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Research Article

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Biosorption of Pb^{2+} from water solution by using of Chroococcus minutus and Chlorococcum aegyptiacum as biosorbents

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ABSTRACT

In this study, the batch experiments (shake flask conditions) existed carried out to investigate the potential of Chroococcus minutus and Chlorococcum aegyptiacum (dead mass) to remove Pb^{2+} ions (5, 10, 15 and 20 mgL^{-1}) from aqueous solution under different pH values (3,4,5,6& 7); different mass amounts (0.5, 1.0, 1.5 & 2.0 g dry wt./L) and also under different shaking time periods (1, 2,3,4,5 & 6 hours). Both biosorbents recorded high biosorption value (96 and 90 % for Chroococcus minutus and Chlorococcum aegyptiacum, respectively) by using 1.6 g dried algal material at the initial concentration of 15 mgL^{-1} Pb^{2+}, pH 6.0 and 28ºC constant temperature for 5 hours of contact time. Analysis of the spectrum obtained with atomic absorption spectrophotometer indicated that the adsorbents have great potentials to remove Pb^{2+} from aqueous media and can be used as an eco-friendly technology for efficient bioremediation in the natural environment.

Keywords :*Biosorption ; Pb^{2+}; Chroococcus minutus; Chlorococcum aegyptiacum.*

INTRODUCTION

Heavy metal pollutants become a health hazard and a source of growing concern because of health risks on living organisms and humans. Therefore, the heavy metal pollution is one of the most serious environmental problems in the world [1-4]. The increased industrial activities are the main reason for most of the problems of pollution which damages the ecosystem due to the accumulation of toxic metals pollutants such as chromium [5].

Heavy metal removal from aqueous solutions is an important issue faced by industries discharging waste water containing heavy metals. Thousands of tons of heavy metals are discharged from industrial processes such as electroplating, plastics manufacturing, mining and metallurgical processes [6]. A number of physicochemical methods, such as chemical precipitation, adsorption, solvent extraction, ion exchange, membrane separation, etc., have been commonly employed for stripping toxic metals from wastewaters [7]. However, these methods have several obstacles, such as inadequate metal discharge, costly apparatus and monitoring regularity requirements, special reagent or energy demands and generation of toxic sludge or other waste products that require clearance. Moreover, they may be worthless or extremely expensive when the metal concentration in wastewater is in the range 10-100 mgL^{-1}[8].

For more than a decade, researchers have been looking for inexpensive and more effective methods to remediate heavy metal contaminated waters and reduce the growing danger hazard on the public health. With the expanding attention around heavy metal contamination and allow to make great efforts to find effective means to remove metal contaminants using biological methods especially dynamic adsorption to be a substitute for the physical techniques such as sedimentation, ion exchange and membrane processes [9]. Biosorption of heavy metals from aqueous effluents is a process that has proven very encouraging. The significant benefits of biosorption over conventional treatment methods include regeneration of biosorbent and the possibility of metal recovery, high efficiency of metal removal from dilute solution, low cost, minimization of chemical and/or biological sludge and no additional nutrient requirement [10-13].

Algae are therefore readily available in large quantities for the development of highly effective biosorbent materials. This is due to the presence of different functional groups such as carboxyl group (COOH) and Secretary (NH_2) and sulfate (SO_4) and hydroxyl (OH), which serves as binding sites for metals [14].

The intention object of the present work was to assess the lead biosorption by one blue-green algal taxon (*Chroococcus minutus*), and one green algal taxon (*Chlorococcum aegyptiacum*), also to evaluate the influence of different factors such as pH, temperature, concentration of biomass, concentration of metal ions and the contact time on the biosorption capacity of the algal mass.

MATERIALS AND METHODS

Microalgae isolates

Two micro-algal taxa were kindly supplied by Prof. Dr. Ibraheem, I.B.M., Manager of *Phycological laboratory, Faculty of Science, Beni-Suef University, Egypt*. There were *Chroococcus minutus* and *Chlorococcum aegyptiacum*.

