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Research Article

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Calcium alginate immobilized sugar palm fruit (*Arenga pinnata* Merr) Shell for the removal of Pb(II) and Cd(II) ions

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ABSTRACT

Biosorption of Pb(II) and Cd(II) from Aqueous solution was studied using Arenga pinnata shell immobilized in Calcium Alginate in batch mode. Uptake of metal was very fast initially and equilibrium was attained within 15 min. Sorption data conformed well both Langmuir and freundlich isoterm model for Pb(II), while for Cd(II), the langmuir is better than the freundlich isoterm model. Highest Pb(II) uptake (78,957 %) and Cd(II) uptake (51,022 %) by selected biomass (1 %) immobilized in 1 % Calcium Alginate occured at pH 4, 100 rpm for Pb(II) and 150 rpm for Cd(II) when both initial concentration was 10 mg/L.

Keywords: Calcium algiante, Immobilized Sugar Palm Fruit (*Arenga pinnata Merr*) Shell, Pb(II) and Cd(II) biosorption, SEM, FTIR

INTRODUCTION

The presence of metal ions in natural and industrial wastewater, and their potential health implications to man and his environment has been a subject of environmental concern in the last three decades [1]. The release of large quantities of heavy metal from industries into the environment has resulted in a number of environmental problems [2-3]. The adverse effects of heavy metals affect not only the ecosystems, but also human life via bioaccumulation and bioaugmentation in the food chain ([4]. Several technologies have been developed for the removal of metal ions from industrial wastewater, such as chemical precipitation, ion exchange, coagulation, electrolysis, reverse osmosis processes, adsorption, membrane separation and evaporation. These processes are inefficient or expensive in which some technological problems exist especially when applied to diluted metal solutions and when heavy metal exist in low concentrations. Therefore, the search for clean and competitive technologies is strongly recommended [5-9].

Biosorption for heavy metals and various organic pollutants has emerged as a potential alternative to the conventional techniques because it more efficient, cost-effective and environmentally friendly [10]. Most studies about biosorption have focused on the use of dead biomass in powdered form. This has practical problems, such as low mechanical strength, small particle size, difficulty in separating biomass from liquid stream after biosorption, and mass loss in post-separation. These problems can be solved through the immobilization of biomass on natural or synthetic polymers, which provides additional advantages over freely suspended cells. The immobilization of native biomass improves its mechanical strength, rigidity, size, porosity characteristics, resistance to environmental restraints, convenience for regeneration and reuse of biomass and easy solid–liquid separation [10-11].

Recently, he utilization of banana and orange shells immobilized by Ca-alginate has been studied [12], Sargassum sp. macroalgae that was immobilized by polyethylenimine (PEI) [13], algae that was immobilized by Ca-alginate [14], and Saccharomyces cerevisiae that was immobilized on the chitosan surface [6].

In this research, a biosorbent from Arenga pinnata shell was immobilized by using alginate compound (sodium salt). This waste can be used as a biosorbent because it contain the active compounds such as carbohydrates, proteins, fats, and the other minerals that play a role in the absorption of metal ions. The immobilization of Arenga pinnata is expected to increase the absorption capacity of metal ions to compare with the absorption of metal ions by using batch method that has been done before [15]. The concentration of metal ions was measured by using AAS (Atomic Absorption Spectrometer). The morphology and the surface characteristic of biosorbent before and after the absorption was analyzed by SEM (Scanning Electron Microscope), while the interaction between the metal ions and biosorbent was observed by using FTIR (Fourier Transform Infra Red).

EXPERIMENTAL SECTION

Equipment and Materials

Field Emission Scanning Electron Microscope (FE-SEM) (Inspect F50, FEI Company, USA), Atomic Absorption Spectrophotometer (WFX-320 Raylight, BRAIC, China), FTIR (FT/IR-460 Plus, Jasco, Japan), a digital balance. Arenga pinnata shell was collected from Batusangkar district, West Sumatra province, Indonesia, All reagents used are in pure analytical grade obtained from E-Merck (Germany) unless otherwise noted. Sodium Alginate, $CaCl_2$, $Pb(NO_3)_2$, $Cd(NO_3)_2$, HNO_3 65% and NaOH, , distilled water was laboratory made.

