European Science Review 2024, No 1–2.
ISSN 2310-5577

PREMIER Publishing
ppublishing.org

# Section 2. Engineering science in general

DOI:10.29013/ESR-24-1.2-10-15



## STUDY OF THE ADSORPTION PROCESS OF HEAVY METAL IONS BY MODIFIED RICE HUSK

***Maksudova Aziza*** [1], ***Mutalov Shukhrat*** [2] ***and Adilova Klara*** [1]

[1] "Industrial Ecology" Department, Tashkent Institute of Chemical Technology

[2] "Industrial Ecology" Department, Branch Tashkent Institute of Chemical Technology in Shakhrisabz city

***Cite:*** *Maksudova, A., Mutalov, S. Adilova K. (2024). Study of the adsorption process of heavy metal ions by modified rice husk. European Science Review 2024, No 1–2.* https://doi.org/10.29013/ESR-24-1.2-10-15

**Abstract**

Adsorption of heavy metal ions is an important aspect for purifying water from pollutants and ensuring environmental safety. In this study, the adsorption process of heavy metal ions was studied using modified rice husk as an adsorbent. Experimental studies included determining optimal conditions for maximum removal of metals from aqueous solutions, including varying parameters such as contact time and pH of the medium, as well as studying changes in the structure of the surface layer of the resulting adsorbent. The results showed the effectiveness of modified rice husk in the adsorption process of heavy metal ions, highlighting its potential as a promising material for wastewater treatment.

**Keywords:** *adsorption, heavy metal ions, rice husk, monoethanolamine, wastewater, pH, kinetics.*

### Introduction

In recent years, the problem of rational use of water resources necessary to support various aspects of human life has become increasingly urgent. For the countries of Central Asia, located in an arid zone with low humidity, this problem is not limited only to a shortage of water resources, but is also associated with a deterioration in their quality. Along with the lack of drinking water, pollution of surface and groundwater by wastewater from industrial enterprises becomes an important aspect.

According to many studies conducted to monitor the condition of the Chirchik and Akhangaran rivers, which are the main sources of industrial and municipal drinking water supply for a significant part of the population, it was revealed that the water quality parameters in them do not meet the established standards in terms of biochemical oxygen demand (BOD), chemical oxygen consumption (COD), nitrogen content and heavy metals exceeding the maximum permissible concentrations (Usmanov et al., 2019).

Among the main sources of river pollution are discharges of insufficiently treated industrial wastewater from enterprises involved in the production of mineral fertilizers, such as JSC "Maksam-Chirchik" and the Almalyk Mining and Metallurgical Combine.

The wastewater from these enterprises contains particularly dangerous heavy metal ions, such as copper, zinc, nickel, and lead, which have toxic, carcinogenic and mutagenic properties. They can accumulate in the body, causing serious illness. Therefore, the problem of cleaning industrial and domestic wastewater, as well as preparing water for technical and municipal drinking needs, is becoming more and more important every year.

The most common methods for treating wastewater from heavy metal ions are reagent methods, which consist in converting them into insoluble metal hydroxides and their precipitation in the form of sludge. However, with the increase in the volume of wastewater generated and the tightening of sanitary requirements for the quality of treated water, these methods currently do not provide the required degree of water purification. This leads to pollutants entering natural water bodies and, as a result, entering the human body through the food chain.

Another significant problem is the use of outdated treatment plants in many plants. These installations require upgrades to improve efficiency, which entails significant costs. Ensuring compliance with hygiene standards under such conditions becomes extremely challenging. In such situations, the most reasonable solution is to use wastewater tertiary treatment methods after the reagent treatment process. One of the effective post-treatment methods is the adsorption method.

Bioadsorbents are increasingly used in wastewater treatment practice, they have significant efficiency and a number of advantages over synthetic sorbents, such as high adsorption capacity, environmental safety, availability, low cost, the possibility of reuse and regeneration, as well as a wide range of applications (Kyzas, Kostoglou, 2014).

The main objective of this study was to obtain rice husk based adsorbent through chemical modification using monoethanolamine for purification of wastewater from heavy metal ions generated at the JSC "Maksam-Chirchik" during the production of mineral fertilizers.