Preparation of bio sorbents

For the removal of metal ions from aqueous solutions was prepared using the two micro-algal taxa. The two strains were cultivated using BG-11 medium [15] under controlled conditions (28 ± 2ºC, 2200 Lux, 12h/12h light and dark cycle). The sun-dried biomass was rinsed with deionized water to remove the remaining alkalinity. Then, it was dehydrated in an oven originally at room temperature for 24h and subsequently at 80°C for 12h. The dried biomass was then ground well and passed through a 150–200 mesh sieve to obtain a powder pattern. Subsequently, the contents were saved in a desiccator at room temperature to be used as a powdered biosorbent [16]. Dehydrated algal biomass was employed for the studies subsequent rehydration. Re-hydrated biomass was developed by dissolving the provided dry biomass in 100 ml of deionized water taken in 250-ml- Erlenmeyer flasks. After a disturbance on a rotary shaker (150 rpm) at ambient heat for 60 minutes, the biomass was collected by filtration through a 0.45 um membrane filter (type Millipore Corporation, USA) and quickly used in adsorption studies [17].

Preparation of stock solution of Pb^{2+}

A stock solution of 1000 ppm Pb^{2+} solution was prepared by suspending 3.31g of lead nitrate $Pb(NO_3)_2$, in one liter of deionized distilled H_2O. Different concentrations of test solutions were prepared by appropriate dilution of the property suspension. The original pH of various suspensions was later adjusted to the required value with different concentrations of HCl and NaOH solutions before mixing the biosorbents suspension.

Factors affecting heavy metal bio sorption

Batch mode adsorption studies were carried out to investigate the effect of different parameter such as initial concentration of Pb^{2+}, via biomass, pH, temperature, and contact time. The solution containing adsorbate and adsorbent was taken in 250 ml capacity flasks and agitated at 150 rpm in an environmental Shaking Incubators (49L, 71L, Bench top) at proposed time periods. The adsorbate was separated from the adsorbent after processed by centrifuge at 6000 rpm, for 30 minutes followed by filtration by using 0.45 um membrane filters (type Millipore Corporation, USA).

Effects of contact time

The impact of contact time on adsorption ability for $Pb^{2+}$by biomass was determined at varying periods of incubation time (1,2,3,4,5 and 6 hours), with an initial concentration of Pb^{2+}, 10 mg/L in an environmental Shaking Incubators (49L, 71L, Bench top). After incubation for specified period, the supernatant was analyzed for remaining metal concentration in the solution. The pH (5) and the adsorbent concentration of the biomass (1 gL^{-1} dry wt.) were kept constant.

Effect of pH

To identify the most suitable pH for the effective biosorption of Pb^{2+} onto the experimental microalgae, sorption experiments were performed at different pH values (3, 4, 5, 6 and 7). The pH of solutions was adjusted with 0.1 M of HCl and 0.1 M of NaOH. Due to the formation of soluble hydroxylated complexes of the metal ions, no experiments performed at higher pH [18].The equilibrium time, temperature and biomass concentrations were maintained constant throughout the study. The Erlenmeyer flasks containing 1g L^{-1} dry wt. biomass were kept in a shaker at 200 rpm and 28°C for 5 hours of contact time.

Effect of biosorbent dose

The effect of biosorbent dose on adsorption of $Pb^{2+}$was studied using different biomass concentrations (0.4, 0.8, 1.2, 1.6 and 2 g dry weight /L^{-1}) with 10 mgL^{-1} of Pb^{2+}. The equilibrium time (5 hours) and the pH 6 of the test solution were kept constant [19]. The Erlenmeyer flasks were kept in a shaker at 200 rpm and 28°C.

Effect of metal ions concentration

To study the effect of metal ions concentration on the amount of the metal absorption, initial experiments were carried out by using 100 ml solution of Pb^{2+} at different concentrations (1,5,10,15, and 20 mgL^{-1}). Thin 1.6 g (dry weight) of algae biomass was added to all solutions. The equilibrium time (5 hours) and the pH 6 of the test solution were kept constant. The Erlenmeyer flasks were kept in a shaker at 200 rpm and 28°C.

Effect of presence of biosorbent

The plot of metal concentration using alginate beads (1.6gL^{-1}) without biomass against that by using microalgal biomass (1.6 gL^{-1}) as biosorbent was conducted. The equilibrium time (5 hours) and the pH 6 of the test solution were kept constant. The Erlenmeyer flasks were kept in a shaker at 200 rpm and 28°C.

