CU(II) ION ISOTHERMS AND THERMODYNAMIC ANALYZES OF BIOSORBENT OBTAINED ON THE BASIS OF RICE HUSK

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Abstract: *In this study, absorption isotherms of toxic Cu^{2+} ions of biosorbent obtained by modification of rice husk biomass with urea were studied. Based on the analysis of the adsorption isotherm, it was concluded that the Freundlich isotherm model (0.97-0.99) is more suitable than the Langmuir isotherm model (0.95-0.98). In addition, the process isotherm was calculated from the sorption results.*

Key words; *isotherm, thermodynamics, free energy, enthalpy, entropy*

Copper is considered a toxic metal and has a toxicological effect on many living organisms. Its permissible amount is 2 mg. Metallurgy and similar plants are one of the main sources of its accumulation in the environment [1]. Many materials and methods are used to prevent its spread into the environment. These include systems such as ion exchange resins, electrochemical processes, and activated carbon [2-3]. Recently, many researchers have been researching inexpensive adsorbents capable of binding metal ions. In our study, we studied the sorption isotherms and thermodynamic aspects of Cu^{2+} ions onto the biosorbent modified from rice husk with urea.

Adsorption isotherms are the most important tool for the analysis of equilibrium processes. Of the many models used to represent equilibrium processes in liquid and solid systems, the most widely used and convenient are the Langmuir and Freundlich models [4].

Langmuir isotherm model. It is represented by the following equation (1):

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

here: q_e- the amount of metal ion absorbed into the ion exchanger mol/g, C_e- the equilibrium concentration of the solution (mol/g), q_{Max} – the maximum amount of metal absorbed in a sorbent of a certain mass (mol/g). To find the Langmuir constant (K_L), a linear form of Langmuir's equation (1) is used, where the values of q_{max} and K_L are determined from the C_e dependence graph of C_e/q_e (2).

$$\frac{C_e}{q_e} = \frac{1}{q_e K_L} + \frac{1}{q_{\max}} \times C_e \quad (2)$$

An important feature of the Langmuir isotherm parameters is that the separation coefficient "R_L" can be used to conclude the relationship between the adsorbent and the adsorbate.

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

In this case, according to (4), the adsorption process $0<R_L<1$ is comfortable, $R_L>1$ is uncomfortable, $R_L=1$ is linear, and $R_L=0$ is irreversible [5].

Freundlich isothermal model. It is represented by the following equation (4)

$$q_e = K_F C_e^{1/n} \quad (4)$$

By using the Freundlich isotherm equation, it is possible to study sorption processes occurring in various (non-ideal) solutions. The linear equation of this model can be expressed as follows (5).

$$\log q_e = \log K_F + (\frac{1}{n}) \log C_e \quad (5)$$

In this (9) equation: q_e – the amount of metal absorbed into the sorbent of a certain mass (mg/g), K_F- The Freundlich constant, C_e- the equilibrium concentration of a solution (mg/L), 1/n – the sorption intensity. The values K_F and n (n≈1–10) of the Freundlich constant are found by the angular value of the slope of the intersection on the linear graph of $\log q_e$ with $\log q_t$ [6, 7].

Thermodynamic analysis. In this study, the adsorption process at 293, 303, and 313 K temperatures was studied. It is possible to calculate the change in free energy of the process (6)

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

In the linear graph of $\ln K_e$ and 1/T, the values (11) of ΔH° and ΔS° are found by the angular value of the intersection slope [8].

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

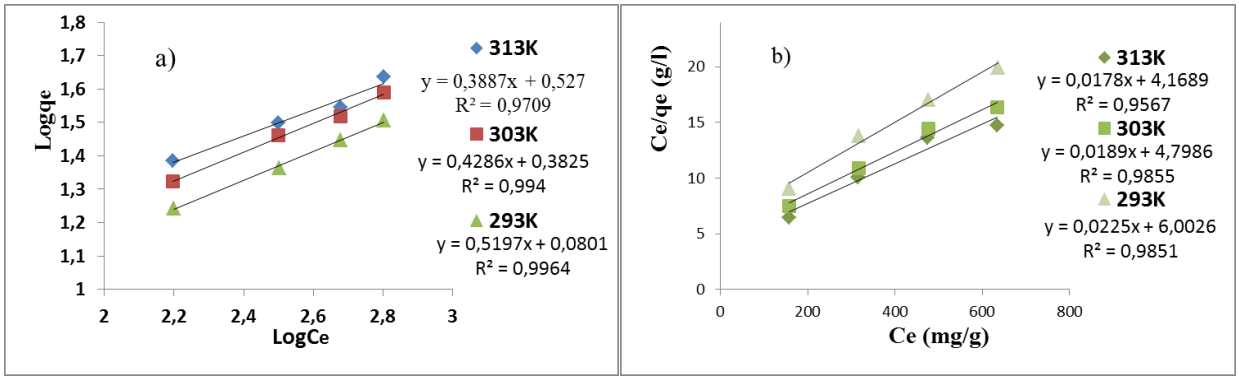

Figure 1 Friendlich (a) and Langmuir (b) isotherm models.

Correlation coefficients of Freundlich and Langmuir of absorption of metal ions to biosorbent are presented in the table below (Table 1).

Table 1. Freundlich and Langmuir correlation coefficients of adsorption.

