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Efficiency of Pre-Treated Immobilized Chara Algae (C. vulgaris) for Biosorption of Copper and Lead from Aqueous Solutions

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ABSTRACT

The present study evaluates the potential of chemically modified, immobilized Chara algae (C. vulgaris) to remove copper and lead from aqueous solutions. Chara algae were prepared and studied for their ability to remove heavy metal ions prepared solutions. In a batch mode, several factors affecting the adsorption process such pH, temperature, contacting period and algal dose on adsorption efficiency were studied. Results showed that the metal adsorption process takes place quickly at pH values (5.0-6.0), temperature level (25-30) ^{o} C and the order of the accumulated metal ions is Cu>pb. The results showed that the handling with low concentration of nitric acid at 0.05 normality was effective in the process of desorbing metal ions. So as for regeneration of algae, 0.2 M sodium hydroxide is very effective. The regenerative algae were used for five cycles of biosorption, without losing its demineralization efficacy. FTIR absorption spectroscopic analyzes showed that all groups that present in the algae are responsible for the main biological absorption of metal ions. Adsorption process specifications are more effective when using modification processes, as the maximum adsorption of algae for both lead and copper was within a range of 6.5-10.3 mg per gram of algae when using the alkaline treatment. While the acid treatment reduced the amount of adsorbent by 4.2-5.8 mg per gram algae; The adsorption process is fast and occurs by 90% within the first 15 min. Heavy metal adsorption was observed at very low levels at pH values as low as 2.0. Algae are effective in removing lead, copper and other light metal ions from wastewater.

1. Introduction

Environmental poisoning by heavy metals and various organic compounds and reducing its environmental impact has become a worrying problem in recent years. As a result of various human activities, these substances are released into the ecosystem in large quantities annually. [1] These pollutants enter the environmental system through these human activities through wastewater to soil and sediments [2]. Heavy metals are present in the eco system with different levels of oxidation states, as well as different states of toxicity depending on their quantity. Toxic effects are produced by interfering with the cellular biomolecules of living being, which leads to various metabolic problems [3]. The process of entry of pollutants into the ecosystem takes place through various mechanisms, including absorption or through contact with the skin and soil diet or through inhalation, or through oral. These pollutants participate in environmental processes largely, as either oxidizing or reducing agents, and cause inhibition of normal cell work, and because of their cumulative property, they may eventually lead to the death of living organisms at certain doses [4- 5].

Most of the health effects of heavy metal accumulation on the ecosystem and humans

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have been briefly explained in various studies [6]

Conventional methods such as chemical precipitation, ion exchange, reverse osmosis and extraction with organic solvents are among the most used methods for removing heavy metals from wastewater [7].

These methods have many limitations such as incomplete removal and the fact that they have high-energy requirements, which may cause the generation of new waste in addition to their inability to remove pollutants with low concentrations [8].

The biological method which defined as the use of specific microorganisms that have the ability to break down pollutants or reduce their concentrations to an acceptable level. The process known as biosorption, it is a convenient technology as it is cheap and highly effective in removing contaminants. [9].

Microorganisms including bacteria, algae, fungi and yeasts have a high ability to remove heavy metal ions through multiple mechanisms including cellular adsorption within the cell or on its cell walls [10].

Biological treatment is nowadays considered a successful alternative to recover heavy metals as well as phosphorous and sulfur contained in wastewater compared to traditional methods [11,12].

The use of immobilized algae gives positive advantages to the removal process, as it possesses resistance in the chemical environment, ease of separation processes, as well as mechanical strength and the possibility of reuse for multiple times [13].

The process of recovering metal ions depends on the nature of the materials used in the recovery [14]. With the lowering the pH value, the process of extracting metal ions from the adsorbent medium accelerates, where competition occurs between protons and metal ions within the active sites that cause bonding. Therefore, mineral acids such as H_2SO_4, HNO_3 and CH_3COOH are considered as highly effective recovery agents. [15].

Cell trapping is one of the most commonly used techniques, whereby cells are entrapped through a polymeric matrix porous enough to allow diffusion and is widely used to remove heavy metals from aqueous solution [16].

The aim of this research is to verify the efficiency of Chara vulgaris with treated and immobilized state to remove copper and lead ions from wastewater.

