

KINETIC STUDY OF COPPER IONS BIOSORPTION ONTO BARLEY STRAW

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ABSTRACT – In this paper, the kinetic study of the copper ions biosorption onto barley straw is presented. The obtained experimental data were modeled using three kinetic models: pseudo-first order kinetic model, pseudo-second order kinetic model, and the intraparticle diffusion kinetic model (Weber-Morris model). Change in the adsorption capacity with process time was also monitored. Analyzing the obtained results, it can be concluded that the pseudo-second order kinetic model shows the best agreement with the analyzed data, which leads to a conclusion that chemisorption is a possible mechanism of binding the copper ions onto the surface of the barley straw.

Keywords: Kinetic Study, Copper Ions, Barley Straw, Biosorption, Chemisorption.

INTRODUCTION

Heavy metals can be removed from wastewaters by conventional methods, such as: coagulation and flocculation, flotation, aeration, oxidation, adsorption, ion exchange, membrane processes, and electrochemical methods [1].

These conventional methods don't always give satisfactory results. Due to the tendency of every industrial process to be more economical and efficient, different possible methods of wastewater treatment are being investigated. Biosorption is one of the possible alternative method to conventional technologies for wastewater treatment, especially those with low heavy metal ions content [2].

Many biological waste materials, such as fungi, algae, peat, yeasts, and different agricultural wastes are being tested as potential adsorbents for heavy metal ions adsorption from water solutions [3].

Kinetic models are often used for analyzing the experimental data in order to determine the rate of the adsorption, its mechanism, as well to determine the step that dictates the rate of the process [4].

There are a large number of kinetic models that are used to describe the adsorption processes. Models that are most often used in relevant literature are: pseudo-first model, pseudo-second order model, and the intraparticle diffusion kinetic model [5].

In this paper, the three above mentioned kinetic models were used for modeling the experimental results of Cu²⁺ ions biosorption onto barley straw.

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EXPERIMENTAL

The change in the adsorption capacity with process time was determined by performing the following experiment: 0.5 g of barley straw was brought into contact with 50 mL of synthetic copper solutions of initial concentration 0.2 g dm^{-3} , for different contact time, ranging from 1 to 90 minutes, considering it a process time long enough to reach the equilibrium between phases [2].

RESULTS AND DISCUSSION

Change in the adsorption capacity with process time

The change in the adsorption capacity with a process time for copper ions biosorption onto barley straw is shown on Fig. 1. As can be seen from Fig. 1, the adsorption capacity rises rapidly in the first 10 minutes, as a result of a large number of available active sites in the structure of the adsorbent. After this period, the adsorption capacity further changes slowly over time, reaching its maximum value after 90 minutes.

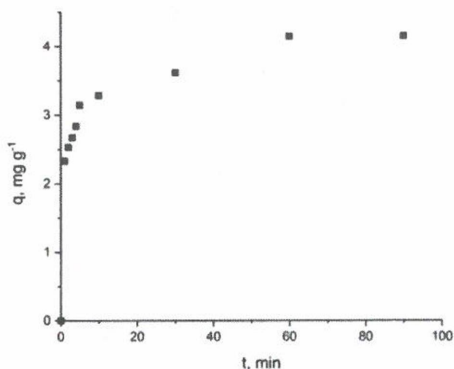


Figure 1 The change in the adsorption capacity with process time for copper ions biosorption onto barley straw

Pseudo-first order kinetic model

Pseudo-first order kinetic model was determined by Lagergren, and its often-named in literature as Lagergren's model. This model assumes that adsorption is a reversible process [6].

The pseudo-first order model is given as:

$$\frac{dq(t)}{dt} = k_1(q_e - q(t)) \quad (3)$$

where: $q(t)$ - is the adsorbent capacity defined as the mass of the adsorbed metal per unit mass of the adsorbent (mg g^{-1}) at time t ; q_e - is the adsorption capacity defined as mass of the adsorbed metal per unit mass of the adsorbent (mg g^{-1}) at equilibrium; k_1 - is the adsorption rate constant for the pseudo-first order kinetic model (min^{-1}).

