

Removal of Copper(II) and Zinc (II) ions from aqueous solution using modified rice husk as an adsorbent

Asha R* and Avila Thanga Booshan S.

Department of Chemistry and Research Centre, Women's Christian College, Nagercoil, Tamilnadu, India.

*Corresponding Author: E-Mail: ashasicily@gmail.com

Received: 17 Jun 2015, Revised and Accepted: 25 Jun 2015

ABSTRACT

An increase in population initiating rapid industrialization was found to consequently increase the effluents and domestic wastewater into the aquatic ecosystem. Heavy metals are major toxicants found in industrial wastewaters they may adversely affect the biological treatment of wastewater. Various methods adopted for removal of heavy metals include chemical precipitation, membrane separation, ion exchange and adsorption. In the case of adsorption, the generally used adsorbents like activated carbon, silica, alumina etc are expensive. This has prompted the use of natural materials as adsorbents in order to develop cheaper alternatives, which can be disposed off without regeneration due to their lower cost. Rice husk is tried for the removal of copper and zinc. For chemically modified method rice husk were treated with 0.1M NaOH. The newly developed adsorbents should be as effective as the conventional ones. Hence in the present work, 0.1 M NaOH modified rice husk (MRH) is studied for their adsorptive capacity to remove copper (II) and zinc (II) from aqueous solution. The effect of various parameters such as, contact time, pH, mixing speed and initial metal concentration for the adsorption of Cu(II) and Zn(II) on MRH is investigated. Experimental results are analyzed using Langmuir and Freundlich isotherms.

Keywords: Biosorption, Rice husk, Copper(II), Zinc (II), Isotherms.

1. INTRODUCTION

The increase in industrial activity during recent years is greatly contributing to the increase of heavy metals in the environment, mainly in the aquatic systems. Water pollution due to heavy metals is an issue of great environmental concern. Industrial wastewater containing metal ions such as nickel, lead, copper and zinc are common because their metals are used in a large number of industries such as electroplating, batteries manufacture, mining operations, paint and pigments, pharmaceutical and so on. Metals are of special concern because they are non-degradable and therefore persistent. The effect of metals in water and wastewater range from beneficial through troublesome to dangerously toxic. Therefore, the elimination of heavy metals from water and wastewater is important to protect public health and wild life.

The conventional methods used to remove heavy metals include chemical precipitation, ion exchange and electrochemical treatment [1-3]. The search for new, effective and

economical technologies involving the removal of toxic metals from wastewater has directed attention to biosorption based on metal binding capacities of various biological materials at little or no cost. Different types of biomass have been investigated for the biosorption of metal ions, including yeast [4], algae [5], fungi [6], bacteria [7] and agricultural by-products (inexpensive plant material) such as dried leaves [8], peanut hull [9], sugar-beet-pulp [10], tea waste [11], coconut husk [12], apple wastes [13], maize leaf [14], grape stalk wastes [15].

These agricultural by-products are relatively cheap and show quite high biosorption potential. However, the direct use of the raw plant wastes as adsorbents has been found to be limited due to leaching of organic substances such as lignin, tannin, pectin and cellulose into the solution. To resolve these problems chemical modification on solid adsorbents have been used as a technique to improve their physical, chemical properties and biosorption capacity.

Rice husk is a by-product of the rice milling industry and the amount of rice husk available is far in excess of any local uses, thus frequently causing disposal problems. Therefore, rice husk is very inexpensive and thus its use would significantly lower the cost of wastewater treatment. In addition, the use of rice husk would represent effective utilization of waste water. The aim of this work is to study the biosorption capacity of rice husk that was chemically modified with sodium hydroxide for biosorption of Cu(II) and Zn(II) ions from aqueous solutions. The effects of contact time, pH, mixing speed, initial concentration of metal ions and adsorption isotherms were investigated.

2. MATERIALS AND METHODS

2.1. Preparation of adsorbent

The rice husk was received from a local rice mill, the rice husk were crushed and thoroughly washed with distilled water to remove all dirt and then were heated in an oven at 80-85°C for 2 h. About 25 g of oven-dried rice husk were poured into 500 ml flask containing 250 ml of 0.1 M NaOH solution, and then were shaken at 200rpm for 4h at room temperature. The mixture was left overnight, and then was filtered to remove the sorbent, which was washed several times with distilled water to provide neutral pH. The adsorbent was then oven dried at 85°C for 2 h. Finally, MRH was separated and stored in plastic container for the future experiments.

