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Biosorption of Copper and Lead Ions Using Chara Algae

Salah N. Farhan*, Walaa Abid Mahmood, Muataz H. Ismael, Anees A. Khadom, Abdul Munem Abbas Karim

Diyala University, College of Engineering, Chemical Engineering Department, Iraq

* **Corresponding Author:** Email: drsalahchem@gmail.com

Abstract

The current work focused on the possibility of using Chara algae and algae ashes from the Khirisan River in Diyala Governorate as biosorbent material to remove copper and lead ions from prepared aqueous solutions. Batch biosorption experiments were carried out using Chara algae and its ashes as a biosorbent for metal removal to determine optimum biosorption conditions such as pH, different initial concentration for metal ions, amount of the biosorbent material, contact time of biosorbent with metal ions, and temperature. Maximum adsorption uptakes were 93% for lead and 88% for copper at pH 5 and 5.5, respectively. Varying initial metal concentrations (from 20 to 80 ppm) and varying amount of biosorbent were investigated. Removal of the metal ions with high efficiency depends on the pH, and these removals came in order lead > copper. Using FTIR shows that carboxylic group of alginate present in the algae attaches to the metal ions leading to most of the adsorption process. Current study showed that it is possible to use cheap and available in large quantities, Chara algae, to remove toxicity from the effluent stream of any industry. The practical results showed that the time required for adsorption was short, exothermic nature of biosorption process, best pH and high affinity for metal ions was found.

Key Words: adsorption, biosorption, Chara algae, heavy metal ion

1. Introduction

To preserve water quality requirements which can be appropriate for environmental and human health, elimination of heavy metals from commercial effluents has emerged as very important. Recycling and conservation of crucial metals is becoming increasingly more essential [1]. Human health will be threatened seriously by heavy metal ions via bio-concentration, bio-accumulation, and bio-magnification through a biological chain and drinking water [2, 3].

As two of classical toxic heavy metals, lead and copper contamination is derived from wastewater of several industries including plastic and paint manufacturing, mining, petrochemical processes, electroplating, paper and pulp, metallurgical processes, and batteries. Exposure to a higher concentration of copper causes Wilson's disease which is neurotoxicity, while lead causes anemia, encephalopathy, and hepatitis. Ion exchange, chemical precipitation, liquefied lime, reverse osmosis, and electrochemical removal have been used to eliminate heavy metal ions from aqueous solution with significant disadvantages such as cost prohibitive, slurry formation, and high energy requirements. Activated carbon is a very effective method of adsorbing metals but it is limiting due to high cost. Sustainable and effective technology using biologically active or inactive organisms or so-called bio-adsorption (Biosorption) is an emerging way to remove heavy metal ions as its cost is low such as, bamboo dust [4], coconut fiber [5], bagasse [6], saw dust [7], algae [8], silk cotton hull [9], wheat straw (Triticum sativum) [10], yeast [11,12]. In water pollution control, biosorption is a very effective way used to eliminate metal ions from containing solutions [13,14].

One of the most important advantages of the removal process in this way is the possibility of reusing the adsorbent medium with a low selective cost for the metal ions, even if they are present at low concentrations, as well as the non-generation of toxic substances as an accidental product [15]. The present study is conducted to investigate the efficiency of *Chara algae* in removal of lead and copper ions (Pb^{+2} and Cu^{+2}) from prepared solutions.

The optimal conditions for the process of bio-adsorption such as pH function, primary metal concentration, contact time, temperature, and quantity of biomaterial are studied. Biosorption mechanisms of Pb^{+2} and Cu^{+2} ions onto Chara algae are examined through the kinetics of reactivity and thermodynamics.

2. Methods

2.1 Algae Preparation

Chara algae used in the present study is obtained from Khirisan River (Diyala Governorate, Iraq). To remove all the dirt particles, it is washed with tap water and then with distilled water for several times, then left under sunlight for two days for initial drying, then it is placed in an oven at 75 °C for 24 hours to complete the drying process. The dried material is grounded and screened through a set of sieves to get 250 µm, and then stored in a plastic holder before examinations.