Data analysis

After adsorption, the adsorbents – loaded adsorbent were separated from the solution by centrifugation at 6000 rpm for 30 min and then all the samples were filtered immediately through 0.45 um membrane filters (type Millipore Corporation, USA) to remove biomass. Pb^{2+} concentrations in test solutions were analyzed by Atomic Adsorption Spectrometer (AAS; Perkin-Elmer model 3100). The removal efficiency for $Pb^{2+}$was calculated as removal percentage (R%) from aqueous solutions by using the following equation [20]:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

Where:

Co: Initial concentration of Pb^{2+}

Ce: Pb^{2+}concentration remaining in the solution.

RESULTS AND DISCUSSION

Effect of contact time

The equilibrium time required for the biosorption of Pb^{2+} on *Chroococcus minutus* and *Chlorococcum aegyptiacum* with 10 mgL^{-1} of the biosorbent at different time intervals were studied. Figure 1, showed that adsorption capacity sharply increased with increase in time and attains equilibrium in 5 hours for all studied algal biosorbent. However, it remains constant after an equilibrium time of 5 hours, which indicates that the adsorption tends toward saturation. Therefore, the adsorption time was set to 5 hours in each experiment. The rate of adsorption is higher in the beginning due to the large available surface area of the biosorbent. At equilibrium (i.e., after the capacity of the adsorbent gets exhausted), the rate of uptake is controlled by the rate at which the adsorbete is transported from the exterior to the interior sites of the biosorbent particles [21].

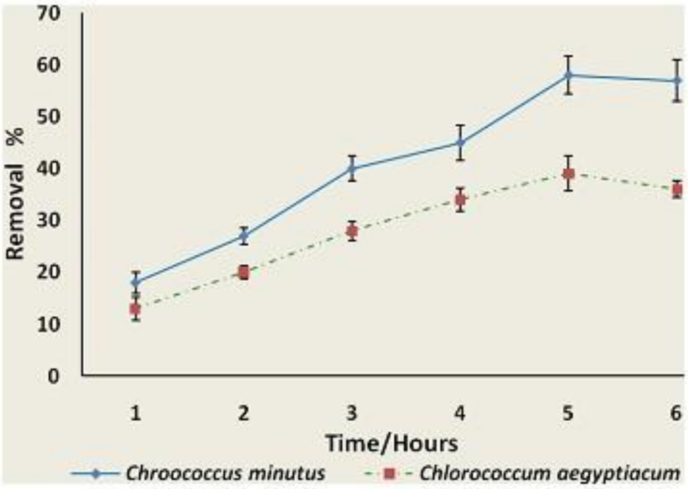

Figure 1. Effect of contact time on biosorption of Pb^{2+}

Effect of pH

In order to establish the effect of pH on the biosorption of Pb^{2+} ions onto the two different biosorbents mentioned above, the batch sorption studies at different pH values were conducted in the range of 3 to 7. It has been shown that the affinity of cationic species for the functional groups presents on the cellular surface is strongly dependent on the pH of the solution. The biosorpitive potential appeared low at low pH values and increases with pH until reaching an optimum pH. It was observed that the maximum adsorption of Pb^{2+} ions was observed at pH 6 for all the biosorbents and significantly decreased by increasing the pH values up to 7 (Figure-2). At lower pH, the biosorbent is positively charged due to protonation and Pb^{2+} ion exists as an ion leading to an electrostatic attraction between them [22]. A definite decrease in adsorption above pH 6 maybe due to the occupation of the adsorption sites by anionic species which retards the approach of such ions further toward the sorbent surface [23, 24]. Uptake of Pb^{2+} increased markedly with increasing pH. At pH 5 and 6 corresponding uptake yield values were found to be 49 and 68 % for *Chroocuccus minutus*; 39 and 58 % for *Chlorococcum aegyptiacum*. So, the maximum uptake of $Pb^{2+}$was recorded at pH 6 and thereafter decreased with further increase in pH. These results suggest that pH affects the solubility of metals and the ionization state of the functional groups such as phosphate, carboxylate, and amino groups of the biosorbent cell walls [25].