2.2. Preparation of stock solutions

A stock solution of Copper and Zinc was prepared in double distilled water with Copper(II) Sulphate and Zinc(II) Sulphate. All working solutions of varying concentrations were obtained by diluting the stock solution with distilled water. The pH of the effluent was adjusted by using 0.2 M acetic acid and 0.2 M sodium acetate solutions. The concentration of metal ions in effluent was analyzed by Atomic Absorption Spectrophotometer.

2.3. Biosorption experiments

Biosorption experiments were carried out by shaking a stopper flask containing 25 ml of 100 mg/L metal ion solution and 0.2 g of MRH at 200 rpm for 60 min. The sample was allowed to settle and then it was filtered through a Whatman filter paper. The filtrate of the sample was analyzed in an AAS for the final concentration of metal ions in aqueous solution. The amount of metal adsorbed per unit mass of the adsorbent was calculated using the following equation:

$$q = \frac{(C_i - C_f)V}{M}$$

where, q is the metal uptake (mg/g), C_i is the initial metal concentration (mg/L), C_f is the final or equilibrium metal concentration (mg/L), V is the volume of the metal solution in the flask (L) and M is the dry mass of biosorbent(g). The percentage removal (%R) of metal ions was calculated from the following equation:

$$\%R = \frac{(C_i - C_f)}{C_i} \times 100$$

The same procedure were performed at different contact time (10, 20, 30, 60 and 120 min), pH (3, 4, 5 and 6), mixing speed (100, 150 and 200 rpm) and initial metal-ion concentration (100, 200 and 300 mg/L) to obtain the equilibrium data.

3. RESULTS AND DISCUSSION

3.1. Effect of contact time

Figure 1 shows the effect of contact time on the removal of Cu(II) and Zn(II) on MRH at initial concentration of 100 mg/L at room temperature. The percentage removal of Cu(II) by MRH increased from 24.00% to 58.00% when the contact time of the solution was increased from 10 min to 60 min. In the case of Zn(II) the removal percentage increases from about 19.36% to 34.72% when the contact time was increased from 10 min to 120 min. Thus taking an optimum time and economic considerations into account, a contact time of 60 minutes was used for all experiments.

As the time increases, Cu(II) and Zn(II) getting adsorbed by the adsorbent increases, but a particular point of time, the removal of metal ions is almost constant. During the initial stage of sorption, a large number of vacant surface sites are available for adsorption. After a lapse of some time, the remaining vacant surface sites have difficulty in becoming occupied due to repulsive forces between the adsorbate molecules on the solid surface and in the bulk phase.

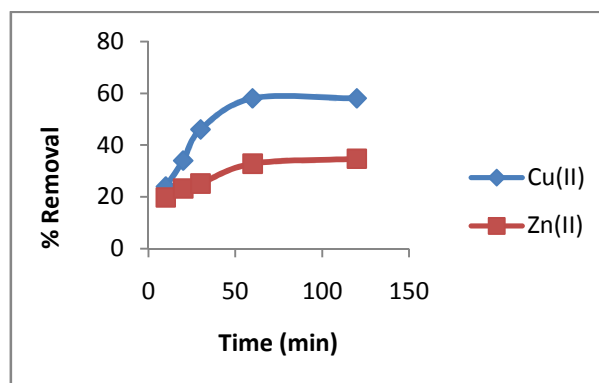


Figure - 1: Effect of contact time on the adsorption of Cu(II) and Zn(II) by MRH.

3.2. Effect of pH

Figure 2 shows the effect of pH on the adsorption of Cu(II) and Zn(II) on MRH at initial concentration of 100 mg/L at room temperature. The percentage removal of Cu(II) by MRH increased from 24.00% to 58.00% when the pH of the solution was increased from 3 to 6. Similarly in the case of Zn(II) the removal percentage increases from about 21.28% to 32.80% when pH was increased from 3 to 6. This shows that at lower pH, the surface charge of the biomass is positive, which is not favorable to cations biosorption. Meanwhile, hydrogen ions compete strongly with metal ions at the active sites, resulting in less biosorption. With increasing pH, electrostatic repulsions between cations and surface sites and the competing effect of hydrogen ions decrease. Consequently, the metal biosorption increases.