2.2 Algal Ashes Preparation

Dried algae are heated at 500 °C for 5 hr for carbonization and then hydrolyzed in 3:1 potassium hydroxide for 2 days. At 500 °C for 3 hours, calcination is performed to obtain algae ashes [16,17].

2.3 Preparation of Synthetic Solution

Standard solutions of 1 $g \cdot L^{-1}$ of Pb^{+2} and Cu^{+2} ions are prepared by dissolving the suitable amount of $CuCl_2$ and $Pb(NO_3)_2$ in deionized, distilled water. For the purpose of preventing the deposition of metal ions, drops of hydrochloric acid are added. By dilution with distilled water, working solutions are prepared. Initial pH is controlled via adding HNO_3 or NaOH droplets.

2.4 FTIR studies of Untreated Chara algae

Binding mechanism of sorption is explained by FTIR studies, which are carried out to confirm the presence of the functional groups. Chara algae powder is mixed with KBr of spectral grade and moisture free pellets. The spectrum of FTIR is recorded by Perkin-Elmer Spectrum 100, in the range of 450 cm^{-1} to 4000 cm^{-1}.

2.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is done by a differential thermal analyzer (Shimadzu DTA-50, Japan) up to 900 °C for both algae and algae ashes.

2.6 Batch Mode of Biosorption Studies

To study the effect of acidity, temperature, contact time and primary concentration of metal ions on equilibrium, batch experiments are conducted at a constant concentration for both of Pb^{+2}, and Cu^{+2} at 10 mg/L. 50 ml of these solutions of known concentrations are placed in conical flasks (250 ml) and biosorbent dose. PHs (2, 3, 5, 6, and 8), and a biosorbent dose of 0.1 g/l for 30 min contact time. The mixture is agitated by rotary shaker (DUBNOOT BSD/DCE) for 1 hr at 200 rpm. The pH is controlled by adding 0.1 M NaOH and/or 0.1 N HNO3 prior to sorbent addition. After that, centrifugation process is done at 300 rpm for 5 minutes in order to separate supernatants from adsorbent media. Residual metal concentration in supernatants is determined by AAS (Scientific Atomic Absorption Spectrophotometer Accu Sys 21), average results are recorded. The biosorption efficiency is measured by the following equation:

$$E = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad (1)$$

The following expression is used to predict metal uptake efficiencies of all adsorbents:

$$q = \frac{V(C_o - C_e)}{m^{*}1000} \qquad (2)$$

Where q represents the amount of metal bonded in mg to 1 g of algae; C_o and C_e represent initial and final metal concentration (after equilibrium); V refers to the volume of solution in milliliter and m denotes the dry weight of the Chara algae added.

2.7 Biosorption Equilibrium

A known amount of Chara algae is put in flasks of 250 mL volume, each flask containing 100 mL of metal ion solution with different initial concentration (20–100 mg/L). These flasks are shaken in a rotary shaker at 200 rpm for 1 hr maintaining a temperature at 25 °C in order to reach saturation condition where the biosorbent is saturated with metal ions.

2.8 Biosorption Kinetics

Kinetics experiments are conducted by using 250 mL flasks containing 100 mL of metal ion prepared solution with specified amount of Chara algae. Flasks are agitated by rotary shaker at 200 rpm with constant temperature at 25 °C. Samples are collected at various intervals (10-150 min), centrifuged, and residual metals in the samples are determined. Pseudo-first and second order models are used to analyzed kinetic results [19,20].

3. Results and Discussion

3.1 Identifying the Peaks on Raw Algae

The wall of algal cells is composed of polysaccharides, proteins, and lipids which offer functional groups that are responsible for metal binding [21]. FTIR analysis in the range of 450 cm^{-1} to 4000 cm^{-1}, shows the presence of characteristic polymeric –OH as in cases of celluloses and hemicelluloses (Xylan), phenolic –OH as in case of tannins and lignins, O=C-O, carboxylate ion as in glucuronates of hemicellulose present in a bark.