Experimental section

The experiment was conducted in some phases. The first is the creation of adsorbent Arenga pinnata shell immobilized in Calcium Alginate. The second is determination of the optimum conditions for sorption Pb(II) and Cd(II) with variation of solution pH, contact time, agitation speed, ratio of alginate: biomass, biosorbent weight, and initial concentration of solution. Last, desorption of metals ion by using HNO_3 with varying pH and determination of adsoprtion capacity both of metal in multicomponent solution in optimum condition resulting from the previous stage.

Preparation of immobilized biosorbent

Alginate solution of 1 % was prepared by dissolving 1 g alginate (sodium salt) in 100 mL of hot distilled water with constant stirring to avoid formation of lumps. The slurry was cooled to room temperature and equal quantity of powdered biomass was added under stirring condition to have a uniform mixture. This mixture was extruded as droplets in 0,2 M $CaCl_2$ solution, using syringe. The gel beads were allowed to cure for 2 h at 4^oC and washed thoroughly with distilled water. The gel beads kept at a temperature of 4^oC until treatment.

Batch Biosorption Studies

The biosorption of Pb(II) and Cd(II) using immobilized Arenga pinnata shell biomass was investigated in batch experiments. Biosorption process was carried out at room temperature in 50 mL glass Erlenmeyer flask which contains 0.5 g of adsorbent and 25 mL of ion solution (PbII and CdII) 10 mg/L. Flask were agitated on a shaker at 100 rpm for 1 hour at room temperature. The pH of solution is adjusted by addition of HCl and NaOH. The solution was filtered and filtrate was analyzed by SSA for calculating the value of absorption capacity factor.

$$q = \frac{Co - C}{m} \times 0.025 \text{ L}$$

RESULTS AND DISCUSSION

SEM Analyses

The surface structures of the Arenga pinnata shell beads before and after adsorption are shown in Fig. 1 with 200x magnification. The surface of the biosorbent beads is irregular and blobs. After absorption, a great deal of crystals metal ion adhered to the surface, this causes a blobs on the surface of the adsorbent be large.

FTIR Analyses

FTIR is an analytical technique that is important to detect the functional groups that involve in the absorption of metal ions by comparing the FTIR spectrum before and after the absorption. The wave number of the functional groups will shift towards smaller wave numbers. The functional group that contained on biomaterials shown in **Fig. 2**.

Based on Fig. 2, the Pb (II) metal ions was bound to the OH group which is characterized by a shift wave number from 3423.57 cm^{-1} to 3422.11 cm^{-1}. In addition, the metal bond with the functional groups also occur in the CO group which is characterized by a shift wave number from 1061.44 cm^{-1} to 1034.91 cm^{-1}. The peak intensity of the immobilized Arenga pinnata shell was higher than the peak intensity of sodium alginate. It also followed by a peak

increase in the immobilized biomass. However, the peak intensity will decrease if it contacts with the metal ions Pb (II).

Effect of solution of pH

Fig. 3 shows that the absorption capacity of the Pb (II) and Cd (II) metal ions increase from pH 2 to pH 4, but it decreases after pH 4. At low pH, functional groups was protonated and it limit the absorption of metal due to the competition of metal ions with H^+. Along with the increase in pH, functional groups such as amino, phosphate, and carboxyl groups will open and carry a negative charge so that the metal ions will be adsorbed.

At higher pH, the amount of adsorbed metal ions will also decrease. This is because there is a competition between the active molecules of negatively charged biosorbent and OH-ions. In these conditions, there is a formation of anionic hydroxide complexes between metal ions Pb (II), Cd (II), and a hydroxyl group that forms a precipitate.

In Fig. 3 it can be seen that the absorption capacity of Pb (II) metal ions is higher than the Cd (II) metal ions, this is because the atomic radius of Pb is larger than the Cd so that the Pb is easier to hand its electrons to bind the active site of the molecule biosorbent.