By integrating the equation (1) for the boundary conditions: $t = 0$ to $t = t$ and $q(t) = 0$ to $q(t) = q(t)$ the following equation can be obtain:

$$\log\left(\frac{q_e}{q_e - q(t)}\right) = \frac{k_1}{2,303} \cdot t \quad (2)$$

For practical use, this equation can be modified into:

$$\log(q_e - q(t)) = \log(q_e) - \frac{k_1}{2,303} \cdot t \quad (3)$$

Plotting $\log(q_e - q(t))$ vs. t gives a linear dependence where the constant k_1 and the equilibrium adsorption capacity q_e can be determined from the slope and the intercept, respectively (Fig. 2). The obtained model data is given in Table 1.

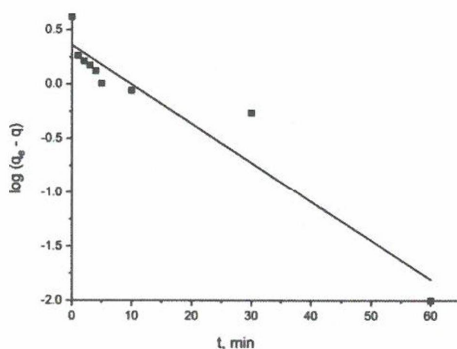


Figure 2 Pseudo-first order kinetic model for copper ions biosorption onto barley straw

Pseudo-second order kinetic model

The pseudo-second order kinetic model is based on the assumption that the rate of the adsorption is controlled by chemisorption [7].

A nonlinear form of the pseudo-second order kinetic model can be represented by the following equation:

$$\frac{dq(t)}{dt} = k_2(q_e - q(t))^2 \quad (4)$$

where: $q(t)$ - is the adsorbent capacity defined as the mass of the adsorbed metal per unit mass of the adsorbent (mg g^{-1}) at time t ; q_e - is the adsorption capacity defined as mass of the adsorbed metal per unit mass of the adsorbent (mg g^{-1}) at equilibrium; k_2 - is the adsorption rate constant for the pseudo-second order kinetic model ($\text{g mg}^{-1} \text{min}^{-1}$).

Rearranging Eq. (4) to obtain its linear form, leads to the following equation:

$$\frac{1}{(q_e - q(t))} = \frac{1}{q_e} + k_2 t \quad (5)$$

For practical use, the equation (5) is modified into:

$$\frac{t}{q(t)} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

By plotting $t/q(t)$ vs t (Fig.3), the pseudo-second order kinetic model parameters can be determined. The obtained model data is given in Table 1.

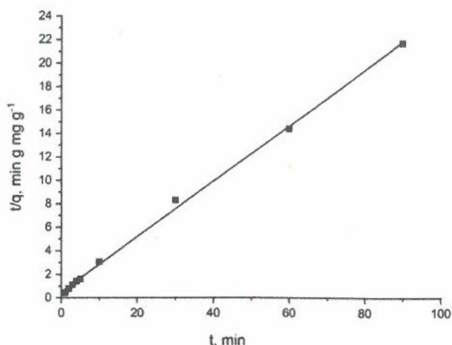


Figure 3 Pseudo-second order kinetic model for copper ions biosorption onto barley straw

Intraparticle diffusion kinetic model (Weber-Morris model)

The intraparticle diffusion kinetic model assumes that adsorption does not take place only on the surface of the adsorbent, but also includes diffusion and adsorption inside the adsorbent structure [8].

Linear form of this model is given by [9]:

$$q(t) = k_i t^{1/2} + C_i \tag{7}$$

where: $q(t)$ - is the adsorption capacity defined as the mass of the adsorbed metal per unit mass of the adsorbent (mg g^{-1}) at time t ; k_i - is the internal particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$); C_i - is a constant that provides insight into the thickness of the boundary layer. If the C_i value is higher, the boundary layer effect is greater, so the effect of surface adsorption in controlling the process rate is higher (mg g^{-1}). The obtained model data is given in Table 1.

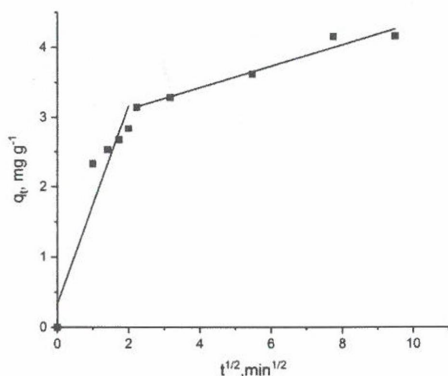


Figure 4 Intraparticle diffusion kinetic model (Weber-Morris model) for copper ions biosorption onto barley straw

The obtained experimental data, shown on Fig. 1, was fitted using the pseudo first-order kinetic model, pseudo-second order kinetic model, and the intraparticle diffusion kinetic model. Equilibrium parameters for the considered models were determined using the Eqs. (3), (6), and (7), and, along with the correlation coefficients R^2 , are given in Table 1.

