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BIOSORBENT BASED ON RICE HUSK FOR REMOVING COPPER AND NICKEL IONS FROM WASTEWATER

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Abstract

The adsorption of Cu (II) and Ni (II) ions from aqueous solutions by an adsorbent obtained by treating rice husks with an aqueous solution of monoethanolamine was studied. The structure of the adsorbent was studied using IR spectroscopy. It has been shown that adsorption reaches equilibrium within 60 minutes at an optimal pH value of 5–6. The adsorption process was found to correspond to the Freundlich model with high correlation coefficients. The resulting adsorbent can be used as an effective, inexpensive and environmentally friendly bioadsorbent for treating wastewater from heavy metal ions.

Keywords: *adsorption, rice husk, monoethanolamine, wastewater, modification, adsorption isotherm*

Introduction

One of the main pollutants of natural water bodies are heavy metals, which have toxic, mutagenic and carcinogenic properties. They tend to accumulate in living organisms, which leads to severe poisoning (Acharya J., Kumar U., & Rafi P.M., 2018). The main method of treating wastewater from heavy metal ions is reagent methods, which do not provide the required degree of water purification and lead to the formation of sludge that requires disposal. Recently, bioadsorbents based on agricultural waste, which are a cheap, annually renewable source of raw materials and do not pose a threat to the environment, are increasingly used to purify wastewater from heavy metal ions. Rice hulls, which are produced as a by-

product of the rice milling process, can also be used as an adsorbent. The composition of rice husks includes cellulose (32%), hemicelluloses (21%), lignin (21%) and silicon oxide (20%), which gives the structure mechanical strength. Due to the presence of three hydroxyl groups in cellulose, it has adsorption properties towards heavy metal ions. However, untreated rice husks have low adsorption capacity because the hydroxyl groups are linked by intermolecular hydrogen bonds, which makes it difficult for metal ions to reach them when extracted from solution. To increase the adsorption capacity of rice husk, methods of treatment with alkali, tartaric acid, and epichlorohydrin have been proposed (Zhang Y., Zheng, R., Zhao J., Zhang, Y., Wong P.K., & Ma F., 2013;

Wong K.K., Lee C.K., Low K.S., & Haron M.J., 2003; Shrestha, B., Kour J., Homagai P.L., Pokhrel M.R., & Ghimire K.N., 2013).

In this work, an adsorbent was obtained by treating rice husks with an aqueous solution of monoethanolamine to purify wastewater from Cu (II) and Ni (II) ions. This treatment leads to the destruction of hydrogen bonds between hydroxyl groups, increasing their availability for binding metal ions, as well as the introduction of amino groups into the structure of the adsorbent. In this case, metal ions bind to the hydroxyl and amide groups of the adsorbent through the mechanisms of ion exchange and complex formation (Sud, D., Mahajan, G., & Kaur, M.P., 2008).

Materials and methods

Rice husk samples were treated with a solution of monoethanolamine in water according to the method (Maksudova A., Adilova K., 2022). Component ratio: rice husk (1g): modifier solution (100ml) = 1:100. The treatment was carried out for 24 hours with con-

stant shaking. Next, the solution was filtered, the rice husks were washed with water and dried. IR spectroscopic studies of the original and modified rice husk were carried out using a Shimadzu “IRAffinity” IR-Fourier spectrometer (Japan). Wastewater solutions containing ions Cu (II) and Ni (II) with a concentration of 5–300 mg/l were prepared from the salts $\text{CuSO}_4 \times 5 \text{H}_2\text{O}$ and $\text{NiSO}_4 \times 7 \text{H}_2\text{O}$ by diluting the initial solution with distilled water.

Adsorption capacity studies were carried out in static mode. 100 ml of wastewater solution of a given concentration was poured into 250 ml flasks and 1 g of adsorbent was added. The flasks were kept for 60 minutes with constant shaking. Next, the solutions were filtered and the content of metal ions in water was determined using the atomic absorption method on an Agilent spectrophotometer Technologies 140 Series AA (France).

Results and discussion

IR spectra of the original and modified rice husk are shown in Figures 1 and 2.

