BIOSORPTION OF COPPER AND LEAD IONS USING WHEAT HUSK

Salah N. Farhan
Department of Chemical Engineering, College of Engineering, University of Diyala, Iraq

ABSTRACT: - The present work focused on the effectiveness of wheat husk for removal of Cu(II) and Pb(II) ions from aqueous solution. A batch biosorption experiments was carried out using wheat husk as a biosorbent for metal removal to determined optimum biosorption conditions including pH, biomass dosage, contact time, and temperature.

Atomic Absorption Spectroscopy (AAS) adsorption results show maximum adsorption capacities of 93.41% for lead and 88% for cupper at pH 4, 5.5 respectively. Various initial metal concentrations (from 20 to 100 ppm) and various amount of biosorbent were investigated.

The effect of pH was significant and varied with each metal. These results were found to be comparable to results reported from previous works. The results show that the removal efficiency of each adsorbent is highly dependent on pH, and metal ion removal occurred in the preferential order lead > cupper.

The FT-IR studies show that the C-O in carboxyl group of alginate directly attaches to the copper ion that leads to most of the adsorption. Langmuir, and Freundlich models were applied to describe the biosorption isotherm of the metal ions by wheat husk biomass. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The monolayer biosorption capacity of wheat husk for Pb(II) and Cr(III) ions was found to be 75.8 mg/g and 52.1 mg/g, respectively. From the D–R isotherm model, the mean free energy was calculated as 12.7 kJ/mol for Pb(II) biosorption and 10.5 kJ/mol for Cu(II) biosorption, indicating that the biosorption of both metal ions was taken place by chemical ion-exchange.

Keyword: - Biosorption, wheat husk, heavy metals.

1-INTRODUCTION

One of the most important environmental issues is the presence of heavy metals contaminated in aqueous streams, arising from the discharge of untreated metal containing effluent into water bodies [1, 2]. Contamination of aqueous environment by heavy metals is the driving force behind a great attention towards metal remediation methods. Among heavy metals in wastewaters, lead and copper are considered having a high priority due to their toxicity and high disposal rate [3, 4].

Main industrial applications, such as storage battery, manufacturing, printing pigments, fuels, and photographic materials passes Pb(II) ions to aquatic bodies [5]. Additionally, copper ion is widely used in electroplating, the light industry, the mechanical manufacturing industry, and architecture. Copper is an indispensable micronutrient element to humans and other life forms. However, it is one of the toxic metals to human beings as excessive copper causes serious lesions in the central nervous system and even permanent damage particularly for children [6].

FT-IR provide good insight into adsorption process at the molecular level. Many researchers adopted to identify the major functional groups of adsorbents and elucidate their
interactions with metal ions. The possible organic functional groups in the metal binding include carboxyl, ether, alcoholic, hydroxyl, and amino functional groups [7-9].

Biosorption is an alternative technology for the treatment of wastewater containing metal ions, biosorption referred to the pollutants uptake by living or nonliving biomass [10]. The rapid growth in global population and urbanization has driven an exponential increase in industrial activities, which is accompanied by an increase in the amount of industrial wastes being discharged into the environment. Hence, the increase in heavy metals such as Cadmium, Mercury, Lead, Copper, Zinc, Nickel and Chromium posing significant risk to soil, water and human health.

Heavy metals are not biodegradable and tend to accumulate in living organisms causing various diseases and disorders, as well as deleterious ecological effects [11]. Various treatment methods have been employed in the removal of heavy metals from industrial effluents. Among them include chemical precipitation, membrane filtration, ion exchange, reverse osmosis, electro dialysis, solvent extraction, evaporation, oxidation, activated carbon adsorption [12, 13]. However, these methods are often expensive and difficult to maintain due to high capital and operational costs, as well as, extra cost of treating the resultant sludge generated before disposal.

The generated secondary waste, apart from requiring additional treatment along with the accompanying cost, also poses disposal hazards and pollution risks to the environment [14]. Studies on cheaper methods of treating metal-enriched industrial wastewater involving the possible use of low-cost and commonly available organic materials with high adsorptive capacities is now a growing research area [15].

Biosorption plays an important role in the elimination of metal ions from aqueous solutions in water pollution control [16, 17]. The main advantages of this technique are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time, and no production of secondary compounds which might be toxic [18].