FTIR spectra analysis suggests that the presence of effective groups such as carboxylic and alcohol bonds can be associated with (N-H) amine bond stretching at peaks extended from 3399 to 3434 cm^{-1}; while amide groups or carbonyl C=O bond between 1080-1090 cm^{-1}; stretching of alcohol and ethers C-O and O-H bond extended from 1000 to 1280 cm^{-1}. At 1400 cm^{-1} lead could be binding at this site, all these groups are related to individual metal binding [22].

The FTIR spectra (Fig. 1) shows that all groups including amino, hydroxyl, carboxylic, and carbonyl groups are present and have some role in the adsorption process.

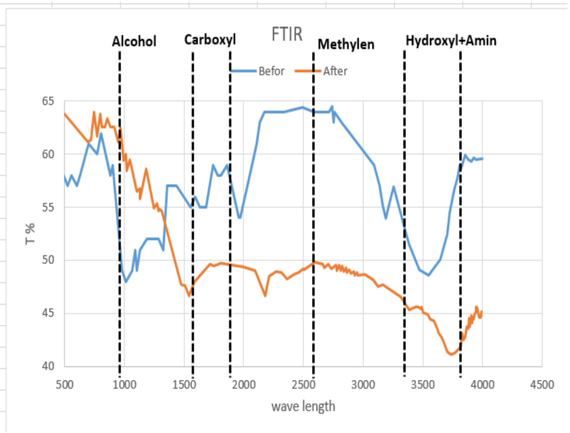

Fig 1: FTIR spectra of algal biomass Chara Algae. Native

3.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) for algae and algae ashes as seen in Fig. 2 shows that from 0 to 150 °C, there is loss in mass of samples by up to 20% due to a removal of humidity. Between 300-400 °C, the loss is very high and that could be attributable to decomposition of algae to gases [23]. In algae ashes, there are more hydrophilic groups, and its surface area are accepted by activation [24].

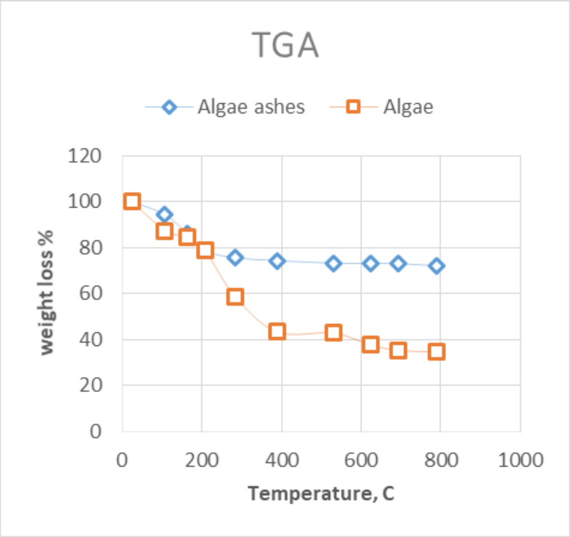

Fig. 2: TGA for algae and algae ashes

3.3 Effect of pH

Chemistry of metals is known to be affected by acidic scale, pH of a prepared solution as well as by functional group protonation of the functional groups existing on Chara algae surface. By increasing the pH, adsorption rate of ions increases to a maximum and then begins to decline sharply.

As the pH increases, this increases the number of active sites that carry a negative charge on the surface of the absorbent material; the best pH was 6 as shown in Fig. 3.

Acidic and basic functional groups existing on Chara algae surface include the sulfate groups, phosphate, carboxyl, amine, and hydroxyl. In general, sulfate and carboxylic groups are the most effective in the adsorption process [25]. When the acid scale pH is less than 5, the active groups in the cell wall and ionic state are responsible for adsorption and since the metals are present in their ionic form and through acid-acid equilibrium theory, the coupling of metal cations is measured by the dissociation of weak acid groups.