Figure 1. IR spectrum of original unprocessed rice husk

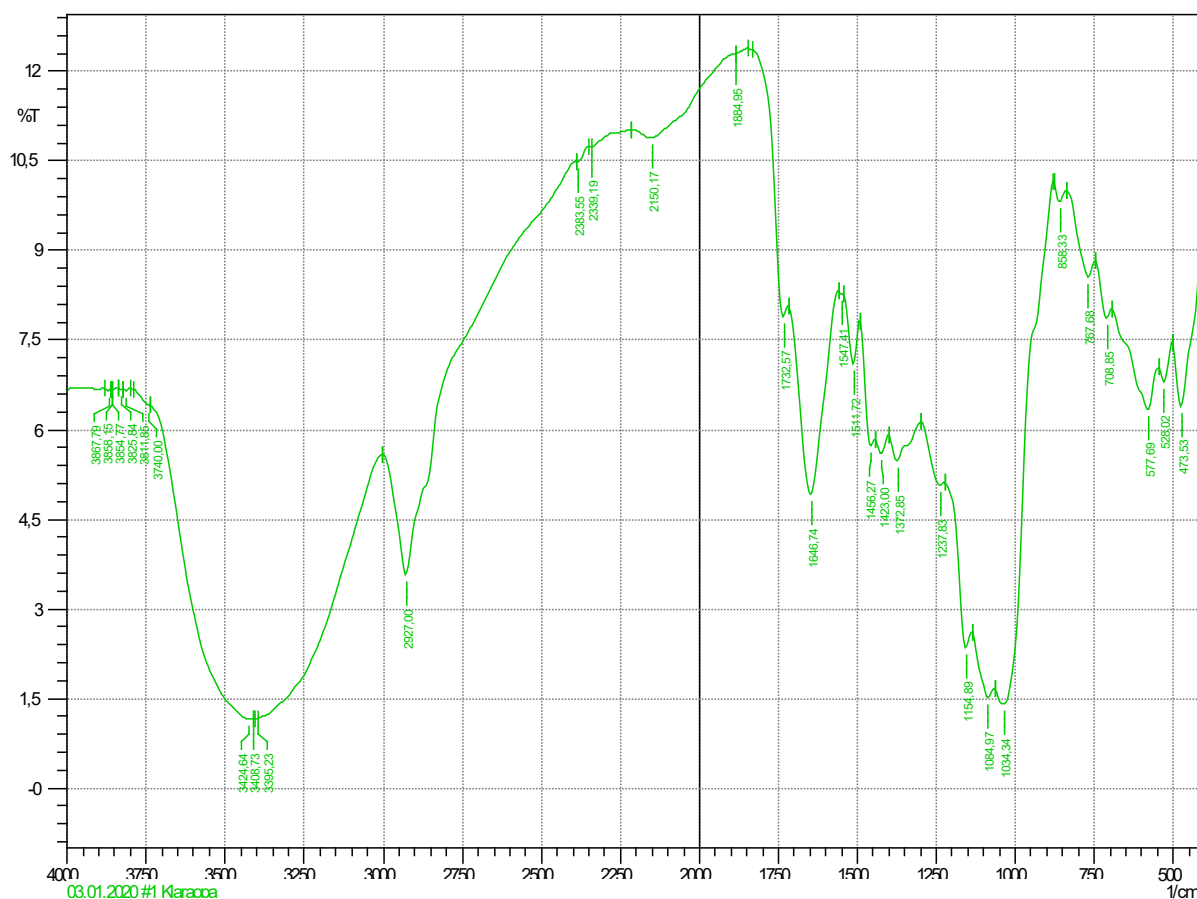
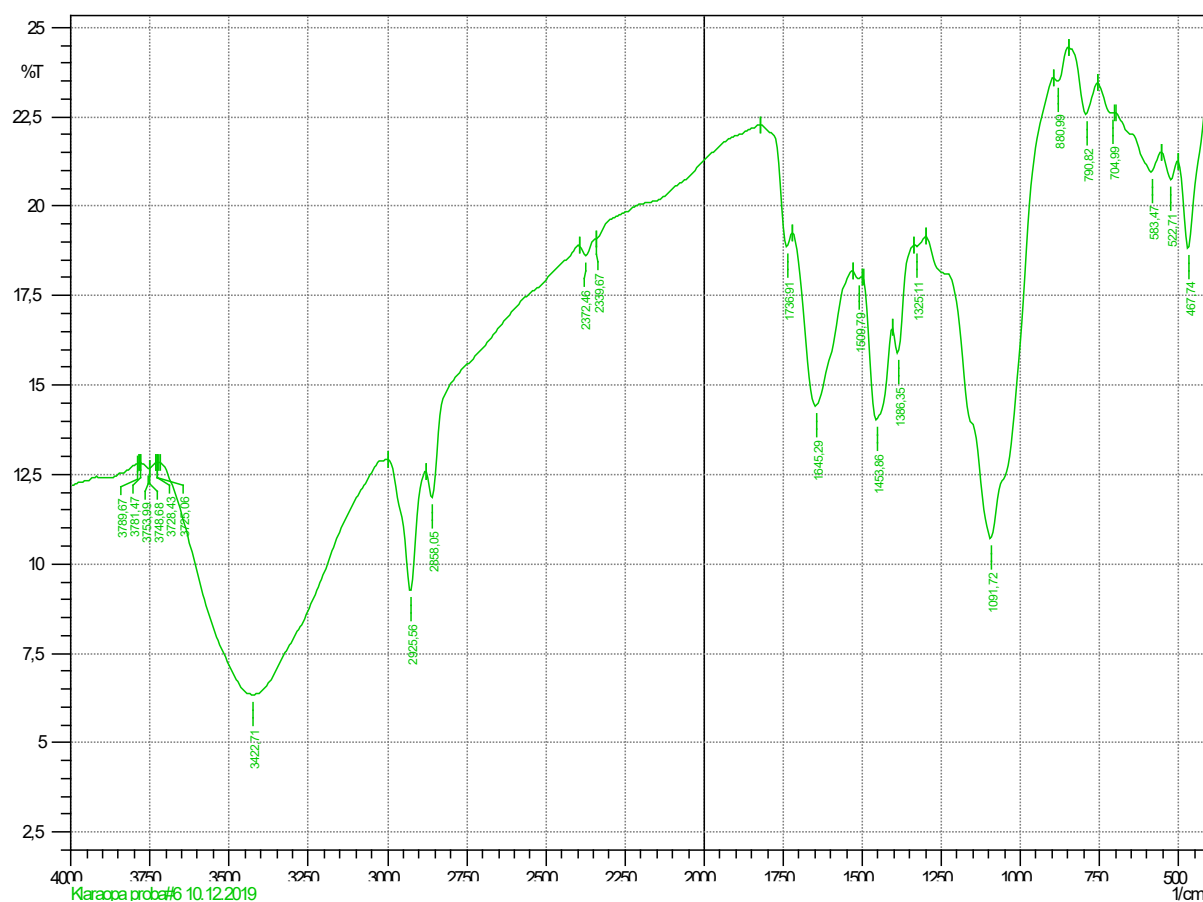