Effect of Contact Time on

Fig. 4 shows that the absorption capacity of the Pb (II) and Cd (II) metal ions increase from 15 minutes to 45 minutes of contact time, although it is not too significant. However, over 45 minutes of contact time, the absorption capacity of metal ions will decrease and it then has a constant value at 60 minutes to 90 minutes of contact time.

Absorption will increase in increasing of interaction time and it will reach the equilibrium at the optimum time. After passing through the equilibrium, the absorption will decrease. This is because the metal ion on the biosorbent's active side molecules was detached again because of the effect of stirring process that cause the unstable bond. In addition to stirring effect, the saturation of the solution will decrease the absorption because the biosorbent's active side molecules have bound all of the metal ion so that there is no active side was empty to bind the remain metal ions in the solution.

Effect of Agitation Speed

Fig. 5 shows that the optimum absorption capacity of Pb was obtained at 100 rpm, while Cd was obtained at 150 rpm. In the Pb curves, the speed over 100 rpm causes the decrease in absorption capacity, whereas in the Cd curves, the speed over 150 rpm will cause the decrease in absorption capacity. This occurs because the agitation process can cause the change in the concentration of metal ions on the biosorbent surface so that it will change the biosorption balance. In the beginning of the agitation process, metal ions and biosorbent particles will move faster and improve its relative concentration so that the biosorption can occur often. But when the agitation speed passes a certain limit, the kinetic energy of metal ions and biosorbent particles increase, so that the biosorption will decrease. The high speed of agitation process causes an increase in kinetic energy value of each particle so that it will weaken the bond between metal ions and biosorbent active groups, in which the absorption capacity of metal ions will decrease.

Effect of ratio of Alginate-Biomass

The next assay in this research is to conduct the variation of alginate ratio: biomass. Alginate concentration was maintained at 1%, while biomass concentration was varied at 0.5%; 0.75%; 1%; 1.25%; and 1.5%. This is done to determine the ratio of alginate: optimum biomass to increase the absorption capacity.

Based on Fig. 6, the optimum absorption capacity of the Pb (II) metal ions are in the ratio of alginate : biomass 1% : 0.5%. The absorption capacity of Pb (II) meta ions decreased from 0.75% to 1.5% of biomass concentration. The absorption capacity of Cd (II) metal ions increased from 0.5% to 1% of biomass concentration. After 1% of biomass concentration, the absorption capacity of Cd^{2+} metal ions will decrease. Based on these data, the ratio of alginate: optimum biomass for each metal is 1% of alginate : 0.5% of biomass for Pb^{2+} and 1% of alginate : 1% of biomass for Cd^{2+}.

Effect of Adsorbent Dossage

Fig. 7 shows the absorption capacity will decrease in increasing of biosorbent number. It means that the absorption of metal ions per weight unit will decrease in increasing of biosorbent number. The decrease in the absorption capacity was caused by decreasing of total amount of adsorbent surface area and extending of diffusion path due to the adsorbent particle aggregation [16].

Meanwhile, the absorption efficiency increase in increasing of biosorbent number. If the biosorbent number is increased, the functional groups will also increase. Figure 8 shows that the absorption efficiency of Pb and Cd in 0.5

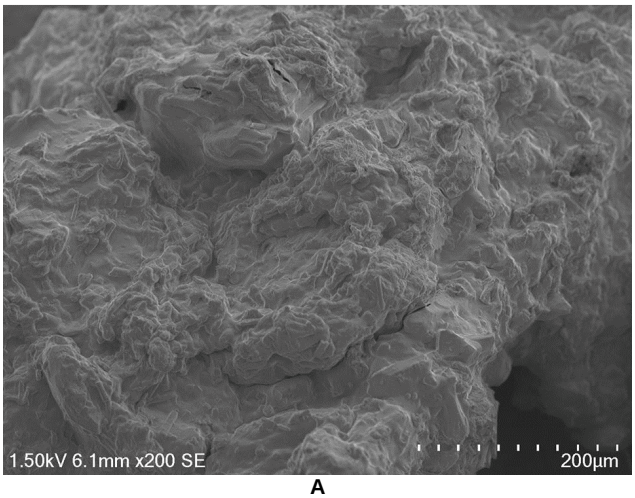
g of biosorbent was only 65.5%, whereas the absorption efficiency in 1.75 g of biosorbent increased to 78.957%. The same thing happened to the Cd ions.