Rice husk has attracted the attention of researchers due to its availability and low cost. It is insoluble in water, has high mechanical strength and chemical stability. Its feed value is low, and transportation costs are significant, especially when used at a considerable distance from the place of formation.

Rice husk consists of lignin (21%), cellulose (42%), hemicellulose (21%), and the inorganic part consists of silica (20%) (Sud et al., 2008).

## Research methods

The process of binding metal ions is due to the presence of hydroxyl groups in the structure of the adsorbent. To increase the adsorption capacity of rice husks, treatment with alkaline reagents is most often used.

In this study, the adsorbent was obtained by chemical modification of rice husk using an aqueous solution of amino alcohol (monoethanolamine) at a certain component ratio: 1 g of rice husk per 100 ml of modifier solution. The treatment process was carried out for 24 hours at room temperature. The solution was then filtered, and the rice husks were washed with water and dried.

The resulting adsorbent was used to purify wastewater from copper ions Cu (II) and nickel Ni (II). To analyze the adsorption capacity, 100 ml of a wastewater solution of a given concentration and 1 g of adsorbent were added to 250 ml flasks. The flasks were kept for 60 minutes with constant shaking. Then the solutions were filtered, and the content of metal ions in water was determined using the atomic absorption method using an Agilent spectrometer Technologies 140 Series AA (France).

## Effect of pH on adsorption

The impact of pH on adsorption was investigated using a PXSJ-216 F pH-meter (manufactured in China). For the experiment, 100 ml of a solution containing Cu(II) and Ni(II)ions at a concentration of 50 mg ×

× l–1, along with 1 g of the adsorbent sample, were placed in 200 ml flasks. The pH of the water in each flask was adjusted within the range of 2 to 8 using 0.1N HCl and NaOH solutions. The flasks' contents were then agitated on a PS-1 BioSan shaker at 150 rpm for 60 minutes at a temperature of 20 °C. Subsequently, the water was filtered, and the metal content was determined using flame atomic absorption spectrophotometry.

### Characteristics of surface morphology

Studying the surface of rice husks allows one to analyze changes in the surface structure after treatment, assess the possibility of the formation of a porous structure, and also evaluate the structural features of adsorbed molecules. A high-magnification microscope allows one to visualize the "fixation" of molecules of adsorbed substances on the surface of rice husk grains. To analyze the surface structures of rice husk grains, a ZEISS EVO LS15 SEM microscope (Germany) was used in this study.

### Effect of contact time on adsorption

The study of the influence of the contact time of the test solution on adsorption was carried out in flasks with a volume of 250 ml containing 100 ml of waste water of a given concentration and 1 g of adsorbent. The contents of the flask were continuously stirred on a shaker at a temperature of 20 °C for a certain time. The contact time ranged from 2 minutes to 2 hours. At certain intervals, water samples were filtered and the metal content in water was determined by the atomic absorption method.

The kinetic data on the sorption of metal ions were analyzed in accordance with the pseudo-first and pseudo-second order kinetic equations.

Pseudo-first-order kinetic equation (Lagergren's equation) has the form of (Thajeel, 2013):

$$\frac{dq_t}{dt} = K_1\left(q_e - q_t\right), \qquad (1)$$

where $q_t$ and $q_e$ — the amount of metal ions adsorbed at a given time and in a state of equilibrium (mg × g$^{-1}$); $K_1$ is the rate constant of the sorption process of the first order (min$^{-1}$).

