

Green Approach for Heavy metals removal from Polluted Water

Huda Yousif, Kafia M. Surchi
Department of Chemistry, College of Science, Salahaddin University
Erbil, Kurdistan, Iraq

Abstract - Natural agricultural waste like rice husk without chemical treatment provides sustainable, safe, and non-polluting procedure for heavy metal removal from aqueous systems. The goal of the present study was to provide information about adsorptive affinity of locally available rice husk for heavy metals removal. The influence of different adsorption parameters on the selectivity and sensitivity of the removal process was investigated. The studied parameters were: pH, contact time, initial metal concentration, adsorbent/metal ion ratios and interfering ions (0.1-0.4 M) Na, K, and Ca. The efficiency of rice husk for Cu, Ni, and Zn removal were; 85.0, 63.5 and 88.3 respectively at 0.8 gml⁻¹adsorbent dose. The experimental kinetic data were analyzed using pseudo-first order, pseudo-second order, and Elovich models. The pseudo-second-order kinetic model gave a better fitting of the kinetic data for Cu, Ni, and Zn removal. Fourier Transform Infra Red (FTIR) analysis confirms the complexation of Cu, Ni, and Zn with functional groups present in the RH.

Keywords- Adsorption kinetic, Rice husk, heavy metals, wastewater

1 Introduction

The problem of removing pollutants from water is an important process and is becoming more important with increasing industrial activities. The greater environmental awareness in both the public and regulatory sphere in recent years has necessitated greater treatment of industrial effluent. As such there has been a great deal of research into finding cost-effective methods for the removal of contaminants from wastewater [1].

Adsorption has advantages over other methods for remediation of heavy metals from wastewater because it's simple design, it is sludge-free and can be of low capital intensive [2-4].

In recent years considerable attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using agricultural materials. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, renewable, and reduce the residues whose disposal becomes major costly problem, and are more efficient are seem to be viable option for heavy metal remediation.

Many researchers utilized agricultural wastes such as pecan, walnut, sugarcane bagasse, cotton, coconut coir in natural or modified form for metal adsorption [5,6].

Agricultural wastes such as rice husk are environmentally friendly due to their unique chemical composition. Rice husk contains high property of cellulose (28-36%), Hemicelluloses and lignin as main component in addition to ash [7-9].

Our goal in the present study was to determine whether, locally present rice husk would have an acceptable efficiency for removing Cu, Ni, and Zn.

Using rice husk without chemical modification (additives free) offered several advantages including cleaner system as well as a simple experimental and work-up procedure which provides sustainable, safe, and non-polluting procedure for heavy metal removal from aqueous systems

2 Materials and methods

Locally available rice husk was collected from a pre-consumer agricultural product process industry located at Aqrea, Erbil, Kurdistan, Iraq. The adsorbent material was washed, oven dried at 100°C for 24 hours, ground and then sieved to various size (10, 40, 60 mesh) thereafter stored at room temperature until use [10].

FTIR spectra were obtained on powdered rice husk (before and after adsorption) mixed with KBr and placed in a diffuse-reflectance cell of an Infinity Avatar 360 FTIR-8201PC (Shimadzu).

Preliminary experiments were done to find out suitable condition for efficient removal of the studied metal ions. In each kinetic experiment, 0.8g of rice husk was mixed with 10 mL of metal ion solution at different initial concentrations (10, 20, and 30 µgml⁻¹). The mixtures were shaken continuously at temperature controlled (20±1°C) water bath shaker (MODEL YCW-012S, GEMMYCO) at 185rpm. The samples were removed at different time periods (10, 20, 30, 40, 60, 90, 120, 180, 300, 630, 1440 min). At the end of each time, adsorbent was separated from the solution and the remaining metal ion concentrations were analyzed by Atomic Absorption Spectrophotometer, AAS11. The same procedure was followed to study the effect of pH (2-10), contact time, initial metal ion concentrations, solid: liquid ratio, interfering ions (0.1-0.4 M) Na, K and Ca ions and adsorption of each studied ion from mixture of their ions.