Figure 2. IR spectrum of modified rice husk



The IR spectra show that the band at 3395–3408 cm^{-1} , responsible for OH groups linked by hydrogen bonds, shifts to a value of 3422 cm^{-1} , which indicates the destruction of intermolecular hydrogen bonds. The absorption band in the region of 1732–1736 cm^{-1} corresponds to vibrations of the carbonyl group C = O of lignin. After treatment with monoethanolamine, the intensity of this peak decreases, indicating a decrease in the number of C = O groups that enter into chemical interaction with monoethanolamine molecules. The appearance of a specific absorption band at 1091 cm^{-1} in the IR spectra of the modified samples is associated with stretching of the C- N bond, which lies in the region of 1230–1030 cm^{-1} . This indicates the introduction of amino groups into the structure of the biosorbent.

When carrying out adsorption studies, the optimal pH values and adsorption time were determined at which the maximum absorption of metal ions was observed.

The adsorption value A ($\text{mg} \times \text{g}^{-1}$) was determined using the formula (Bonilla- Petrici-

olet A., Mendoza-Castillo D.I., & Reynel-Ávila, H.E., 2017):

$$q_e = \frac{(C_0 - C_e)V}{m \times 1000}$$

V – volume of the test solution, ml;

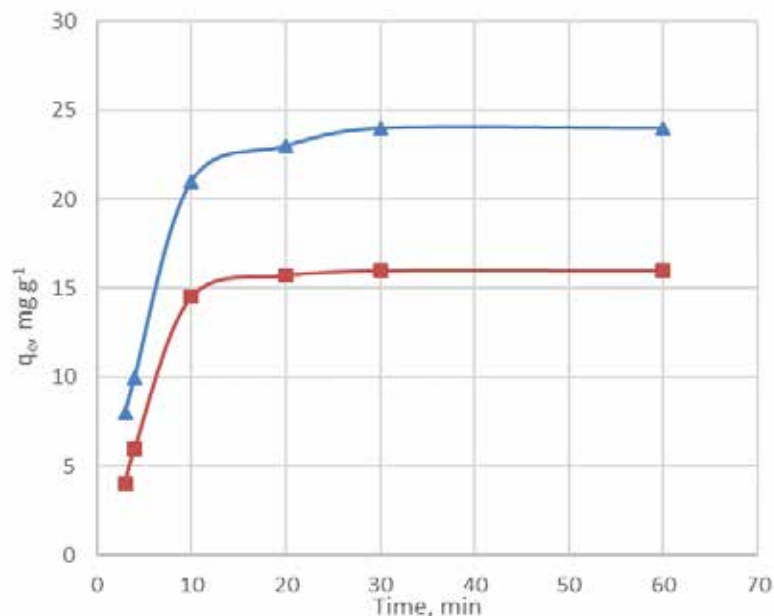
C_0 and C_e – initial and equilibrium concentration of metals in water, $\text{mg} \times \text{L}^{-1}$;

m – mass of adsorbent, g.

A study of the effect of pH on adsorption showed that the optimal pH value is in the range of 5–6. At low pH, H^+ ions, which have high mobility, are predominantly adsorbed on the surface of the adsorbent. This leads to the formation of a positively charged adsorbent surface, which reduces the adsorption of metals. With increasing pH, the concentration of H^+ ions in the solution decreases and the adsorption of metal cations increases due to electrostatic attraction to the negatively charged surface.

The dependence of adsorption on time is shown in Figure 3.

Figure 3. Dependence of adsorption of metal ions on contact time for \blacktriangle – Cu^{2+} ions and \blacksquare – Ni^{2+} ions



From Figure 3 it can be seen that at the beginning of the process, adsorption increases within 60 minutes balance is achieved. This is explained by the fact that at the beginning of the cleaning process there are enough active centers on the surface of the adsorbent capable of binding metal, after filling which the adsorption does not change. With an increase in the initial concentration of

solutions, an increase in adsorption was observed due to an increase in the driving force necessary for metal ions to overcome the forces of resistance to mass transfer between the aqueous and solid phases. But at the same time, the degree of purification decreases, which is explained by the limited number of active centers on the surface of the adsorbent.

Figure 4. Dependence of the degree of purification on the initial concentration of the solution: 1 – for Cu^{2+} ions, 2 – for Ni^{2+} ions

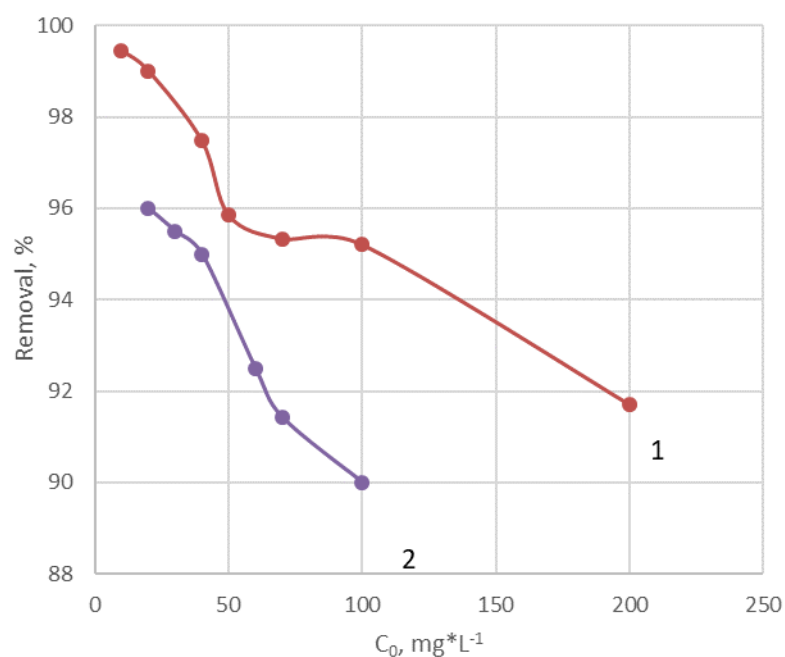


Figure 5. Adsorption isotherms: 1,2 – modified rice husk for copper and nickel ions, respectively, 3,4 – untreated rice husk for copper and nickel ions, respectively