Effect of Initial Concentration

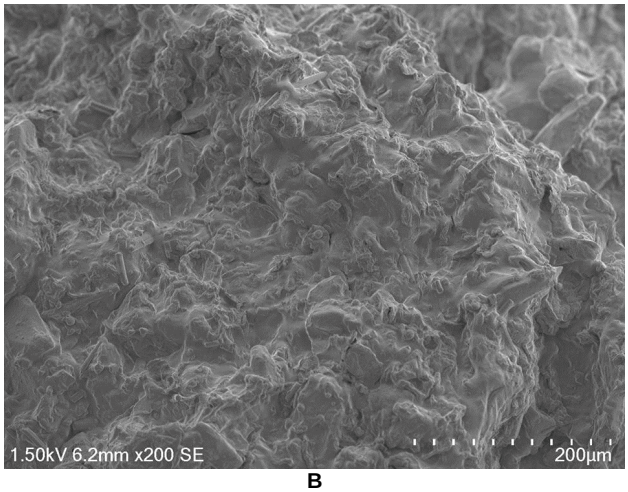
In theory, an increase in metal ions concentration will increase the absorption capacity because more metal ions will bind the functional groups of biosorbent. The absorption capacity will increases in increasing of metal ions concentration. The absorption of Pb (II) metal ions increased until 200 mg/L with 4.515 mg/g of absorption capacity, while the absorption of Cd (II) metal ions initially increased until 150 mg/L with 3.545 mg/g of absorption capacity, but it will saturate at 200 mg/L. The absorption capacity of Cd (II) metal ions using an unimmobilized Arenga pinnata biosorbent (15) was lower than using immobilized Arenga pinnata biosorbent. In the previous research, researchers obtain the absorption capacity of Cd at 100 mg /L was 1.162 mg/g, whereas in this research, the absorption capacity that was obtained at the same concentration was 2.046 mg/g. It proves that the immobilized biosorbent can increase the absorption capacity.

Isotherm Adsorption

Isotherms adsorption was performed at pH 4 with the 10 mg/L to 200 mg/L of metal ions initial concentration. The study about the adsorption equilibrium showed the biosorbent capacity, in which the adsorption equilibrium was illustrated by the isotherm adsorption with the particular constant.



A



B

Fig. 1. Scanning Electron Images of *Arengap innata* Shell beads before (A) and after (B) adsorption

Langmuir isotherm models assume that the structure of biosorbent was homogeneous. Active group on biosorbent have a similar affinity for the monolayer adsorption. The bonding in the functional groups can be either chemical or physical bond, but it has to strong enough to prevent the movement of adsorbed molecules [6]. Langmuir isotherm show that the absorption capacity value will increase in increasing of metal ions concentration. Based on Figure 10, the value of the maximum absorption capacity (Qm) of immobilized Arenga pinnata in theory is 4.76 mg/L for Pb (II) and 1.92 mg/L for Cd (II) whereas the Qm value of unimmobilized Arenga pinnata is 0.15 mg/L for Cd (II). It

proves that the utilization of immobilized biosomass can increase the absorption capacity. On the other hand, Freundlich isotherm models describe the adsorption process occurs on the multilayer surface. Based on the R^2 values that obtained from the two models above, the absorption of Pb (II) and Cd (II) metal ions was a Freundlich isotherm models, although the two values do not have a significant differences.

