ADSORPTION ISOTHERMS FOR COPPER IONS ADSORPTION ONTO WALNUT SHELLS

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Abstract

In this paper Langmuir, Freundlich, and Temkin adsorption isotherm models were used for describing the adsorption of copper ions onto walnut shells. The adsorption was performed in a batch system. The obtained isotherm data were fitted using the mentioned models, and the isotherm parameters were calculated from the linearized plots corresponding to each model. The Langmuir adsorption isotherm model showed the best agreement with the analyzed experimental data, with the correlation coefficient R^2 = 0.993. According to this model, the adsorption process occurs until a complete monolayer of copper ions is formed on the surface of the walnut shells. The maximum adsorption capacity, according to this model, was 7.71 mg g^{-1}.

***Keywords**: Adsorption isotherms, walnut shells, adsorption capacity, copper ions, batch system.*

1. INTRODUCTION

Environmental pollution, which includes water, air, and soil pollution, is a serious environmental problem. Waters contaminated with heavy metals are one of the biggest environmental problems of today. These waters affect the flora and fauna, and through the food chain also human health. Many industries, for example, metallurgy processing plants,discharge heavy metals into their wastewaters, thus polluting the environment[1, 2].Conventional technologies which are used for the removal of heavy metals from wastewaters including chemical precipitation, cementation, ion exchange, solvent extraction, adsorption, different membrane processes, etc, are already in use on an industrial level. These methods have their downsides, including an insufficient degree of metal ions removal, high costs, the need for excessive amounts of chemicals used in the process, and the formation of significant amounts of sludge. As a potential alternative method to conventional technologies for the removal of heavy metals from wastewaters emerges biosorption [3]. To describe the mechanism of the adsorption process as well as to obtain the information about the maximum adsorption capacity of selected adsorbent, the adsorption isotherms are used [4].

In this paper, the adsorption isotherm data of copper ions adsorption onto walnut shells was fitted using the Langmuir, Freundlich, and Temkin adsorption isotherm models.

2. EXPERIMENTAL

Walnut shells were used as an adsorbent for the adsorption experiments. Adsorption isotherm data was obtained by bringing into contact 0.5 g of walnut shells with 50 mL of synthetic solutions of copper ions with different initial concentrations ranging from 5 to 500 mg dm^{-3}. The suspension was stirred using a magnetic stirrer for 60 minutes, assuming that this process time is long enough to reach the equilibrium between phases [3]. After that, the suspension was filtered, and the filtrate was analyzed for the residual amount of copper ions.

3. RESULTS AND DISCUSSION

3.1 Langmuir adsorption isotherm model

This model was implemented theoretically assuming that the adsorption occurs in a monolayer, at a finite number of localized sites [5].

The Langmuir model can be expressed in the following form:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{1}$$

Linearization of the equation (1) results in the following expression:

$$C_e / q_e = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{2}$$

where C_e is the equilibrium concentration of metal ions (mg dm^{-3}), $q_e$is the equilibrium adsorption capacity (mg g^{-1}), $q_m$is the maximum adsorption capacity (mg g^{-1}) and K_L (dm^3 g^{-1}) is the Langmuir equilibrium constant.

Graphical dependence of C_e/q_e in function of C_e, shown on Figure 1b, gives the straight-linewith the slope $1/q_m$and the intercept $1/K_Lq_m$.

3.2 Freundlich adsorption isotherm model

This model is often used to describe the non-ideal and reversible adsorption processes. The Freundlich model can also be applied to multilayer adsorption [5].

This model is represented by the following expression:

$$q_e = K_f C_e^{1/n} \tag{3}$$

Linearization of the Eq. (3) gives:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where $C_e$is the equilibrium concentration of copper ions in the solution (mg dm^{-3}); q_e is the adsorbent capacity defined as mass of the adsorbed metal per unit mass of the adsorbent (mg g^{-1}) at equilibrium; K_F is the Freundlich equilibrium constant ((mg g^{-1}) (dm^3 mg^{-1})$^{1/n}$), and $1/n$ is the coefficient of heterogeneity in the Freundlich adsorption isotherm equation.