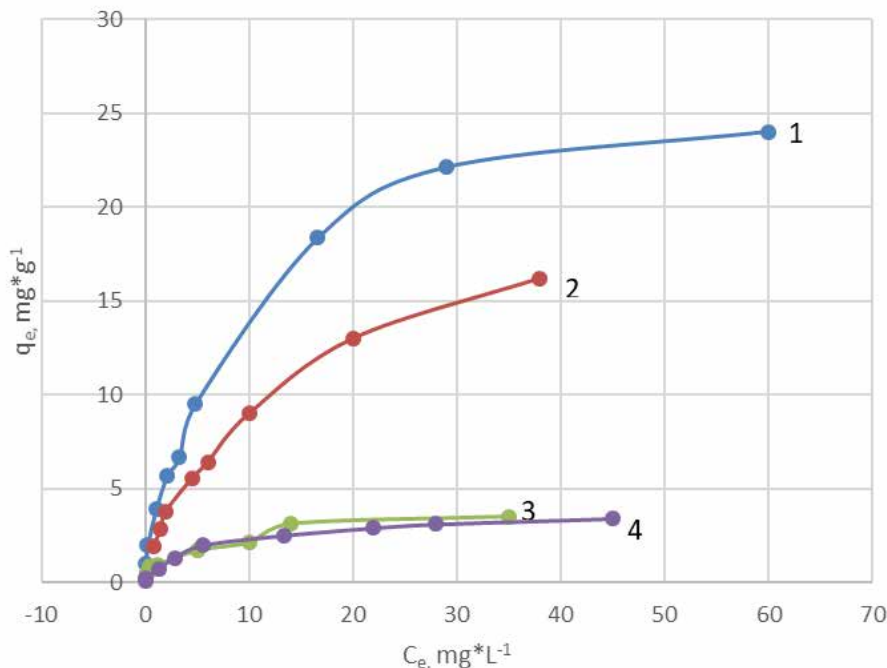


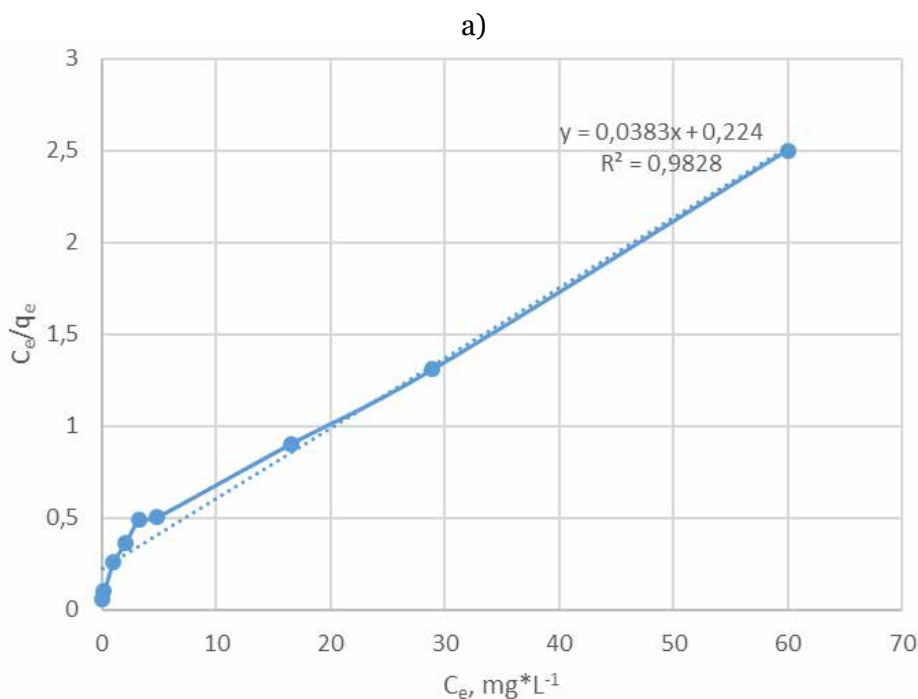
Figure 5 shows the adsorption isotherms of copper and nickel for the original and modified rice husks.

