | 1.312 | 17.793 | 11.025 | 5.519 | 0.130 | 13.456 | 3.464 | 8.897 | 3.162 | 3.45 | 4.74 |
| 23.764 | 7.834 | 27.070 | 18.227 | 8.994 | 0.559 | 21.258 | 9.463 | 12.844 | 7.059 | 3.25 | 4.62 |

4. Mathematical processing of experimental results

To approximate the experimental data (as it is shown in Table 1), the Langmuir, Freundlich, Redlich-Peterson, Toch, Langmuir-Freundlich equations were used to select the isotherms that most adequately describe the experiment results and determine the corresponding sorption coefficients (see Table 2). Figure 2 shows the obtained graphs. The determination coefficient R² was used to compare the accuracy of the approximation for each metal and the equation. All equations, with the exception of the Langmuir equation, involve three adjustable parameters and their values cannot be determined by linear regression or by any other reliable graphical method [15]. For this reason, the initial value of the sorption capacity M was set on the basis of the experimental results. The parameters k, β and the exact value M were calculated by the least-squares method using MS MathCAD Professional and SciDAVis software programs. The obtained results are correct for concentrations within the range of studies.

Table 2. Adsorption Isotherms

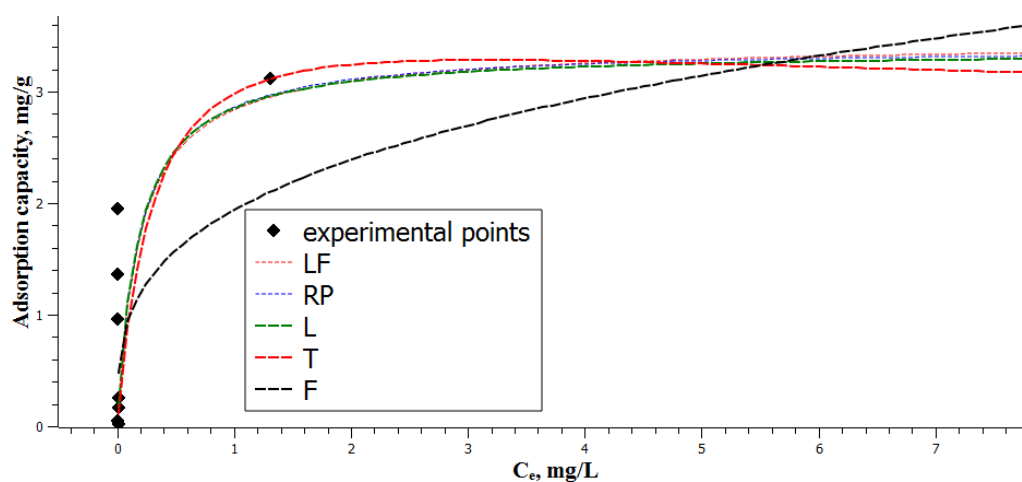
| Adsorption isotherms | Symbol | Formula |
|----------------------|--------|---|
| Langmuir | L | $f = \frac{k \times M \times C_{ex}}{1 + k \times C_{ex}}$ |
| Langmuir-Freundlich | LF | $f = \frac{M \cdot (k \cdot C_{ex})^\beta}{1 + (k \cdot C_{ex})^\beta}$ |
| Redlich-Peterson | RP | $f = \frac{M \cdot k \cdot C_{ex}}{1 + (k \cdot C_{ex})^\beta}$ |
| Toch | T | $f = \frac{M \cdot k \cdot C_{ex}}{(k + C_{ex})^{1/\beta}}$ |
| Freundlich | F | $f = M \cdot k \cdot C_{ex}^\beta$ |

Note: Here, C_{ex} is the equilibrium ion concentration (mg / l); M is the maximum adsorption capacity (mg/g); β -is the degree of non-homogeneity (0 < β < 1); k is the constant.

Sorption on modified clay is a complex process due to the porous structure, internal and external charged surfaces, mineralogical heterogeneity, the existence of crystal edges and broken bonds, which also have a high sorption capacity. The most common and frequently used Langmuir equation is unable to describe all these sorption processes in a wide range of concentrations. Experimental results often show nonlinear graphs that are better approximated by more complex models. The Langmuir-Freundlich equation better describes a sorption model for the low-concentration range as shown in Figure 2 (A-I).