Graphical dependence of *log* $q_e$in function of *log* C_e, shown on Figure 1c, gives the straight line, with the slope $1/n$ and the intercept K_F.

3.3 Temkin adsorption isotherm model

Temkin adsorption isothermmodel is based on the assumption that the heat of adsorption in all layers of molecules decreases linearly with coverage, and that there is a uniform distribution of ion binding energy in the adsorbent-adsorbate system [6].

Temkin isotherm model is represented by the following expression:

$$q_e = B \ln\left(K_T C_e\right) \tag{5}$$

Linear form of the equation (5) is:

$$q_e = B \ln K_T + B \ln C_e \tag{6}$$

where $B = RT/b$ is the Temkin constant, which refers to the adsorption heat (J mol^{-1}); b is the variation of adsorption energy (J mol^{-1}); R is the universal gas constant (J mol^{-1} K^{-1}); T is the temperature (K); K_T is the Temkin equilibrium constant (dm^3 g^{-1}); q_e is the adsorption capacity defined as mass of the adsorbed metal per unit mass of the adsorbent (mg g^{-1}) at equilibrium; $C_e$is the equilibrium concentration of copper ions in the solution (mg dm^{-3}). Constants B and K_T can be determined from the graph $q_e = f(ln\ C_e)$, which is shown in Figure 1d, where B is the slope, and $K_T$the intercept.