Ho and McKay's model (Ho & Mckay, 1999) describes the kinetic patterns of adsorption in terms of pseudo-second order rates (Ho & Mckay, 1999; Ho & McKay, 2002; Thajeel, 2013).

$$v = \frac{dq_e}{d\tau} = k_2\left(q_{e\infty} - q_{e\tau}\right)^2, \qquad (2)$$

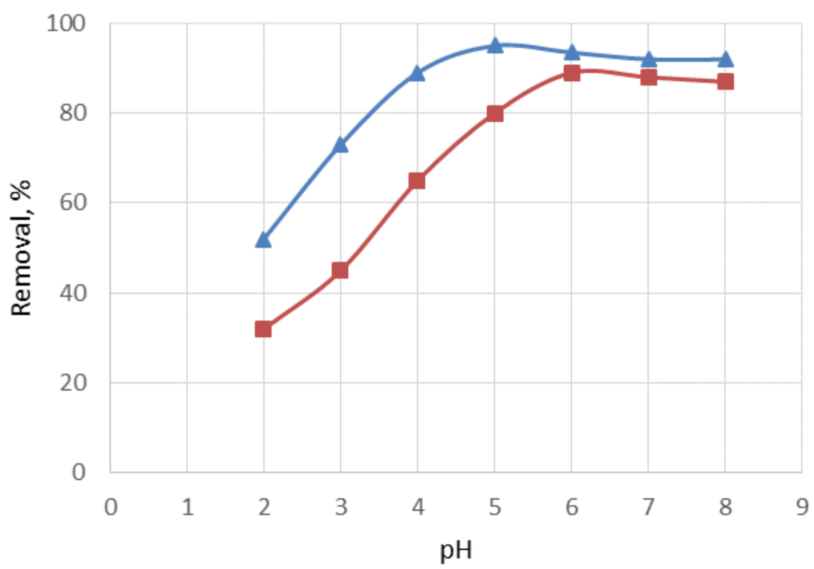
where $k_2$ is the pseudo second order rate constant (g × mg$^{-1}$ × min$^{-1}$, g × mg$^{-1}$ × h$^{-1}$).

## Results

### *Effect of pH on the adsorption*

As noted in the literature (Witek-Krowiak et al., 2011), the pH of the solution plays a significant role in the adsorption process. To assess the effect of solution pH on the adsorption of metal ions, studies were carried out in the range of values from 2 to 8.

**Figure 1.** *Dependence of adsorption on pH for ions ▲ — $Cu^{2+}$ and ions ■ — $Ni^{2+}$*



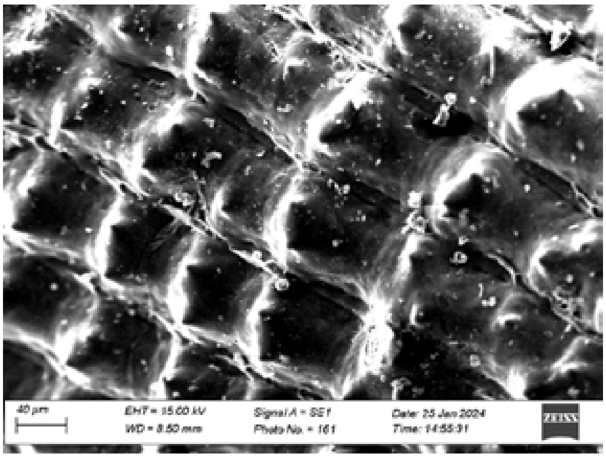
With an increase in the pH of the solution, an increase in the degree of purification of wastewater from copper ions is observed from 52% at pH = 2 to 95% at pH = 5, and for nickel ions — from 32% to 89%, respectively. Further, adsorption remains practically unchanged at pH values of 6 and higher. Changes in pH affect the surface charge of the adsorbent and the degree of ionization of metal compounds in solution. At low pH values, $H^+$ ions, which have high mobility, predominate, which leads to the formation of a positively charged adsorbent surface and a decrease in the adsorption of metal cations. With increasing pH, the concentration of $H^{+}$ ions in the solution decreases, which leads to the formation of a negatively charged adsorbent surface and an increase in the adsorption of metal cations due to an increase in electrostatic attraction. Based on this, all subsequent experiments were carried out at optimal values of pH = 5 for copper ions and pH = 6 for nickel ions.