T, K	Freundlich isotherm model	Langmuir isotherm model

	n	K_f	R^2	q_{max}	K_l	R^2_l	
293	1,924	1,202	0,99	44,44	0,24	0,07	0,98
303	2,336	2,412	0,99	52,63	0,253	0,076	0,98
313	2,577	3,365	0,97	56,18	0,273	0,08	0,95

Table 1 shows the correlation values of Freundlich and Langmuir sorption isotherms. From the results, Freundlich parameter (n) values were n=1.924, 2.336, 2.577. This indicates that the sorption of metal ions to the biosorbent is high. Langmuir isotherm R_L (R_L<1) values explain the favorable sorption. The R2 correlation values indicate that the adsorption process obeys the theory of Freundlich adsorption.

4.2. Thermodynamic analyses

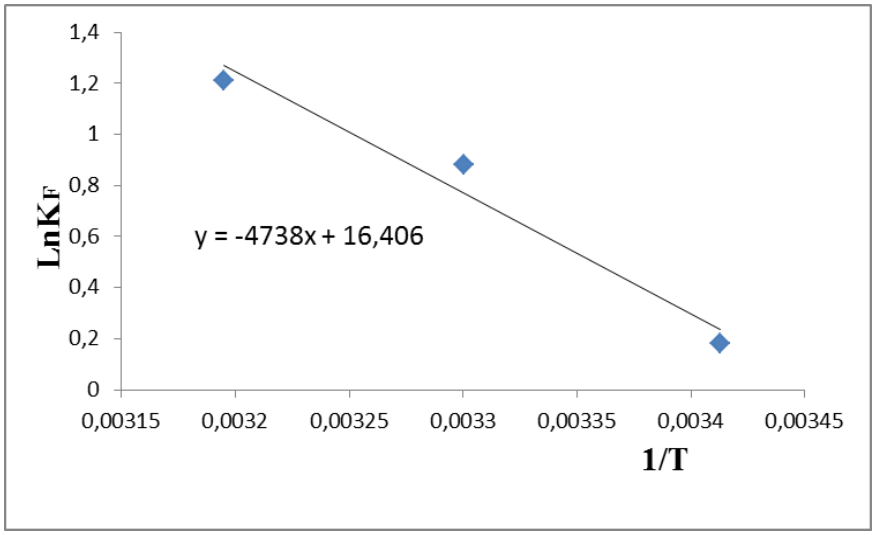

Figure 4.2.1. Thermodynamics of adsorption of Cu^{2+} ions on biosorbent.

Changes in thermodynamic parameters during the sorption of Cu^{2+} ions from solutions to biosorbent at temperatures of 293, 303 and 313 K were calculated (Table 2).

2 tables. Thermodynamic parameters of sorption of metal ions.

T, K	K_F, L/mol	$-\Delta G^0$, kJ/mol	$-\Delta H^0$, kJ/mol	ΔS^0 kJ/mol ·K
293	1,2	-0,444135677	-39,39173	136,35
303	2,41	-2,215904684		

313	3,36	- 3,153812182		

In the table, we can see that the values of free energy ($-\Delta G^0$) decrease with increasing temperature. This means that the process went by itself. A decrease in entropy ($-\Delta H^0$) indicates that adsorption is exothermic. A positive value of entropy (ΔS^0) indicates that there is an ion exchange process between the NH_2 functional group of the biosorbent and Cu^{2+} ions.

Conclusion

Based on the results, we can see the suitability of the Freundlich isotherm model for the sorption of Cu(II) ions to the biosorbent obtained by modifying the rice husk with urea. That is, it explains that the sorption took place between a solid-liquid medium and a decrease in free energy indicates that the process is spontaneous.

References

8. Singh, N. B., Nagpal, G., Agrawal, S., & Rachna. (2018). Water purification by using Adsorbents: A Review. Environmental Technology & Innovation, 11, 187–240. doi:10.1016/j.eti.2018.05.006

9. Phueng phai, P., Singjanusong, T., Kheangkhun, N., & Wattanakornsiri, A. (2021). Removal of copper(II) from aqueous solution using chemically modified fruit peels as efficient low-cost biosorbents. Water Science and Engineering. doi:10.1016/j.wse.2021.08.003

10. Bekcha nov, D., Mukhamediev, M., Lieberzeit, P., Babojonova, G., & Botirov, S. (2021). Polyvinylchloride-based anion exchanger for efficient removal of chromium (VI) from aqueous solutions. Polymers for Advanced Technologies, 32(10), 3995–4004. doi:10.1002/pat.5403

11. J. P. Simonin, (2016) "On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics," Chemical Engineering Journal, vol. 300, pp. 254–263.

12. N. Adina, G. Andreea, M. D. Corneliu, C. Mihaela, N. Petru, D. Narcis, and B. Alina. (2018) "Rare Earth Elements Removal from Water Using Natural Polymers," Scientific reports, vol. 8, no. 1, pp. 1-11.

13. K. R. Harikishore, Y. Harinath, K. Seshaiah, A.V.R. (2010) Reddy, "Bio-sorption of Pb(II) from aqueous solutions using chemically modified Moringa oleifera tree leaves," Chemical Engineering Journal vol. 162, no. 2, pp. 626–634.

14. Krstić, V., Urošević, T., & Pešovski, B. (2018). A review on adsorbents for treatment of water and wastewaters containing copper ions. Chemical Engineering Science, 192, 273–287. doi:10.1016/j.ces.2018.07.022

15. Ahmad , R., Kumar, R., & Haseeb, S. (2012). Adsorption of Cu^{2+} from aqueous solution onto iron oxide coated eggshell powder: Evaluation of equilibrium, isotherms, kinetics, and regeneration capacity. Arabian Journal of Chemistry, 5(3), 353–359. doi:10.1016/j.arabjc.2010.09.003