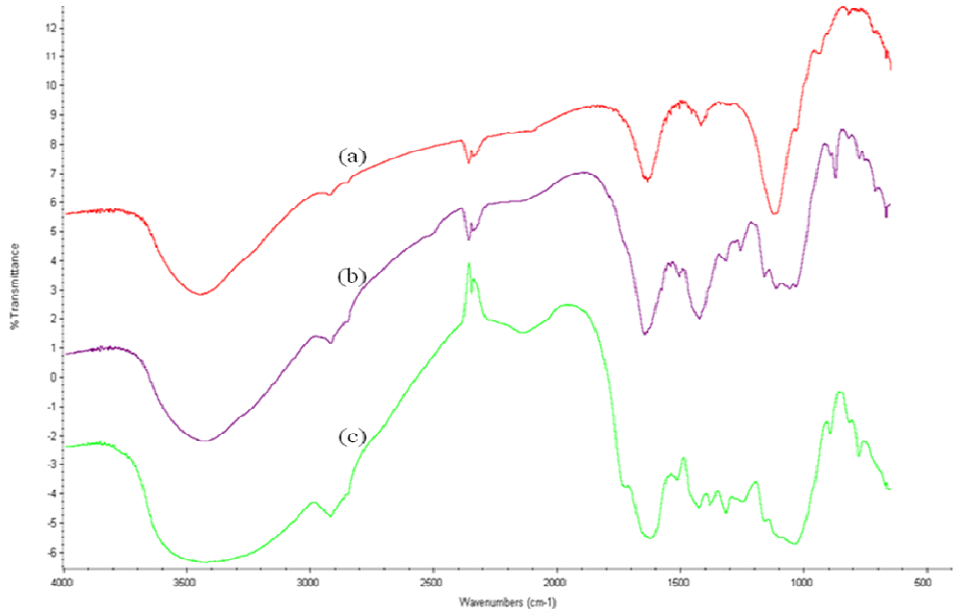


Fig. 2. FTIR spectra of *Arenga pinnata* shell beads sodium alginat (a), before (a) and after (b) adsorption

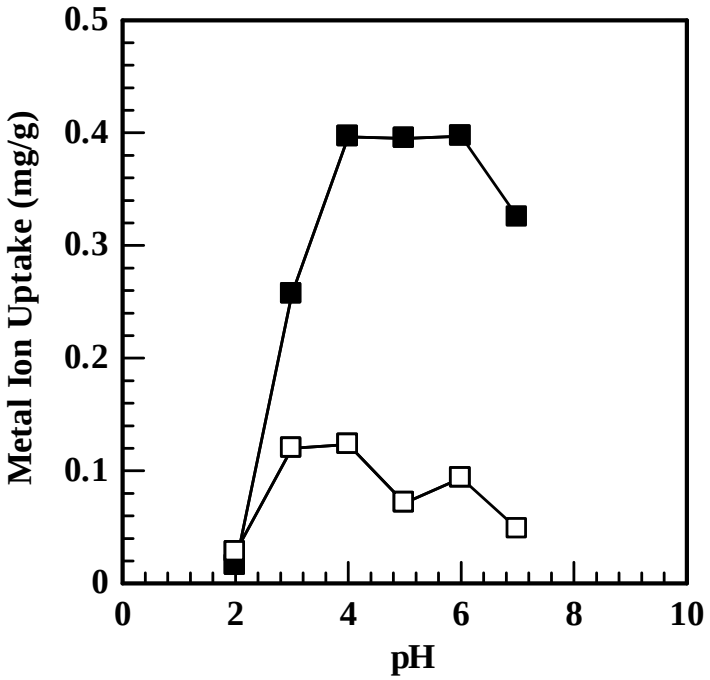


Fig. 3. Effects of initial pH on Pb(II) (■) and Cd(II) (□) biosorption; metal ions solution volume 25 mL; concentration of solution 10 mg/L; adsorbent weight 0,5 g; contact time 60 min; agitation speed 100 rpm