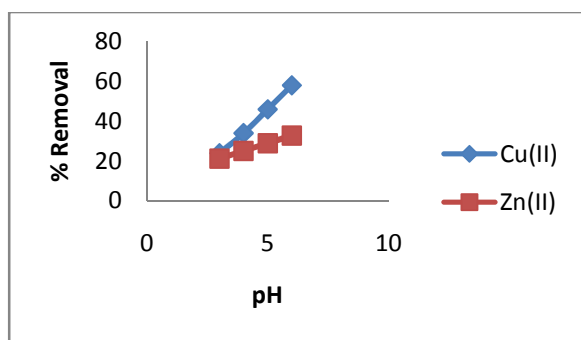


Figure - 2: Effect of pH on the adsorption of Cu(II) and Zn(II) by MRH.

3.3. Effect of mixing speed

Figure 3 shows the effect of mixing speed on the removal of Cu(II) and Zn(II) on MRH at initial concentration of 100 mg/L at room temperature. Adsorption studies were carried out at varying mixing speeds (100-200) rpm. It was observed that the percent removal metal ions increases with the increase of stirring speed upto 200 rpm. At this mixing speed the maximum removal of Cu(II) was 58.00% whereas 32.80% of Zn(II) were obtained under optimum conditions.

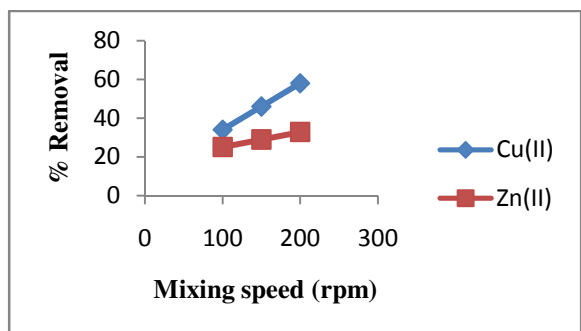


Figure - 3: Effect of mixing speed on the adsorption of Cu(II) and Zn(II) by MRH.

The increase of adsorption efficiency with the increase of mixing speed could be mainly due to resistance to mass transport in the bulk solution at lower mixing speeds. A thin liquid film surrounding the adsorbent particles offered resistance to mass transport by diffusion. As the mixing speed increased, there would be decrease in the thickness of the boundary film there by decreasing the effect of film diffusion.

3.4. Effect of initial metal concentration

Figure 4 shows the effect of metal initial concentration on the adsorption of Cu(II) and Zn(II) on MRH at room temperature. The percentage removal of Cu(II) by MRH decreased from 58.00% to 52.00% when the initial concentration of the solution was increased from 100 to 300 mg/L. Similarly in the case of Zn(II) the removal percentage decreases from about 32.80% to 24.48% when the concentration of the solution was increased from 100 to 300 mg/L. This shows that the suitable initial metal ions (Cu(II) and Zn(II)) concentration is 100 mg/L. At low concentrations, metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and exchange sites are filled.

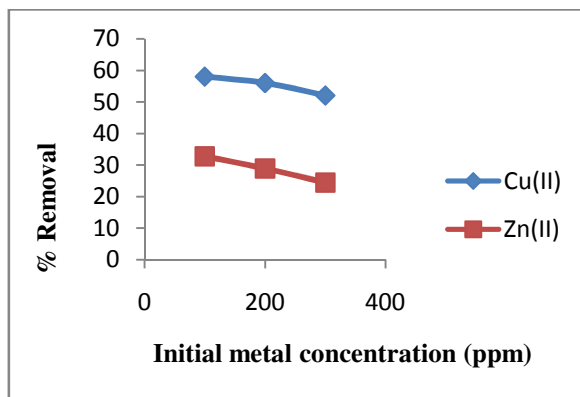


Figure - 4: Effect of metal concentration on the adsorption of Cu(II) and Zn(II) by MRH.

3.5. Adsorption Isotherm

The adsorption isotherms for the Cu(II) and Zn(II) were studied using initial concentration of Cu(II) and Zn(II) from 100 mg/L to 300 mg/L at room temperature. In this research, two isotherm models were used to study the equilibrium sorption as Langmuir and Freundlich models. The Langmuir model assumes that the uptake of metal ions on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions.