2. Materials and methods

2.1. Chara algae

The algae (C. vulgaris) used in this study were collected during the month of April from Khurasan River in Baqubah, Iraq and washed with normal water and then with distilled deionized water many times to remove the suspended dirt. The drying process done by leaving them under the sun light for two days, and then they were placed in an oven at a temperature 75 ^oC for a full day to finish the drying process. The dried algae were milled and isolated using molecular sieves to obtain (300-600) micrometre, then stored in a plastic bottle prior to use. Table (1) shows the different treatment methods that were carried out on samples of algae with an amount of 10 g of algae with a size of (300) micrometres. The samples were slowly soaked in chemical solutions, stirred for an appropriate period, then washed with distilled deionized quantity of water prior to drying in an oven in an oven at 60°C for 6 h. It was determined whether algae cells were alive or dead by taking 0.1 ml of algae solution. The resulted solution then diluted with ringar solution of 1:10, then taking 0.1 ml of this solution and mixing it with 0.9 ml of methylene blue solution. Dead algae were coloured.

Table 1: Treatment methods applied to Chara Algae

Method Number	Solution (100 ml)	Interval (min)
1	Without treating	120
2	0.1 N NaOH	120

2.2 Procedure for immobilization of algae

The immobilization process of algae is the same as that used in [17, 18]. Where 70 g of the washed algae suspended in distilled water at 50% w/v. Then an aqueous solution of 20% (w/v) of polyvinyl chloride of molecular weight 70000-100000, was prepared by adding 33 g of PVA in deionized distilled water. The resulting suspension then heated to 70 °C.

In order to dissolve the polymer, the resulting mixture was heated to 70°C, then cooled to 55°C before mixing it with the algae suspension, then the resulting suspension was cooled to 45°C before it was extruded via nozzles into a solution of saturated boric acid and then stirred for two hours. The formed granules with a diameter of 3 mm were transferred to a boric acid solution until crystallization occurred and hardness gained, then they were washed with distilled water and freeze-dried for 36 h.

2.3 Metal solutions

All chemicals used in this work were all of analytical grade when available and obtained from DIFCO, Sigma, Mallinckrot, or Fisher.

One liter of standard solutions of copper and lead ions was prepared by dissolving specific amounts of lead nitrate and copper chloride in water, which was distillated several times and passed over specific resins to remove ions. In order not to allow the precipitation process to occur, few drops of acid were added. By diluting with distilled water, a solution of different concentration was prepared from the prepared standard solution. The process of controlling the pH was done by adding drops of HNO_3 or NaOH.

2.4. Elutants

Distilled deionized water and hydrochloric acid at a concentration of 0.05 N were used to recover the ions from the algae after the adsorption process.

2.5 Metal uptake

The adsorbed metal ions, q was calculated from the following equation: -

$$q = \frac{v\,(C_o - C_e)}{m * 1000} \quad (1)$$

where: q represents amount of metal adsorbed on algae in (mg/gram); C_0 and C_e represent the concentration at time zero, and final concentration (equilibrium concentration) of ions mg/L; V is the mixture volume in ml and m is the weight of the algae used.

2.6 Metal binding experiments

2.6.1 Effect of pH

Adsorption experiments carried out to study the effect of pH at 25 °C by mixing 0.1 g of algae with 100 ml of a solution containing metal ions at a concentration of 10 mg/L in conical flasks.

The flasks were placed on a DUBNOOT BSD/DCE rotary shaker with speed of 200 rpm for 2 hours. The pH was controlled to the desired value via 0.1 N HNO_3 and/or 0.1 M NaOH prior to adding the algae.

Experiments were performed within ranges of pH 3, 4, 5.5 and 6. A control sample was prepared without treatment with algae. The pH during the mixing process was not controlled or measured.

At different time intervals (5, 15, 30, 50, 80, 120, 150, and 180 min.), samples were drawn from the flasks and the separation process was carried out using a centrifuge at 3000 rpm for 10 min., then filtration was carried out to separate the algae from the solution. Measure the concentration as well as the pH.

2.6.2 Elution of algae and reuse

After the end of the adsorption process, separation of the algae with centrifugation, the separated algae were eluted with several chemical solutions to remove the adsorbed ions, the samples of 0.1 g treated with 25 ml of chemical solutions (deionized water, 0.05N HNO3) and placed in conical flasks on the shaker device for 10 min. at 3000 rpm.

The concentration of metal ions in the medium was measured and then two methods were used to regenerate the algae, the first was using distilled water only and the second was using 2% sodium hydroxide solution. The process aims to get rid of positive hydrogen ions until the pH reaches 5. immediately; the regenerated algae were washed with large amounts of deionized water until the pH was neutralized and then the drying process was carried out at 60°C for reuse in the new adsorption processes.

2.6.3 Charactrization of bioadsorbent

FTIR analysis used to detect the effective groups in the algae after exposure to heavy metals, where 5 ml was taken from the medium and filtered using a 0.2 µm filter and dried for 48 h. The analysis was conducted at the length of 400-4000 cm^{-1}.