Low–cost organic materials which have been found to possess potentials for viable use in the treatment of industrial wastewater include reed plant, tree bark, moss, cotton wool, reed plant, corn hobs, rice husk, orange peel, banana peel, sawdust, apple-waste, mango peel, etc. [10, 19]. The choice of an organic adsorbent usually depends on a number of factors which include availability, location, locality, seasonality, cost-effectiveness, etc. Apart from availability, location, seasonality and cost-effectiveness, studies have demonstrated that the use of low cost adsorbents has distinct advantages over conventional methods of metal removal from industrial wastewater [20, 21].

This property has fuelled the growing attraction for researchers towards the use of readily available organic adsorbents for the removal of heavy metals from wastewater. These advantages include: low cost, high efficiency, reduced production of sludge, ease of regeneration of biosorbents and metal recovery [22].

The use of biological materials, including living and non-living micro-organisms, to remove and recover toxic or precious metals from industrial waste waters has gained popularity over the years due to good performance, availability and low cost of raw materials [23].

The objective of the present work is to investigate the biosorption potential of wheat husk in the removal of Pb(II) and Cu(II) ions from aqueous solution. Optimum biosorption conditions were determined as a function of pH, biomass dosage, contact time, and temperature. The Langmuir, and Freundlich models were used to describe equilibrium isotherms. Biosorption mechanisms of Pb(II) and Cu(II) ions onto wheat husk were also evaluated in terms of thermodynamics and kinetics.

2- MATERIALS AND METHODS
2.1. Materials
The wheat husk used in the present investigation was obtained from the local countryside. The collected materials were washed with distilled water several times to remove all the dirt particles. The washed material was dried in sunlight for 8 h and then in an oven at 378 K for a period of 24 h. Then grounded and screened through a set of sieves to get the geometrical sizes (40) mesh. This produced a uniform material for the complete set of adsorption tests which was stored in an airtight plastic container for all investigations. The wheat husk is mainly composed of carbohydrates, lignin, cellulose, and volatile substances which are 91% of the total weight [24].

2.2 Metal Solutions

All metal salts and chemical reagents used were of analytical grade obtained from Merck. Standard Stock solutions of 1g·L⁻¹ of Cu(II) and Pb(II) were prepared by dissolving the appropriate amount of metal compounds CuCl₂ and Pb(NO₃)₂ in distilled, deionized water containing a few drops of concentrated HCl to prevent the precipitation of these ions by hydrolysis. All working solutions were prepared by diluting the stock solution with distilled water to the needed concentration. The initial pH of the working solution was adjusted by addition of HCl or NaOH solution. in de-ionized water.

2.3 Instrument and Apparatus

A pre- and post-adsorption determination of the types and distribution of functional groups present in the dry adsorbent samples was carried out by Perkin Elmer Fourier Transform Infrared (FTIR) RX1 spectroscopy, using Potassium Bromate (KBr) disc to prepare the feedstock. The spectral range varied from 4000 to 400 cm⁻¹. The Pb²⁺, and Cu²⁺, concentrations were determined by using Perkin-Elmer Model Atomic Absorption Spectrometer (AAS) equipped with deuterium lamp background correction. All pH measurements were taken with a Hanna Educational HI 208 ion-meter.

3. BIOSORPTION EXPERIMENT

Batch mode biosorption experiments were conducted to investigate the effects of process parameters such as pH, biosorbent amount, initial metal concentration, and contact time on the biosorption of Pb(II), and Cu(II)). Conical flasks (250 ml) containing 50 ml of these ions of known pH, concentration and biosorbent dose were prepared. To study the effect of pH, pHs (2, 3, 5, 6 and 8), and adsorbent dose of 0.1 g/l, for a contact time of 30 min. For each 50 ml of metal (Pb(II), and Cu(II)) solution of 60, 10 mg/l respectively used and pH adjusted before adding adsorbent. The mixture was agitated on a rotary shaker (DUBNOTT BSD/DCE) at 200 rpm for 1 h. The pH was adjusted to the required value using 0.1 M NaOH and/or 0.1N HNO₃ before the addition of the sorbent. After that, the mixture was centrifuged for 10 minutes at a speed of 300 rpm using an Impact-5 Centrifuge to separate the supernatants from the adsorbent. The residual concentration of metals in the supernatant was determined using AAS. All the experiments were done in replicated and results averaged. The percentage removal and metal uptake efficiencies of all adsorbents were determined with following expressions:

$$q = \frac{V(C_0 - C_e)}{m*1000}$$

where q is the quantity of metal uptake by biomass (the amount of ions adsorbed per unit mass of dry wheat husk) in mg·g⁻¹; C₀ and Cₑ are the initial and final (after sorption at equilibrium) metal concentration, respectively; V is the volume of solution in ml and m is the dry weight of the wheat husk added in grams.