Corresponding author
Tel.:00964 750 455 8666
E-mail address: ksvme@yahoo.com, kafia.surchi@yahoo.com
Azady, Hady Jawshly Street, Erbil, Kurdistan, Iraq

3 Results and Discussion

Batch experiments were carried out to find out the optimum condition for adsorption of Cu, Ni and Zn on Rice husk, adsorption capacity $q_t, \mu\text{gg}^{-1}$, was determined using the formula[11]:

$$q_t = \frac{C_o - C_t}{m} * V \quad (1)$$

Where C_o and C_t (μgml^{-1}) are the initial and final concentration of metal in solution, V (ml) is the volume of solution and m (g) is the adsorbent mass. All kinetic experiments were done at $20 \pm 1^\circ\text{C}$, 0.8 g/10ml and adsorption particle size of 60 mesh.

3.1 Factors Affecting the Adsorption Capacity

3.1.1 Effect of contact time

Aqueous metal ion solutions with different C_o were kept in contact with the adsorbent for 24h. The removal of Cu, Ni, and Zn by rice husk was increased with time and attained a maximum value at about 180 min thereafter, it remained almost constant. During the first minutes of contact time, the rate of metal ion removal is found to be very rapid (Fig.1). During the initial stage of adsorption, a large number of vacant surface sites are available for adsorption. After lapse of sometime, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute species on the solid surface and the bulk phase[10].

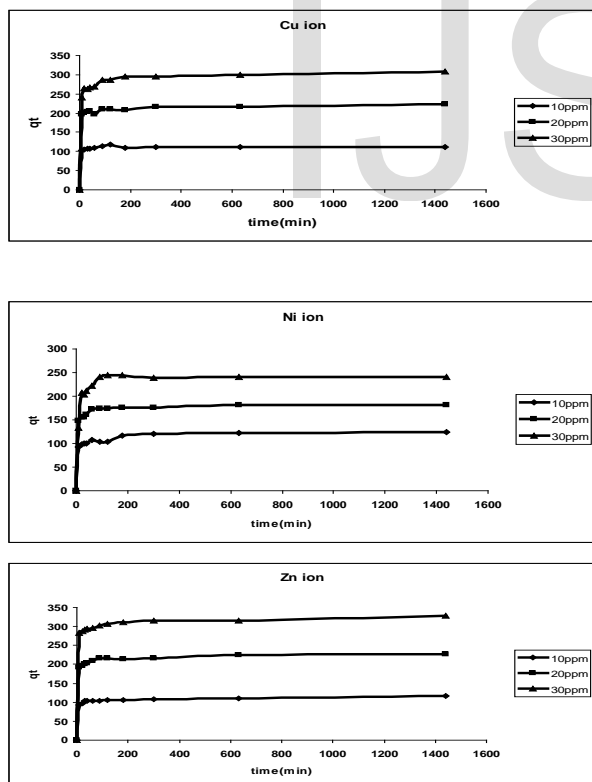


Fig. 1- Effect of contact time on Cu, Ni and Zn removal by rice husk.

3.1.2 Effect of initial metal ion concentration

The effect of C_o on the extent of adsorption of Cu, Ni, and Zn by rice husk is shown in Fig. 1. Adsorption capacity of rice husk was increased with increase in initial metal ion concentration.

The metal uptake mechanism is particularly dependent on C_o , at low metal ions are adsorbed by specific sites, while with increasing the concentration the specific sites are saturated so the exchange sites are filled[10].

3.1.3 Effect of adsorbent dose

Adsorption experiments were carried out at the different adsorbent dose values of 0.3, 0.5, 0.8, 1 g while keeping the volume of the metal solution constant (10ml). The results of the effect of adsorbent dose on the percentage of removal of Cu, Ni, and Zn showed that adsorption percentage increases with the increase in the amount of the adsorbent (Table 1). This can be explained by a greater availability of the exchangeable sites or surface area at higher amount of the adsorbent[10].

Table 1- Effect of adsorbent dose on its removal efficiency.

Adsorbent dosage(g/10ml)	Cu %	Ni %	Zn %
0.3	84.0	60.4	78.1
0.5	84.4	61.4	83.0
0.8	85.0	63.5	88.3

3.1.4 Effect of adsorbent particle size

Adsorption of Cu and Zn was found to increase with the increase in the mesh sizes (decrease in particle size). This is due to increase in the surface area of the adsorbents and accessibility of the adsorbent pores towards the metal ion. Other low cost adsorbents such as saw dust showed similar effect of particle size[6].

