

KINETIC ANALYSIS OF COPPER IONS ADSORPTION ON SUNFLOWER HULLS

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Abstract

This paper presents the kinetic analysis of the adsorption process of copper ions on sunflower hulls. Three theoretical kinetic models were used to analyze the experimental results: the pseudo-first order kinetic model, the pseudo-second order kinetic model and the Elovich kinetic model. The results showed that the pseudo-second order kinetic model is the best fit for the analyzed data.

Keywords: sunflower hulls, copper ions, kinetic

1. INTRODUCTION

Heavy metals such as cadmium (Cd), chromium (Cr), arsenic (As), lead (Pb) and mercury (Hg) are persistent environmental pollutants that do not degrade naturally and accumulate in the environment. If they are found in the human body, even in traces, their toxicity has a negative effect on the function of the organs and damages them [1].

Many conventional methods are used to remove heavy metals from wastewater, including chemical precipitation, ion exchange, ultrafiltration, reverse osmosis and membrane filtration [2]. However, these methods do not always provide satisfactory results, which is why it is necessary to develop a new, alternative process.

An emerging and promising alternative is biosorption, a physico-chemical process in which biological materials such as plant biomass and microorganisms are used as adsorbents to bind heavy metal ions from aqueous solutions [3]. In contrast to conventional methods, biosorption offers several advantages, including high removal efficiency even at low metal concentrations, cost efficiency and minimised secondary waste production [4].

2. EXPERIMENTAL

The sunflower hulls were first ground and sieved on a set of laboratory sieves. The fraction -1+0.4 mm was used for the experiments. Each sample was rinsed with distilled water before experiments. Adsorption experiments were carried out using a synthetic solution of Cu²⁺ ions, prepared from CuSO₄·5H₂O (LACHEMA, Czech Republic).

3. RESULTS AND DISCUSSION

3.1 Kinetic study

The study of adsorption kinetics provides information about the rate of uptake of solutes at the solid-liquid interface and the possible mechanism of the adsorption process [5]. To obtain the

experimental kinetic data, 0.5 g of sunflower hulls were brought into contact with the copper ion solutions with an initial concentration of 0.2 g dm⁻³ for different contact times between 1 and 90 minutes.

The change in adsorption capacity over time is shown in Figure 1. Figure 1 shows that at the beginning of the process, i.e. in the first 5 minutes, the capacity increases rapidly with the phase contact time. It then continues to increase, but at a slower rate. The sudden increase in adsorption capacity right at the beginning of the process is due to the availability of a large number of active sites in the structure of the adsorbent [6].

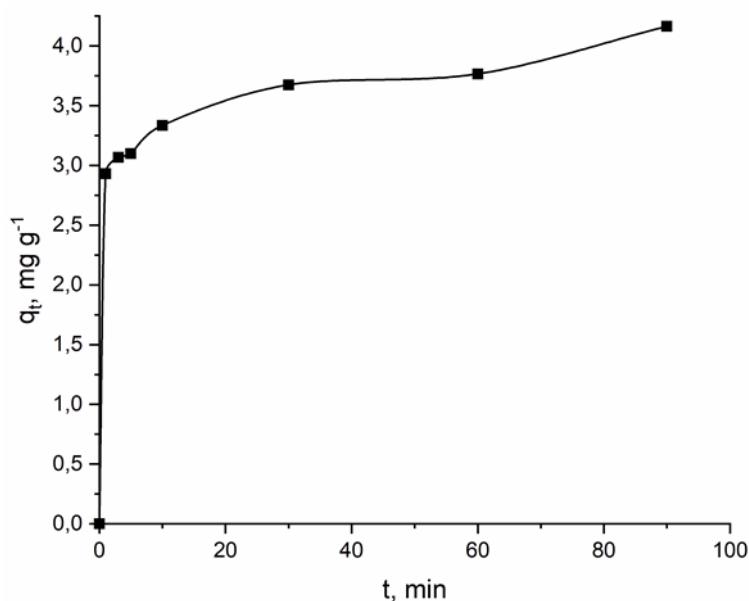


Figure 1. Change in the adsorption capacity for copper ions with time

In this paper, the pseudo-first order kinetic model, the pseudo-second order kinetic model and the Elovich kinetic model were used to analyze the obtained kinetic adsorption data.