Table 1 Obtained parameters for the pseudo first-order model, pseudo-second kinetic model, intraparticle diffusion model, and the Elovich model for copper ions biosorption onto barley straw

Model	Parameters	Values
Pseudo-first order kinetic model	k_1 (min^{-1})	0.083
	$q_{e,\text{exp}}$ (mg g^{-1})	4.16
	$q_{e,\text{cal}}$ (mg g^{-1})	2.28
	R^2	0.917
Pseudo-second order kinetic model	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.116
	$q_{e,\text{exp}}$ (mg g^{-1})	4.16
	$q_{e,\text{cal}}$ (mg g^{-1})	4.23
	R^2	0.998
Intraparticle diffusion kinetic model	k_{i1} ($\text{g mg}^{-1} \text{min}^{-0,5}$)	1.415
	C_{i1} (mg g^{-1})	0.332
	R_1^2	0.889
	k_{i2} ($\text{g mg}^{-1} \text{min}^{-0,5}$)	0.152
	C_{i2} (mg g^{-1})	2.812
	R_2^2	0.960

CONCLUSION

In this paper, a kinetic study of copper ions biosorption onto barley straw was performed. Four kinetic models were used for modeling the experimental data: pseudo-first order kinetic model, pseudo-second order kinetic model, and the intraparticle diffusion kinetic model (Weber-Morris model). The obtained results showed that the pseudo-second order kinetic model gives the best fit for the analyzed experimental data, indicating that chemisorption is a possible mechanism of binding the copper ions onto the surface of the barley straw.

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REFERENCES

1. Šećerov Sokolović, R., Sokolović, S. (2002) Inženjerstvo u zaštiti okoline, Univerzitet u Novom Sadu Tehnološki fakultet, Novi Sad, 1-299.
2. Gorgievski, M., Božić, D., Stanković, V., Štrbac, N., Šerbula, S. (2013) Kinetics, equilibrium and mechanism of Cu^{2+} , Ni^{2+} and Zn^{2+} ions biosorption using wheat straw, *Ecological Engineering*, 58, 113-122.
3. Nemes, L. N., Bulgariu, L. (2016) Optimization of process parameters for heavy metals biosorption onto mustard waste biomass, *Open Chemistry*, 14, 175-187.
4. Guša, A., Đolić, M., Lekić, B., Rajaković-Ognjanović, V. (2015) Komparativna sorpcija jona teških metala na različitim tipovima sorbenata, Originalan naučni rad, Građevinski fakultet Univerziteta u Beogradu, Beograd, Srbija, Institut za nuklearne nauke Vinča, Univerzitet u Beogradu, Beograd, Srbija, 67-77.
5. Pap, S. (2017) Novi adsorpcioni medijumi za separaciju neorganskih polutanata otpadnih voda bazirani na termohemijskoj konverziji biomase (Doktorska disertacija), Univerzitet u Novom Sadu, Fakultet tehničkih nauka, Departman za inženjerstvo zaštite životne sredine i zaštite na radu, Novi Sad, 1-211.
6. Lagergren, S. (1898) About the theory of so-called adsorption of soluble substances, *Kungliga Suensk Vetenskapsakademiens Handlingar*, 241, 1-39.
7. Lu, N., Hu, T., Zhai, Y., Qin, H., Aliyeva, J., Zhang, H. (2020) Fungal cell with artificial metal container for heavy metals biosorption: Equilibrium, kinetics study and mechanisms analysis, *Environmental Research*, 182, 1-10.
8. Cheung, W. H., Szeto, Y. S., McKay, G. (2007) Intraparticle diffusion processes during acid dye adsorption onto chitosan, *Bioresource Technology*, 98, 2897-2904.
9. Weber, W.J., Morris, J.C. (1963) Kinetics of adsorption on carbon from solution, *Journal of the Sanitary Engineering Division*, 89(2), 31-59.