### ***Characteristics of surface morphology***

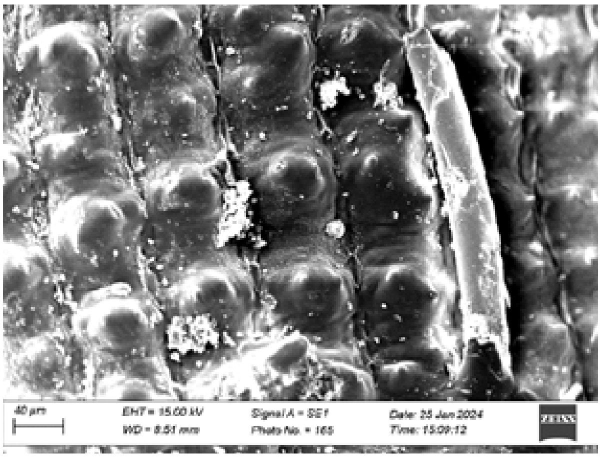
Scanning electron micrographs of untreated rice husk and modified rice husk are shown in Figure 2.

**Fig 2.** *Scanning electron micrographs of: a) unprocessed rice husk and b) modified rice husk*

*a)*




*b)*




At low magnification of the electron microscope, some cone-shaped and raised contours can be observed on the surface of the untreated rice husk in Figure 2(a). The morphological structure of the surface of the modified rice husk is shown in Figure 2(b). Numerous “dot spots” are observed on the cell wall, which may indicate a violation of the integrity of the surface structure of the adsorbent, which helps to increase the adsorption of metal ions by increasing the number of active binding sites.

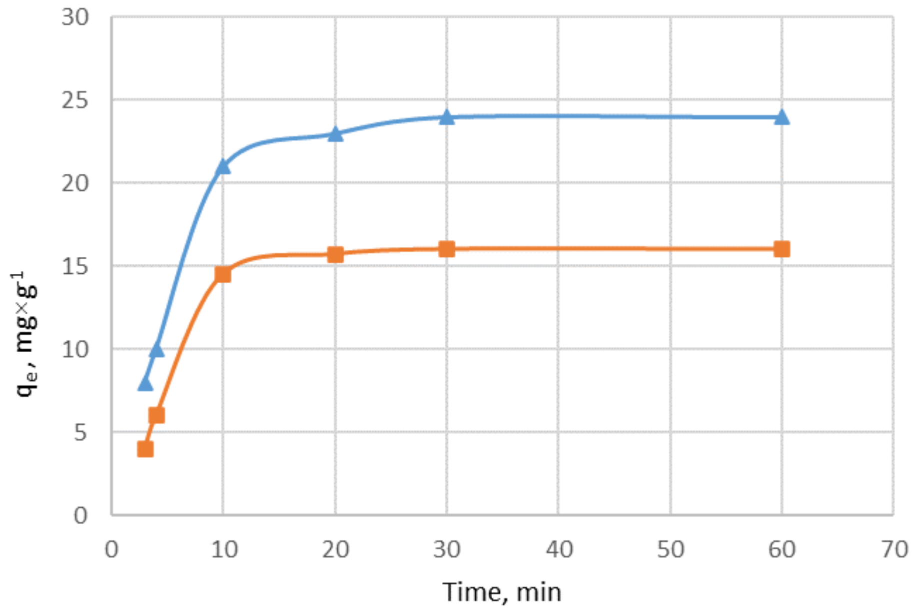
Apparently, the fats, proteins and soluble polysaccharides in the rice husk were dissolved after treatment with monoethanolamine, resulting in an improvement in the physicochemical properties of the rice husk and an increase in its adsorption capacity.

### **Effect of contact time on adsorption**

The influence of the contact time at different initial concentrations of solutions was studied. The dependence of adsorption on time is shown in Fig. 3.

Figure 3 shows that during the first 10 minutes there was a rapid increase in adsorption, which amounted to 21 mg × $g^{-1}$ for copper ions and 14.5 mg × $g^{-1}$ for nickel ions, then there is a slowdown in the adsorption rate up to 30 minutes, and then the adsorption changes insignificantly up to 60 minutes, after which it remains constant, indicating that equilibrium has been reached. This is explained by the fact that at the beginning of the purification process, there are enough active centers on the surface of the adsorbent capable of binding the metal, and after the filling of the surface layers, the internal pores of the adsorbent are filled.