Table 3. Adjustable isotherm parameters and determination coefficient calculated by using experimental data

| ITM | Types of isotherms | k | β | M | R ² |
|-----|--------------------|-------|---------|-------|----------------|
| Fe | L | 5.49 | - | 3.37 | 0.994 |
| | LF | 5.29 | 1 | 3.4 | 0.992 |
| | RP | 5.54 | 0.99 | 3.3 | 0.992 |
| | T | 0.39 | 0.89 | 11.12 | 0.998 |
| | F | 1.61 | 0.3 | 1.2 | 0.847 |
| Zn | L | 13.45 | - | 1.4 | 0.842 |
| | LF | 0.49 | 0.28 | 3 | 0.911 |
| | RP | 11.25 | 1 | 1.45 | 0.833 |
| | T | 1.16 | 1 | 1.4 | 0.624 |
| | F | 0.65 | 0.19 | 1.4 | 0.912 |
| Mn | L | 0.37 | - | 1.7 | 0.942 |
| | LF | 0.37 | 1 | 1.7 | 0.944 |
| | RP | 0.38 | 1 | 1.7 | 0.942 |
| | T | 6.41 | 0.61 | 1.9 | 0.952 |
| | F | 0.26 | 0.516 | 1.78 | 0.906 |
| Cu | L | 3.6 | - | 2.27 | 0.865 |
| | LF | 0.32 | 0.24 | 6.45 | 0.875 |
| | RP | 3.94 | 0.99 | 2.2 | 0.872 |
| | T | 0.32 | 0.97 | 7.4 | 0.861 |
| | F | 0.93 | 0.17 | 1.68 | 0.875 |
| Pb | L | 239 | - | 1.65 | 0.813 |
| | LF | 0.86 | 0.3 | 4.07 | 0.865 |
| | RP | 252 | 0.99 | 1.6 | 0.816 |
| | T | - | - | - | - |
| | F | 1.33 | 0.22 | 1.41 | 0.874 |

**Figure 2A.** Comparison of adsorption isotherms with experimental points for the following ions: A – iron

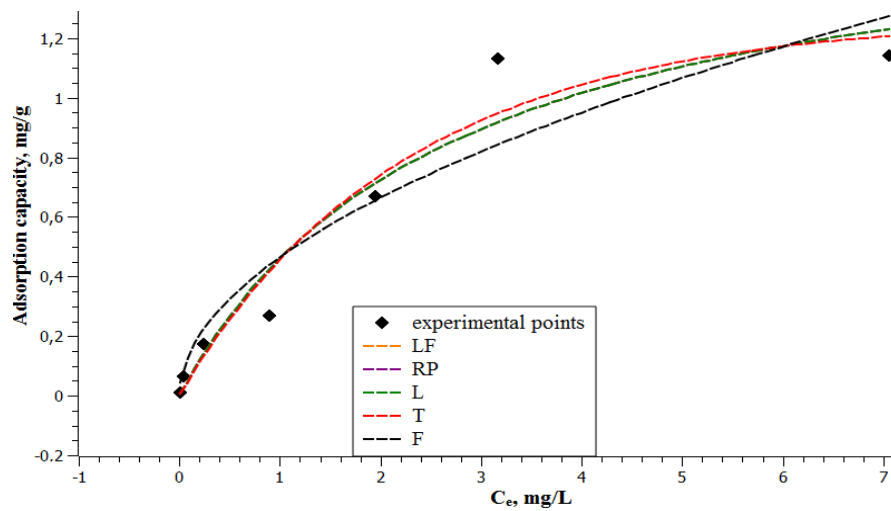


Figure 2B. Comparison of adsorption isotherms with experimental points for the following ions: **B** – manganese

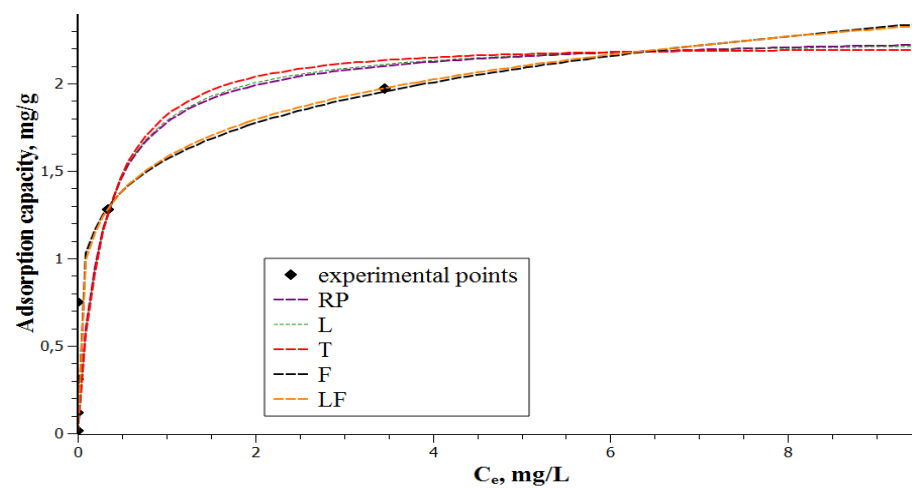


Figure 2C. Comparison of adsorption isotherms with experimental points for the following ions: **C** – copper