Pseudo-first order kinetic model

The pseudo-first order kinetic model assumes that the adsorption rate is directly proportional to the number of unoccupied adsorption sites [7]. This kinetic model was proposed by Lagergren and it can be expressed in integral form as follows [8]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} \cdot t \quad (1)$$

where: q_t and q_e are the adsorption capacity defined as the mass of adsorbed metal per unit mass of adsorbent (mg g⁻¹) at time t and at equilibrium, respectively; k_1 (min⁻¹) is the rate constant for the pseudo-first order model.

A plot of $\log(q_e - q_t)$ against t gives a linear dependence, from which the constant k_1 and the equilibrium adsorption capacity q_e can be determined from the slope and intercept, respectively.

The experimental data were fitted using this model (Figure 2), and the kinetic parameters were determined and shown in Table 1.

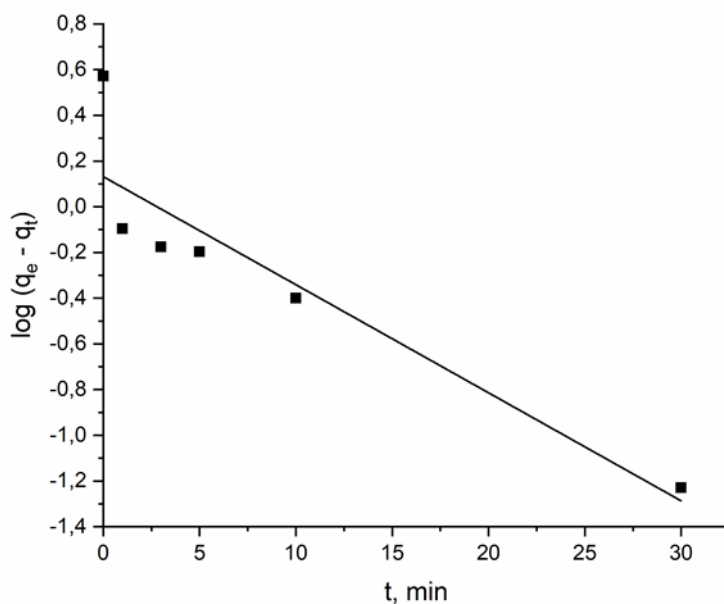


Figure 2. Pseudo-first order kinetic model for the adsorption of copper ions on sunflower hulls

Pseudo-second order kinetic model

The pseudo-second order kinetic model is based on the assumption that the rate-determining step of the adsorption process is chemisorption, i.e. the chemical interaction between the functional groups of the adsorbent and the heavy metal ions [9, 10]. This model can be expressed by the following equation [11]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) \cdot t \quad (2)$$

where: q_t and q_e are the adsorbent capacity defined as mass of the adsorbed metal per unit mass of the adsorbent (mg g^{-1}) at time t and at equilibrium, respectively; k_2 is the rate constant for pseudo-second order kinetic model.

The values of k_2 and q_e can be calculated from the slope and intercept of the plot of t/q_t vs. t (Figure 3).

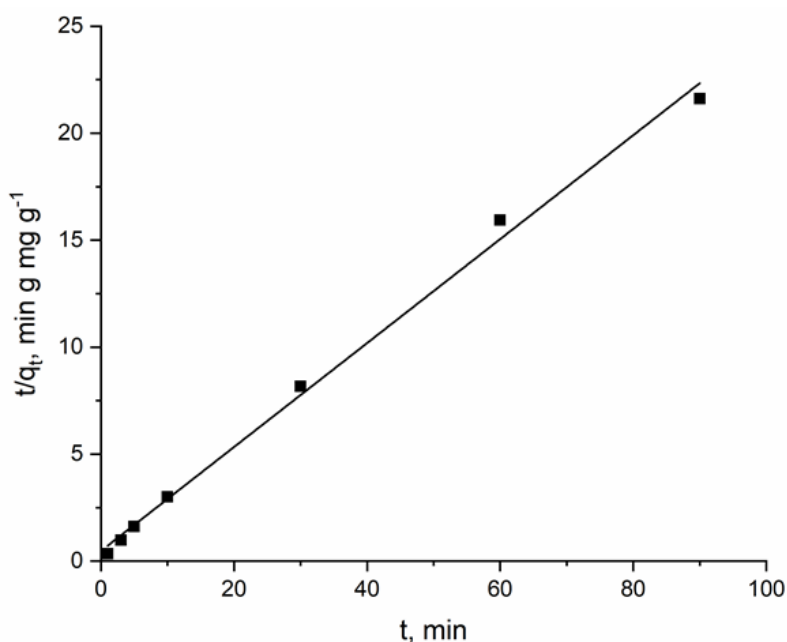


Figure 3. Pseudo-second order kinetic model for the adsorption of copper ions on sunflower hulls