The linear form of the Langmuir equation (Langmuir I., 1916) is as follows:

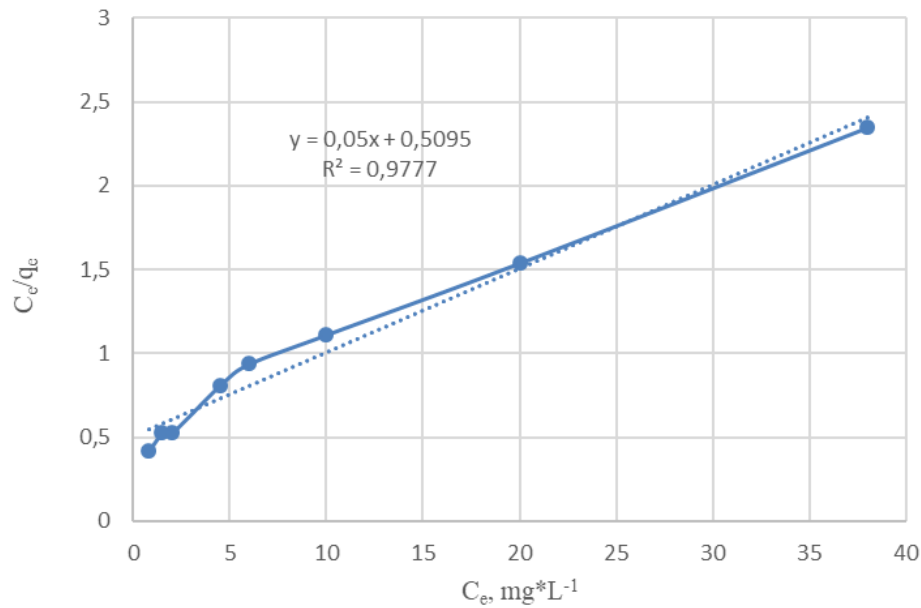
$$\frac{C_e}{q_e} = \frac{1}{q_m \times K_L} + \frac{C_e}{q_m}$$

To determine the coefficients of the Langmuir equation, a graph of the dependence of C_e/q_e on C_e was plotted in linear form. The value of q_m and the Langmuir constant were found from the tangent of the slope of the straight line and the section cut off on the axis of values C_e/q_e .

Figure 6. Graphs of the dependence of C_e/q_e on C_e : a – for copper ions, b – for nickel ions.



b)



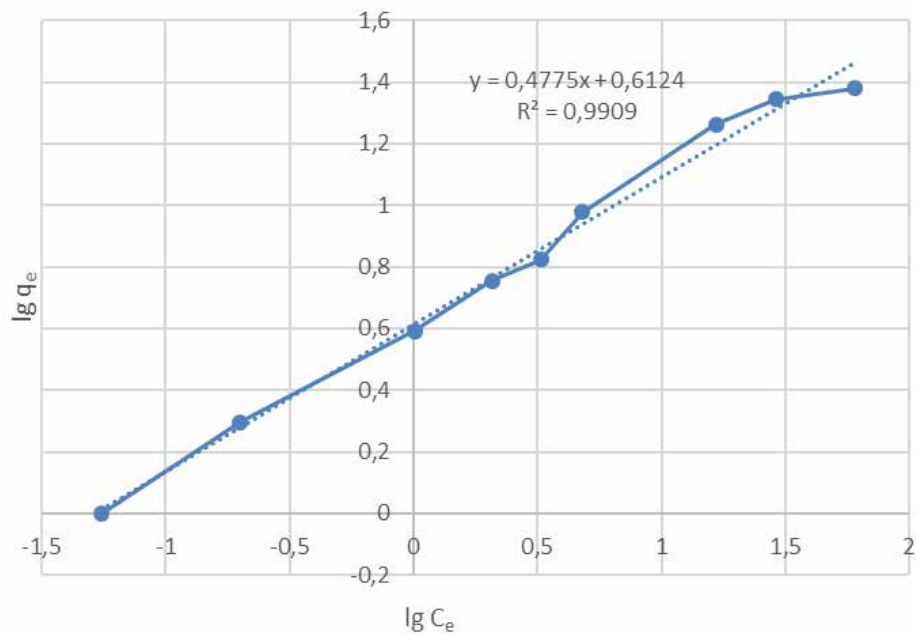
The Freundlich equation (Freundlich H. M. F., & Freundlich, H. M. F. (1906) in logarithmic form has the form:

