

EQUILIBRIUM AND THERMODYNAMIC ANALYSIS OF THE ADSORPTION OF COPPER IONS ON SUNFLOWER HULLS

Milan Gorgievski^{1a}, Marina Marković^{1b}, Miljan Marković^{1c}, Vesna Grekulović^{1d},
Nada Štrbac^{1e}, Kristina Božinović^{1f}, Milica Zdravković^{1g}

¹ Technical Faculty Bor, University of Belgrade, V.J. 12, 19210 Bor, Serbia

^{1a} mgorgievski@tfbor.bg.ac.rs, 0000-0002-9899-719X

^{1b} marina.markovic@tfbor.bg.ac.rs, 0009-0007-7553-6423

^{1c} mmarkovic@tfbor.bg.ac.rs, 0000-0002-4734-1481

^{1d} vgrekulovic@tfbor.bg.ac.rs, 0000-0001-6871-4016

^{1e} nstrbac@tfbor.bg.ac.rs, 0000-0003-4836-1350

^{1f} kbozinovic@tfbor.bg.ac.rs, 0000-0002-9834-448X

^{1g} mzdavkovic@tfbor.bg.ac.rs, 0000-0001-9488-9151

Abstract

This paper presents the equilibrium and thermodynamic study of the adsorption of copper ions on sunflower hulls. The results of the equilibrium analyses showed that Temkin's isothermal model was the best fit the analysed data. The calculated thermodynamic data showed that the sorption reaction is not spontaneous at the given temperatures, that the process is endothermic and that there is a reduced randomness at the solid-solution interface.

Keywords: copper ions, sunflower hulls, isotherms, thermodynamic

1. INTRODUCTION

The contamination of water bodies with heavy metals, mainly from the metallurgical and mining industries and battery production, has become a serious problem. Due to their toxicity, heavy metals in wastewater threaten global ecosystems and global health. However, they are also valuable resources that should be recycled. For this reason, but above all for environmental reasons, the development of highly efficient methods for the treatment of industrial wastewater contaminated with heavy metals is very important [1, 2].

One of the most promising methods for treating industrial wastewater with low concentrations of metal ions is adsorption using natural adsorbents, known as “biosorption”. This process has several advantages over conventional technologies, such as the use of inexpensive and sustainable materials, the metabolic independence of the process, the effective utilization of waste materials and the high removal efficiency even at low heavy metal concentrations [3].

2. EXPERIMENTAL

The sunflower hulls were first ground and sieved on a set of laboratory sieves, and the fraction -1+0.4 mm was used for the adsorption experiments. Before the adsorption experiments, the sunflower hulls were rinsed with distilled water. Stock solutions of Cu²⁺ ions were prepared with CuSO₄·5H₂O from LACHEMA (Czech Republic).

3. RESULTS AND DISCUSSION

3.1 Adsorption isotherms

Adsorption isotherms represent the amount of adsorbed material as a function of the equilibrium concentration after adsorption at a constant temperature [4].

Langmuir isotherm model

Langmuir isotherm model assumes monolayer adsorption on a homogeneous surface. It also assumes that there are no interactions between the adsorbed molecules [5]. In non-linear form, the Langmuir adsorption isotherm model can be expressed as follows [6]:

$$q_e = q_m K_L \frac{C_e}{1 + K_L C_e} \quad (1)$$

where: C_e is the equilibrium concentration of metal ions in the solution (mg dm^{-3}); q_e is the equilibrium adsorption capacity, defined as the mass of metal ions per unit mass of adsorbent when the system is at equilibrium (mg g^{-1}); q_m (mg g^{-1}) and K_L ($\text{dm}^3 \text{mg}^{-1}$) are constants related to the adsorption capacity and the energy or net enthalpy of adsorption.

Freundlich isotherm model

Freundlich isotherm model is based on the assumption that the surface energy of the adsorbent is heterogeneous and that the stronger binding sites are occupied first. It is also assumed that the binding strength decreases as the degree of site occupation increases [7]. This model can be expressed by the following equation [8]:

$$q_e = K_F C_e^{1/n} \quad (2)$$

where: C_e is the equilibrium concentration of metal ions (mg dm^{-3}); q_e is the equilibrium adsorption capacity (mg g^{-1}); K_F is the Freundlich equilibrium constant ($\text{dm}^3 \text{g}^{-1}$). $1/n$ is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption.