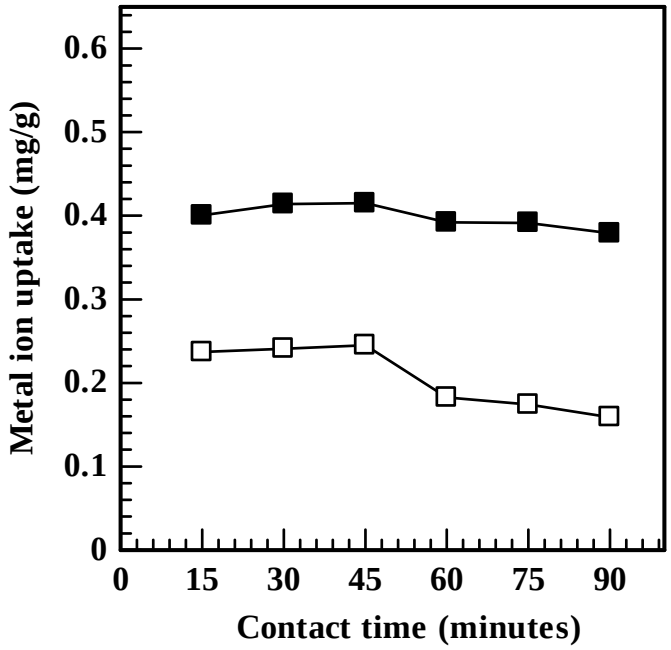


Fig. 4. Effects of contact time on Pb(II) (■) and Cd(II) (□) biosorption; metal ions solution volume 25 mL; concentration of solution 10 mg/L; pH of solution 4; adsorbent weight 0,5 g; agitation speed 100 rpm

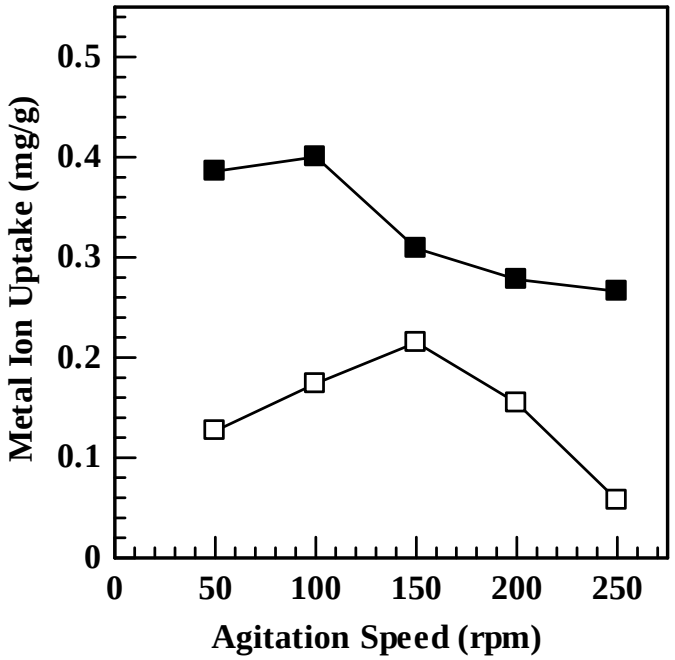


Fig. 5. Effects of agitation speed on Pb(II) (■) and Cd(II) (□) biosorption; metal ions solution volume 25 mL; concentration of solution 10 mg/L; pH of solution 4; adsorbent weight 0,5 g; contact time 15 min

