



## Removal of Pb(II), Cd(II) and Co(II) from aqueous solution using *Garcinia mangostana* L. fruit shell

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### ARTICLE INFO

#### Article history:

Received 5 May 2009

Received in revised form 5 April 2010

Accepted 19 April 2010

Available online 24 April 2010

#### Keywords:

Mangosteen shells

Biosorption

Toxic metals

FTIR

### ABSTRACT

This study examines the possibility of using mangosteen shell to remove low concentrations of lead, zinc and cobalt (less than 100 mg/l) from aqueous solution.

It was found that the biosorption capacities were significantly affected by solution pH, contact time and initial metal ions concentration. Un-extracted and extracted dyes of mangosteen shell were investigated. Moreover higher pH up to 5 favoring higher metal ion removal. Kinetic and isotherm experiments were carried out at the optimal pH: at pH 5.0 for lead and zinc, and at pH 4.0 for cobalt. The metal removal rates were rapid, with 90% of the total adsorption taking place within 60 min. *Mangosteen shell* showed the highest potential for the removal of toxic metals in aqueous solution.

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## 1. Introduction

Pollution of the natural environment by heavy metals has become a serious problem in some industrialized countries [1–3]. The release of large quantities of heavy metals from industries into the environment has resulted in a number of environmental problems [2]. Heavy metal such as lead, cadmium and cobalt from the anthropogenic sources, metal plating, mining operations and other industries are among the most common pollutants found in industrial effluents, and become an environmental problem of worldwide concern [4,5]. The main techniques, which have been utilized to reduce the heavy metal ion content of effluents, include ion-exchange, adsorption into activated carbon, membrane process, and electrolytic methods. However, the effectiveness, and particularly the cost effectiveness, of the most common physical–chemical processes are limited [6–8]. Hence, a search is on world wide for a low-cost alternative. Research in the recent years has indicated that some natural biomaterials including agricultural products and by-products can accumulate high concentration of heavy metals. Adsorbent generated from these biomass are cost effective and efficient. Low-cost agricultural products and by-products have been reported to be effective in removing toxic metals. Waste beer yeast [9], algae [10,11], rice husk [12], citrus peels [13], grapes stalks [14], barley straw [15] and cocoa shells [16] to name a few. Indonesia produces large amounts of biowaste material every year such as rice husk, palm

press fiber, saw dust, coconut shells and fiber and other agricultural by-products. Some of this biomass is just burnt in air; some like rice husk and palm press fiber are mostly dumped into huge mountains of waste. Mangosteen (*Garcinia mangostana*) fruit (Fig. 1A) are well known over the world as a king of fruit with many function for diseases treatment. Natural xanthenes from *G. mangostana* has been use as antifungal and antioxidant [17,18]. Indonesia is main mangosteen exporter country with total production 72.634 ton in 2006. Most of the mangosteen shells has been remove as waste. Although mangosteen shells has a potential to be use as biomaterial for removal of heavy metals, to the best of our knowledge there is no literature describe the function of mangosteen shells for removal of toxic metals from aqueous solution. The aim of the present research is to study the capability of mangosteen shells before and after dyes extraction as biosorption material for toxic metals.

## 2. Materials and methods

### 2.1. Treatment of mangosteen shells

Mangosteen shells (Fig. 1B), a by-product of mangosteen (*G. mangostana* L.) was collected from the local market of West Sumatra Province, Indonesia. The mangosteen shells then washed exhaustively with water and finally with deionized water to remove dirt, sand, clay and the particulate material from their surface. After washing it was dried under the sunlight. Dried mangosteen shells was cuted, ground in a pestle and mortar and then screened to particle size of 150–425  $\mu\text{m}$ . The powder (Fig. 1C) then collected in a bottle for use as a sorbent. To remove dyes from mangosteen shell, the powder then rinsed with hexane and ethanol (Fig. 1D).

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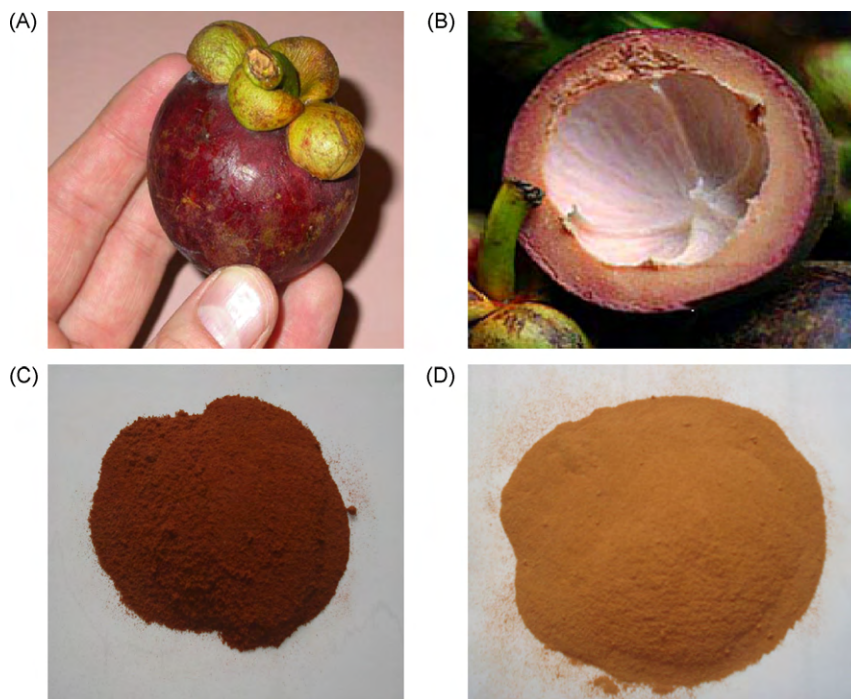


Fig. 1. Mangosteen fruit (A), mangosteen shell (B), un-extracted dyes shell (C) and extracted dyes shell (D).