The Langmuir isotherm can be expressed as:

$$q = \frac{q_{max} b C_f}{(1 + b C_f)} \quad \text{-----(1)}$$

where, q is the metal uptake (mg of metal ion/g of adsorbent), q_{max} is the maximum metal uptake per unit mass of adsorbent (mg/g), b is Langmuir constant (L/mg) related to energy of sorption which reflects quantitatively the affinity between the adsorbent and metal ions. The values of q_{max} and b are characteristics for the Langmuir model. They can be determined by linearized Eq (1) as shown in Eq (2)

$$\frac{C_f}{q} = \frac{1}{q_{max}b} + \frac{C_f}{q_{max}} \quad \text{----- (2)}$$

Therefore, a plot of C_f/q versus C_f gives a straight line of slope $\frac{1}{q_{max}}$ and intercept $\frac{1}{q_{max}b}$. The Langmuir parameters, q_{max} and b are calculated from the slope and intercept of the graph.

The Freundlich model is chosen to evaluate parameters associated to the sorption behavior. The equation is commonly represented by:

$$q = KC_f^{1/n}$$

where, K and n are Freundlich constants, indicating the adsorption capacity and the adsorption intensity respectively. The above equation is rearranged in linear form to give:

$$\log q = \log K + \frac{1}{n} \log C_f$$

K and n are, respectively, determined from the intercept and slope of plotting $\log q$ versus $\log C_f$

The linearised Langmuir and Freundlich isotherms of Cu(II) and Zn(II) are shown in Fig 5a, 5b and Fig 6a, 6b. The Langmuir and Freundlich parameters and correlation coefficients(R^2) for the adsorption of Cu(II) and Zn(II) by MRH are shown in table 1.

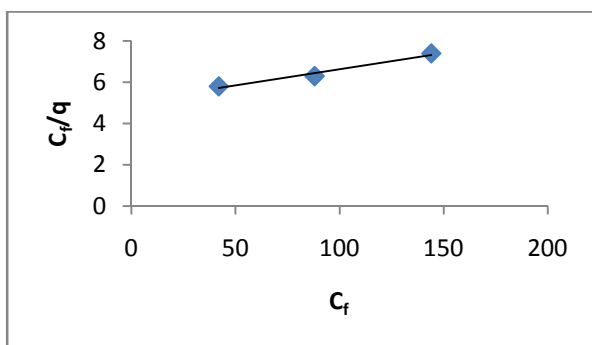


Figure - 5a: Langmuir isotherm plot for the adsorption of Cu(II) by MRH.

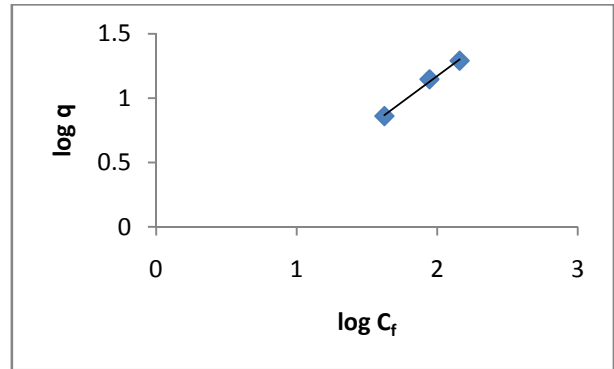


Figure - 5b: Freundlich isotherm plot for the adsorption of Cu(II) by MRH.

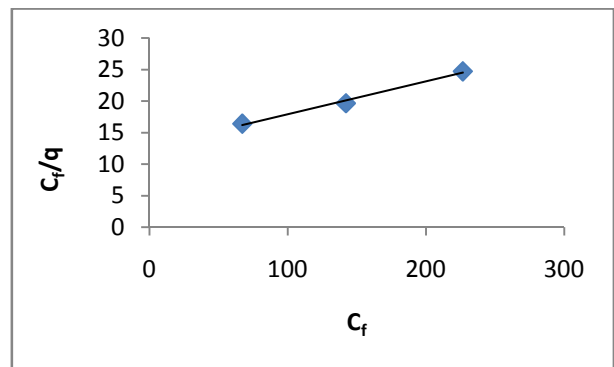


Figure - 6a: Langmuir isotherm plot for the adsorption of Zn(II) by MRH.

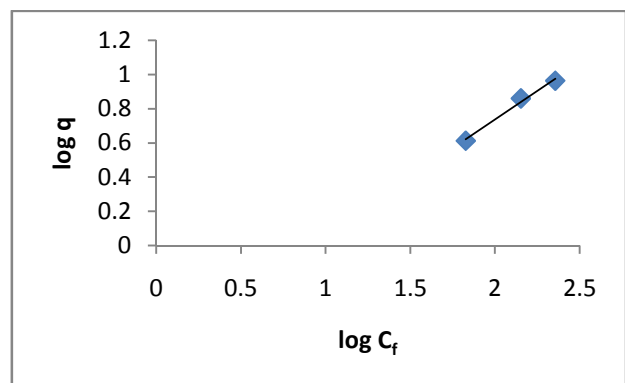


Figure - 6b: Freundlich isotherm plot for the adsorption of Zn(II) by MRH.