**Figure 3.** *Dependence of the adsorption of metal ions on the contact time for ions ▲ C u(II) and ■ Ni(II)*




The kinetic parameters of the process of adsorption of Cu(II) and Ni(II) ions by an adsorbent based on rice husks are shown in Table 1.

**Table 1.** *Kinetic parameters of the process of adsorption of Cu(II) and Ni(II) ions*

| Adsorbent | Metal | Temperature (K) | Pseudo first order equation | | | Pseudo second order equation | | |
|---|---|---|---|---|---|---|---|---|
| | | | $K_1$ ($min^{-1}$) | $q_e$ ($mg \times g^{-1}$) | $R^2$ | $K_2$ ($g \times mg^{-1} \times min^{-1}$) | $q_e$($mg \times g^{-1}$) | $R^2$ |
| Modified rice husk | Cu (II) | 293 | –0.095 | 24 | 0.976 | 0.00539 | 27.3224 | 0.990 |
| | | 303 | 0.064 | 26 | 0.9382 | 0.0090 | 27.7777 | 0.998 |
| | | 313 | 0.079 | 27.5 | 0.9437 | 0.01667 | 28.490 | 0.999 |
| | Ni(II) | 293 | –0.084 | 16 | 0.971 | 0.00548 | 19.0839 | 0.974 |
| | | 303 | –0.080 | 18 | 0.9329 | 0.010903 | 19.56947 | 0.996 |
| | | 313 | –0.076 | 20 | 0.9167 | 0.01553 | 21.0526 | 0.999 |

It can be seen from the data presented that the values of the correlation coefficients $R^2$ equal to 0.990 for Cu (II) ions and 0.974 for Ni(II) ions for the pseudo-second order model is higher than for the pseudo-first order model with $R^2$ 0.976 and 0.971 for Cu(II) ions Ni (II), respectively, which indicates that the adsorption process is better described by the pseudo second order kinetic model.

## Discussion

Research has confirmed that adsorbents prepared by chemically treating rice husks with an aqueous solution of monoethanolamine are significantly effective in removing copper and nickel ions from aqueous solutions. This rice husk modification method exhibits excellent adsorption properties, especially under optimal conditions such as certain pH values and contact times. Moreover, this approach offers a cost-effective solution given the availability and low cost of the starting material. Thus, modified rice husk with monoethanolamine can be considered as a promising adsorbent for effective water purification from heavy metal ions, which opens up potential for widespread use in industry and in the field of environmental safety.

## References

Usmanov, I. A., Makhmudova, D. I., Khodzhaeva, G. A., Musaeva, A. K. (2019). Environmental monitoring of the state of the Chirchik and Akhangaran rivers to develop measures for their protection. Ecology and aquatic economics,– No. 1(01).– P. 30–45.

Kyzas, G. Z., Kostoglou, M. (2014). Materials,– 7,– P. 333–364. Doi:10.3390/ma7010333

Sud, D., Mahajan, G., Kaur, M. P. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqu eous solutions – A review. In Bioresource Technology (Vol. 99, Issue 14). URL: https://doi.org/10.1016/j.biortech.2007.11.064

Thajeel, A. S. (2013). Isotherm, Kinetic and Thermodynamic of Adsorption of Heavy Metal Ions onto Local Activated Carbon. *Aquatic Science and Technology,*– 1(2). URL: https://doi.org/10.5296/ast.v1i2.3763

Ho, Y. S., & Mc Kay, G. (1999). Pseudo-second order model for sorption processes. In *Process Biochemistry* (Vol. 34).

Ho, Y. S., & Mc Kay, G. (2002). Application of kinetic models to the sorption of copper (II) on to peat. *Adsorption Science and Technology,*– 20(8). URL: https://doi.org/10.1260/026361702321104282

Witek-Krowiak, A., Szafran, R. G., & Modelski, S. (2011). Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent. *Desalination,*– 265(1–3).– P. 126–134. URL: https://doi.org/10.1016/j.desal.2010.07.042

submitted 10.02.2024;
accepted for publication 28.02.2024;
published 23.03.2024

Contact: aziza.maksudova2015@gmail.com