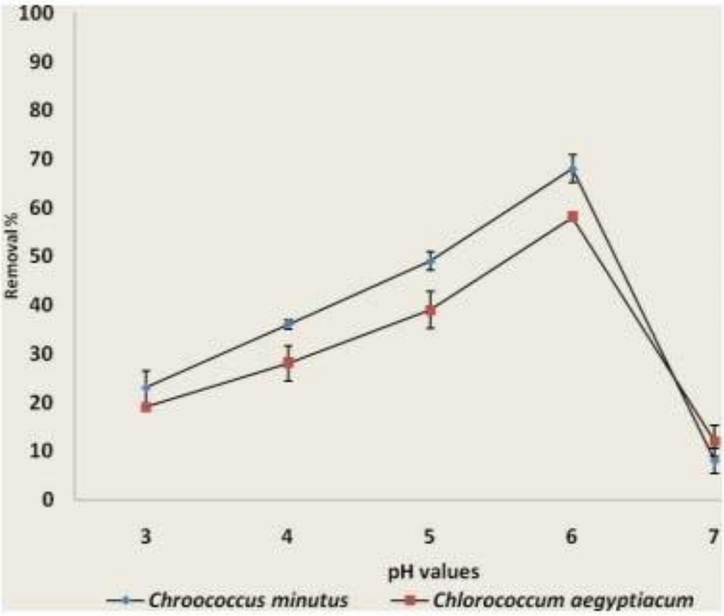

Figure 2. Effect of different pH values on biosorption of Pb^{2+}

Effect of biomass dosage

The effect of biosorbent dosage on the removal of Pb^{2+} was shown in Figure 3. The amount of sorbent was varied from 0.4 to 2.0 gL^{-1}. The results indicated that the percent removal of Pb^{2+} ions increased with the increase in the amount of adsorbent up to 1600 mgL^{-1} and removal efficiency for *Chroococcus minutus* and *Chlorococcum aegyptiacum* were 88 and 79 % of Pb^{2+}, respectively. The removal efficiency attained decreasing after that. This is due to the availability of more biosorbent as well as greater availability of surface area [26]. More quantity of biosorbent results in increasing of surface area and biosorption regions which cause removal of more Pb^{2+}. Moreover, the high blocks of adsorbent particles lead to the lower surface area available for the Pb^{2+} ions, so the decrease in Pb^{2+} uptake at higher adsorbent dose may be due to the competition of the Pb^{2+} ion for the sites available[27,28].

The impact of the initial concentration of metal

Influence of different concentrations of Pb^{2+}on the adsorption process was also studied in this work. It was cleared from the obtained results as shown in Figure 4, that the rate of adsorption of Pb^{2+}ions was increased in the range of 15 mg L^{-1} in all the studied microalgae. The efficiency of adsorption depends on two reasons; lower concentrations of Pb^{2+} ions can provide a positive force which enhances the adsorption process, or the greater number of Pb^{2+} ions can lead to competition for binding sites available in the biomass [29]. Increasing concentrations of Pb^{2+}above 15 mgL^{-1} leading to declining in the removal percentage gradually which can be attributed to the saturation of all binding sites on the surface of the biomass of algae [30].

Effect of presence of biosorbent

The plot of metal concentration in aqueous solution using alginate beads without algal biomass and with biomass (Figure 5) shows that the microalgal biomass is more metal compared to alginate beads without biomass. The increase in metal uptake in many folds higher with microalgal biomass gives the evidence of the biomass efficiency for Pb^{2+} uptake from solution medium.