The biosorption efficiency was measured by the following equation:

$$E = \left(\frac{C_0 - C_e}{C_0}\right)\times100$$

$$E = \left(\frac{C_0 - C_e}{C_0}\right)\times100$$

$$E = \left(\frac{C_0 - C_e}{C_0}\right)\times100$$

$$E = \left(\frac{C_0 - C_e}{C_0}\right)\times100$$
3.1. Biosorption equilibrium

Taking known amount of wheat husk in 250-mL flasks containing 100 mL of the metal ion solution of different initial concentration (20–100 mg/L). The mixture was shaken in rotary shaker at 100 rpm keeping temperature constant (303 K). The agitation was made for 1 h, in order to reach the equilibrium. Langmuir, and Freundlich, models are commonly employed adsorption isotherm models that applied in this present investigation [25].

3.2. Biosorption kinetics

Biosorption kinetics experiments were carried out in 250 mL flasks containing 50 mL of the metal ion solution using a known amount of wheat husk. The flasks were agitated for various time intervals (5–180 min) on a rotary shaker at 100 rpm under constant temperature (303 K). The samples were taken at different time intervals, centrifuged and analyzed for remaining concentrations. The kinetic data was analyzed using pseudo-first order, and pseudo second order models [27, 28].

3.3. Biosorption thermodynamics

Biosorption of Pb(II) and Cu(II) onto wheat husk were investigated at different temperatures (30, 40, 50, and 60 °C) in the orbital shaking incubator under preoptimized conditions. Thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) can be estimated using equilibrium constants changing with temperature. The free energy change is given by the following equation [29]:

\[ \Delta G^0 = -RT \ln K_D \]  

\[ K_D = \frac{q_e}{C_e} \]

Where \( K_D \) is the distribution constant, T is absolute temperature and R is gas constant. Free energy change (ΔG°) varies with temperature according to:

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]  

4. RESULTS AND DISCUSSION

4.1. Effect of Solution pH on Biosorption

The pH of the solution influences the properties of wheat husk, affects the adsorption mechanisms and dissociation of the metal ions. It is an important variable in the adsorption process. The charge of the adsorbate and the adsorbent often depends on the pH of the solution. Figure 1 shows the variation of Pb(II) and Cu(II) adsorption on wheat husk at varying solution pH. For Cu(II), adsorption increases with increasing pH from 2 to 5. For Pb(II), adsorption also increases as pH is increased before pH 4 and then keeps nearly constant between 4 and 10.

The functional groups found to occur on the binding surface wheat husk include the carboxyl, hydroxyl, amine, phosphate and sulphate groups, however, the carboxyl and sulphate groups are thought to be the most active groups in the binding of metals during adsorption [30]. The functionalities of these groups in adsorption have been reported to be pH-dependent. At low pH, Pb(II) and Cu(II) removal is inhibited as a result of a competition between hydrogen and metal ions on the sorption sites. As the pH increases, the negative charge density on the wheat husk surface increases due to deprotonation of the metal binding sites, and thus the adsorption of metal ions increases. The increase in adsorption with the decrease in H+ ion concentration (high pH) indicates that ion exchange is one major adsorption process. Biosorption decreases at higher pH (pH > 5) is due to the formation of soluble hydroxilated complexes of the metal ions and their competition with the active sites, and as a consequence, the retention would decrease again as PH reaches 5-8[31-33].

The poor adsorption of metal ions onto the adsorbent surface at acidic pH may depend on ionic attractions as the ligands on the adsorbent surface are positively-charged due to close association with hydronium ions (H_3O^+) or H^+, causing reduced attraction for the cadmium cations and as such, a reduced rate of adsorption [34]. However, as pH increases, more
negatively-charged ligands such as the carboxyl or amino groups are progressively exposed as a result of proton release. This increases the negative charge density on the wheat husk surface, thereby attracting the lead cations onto the adsorbent binding sites until equilibrium is attained and adsorption begins to decline due to possible precipitation of insoluble hydroxides of the metal ions which has been reported at alkaline pH values [35, 36]

4.2 Fourier Transform Infrared Analysis of Adsorbents.

The FTIR spectral of adsorbent (wheat husk) before and after adsorption of metals were used to determine the vibration frequency changes in the functional groups as shown in the following table:

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Before handling</th>
<th>After handling</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH stretching</td>
<td>3399</td>
<td>3434</td>
<td>35</td>
</tr>
<tr>
<td>C-O stretching</td>
<td>1080</td>
<td>1092</td>
<td>12</td>
</tr>
<tr>
<td>Pb-O stretching</td>
<td></td>
<td>471.99</td>
<td></td>
</tr>
</tbody>
</table>

The pre-adsorption FTIR analysis results suggested the presence of such functional groups as the carboxylic acid or alcoholic O-H bond stretching which may overlap with amine (N-H) bond stretching at peaks between 3399-3434 cm⁻¹; possible C=O bond of carbonyl or amide groups within 1080-10920 cm⁻¹; C-O and O-H bond stretchings of alcohol and ethers at 1000-1260 cm⁻¹ of the finger-print region. A deeper trough was observed at 1400 cm⁻¹ suggesting possible binding of lead at this site. These identified regions may be indicative of functional groups responsible for the individual metal-binding activity of the adsorbent, apart from the groups indicated in previous studies [19].

4.3 Effect of temperature

Temperature has an influence on the biosorption of metal ions to a limited extent under a certain range of temperature. The increase of temperature indicating a decrease of sorption capacity and the maximum equilibrium uptake occurred at 30 °C as shown in Fig. 2. Since adsorption reactions are normally exothermic, biosorption capacities increase with decrease in temperature. The decrease in biosorption capacity between 27 and 62 °C may be due to the damage of active sites in the wheat husk. Many other researchers have also observed the same results [37, 38].

4.4 Effect of contact time

Fig. (4) that more than 75% of metal ion adsorption was completed within 15 min and equilibrium was reached after 30 min and the adsorption did not change significantly with further increase in contact time. Microbial metal uptake by nonliving cells, which is metabolism-independent passive binding process to cell walls (adsorption), and to other external surfaces, and is generally considered as a rapid process, taking place within a few minutes [39]. The rapid metal sorption is also highly desirable for successful deployment of the biosorbents for practical applications [40].

Effect of initial concentrations of metal ions

As seen in Fig. 5, 6, biosorption increase as initial concentration increases; this may be attributed to the active binding sites available for available sorbate ions and biosorption is very fast for both metal ions in the first 15 min, while for the remaining time period, the metal concentrations in the liquid continued to diminish and reach an equilibrium concentration value. The faster first phase of metal biosorption may be attributed to the
surface adsorption due to the action of ion exchange with the participation of some functional groups, while the second lower phase may represent diffusion of metal ions into the cell. Studies were carried out on 100 mL solution having concentration range 10–60 mg/L under best conditions of pH with yeast dosage of 0.1 g/L.

5- CONCLUSION

The present study shows that the use of inexpensive and efficient materials, wheat husk, is capable to remove effluent toxicity. The experimental results demonstrate that relatively shorter contact time, endothermic nature of biosorption process (in most cases), acidic pH range and high affinity for metal ions was found. The use of wheat husk needs further investigation. Biosorption requires investigation in structural studies of biosorbents, multi-metal studies, mechanistic modeling, recovery of metal ions, enhancement of biosorption capacity through modification of biosorbents and continuous flow studies.

6- REFERENCES

10. Salah N. Farhan” Biosorption of Hg and Ni ions on Bakers Yeast” first conference, college of science, University of diyala, 2009.
BIOSORPTION OF COPPER AND LEAD IONS USING WHEAT HUSK

27. Plazinski et al., 2009 (Theoretical models of sorption kinetics including a surface reaction mechanism: A review. Advances in Colloid and Interface Science 152 (2009) 2-13)

Diyala Journal of Engineering Sciences, Vol. 08, No. 04, Special Issue
841


BIOSORPTION OF COPPER AND LEAD IONS USING WHEAT HUSK

**Fig (1):** Metal uptake, q (mg/g) for lead and copper at different pH

**Fig. (2):** Effect of temperature on biosorption of metal ions, reaction volume = 100 mL, yeast weight = 0.1 g, C0 = 10 mg/L
**Fig. (3):** Metal uptake with increasing Biosorbent dose.

**Fig. (4):** Concentration drop with time.
Fig. (5): Lead uptake, $q$ with time at different initial concentration.

Fig. (6): Copper uptake, $q$ with time at different initial concentration.