3. Results and discussion

3.1 pH

Figure 1 shows that the adsorption process increases steadily with increasing pH and reaches its maximum at pH 6 and then starts decreasing between 6-8 due to the precipitation process due to the fact that the medium turns into an alkaline medium. The main reason for the fact that the adsorption process is decreases at low levels of the acidity scale is due to the competition between heavy metal ions and the H_3O ion for the active sites in the algae [19-20].

This means that at a low level of pH, an increase in protons occurs that compete with heavy metal ions for active sites, resulting in reduced or even no adsorption process. Other researchers obtained the same results [21-22].

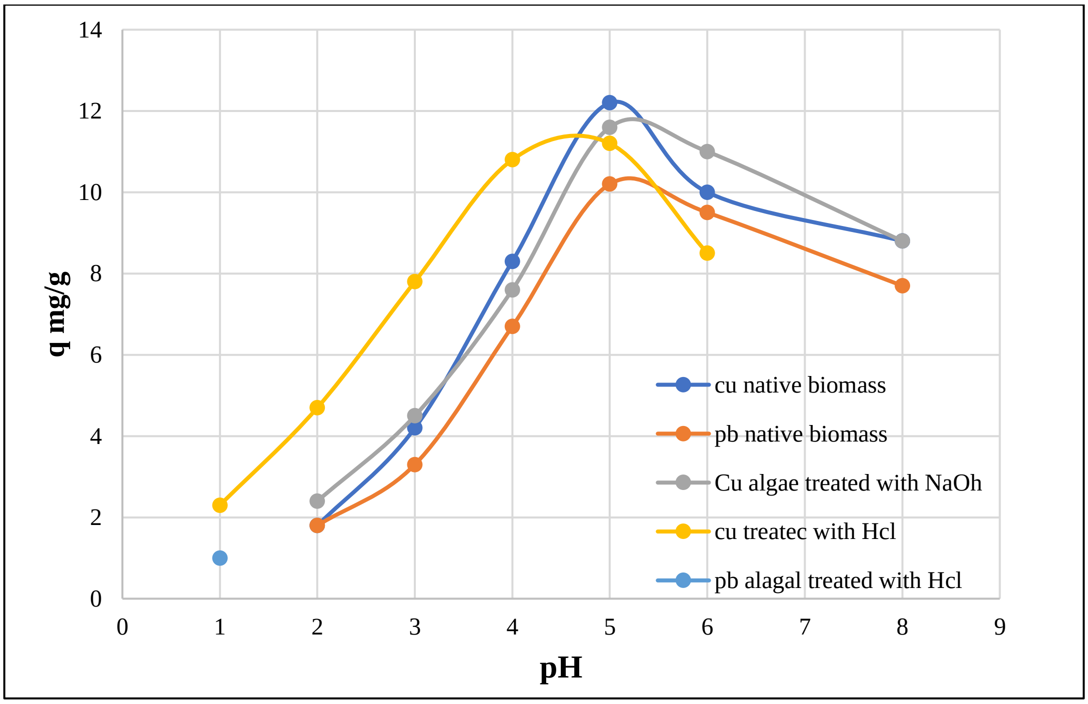

Figure 1. Metal uptake(q) with pH

3.2 Temperature

Temperature is an important environmental factor that has a significant impact on the process of removing heavy metals, as it is closely related to the growth process and the metabolism process. Figure2 show the increase in temperature indicated a decrease in the biological adsorption process of heavy metal ions, where at temperatures higher than 37 ° C, damage to the active sites in algae may occur. The adsorption process is basically an exothermic process. It is necessary to note that the adsorption process does not usually work at a high level of temperature due to the increased operational cost [23].