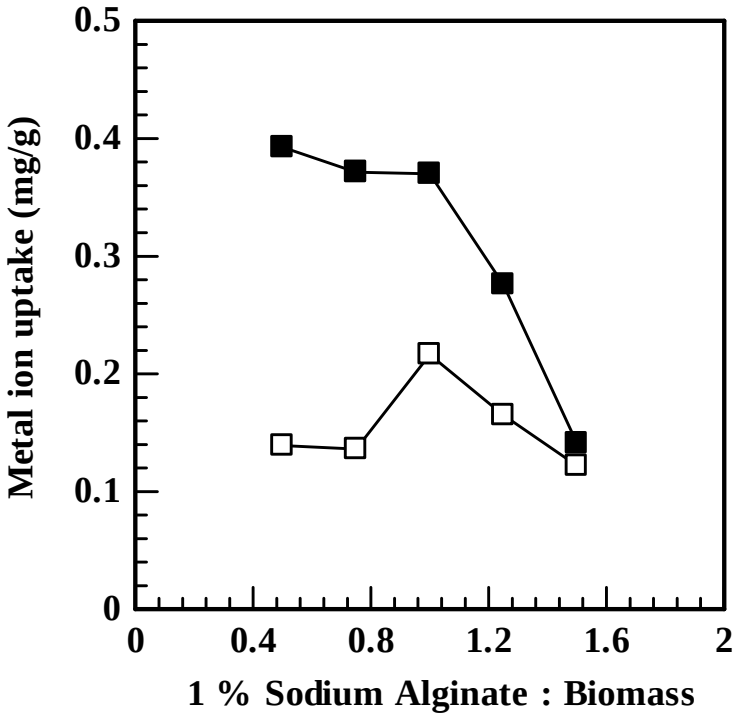


Fig. 6. Effects of ratio alginate : biomass on Pb(II) (■) and Cd(II) (□) biosorption; metal ions solution volume 25 mL; concentration of solution 10 mg/L; pH of solution 4; adsorbent weight 0,5 g; contact time 15 min; agitation speed 100 rpm for Pb(II) and 150 rpm for Cd(II)

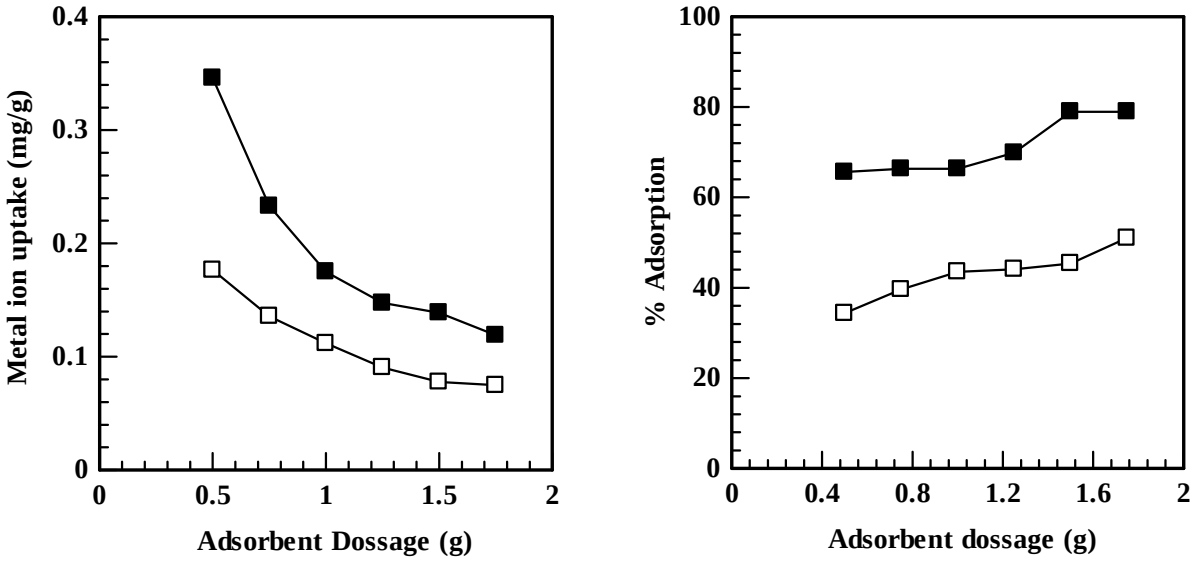


Fig. 7. Effects of adsorbent dossage and % adsorption on Pb(II) (■) and Cd(II) (□) biosorption; metal ions solution volume 25 mL; concentration of solution 10 mg/L; pH of solution 4; adsorbent weight 0,5 g; contact time 15 min; agitation speed 100 rpm for Pb(II) and 150 rpm for Cd(II); ratio alginat : biomass 1:0,5 for Pb(II) and 1:1 for Cd(II)

CONCLUSION

Arenga pinnata shell has important potential for the removal of Cu(II) and Zn(II) ions from aqueous solution. The result show that immobilized Arenga pinnata shell in alginate can be used as biosorbent for the effective removal of heavy metal ions from aqueous solutions. The biosorption capacity of Arenga pinnata shell immobilized into alginate for Pb(II) and Cd(II) is higher than capacity of the non-immobilized powder Arenga pinnata shell.

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