$$\lg q_e = \lg K_F + \frac{1}{n} \lg C_e$$

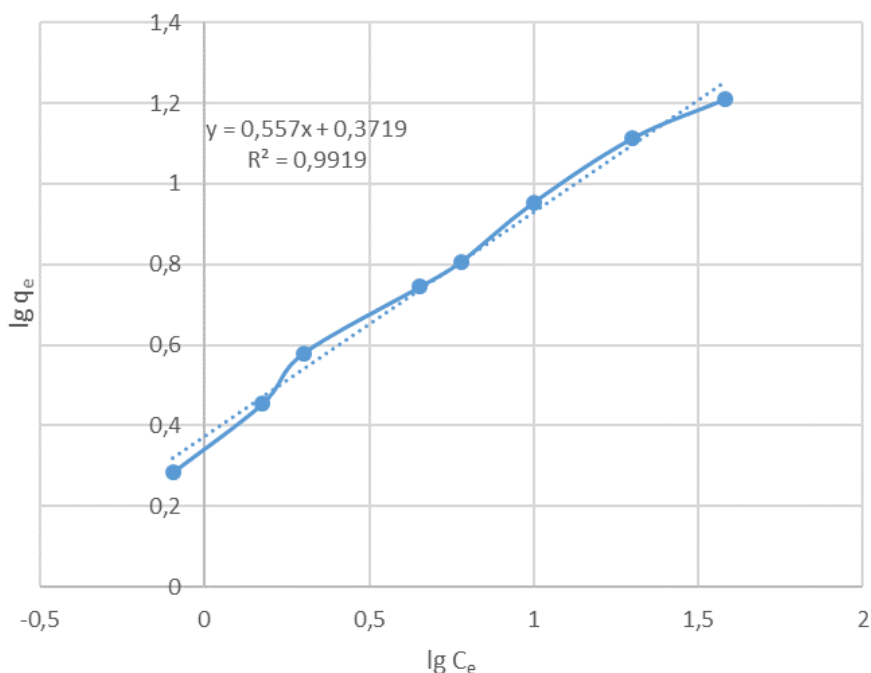
which allows you to graphically determine the constant parameters of the equation K_F and $1/n$.

Figure 7. Graphs of dependence $\lg q_e / \lg C_e$ in linear form: a – for copper ions, b – for nickel ions

a)



b)



The correspondence of each model to the experimental data was determined by the standard deviations R^2 .

The found adsorption parameters are given in Table 1.

Table 1. Adsorption parameters of the Langmuir and Freundlich models and correlation coefficients

Adsorbent	Freundlich model			Langmuir model		
	K_F	$1/n$	R^2	$K_l (l \times mg^{-1})$	$q_m (mg \times g^{-1})$	R^2
	Cu^{2+}					
Initial RH	0.957	0.3686	0.9759	0.392	3.604	0.963
Modified RH	4.096	0.4775	0.9909	0.171	26.109	0.9828
	Ni^{2+}					
Initial RH	0.716	0.4548	0.9893	0.273	3.5486	0.9854
Modified RH	2.355	0.557	0.9919	0.0981	20	0.9777

The correlation coefficients R^2 show that the adsorption process is better described by the Freundlich equation compared to the Langmuir equation. This suggests the participation of functional groups in the inner layers of the adsorbent in the binding of metal ions. Values $n > 1$ indicate the spontaneous nature of adsorption.

Conclusion

The results of the study showed that adsorbents obtained by chemical treatment of rice husks with an aqueous solution of mon-

oethanolamine can be used as effective, inexpensive and environmentally friendly bioadsorbents for treating wastewater from copper and nickel ions. The introduction of amide groups leads to an increase in the number of active sites for the binding of metal ions. Adsorption isotherms are better described by the Freundlich equation than by the Langmuir equation, which suggests the participation of functional groups of the internal layers of the adsorbent in the binding of metal ions.

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