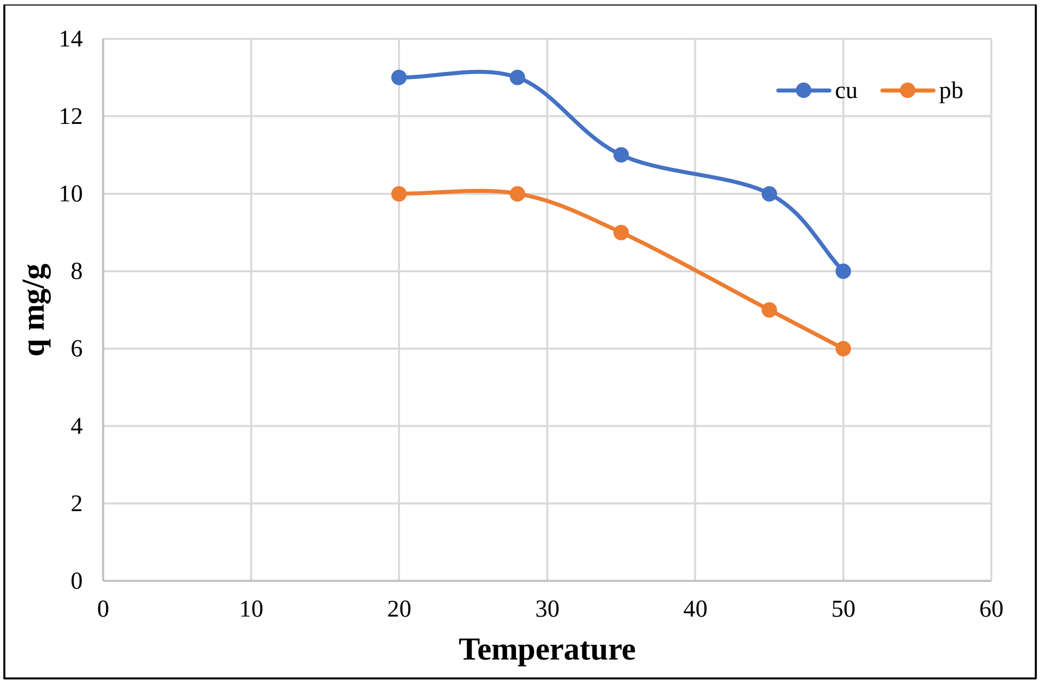

Figure 2. pb and cu sorption capacity with temperature

3.3 Effect of treated alge

Figure 3 shows the effect of the treatment process on adsorption and the ability of the algae to withdraw metal ions. Figure shows that when the treatment with HCl, the adsorption process decreases due to the loss of some effective groups on the algae surface. while the increase in the adsorption process when treated with NaOH, as the alkylation causes inactivation of enzymes that cause algae rot, and alkaline treatment causes removal of fats and proteins, which reflects positively on the efficiency of the adsorption process [24-25].

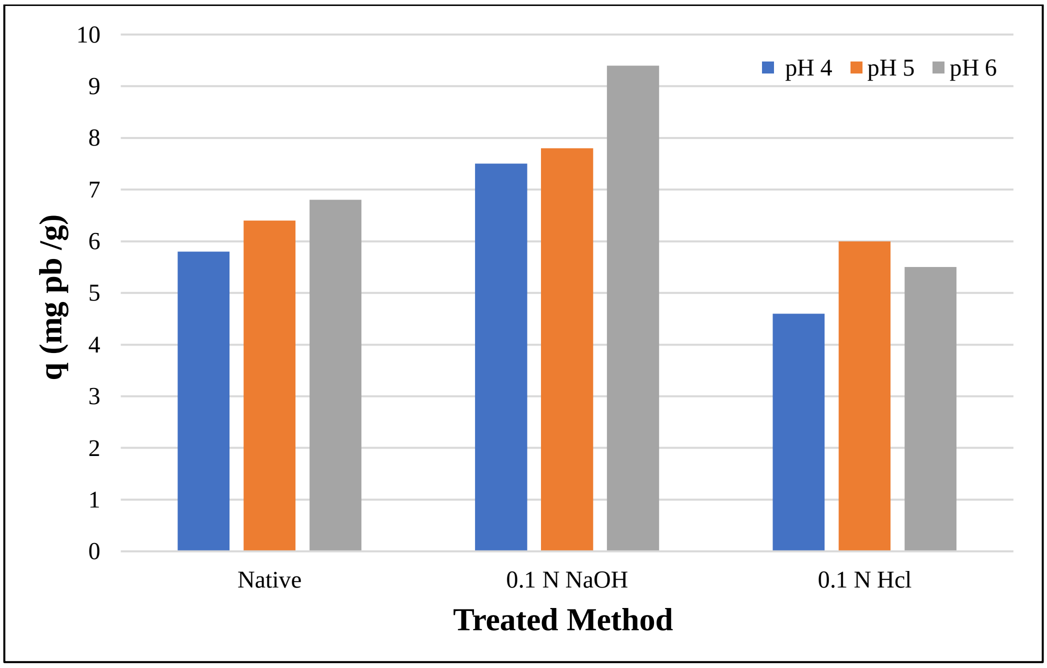

Figure 3. Treated method and its effect on sorption capacity

3.4 FTIR analysis

Algal cell walls are composed of sugars, lipids and proteins, which are in the form of active t groups responsible for the process of bonding with metal ions, FTIR analysis shows within the range of 400-4000 cm^{-1} the presence of the characteristic polymer - OH in cellulose and hemicellulose and the phenol group - OH, and and a carboxyl group O = C-O.