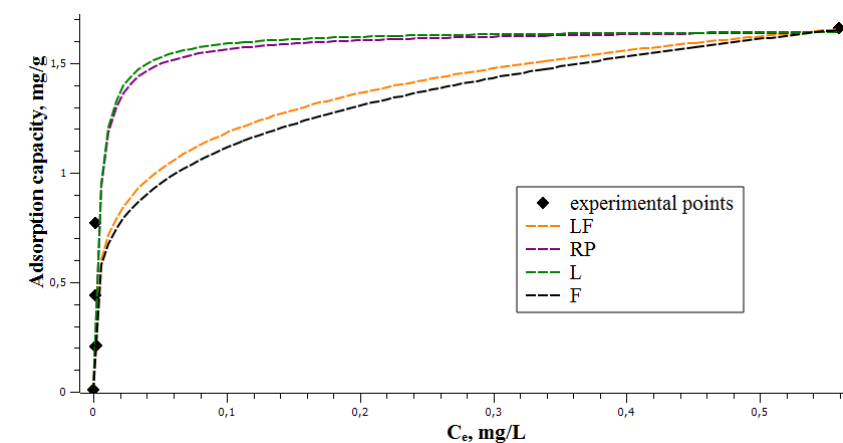


Figure 2D. Comparison of adsorption isotherms with experimental points for the following ions: **D** – lead.

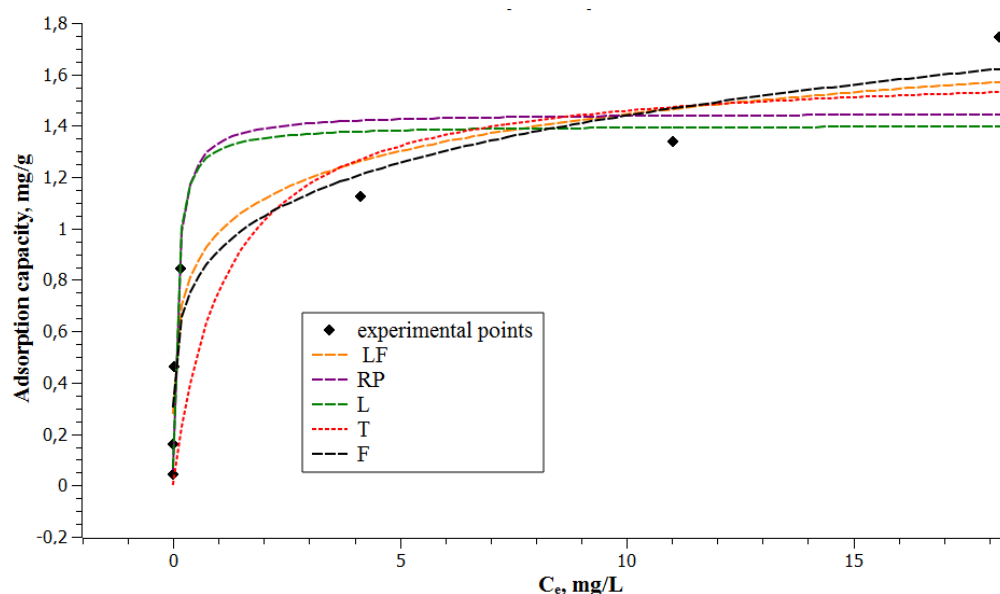


Figure 2E. Comparison of adsorption isotherms with experimental points for the following ions:
I - zinc.

Thus, the highest coefficient of determination for ions is as follows: Cu^{2+} - $R^2=0.875$; Pb^{2+} - $R^2=0.865$; for Zn^{2+} - $R^2 = 0.911$ (see Table 3). To describe the model of manganese and iron sorption, the Toch equation is more suitable. Thus, the highest coefficient of determination according to the Toch equation for ions is as follows: Fe - $R^2=0.998$, Mn - $R^2=0.952$.

5. Conclusion

The research yielded the following conclusions.

1. The values of the sorption capacity for the proposed sorbent, corresponding to MAC for fishery reservoirs in respect of metal ions sorption from a multicomponent solution, are as follows (mg/g): for iron – more than 1.95; for copper – more than 0.75; for zinc – more than 0.464; for manganese – more than 0.011, for lead – more than 0.77.
2. The selectivity range of the developed sorbent is expressed by the dependence $\text{Fe}^{3+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$.
3. For metals with a sorption isotherm ending in a horizontal section, the Langmuir-Freundlich model is better suited, since the maximum sorption capacity according to this equation is: for zinc – 3 mg/g, for copper – 6.45 mg/g, for lead – 4.07 mg/g. The maximum sorption capacity for iron ions is 11.12 mg/g; for manganese ions it is 1.9 mg / g. According to the Toch model, the maximum sorption capacity for iron ions is 11.12 mg/g; for manganese ions it is 1.9 mg/g.

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