Temkin isotherm model

Temkin isotherm model takes into account the interaction of adsorbent and adsorbate and is based on the assumption that the free adsorption energy is a function of the surface coverage, i.e. that the adsorption energy of the molecules decreases linearly with the degree of surface coverage [9].

The Temkin isotherm is represented by the following equation [10]:

$$q_e = \frac{RT}{b} \ln(K_T C_e) = B \ln(K_T C_e) \quad (3)$$

where: T is the absolute temperature (K); R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); K_T is the equilibrium binding constant ($\text{dm}^3 \text{mg}^{-1}$); b is the change in adsorption energy (kJ mol^{-1}); C_e is the equilibrium concentration of the metal ion (mg dm^{-3}); $RT/b = B$ is the Temkin constant related to the heat of adsorption (kJ mol^{-1}).

Adsorption isotherms of copper ions on sunflower hulls

In order to obtain the adsorption isotherm data, experiments were carried out in which 0.5 g of sunflower hulls were brought into contact with 50 mL of copper ion solution, with initial concentrations ranging from 0.05 to 0.3 mg dm^{-3} . The stirring time was 60 minutes. The suspension was then filtered and the copper concentration in the filtrate was determined.

In this work, three of the most common models of the adsorption isotherm in the literature, the Langmuir model, the Freundlich model, and the Temkin model, were used to fit the experimental data of the adsorption of copper ions on sunflower hulls. The obtained results are shown in Figure 1.

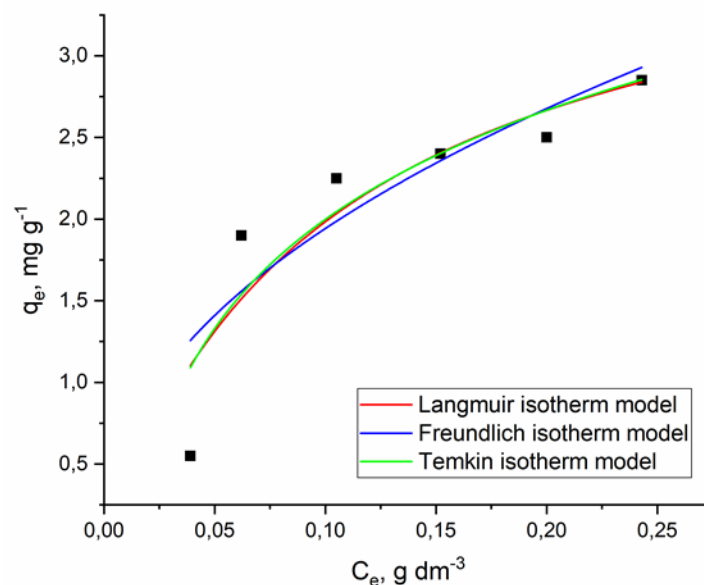


Figure 1. Isotherm data for the adsorption of copper ions on sunflower hulls

Table 1. Isotherm parameters for the adsorption of copper ions on sunflower hulls

Model	Parameters	Values
Langmuir isotherm model	$K_L, \text{dm}^3 \text{mg}^{-1}$	9.537
	$q_{e,\text{exp}}, \text{mg g}^{-1}$	2.850
	$q_m, \text{mg g}^{-1}$	4.064
	R^2	0.838
Freundlich isotherm model	K_F	5.637
	$1/n$	0.463
	R^2	0.987
Temkin isotherm model	$B, \text{J mol}^{-1}$	0.964
	$K_T, \text{dm}^3 \text{mg}^{-1}$	79.397
	R^2	0.988

Based on the values of the correlation coefficients given in Table 1, it can be concluded that Temkin isotherm model shows the best agreement with the experimental data ($R^2 = 0.988$) and is the best model to describe the equilibrium of adsorption of Cu^{2+} ions on sunflower hulls in the observed concentration range.

3.2 Adsorption thermodynamic

The thermodynamic parameters required to determine the spontaneity and feasibility of adsorption, such as the change in Gibbs free energy, the change in enthalpy and the change in entropy, are easy to determine because adsorption is a temperature-dependent process [11].