Spectrum analysis using FTIR results indicated that the presence of different functional groups on the algal surface such as alcohols and carbonates could be associated with amine groups in peaks extending from 3400 to 3436 cm^{-1}.

While the bonding group of amides or carbons was within the peaks of 1090-1098 cm^{-1}; While the extensions of the ethers' aggregates were from 1000 to 1285 cm^{-1}. At 1398 cm^{-1} where lead can be bonded at this location with a single metal bond [26].

The FTIR spectra in Figure 4 show that all existing groups have basic role in the process of adsorption.

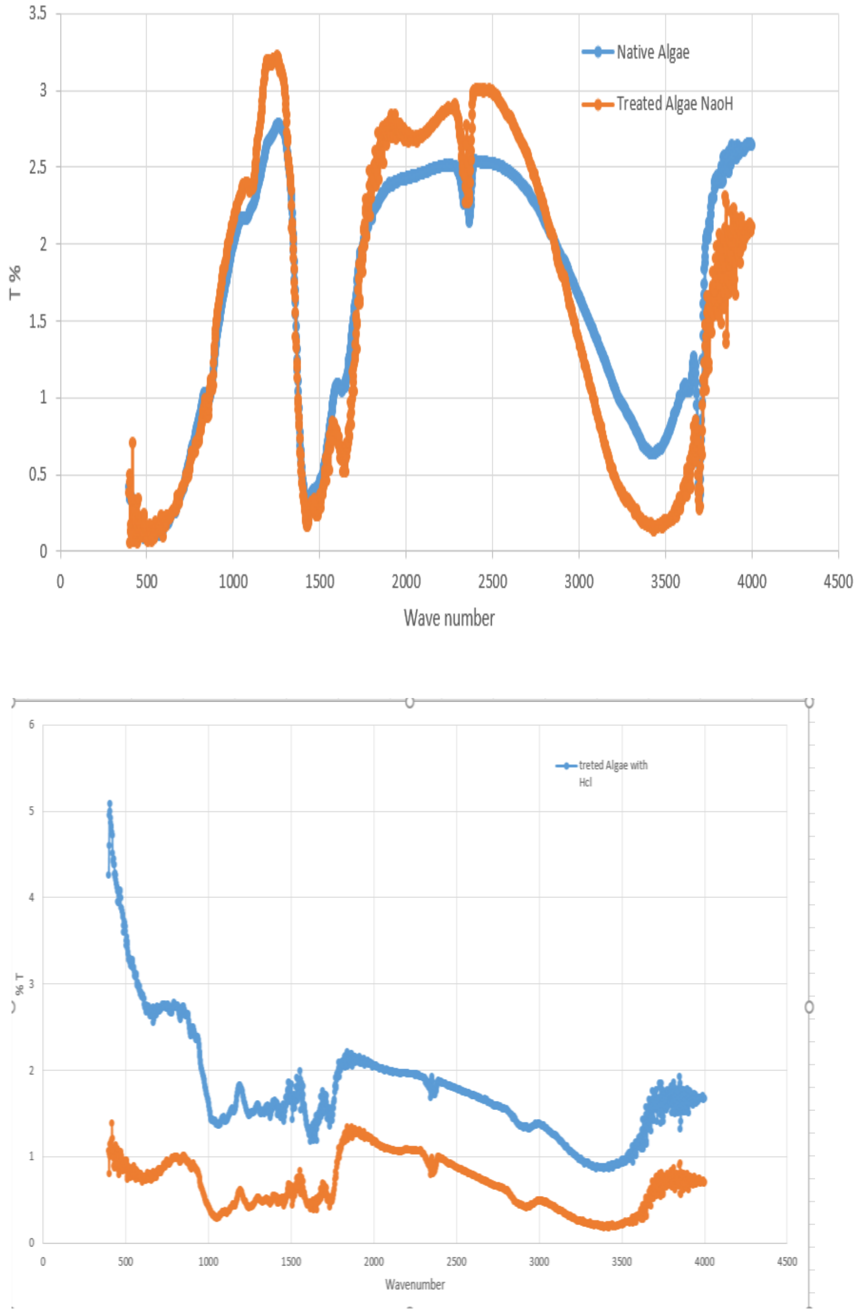

Figure 4. FTIR spectrum results for Algae

4. Conclusions

The study shows that algae used in this research and abundant in environment have the ability to remove heavy metals, and that the process takes place within medium ranges of the pH scale and in an appropriate time. Spectral analysis showed that the aggregates in the algae are responsible for the removal process.

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