3.1.5. Effect of pH

The chemical speciation of metal ions under the influence of the solution pH may partly affect the adsorption efficiency of the adsorbent. The effects of solution pH were examined by varying the initial pH of the solution from pH 2 to 10. Data in table 2 show that adsorption capacity of rice husk for Cu, Ni, and Zn was increased with increasing the suspension pH up to pH 6. Adsorption capacity recorded its minimum values at pH 2, this can be justified on the bases adsorbent surface charge and the presence of H^+ in the solution. At low PH metal ions compete with the H^+ in the solution for active site and therefore lower the adsorption capacity. At high PH, the adsorbent surface has a higher negative charge which results higher attraction force. These data were in agreement with that obtained for other biomasses such as coffee residues[12], coca shells[13] and saw dust [14].

Table 2 Effect of pH on adsorption capacity of rice husk for Cu, Ni, and Zn removal.

pH	Cu q_e	Ni q_e	Zn q_e
2	76.8	10.3	87.5
4	95.3	54.8	123.1
6	99.1	76.8	119.3
8	94.0	88.5	117.0
10	92.9	88.1	115.5

3.1.6 Effect of interfering ions

In reality the contaminated water contains several other ions which can affect the adsorption of heavy metals. Some of the major concerns arising from the adsorption of heavy metals from wastewater is the simultaneous presence of miscellaneous metals such as alkaline, earth alkaline metals such as Na, K, and Ca, and heavy metals in wastewater.

3.1.6.1 Effect of alkaline and earth alkaline metals

Alkaline and earth alkaline metals such as Na, K, and Ca compete heavy metals for adsorption sites, especially for non-specific sites. The effect of the presence of interfering ions on the removal of Cu, Ni and Zn on rice husk was investigated in the presence of 0.1-0.4 M Na, Ca and K. Data in Table 3 show irregular effect of the presence of Na, Ca and K on adsorption capacity of rice husk for Cu removal. Many factors can contribute to this change and the most important factor is the nature of adsorbate and interfering ions.

Table 3 Adsorption capacity of rice husk for Cu, Ni, and Zn removal in the presence of K, Na and Ca.

Conc. of interfering ions	Cu ions q_e			Ni ions q_e			Zn ions q_e		
	K	Na	Ca	K	Na	Ca	K	Na	Ca
0.1	102.3	97.6	98.8	100.7	85.2	55.3	119.2	121.6	106.6
0.2	98.8	99.4	101.6	100.2	87.2	52.7	119.5	118.8	103.6
0.3	101.6	100.5	99.4	98.7	80.7	49.7	119.5	121	92.5
0.4	105.1	98.8	98.8	96.2	72.2	49.2	119.2	120.3	88.4

3.1.6.2 Effect of competitive adsorption

The presence of competing heavy metals is another factor affecting adsorption capacity. Wastewater normally contains many metal ions as a mixture. The presence of rice husk for adsorption of one metal over another has been studied. Tests were performed to investigate the influence of Cu, Ni and Zn on the removal of each studied ion from a mixture of Cu, Ni and Zn, as shown in table 4. The removal percentage of the studied metals was in the following sequence: Zn > Cu > Ni. Removal of Cu and Zn from a mixed solution was found to be lower as compared with their removal from single solution. Higher decrease was found in the efficiency of Ni removal from a mixed solution.

The amount of adsorbed ions depends on the equilibrium between adsorption competition from all ions involving their ionic size, redox potential, electronegativity and stability of bonds between metal ions and adsorbent as well as the distribution of the functional groups on the adsorbents surface[15].

It can also be noticed that total amount of metal adsorbed per unit weight of adsorbent increased in all concentrations of mixed solutions compared to that from single metal solution. This indicates that different adsorption mechanisms may be involved in sorption from mixed solution.

Table 4 Adsorption capacity of rice husk for removal of Cu, Ni, and Zn from their mixture.

Adsorbent	C ₀ μgml ⁻¹	Zn%		Cu%		Ni%	
		Mix ture	Sing le	Mixt ure	Single	Mixt ure	Sing le
Rice husk	10	95.8	89	83.7	84.2	57.8	63.9
	20	95.6	87	83.8	84.5	52.7	62.1
	30	94.9	88.9	83.5	82.4	51.5	60.6
	40	92.1	83	82.2	79	53.6	58.8

3.2 Kinetic models

In order to analyze our kinetics experimental data, the pseudo-first, pseudo-second order, and Elovich kinetic models were applied.