By using biological materials, carboxylic group (COOH) is most effective in removing metal ions [26,27]. At pH 5, there are few hydronium ions that compete with heavy metals ions on free bonds at active sites which are negatively charged resulting in an increase in biosorption. An increase of pH in the range of 6-10 causing precipitation process in solution as well as some dip in the polarity. Several adsorbent materials are used to investigate the effect of pH on the adsorption process [28,29].

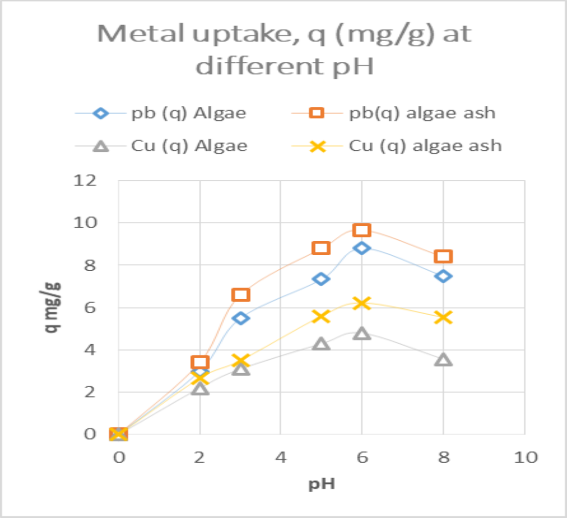

Fig. 3: Metal uptake, for lead and copper at different pH

3.4 Effect of Temperature

The increase in temperature increases the prevalence rate of ions during the external boundary layer, internal limits of pores in absorbent material and the best temperature is 40 °C as can be seen in Fig 4. Results showed that the process of adsorption is an exothermic process and therefore the increase in temperature leads to a decrease in adsorption. Low temperature is indicative of a physical biosorption phenomenon.

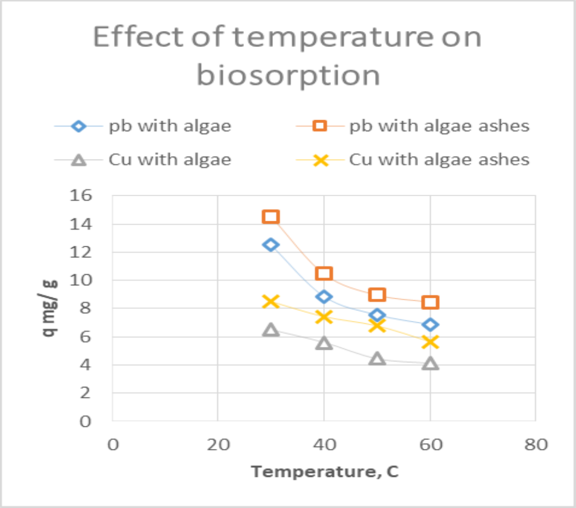

Fig. 4: Temperature effect on metal ion biosorption

3.5 Biosorbent Dose

Using different concentrations of adsorbent material affects the adsorption process as shown in Fig. 5. It can be observed that by increasing the amount of adsorbent, the adsorption rate decreases due to the overlapping of active sites.