4. CONCLUSION

The experimental investigation concluded that MRH could be used as potential biosorbent for removal of Cu(II) and Zn(II) ions from aqueous solutions. The percentage removal of Cu(II) and Zn(II) ions in aqueous solution increased with increase in the mixing speed, pH and contact time.

Table - 1: The parameters of Langmuir and Freundlich isotherms

Metal	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	b (L/mg)	R^2	K	n	R^2
Cu(II)	66.6667	0.00297	0.974	0.3572	1.2360	0.994
Zn(II)	19.2307	0.00411	0.991	0.2466	1.4880	0.990

The percentage removal of Cu(II) and Zn(II) ions in aqueous solution decreased with increasing initial metal concentration. The adsorption isotherm studies showed that both Langmuir and Freundlich adsorption isotherm model fits well with the experimental data. These experimental studies on the specified adsorbent would be quite useful in developing an appropriate technology for the removal of Copper(II) and Zinc(II) ions from contaminated industrial effluents.

5. REFERENCES

1. Matlock MM, Howerton BS and Atwood DA. Chemical precipitation of heavy metals from acid mine drainage. **Water Res.** 2002; 36(19): 4757-4764.
2. Feng D, Aldrich C and Tan H. Treatment of acid mine water by use of heavy metal precipitation and ion exchange. **Minerals Eng.** 2000; 13(6): 623-642.
3. Mohammadi T, Moheb A, Sadrzadeh M and Razmi A. Modelling of metal ion removal from waste water by electro dialysis separate. **Sep. Purificat. Technol.** 2005; 41(1): 73-82.
4. Junxia Yu, Tong Mi, Xiaomei Sun and Buhai Li. Enhanced and selective adsorption of Pb²⁺ and Cu²⁺ by EDTAD-modified biomass of baker's yeast. **Bioresour Technol.** 2008; 99(7): 2588-2593.
5. Feng D and Aldrich C. Adsorption of heavy metals by biomaterials derived from the marine alga *Ecklonia maxima*. **Hydrometallurgy.** 2004; 73(1-2): 1-10.
6. Sag Y, Kaya A and Kutsal T. The simultaneous biosorption Cu(II) and Zn(II) on *Rhizopus arrhizus*: application of the adsorption models. **Hydrometallurgy.** 1998; 50(3): 297-314.
7. Pagnanelli F, Esposito A, Toro L and Veglio F. Metal speciation and pH effect on Pb, Cu Zn and Cd biosorption onto *Sphaerotilus natans*: Langmuir-type empirical model. **Water Res.** 2003; 37(3): 627-633.
8. Benaissa H and Elouchdi MA. Removal of copper ions from aqueous solutions by dried sunflower leaves. **Chem Eng Process.** 2007; 46(7): 614-622.
9. Zhu C, Wang L and Chen W. Removal of Cu(II) from aqueous solution by agricultural by-product: Peanut hull. **Journal of Hazardous Materials.** 2009; 168(2-3): 739-746.
10. Reddad Z, Gerente C, Andres Y and Le Cloirec P. Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. **Environ Sci Technol.** 2002; 36(9): 2067-2073.
11. Amarasinghe BMWPK and William RA. Tea waste as a low cost adsorbent for the removal of Cu and Pb from waste water. **Chemical Engineering Journal.** 2007; 132(1-3): 299-309.
12. Babarinde NAA. Adsorption of zinc (II) and cadmium (II) by coconut husk and goat hair. **J. Pure Appl. Sci.** 2002; 5: 81-85.
13. Maranon E and Sastre H. Heavy metal removal in packed beds using apple wastes. **Bioresour Technol.** 1991; 38: 39-43.
14. Babarinde NAA, Babalola JO and Sanni RA. Biosorption of lead ions from aqueous solution by maize leaf. **Int. J. Phys. Sci.** 2006; 1(1): 23-26.
15. Villaescusa I, Fiol N, Martinez M, Miralles N, Poch J and Serarols J. Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. **Water Res.** 2004; 38(4): 992-1002.