3.2.1 Pseudo-first order model

The Lagergren first order rate equation is one of the most widely used for the adsorption of a solute from liquid solution and is represented as [14, 16]:

$$\log (q_e - q_t) = \log q_e - \frac{k}{2.303} t \quad (2)$$

Where q_e and q_t(μg g⁻¹) are the amount of metal adsorbed at equilibrium and at time t respectively and k is the overall first-order rate constant (min⁻¹).

The slope and intercepts of the plot of log (q_e-q_t) against t for adsorption of Cu, Ni, and Zn on rice husk were used to determine the value of k and q_e.

Values of correlation coefficient (R²) together with the large difference between the experimental and the calculated values of q_e(Table 5) indicated that pseudo-first order model is not suitable to explain our experimental data. Our results were in agreement with those reported in literature [7].

Table 5 pseudo-first order data of Cu, Ni, and Zn removal by Rice husk..

Metal ion	C ₀ μgml ⁻¹	R ²	k min ⁻¹	q _e cal.	q _e exp.
Cu	10	0.9519	0.0225	19.40	117.1
	20	0.6732	0.0225	14.26	209.5
	30	0.888	0.0165	53.26	286.1
Ni	10	0.4584	0.0048	20.08	103.7
	20	0.8908	0.0255	33.79	173.7
	30	0.9587	0.0396	138.23	243.7
Zn	10	0.8556	0.0285	13.24	106.2
	20	0.9793	0.0315	31.99	216.2
	30	0.9717	0.0163	35.05	307.5

3.2.2 Pseudo-second order model

The pseudo-second order kinetic rate equation is expressed in a linear form as [17]:

$$\frac{t}{qt} = \frac{1}{kq_e} + \frac{1}{q_e} t \quad (3)$$

Fig. 2 represents the plot of t/qt versus t, for different studied metal ion concentrations, values of q_e and k₂ were obtained from the slope and intercept of the straight lines. Values of k₂ for Cu, Ni, and Zn removal were; 0.1397, 0.2250 and 0.1389 respectively at 0.8 g/10 ml adsorbent dose and 30 μgml⁻¹ heavy metal initial concentration. Data in table 6 revealed that the values of k₂ were decreased with increase the initial concentrations of the studied heavy metals, correlation coefficients (R²) were higher than 0.999 and the calculated q_e value agreed well with the experimentally measured value. All these indicate that adsorption of Cu, Ni, and Zn on rice husk followed pseudo-second order mechanism. It means that chemisorption is the determining step of the adsorption process. Similar results have been reported by Srivastava [7] and EL-shafey [8].

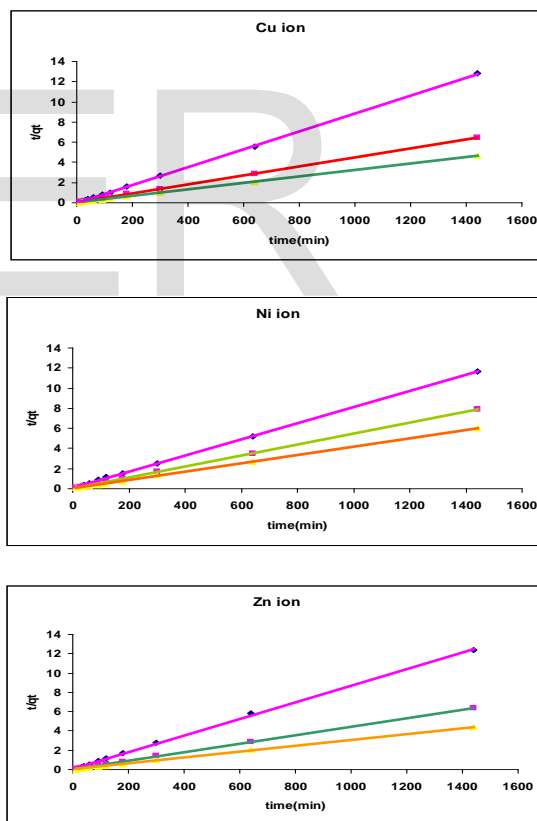


Fig. 2 Application of pseudo-second order model for Cu, Ni and Zn removal by Rice husk.

Table 6 pseudo-second order data for Cu, Ni, and Zn removal by Rice husk.