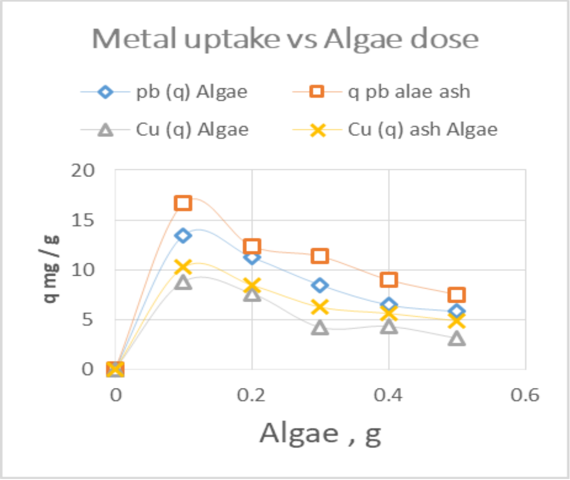

Fig. 5: Metal uptake with increasing biosorbent dose

3.6 Effect of Contact Time

Fig. 6 shows that more than 75% of the metal ions are removed in the first 15 minutes and the equilibrium state can be reached after 60 minutes [30]. And then the change in adsorption status is almost unnoticeable.

Using non-living cells is not dependent on the metabolism and occurs at the walls of these cells and the process of adsorption, in this case, is a quick process and more preferred than the living cells [25].

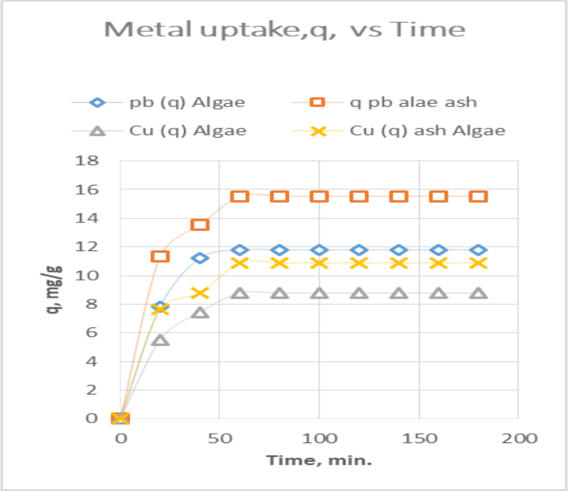

Fig. 6: Metal uptake, q, at varied time

3.7 Initial Concentrations Effects

From observation of Fig. 7, the increase in adsorption is directly correlated with the increase of the primary concentration of metal ions. This can be due to the availability of bonding sites for adsorption of abundant ions. The speed of the adsorption process can be observed in the first 15 minutes. Thereafter a decrease in the concentration of ions occurs to the extent of the occupancy of all the active sites and down to the state of equilibrium.

The speed of the process at first is due to the process of adsorption from the surface of the material obtained by the ion exchange process with the active groups while the second phase is lower and that could be attributed to interstitial fluxes of metal ions into the cell.

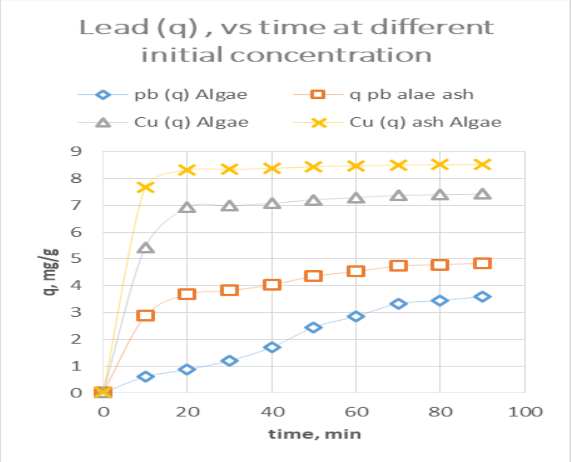

Fig. 7: Metal uptake for lead and copper with time at a varied initial concentration

4. Conclusions

The current study shows that it is possible to use cheap and available in large quantities, Chara algae, to remove toxicity from the effluent stream of any industry. The practical results show that the time required for adsorption is short, exothermic nature of a biosorption process, best pH and high affinity for metal ions is found. The use of algae requires more studies on the level of the presence of more than one metal and the possibility of finding a mathematical model shows the mechanism of the process in addition to the possibility of improving the efficiency of some modification for algae, as well as conducting the process in an open system.

5. Acknowledgments

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