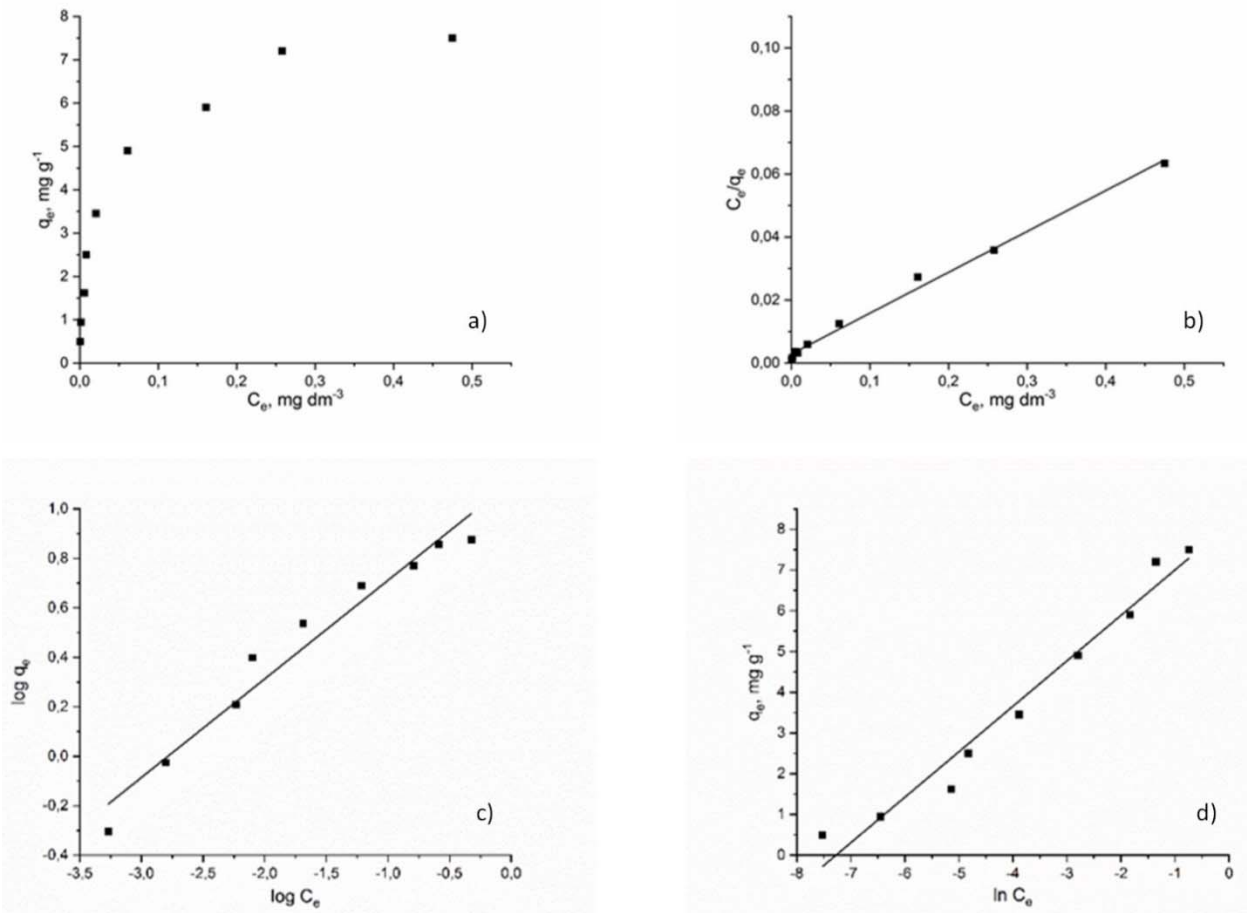

Figure 1. a) Adsorption isotherm data, b) Langmuir adsorption isotherm model, c) Freundlich adsorption isotherm model and d) Temkin adsorption isotherm model for copper ions adsorption onto walnut shells

The obtained adsorption isotherm data, shown in Figure 1a, was fitted using the Langmuir, Freundlich, and Temkin adsorption isotherm models, and the corresponding diagrams are shown on Figures 1 b-d. The equilibrium parameters for the analyzed models were determined using Equations (2), (4), and (6). The obtained parameters and correlation coefficients R^2 are given in Table 1.

Table 1. Obtained parameters for Langmuir, Freundlich and Temkin adsorption isotherm models for copper ions adsorption onto walnut shells

Langmuir				Freundlich			Temkin		
K_L dm^3 mg^{-1}	q_{exp} mg g^{-1}	q_m mg g^{-1}	R^2	K_F	1/n	R^2	B J mol^{-1}	K_T dm^3 g^{-1}	R^2
45.19	7.50	7.71	0.993	12.87	0.4	0.960	1.11	8.11	0.968

According to the data given in Table 1, the Langmuir model shows the best agreement to the analyzed data, with the correlation coefficient R^2 = 0.993. The experimentally determined adsorption capacity, and the maximum capacity determined by the Langmuir model are approximately equal, which further proves very good agreement of the Langmuir model with the analyzed data, and indicates that the adsorbent is almost completely saturated, where all of the active sites areoccupied by copper ions.The maximum adsorption capacity, obtained by the Langmuir adsorption isotherm model was 7.71 mg g^{-1}.

4. CONCLUSIONS

Walnut shells were used as an adsorbent for copper ions adsorption from aqueous solutions. The adsorption isotherm data were fitted using three theoretical adsorption isotherm models, i.e. Langmuir, Freundlich, and Temkin adsorption isotherm model. The obtained results, shown in Table 1, indicate that Langmuir model shows the best agreement with the analyzed experimental data, with the correlation coefficient R^2 = 0.993. This leads to the conclusion that the biosorption process occurs in a monolayer. The maximum adsorption capacity, obtained by the Langmuir adsorption isotherm model,according to Table 1, was 7.71 mg g^{-1}.

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REFERENCES

[1] R. B. Garcia-Reyes, J. R. Rangel-Mendez, Bioresour. Technol. 101 (2010) 8099-8108.
[2] R. Perez-Lopez, J. M. Nieto, G. R. Almodovar, Appl. Geochemistry. 22 (2007) 1919-1935.
[3] M. Gorgievski, D. Božić, V. Stanković, N. Štrbac, S. Šerbula, Ecol. Eng. 58 (2013) 113-122.
[4] M. J. Mohammed-Ridha, A. S. Ahmed, N. N. Raoof, NJES 20 (2017) 298-310.
[5] X. Chen, Information 6 (2015) 14-22.
[6] S. Puttamat, V. Pavarajarn, Int. J. Chem. Eng. 7 (4) (2016).