Elovich kinetic model

Elovich kinetic model assumes that the surface of solids on which the adsorption process takes place is energetically heterogeneous and that with low surface coverage, neither desorption nor the interactions between the adsorbed species can significantly affect the kinetics of adsorption [12]. This kinetic model can be expressed by the following equation [13]:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (3)$$

where: α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$); β is a parameter expressing the degree of surface coverage and the activation energy of chemisorption (g mg^{-1}); q_t is the adsorption capacity (mg g^{-1}), defined as the mass of adsorbed metal per unit mass of adsorbent for time t .

The values for the parameters α and β were calculated from the intercept and the slope of the line $q_t = f(\ln t)$ (Figure 4) and are shown in Table 1 together with the correlation coefficient for copper ions.

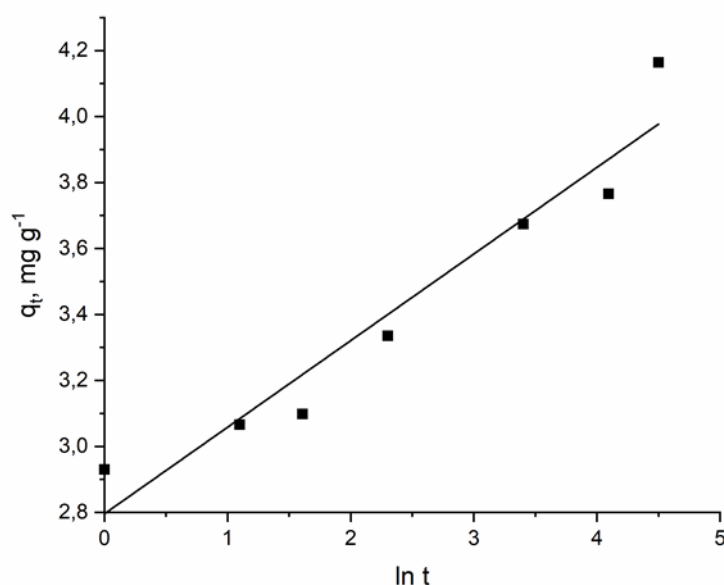


Figure 4. Elovich kinetic model for the adsorption of copper ions on sunflower hulls

Table 1. Parameters of the kinetic models for the adsorption of copper ions on sunflower hulls

Model	Parameters	Values
Pseudo-first order kinetic model	k_1, min^{-1}	0.109
	$q_{e,\text{exp}}, \text{mg g}^{-1}$	4.169
	$q_{e,\text{cal}}, \text{mg g}^{-1}$	1.355
	R^2	0.841
Pseudo-second order kinetic model	$k_2, \text{g mg}^{-1} \text{min}^{-1}$	0.125
	$q_{e,\text{exp}}, \text{mg g}^{-1}$	4.169
	$q_{e,\text{cal}}, \text{mg g}^{-1}$	4.116
	R^2	0.996
Elovich kinetic model	$\alpha, \text{mg g}^{-1} \text{min}^{-1}$	2.795
	$\beta, \text{g mg}^{-1}$	0.263
	R^2	0.931

From the values of the correlation coefficients in Table 1, it can be concluded that the best agreement with the experimental data is achieved by the pseudo-second order kinetic model ($R^2 = 0.996$), indicating that the chemical reaction significantly controls the rate of copper ions adsorption on sunflower hulls.

4. CONCLUSIONS

Kinetic analysis of the copper ions adsorption on sunflower hulls was investigated and presented in this paper. Three kinetic models were used to analyze the experimental results: the pseudo-first order kinetic model, the pseudo-second order kinetic model and the Elovich kinetic model. Based on the obtained values of the correlation coefficients for each model, it can be concluded that the best agreement with the experimental data was achieved by the pseudo-second order kinetic model, which indicates that the chemical reaction significantly controls the rate of adsorption of copper ions on sunflower hulls.

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