To determine the thermodynamic parameters, 0.5 g of adsorbent was brought into contact with 50 mL of a solution of copper ions with a concentration of 0.2 g dm^{-3} , at temperatures of $25 \text{ }^\circ\text{C}$, $30 \text{ }^\circ\text{C}$ and $35 \text{ }^\circ\text{C}$, for 60 minutes. The suspension was then filtered and the concentration of copper ions in the resulting filtrate was determined.

The thermodynamic parameters of the adsorption were calculated using the following equation [12, 13]:

$$K_c = \frac{C_A}{C_S} \quad (4)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (5)$$

$$\Delta G^0 = -RT \ln K_c \quad (6)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

where: K_c is the equilibrium constant; C_A is the concentration of the adsorbed substance at equilibrium (mol dm^{-3}); C_S is the equilibrium concentration of the metal ions in solution (mol dm^{-3}); ΔG^0 is the Gibbs free energy (kJ mol^{-1}); R is the universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$); T is the temperature (K); ΔH^0 is the enthalpy change (kJ mol^{-1}); ΔS^0 is the entropy change ($\text{J mol}^{-1} \text{K}^{-1}$).

Figure 2 shows the dependence of $\ln K_c = f(1/T)$. Based on the given dependence and the experimental data, the thermodynamic parameters of the adsorption process of copper ions on sunflower hulls were calculated and given in Table 2.

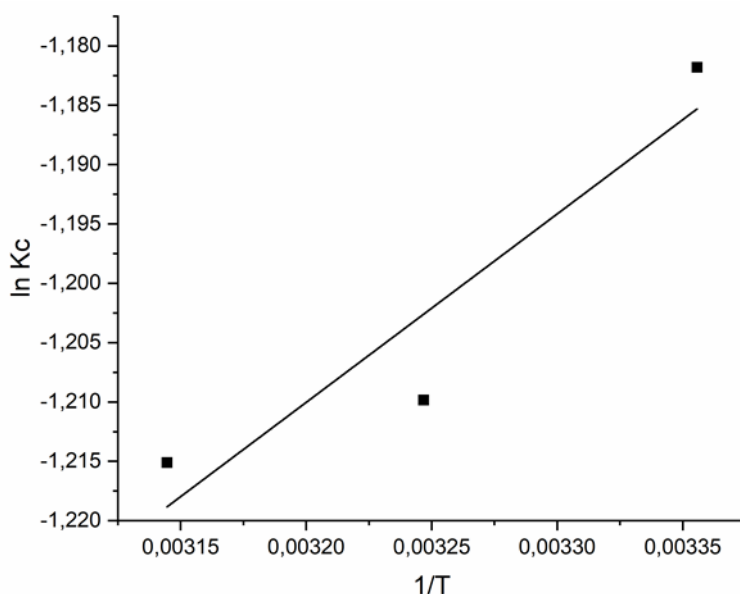


Figure 2. Thermodynamic dependence ($\ln K_c = f(1/T)$) for the adsorption of copper ions on sunflower hulls

Table 2. Thermodynamic parameters of the adsorption process of copper ions on sunflower hulls

T (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 ($\text{J mol}^{-1} \text{K}^{-1}$)
298	2.928	0.158	-1.718
303	3.098		
308	3.212		

The values obtained for the change in Gibbs free energy show that the Gibbs free energy increases with increasing temperature. Positive values of the change in Gibbs free energy indicate that there is an energy barrier for the adsorption of copper ions and that the sorption reaction does not occur spontaneously at the given temperatures. A positive ΔH^0 value indicates that the process is endothermic and a negative ΔS^0 value indicates that there is reduced randomness at the interface between the solid and solution [14].

4. CONCLUSIONS

The adsorption of copper ions on sunflower hulls was investigated and presented in this paper. The equilibrium analysis was performed using Langmuir's isothermal model, Freundlich's isothermal model and Temkin's isothermal model. Temkin's isothermal model fits the analysed data best. This model assumes that the adsorption energy of the molecules decreases linearly with the degree of surface coverage. The calculated thermodynamic data (ΔG^0 , ΔH^0 and ΔS^0) show that the sorption reaction does not occur spontaneously at the specified temperatures, but is favoured at lower temperatures, that the process is endothermic and that decreased randomness is present at the solid-solution interface.

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