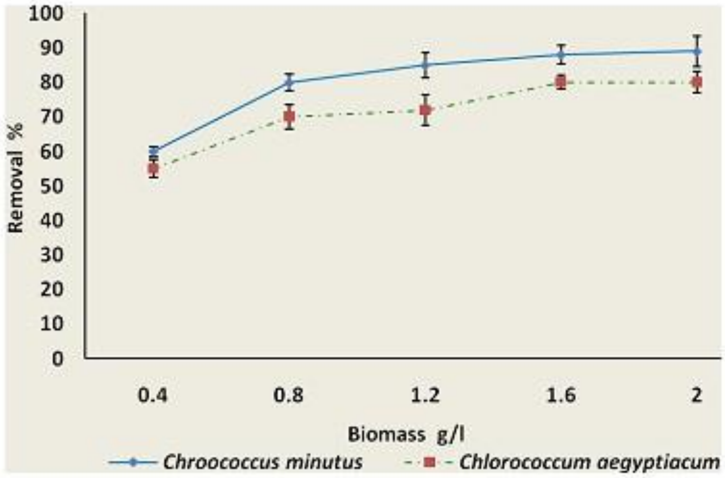

Figure3. Effect of biomass dosage on biosorption of Pb^{2+}

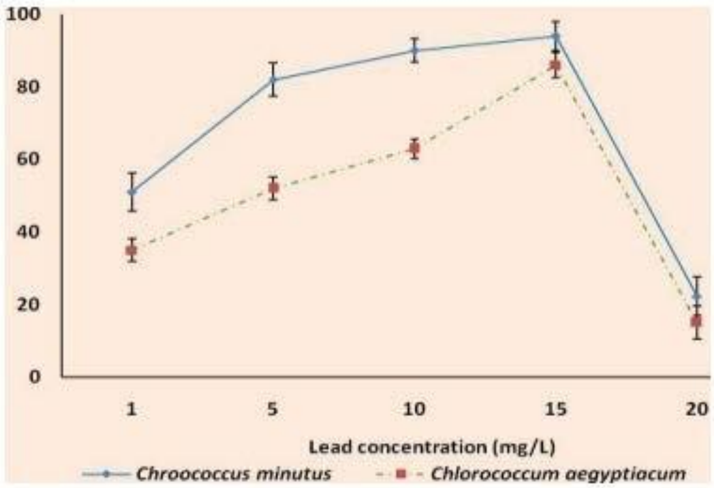

Figure 4.The effect of different concentrations of Pb^{2+}on the rate of removal.

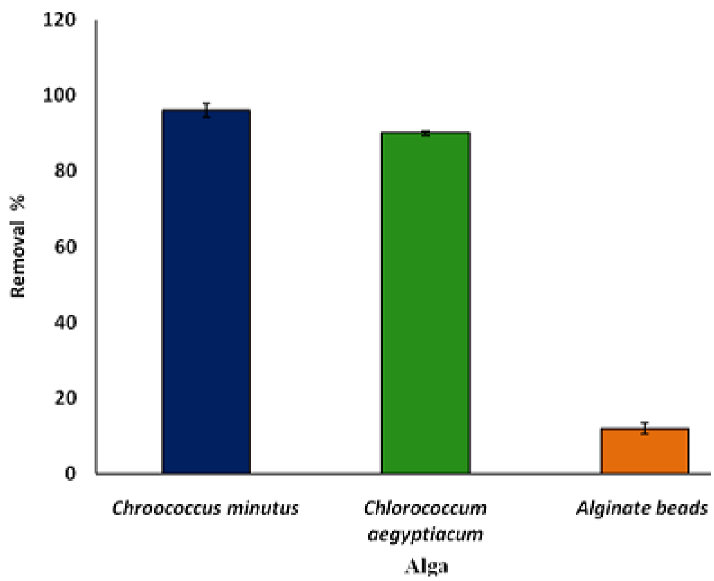

Figure 5.Effect of presence of biosorbent on the Pb^{2+} removal.

CONCLUSION

Biosorption is a process that has been shown to have a considerable potential for the efficient removal of pollutants from aqueous solution. The existing examination provides the evidence of the possible benefits of using the dry biomass of *Chroococcus minutus* and green microalga *Chlorococcum aegyptiacum* for the removal of Pb^{2+} from aqueous effluents. The dried algal biomass, in the batch inspection, was decided to be quite effective in excluding Pb^{2+} ions from aqueous solution by 96 and 90 % by using dried biomass of *Chroococcus minutus* and green microalga *Chlorococcum aegyptiacum* within 5 hours of contact time, respectively. It is concluded that these adsorbents have a great potential for removing Pb^{2+} from aqueous solutions as an eco-friendly process.

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