Metal ion	Co μgml^{-1}	R ²	k ₂ ($\text{ml}\mu\text{g}^{-1}\text{min}^{-1}$)	q _e cal. (μgg^{-1})	q _e exp. (μgg^{-1})
Cu	10	0.9999	0.2968	112.3	117.1
	20	0.9999	0.1679	222.2	209.5
	30	0.9999	0.1397	312.5	286.1
Ni	10	0.9998	0.0908	125.0	103.7
	20	1.0000	0.2030	181.8	173.7
	30	0.9998	0.2250	243.9	243.7
Zn	10	0.9995	0.1029	116.2	106.2
	20	0.9999	0.1555	227.2	216.2
	30	0.09997	0.1389	333.3	307.2

3.2.3 Elovich model

The simple Elovich model may be expressed in the form [5]:

$$q_t = \alpha + \beta \ln t \quad (4)$$

A plot of q_t versus ln t should give a linear relationship for the applicability of the simple Elovich kinetic.

The statistical parameters reported in Table 7 indicated that the kinetics data of adsorption of Cu, Ni, and Zn on rice husk not fitted well to Elovich equation. Our data was in agreement with that of Ashtoukhy [5].

Table 7 Elovich equation data for Cu, Ni, and Zn removal by Rice husk.

Metal ion	Co μgml^{-1}	A	b	R ²
Cu	10	102.47	1.714	0.4312
	20	184.49	5.1223	0.8246
	30	220.11	13.045	0.9243
Ni	10	76.626	6.8611	0.906
	20	136.17	7.1289	0.8706
	30	145.94	15.987	0.5581
Zn	10	86.565	3.9817	0.9128
	20	177.96	7.0523	0.9312
	30	260.63	9.2792	0.9741

4 FTIR Analyses

FTIR spectrophotometer was employed to determine the presence of functional groups in the studied adsorbents [18,19]. FTIR spectrum of RH before and after adsorption (metal loaded) is shown in figure 3 A, B, C & D. The interpretation was complicated due to the fact that each group originated several bands at different wave numbers.

Band around 3317 cm⁻¹ was assigned to OH group represents oxygenated functional groups of cellulose in RH whereas 2920-2854 cm⁻¹ are assigned to the CH₂ and CH₃ whereas 1638 cm⁻¹ was to the C=C (aromatic structures) and C=O stretching (aromatic carboxyl/carbonyl). The band at 1274 cm⁻¹ was assigned to the aromatic C=O and phenolic OH stretching band at 1102 cm⁻¹ is given due to alcohol-OH represents

oxygenated functional groups of cellulose. The band at 855 cm⁻¹ represented the aromatic CH out-of-plan deformation. The transmittance in the 1550-1555 cm⁻¹ indicated N-H bonded peak, in 1157 cm⁻¹ indicate the SO₂ bonded, and the peak at 1095 cm⁻¹ is due to Si-O-Si and -C-O-H and -OH deformation. The spectra display also a number of adsorption peaks indicating the complex nature of the examined adsorbents. The IR spectra of the adsorbents indicated the band at 1600cm⁻¹ may be due to conjugated hydrocarbon bonded carbonyl groups.

The FTIR spectra showed transmittance at 1095cm⁻¹ due to the vibration of CO group this means that the functional groups at these wave numbers participate in the metal adsorption. The presence of polar groups on the surface is likely to give considerable cation exchange capacity to the adsorbents. The surface structures of carbon-oxygen (functional groups) are by far the most important structure influencing the surface characteristics and surface behavior of the studied adsorbent.

The small changes in FTIR spectra confirm the complexation of Cu, Ni, and Zn with functional groups present in the RH. The possible adsorption on this adsorbents may be due to the physical adsorption, complexation with functional groups, ion exchange, surface precipitation and chemical interaction with surface sites.

5 Conclusions

Adsorption of Cu, Ni, and Zn by rice husk is contact time, initial metal ion concentration, adsorbent dose, adsorbent particle size, pH and interfering ions (0.1-0.4 M) K, Na and Ca dependent. The total amount of metal adsorbed per unit weight of adsorbent increased in all concentrations of mixed solutions compared to that at single metal solution. The results revealed that Cu, Ni, and Zn are highly adsorbed on rice husk and it could be an economical method for removal of the studied metal ions from aqueous system as a replacement for costly adsorbents. Adsorption of Cu, Ni, and Zn on rice husk followed pseudo-second order mechanism and chemisorption is the determining step of the adsorption process.

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