## 2.2. Chemicals and apparatus

All reagents used were of analytical grade obtained from Merck (Darmstadt, Germany). The apparatus used were screener Octagon 200 (Endcots, London, England), an analytical balance (AA-200 Denver Instrument Company), a shaker (Haake SWB 20), a pH meter (Denver Instrument Company), FTIR (Bio-Rad FTS 60), and atomic absorption spectrometer (AAS Alpha-4, Analys 100, London, England) Pb(II), Cd(II) and Co(II) working standard solution was prepared from 1000 mg/l stock standard solution.

## 2.3. Batch biosorption studies

Dried mangosteen shells were soaked with 0.1 mol/l nitric acid for ca. 24 h, and then were filtered and finally washed until neutral

by using distilled water before they were dried at room temperature. A stock standard solution of Pb(II), Cd(II) and Co(II) with concentration 1000 mg/l each was prepared and suitably diluted to the required initial concentrations. Adsorption experiments were carried out at various particle size, temperature, solution of pH, contact time and initial concentration ( $C_i$ ) under batch mode. The pH of the solutions was adjusted to the required value (range: 2–6) by adding buffer solution at indicated solution of pH placed in a 50 ml Flask. The flasks then were placed on a rotating shaker (haakc SWB 20) with constant shaking, and at the end of experiment, the flasks were removed from the shaker and solutions were separated from biomass by using filter paper. After equilibration, the final concentrations ( $C_f$ ) were measured by atomic absorption spectrophotometric method (AAS Alpha-4, Analys 100, London, England). The percentage removal of dye and amount adsorbed

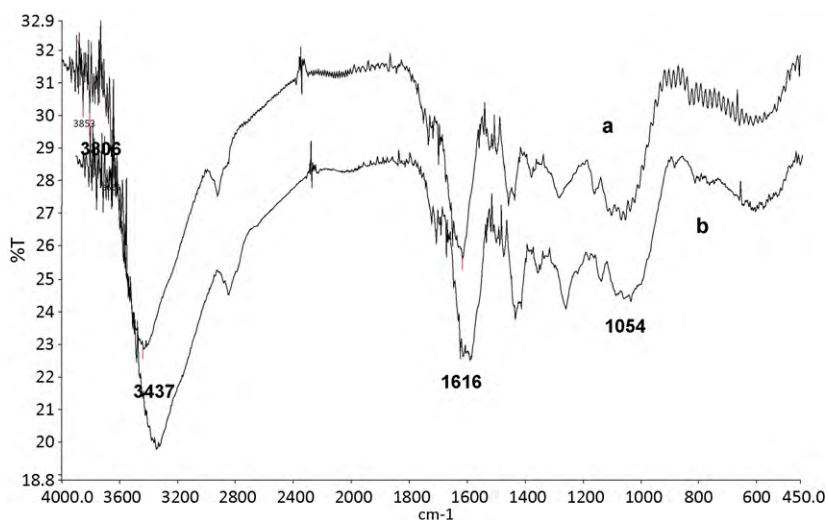


Fig. 2. FTIR spectrum of mangosteen shell before (a) and after (b) dyes extracted.

(in mg/g) was calculated using the following relationships:

$$\text{percentage removal} = 100 \frac{C_i - C_f}{C_i}$$

$$\text{amount adsorbed, } Q = \frac{C_i - C_f}{m}$$

where  $C_i$  and  $C_f$  are the initial and final concentrations (in mg/l) of metal ion, respectively and  $m$  is the mass of mangosteen shells (in mg/l). Blanks containing no metal ions were used for each series of experiments as controls. The average values of duplicate runs were obtained and analyzed. Error in data:  $\pm 1$ –3% for percentage removal and  $\pm 0.005$ –0.01 mg/g for amount adsorbed.

#### 2.4. Fourier transform infrared spectroscopy analysis

For the IR studies, 5% (w/w) of ground and dried of mangosteen shells before and after dyes extraction were pressed to form KBr disc. The FTIR spectra were recorded in the range of 4000–450  $\text{cm}^{-1}$  spectral range using a Bio-Rad FTS 60 instrument. A total of 128 scans were averaged for each sample with a resolution of 2  $\text{cm}^{-1}$ .

### 3. Results and discussions

#### 3.1. Fourier transform infra red analysis

The FTIR spectra of the yields un-extracted and extracted dyes of mangosteen shell are shown in Fig. 2a and b, respectively. It was clear that the carboxylate ions gave rise a strong asymmetrical stretching band at 1616  $\text{cm}^{-1}$  and a weaker symmetrical stretching band at 1419  $\text{cm}^{-1}$ , respectively. The double bands of the carboxylate ion were identical with the observations made on yields extracted of mangosteen shell (Fig. 2b). The bands at 1225  $\text{cm}^{-1}$  (Fig. 2a) and 1227  $\text{cm}^{-1}$  (Fig. 2b) were due to the C–O stretching of ether groups; the bands at 1052  $\text{cm}^{-1}$  (Fig. 2a) and 1054  $\text{cm}^{-1}$  (Fig. 2b) were assigned to the C–O stretching of alcoholic groups. An interesting phenomenon was the sharp decrease in the band intensity of the ether groups after metal binding for both algal materials. From the changes of band areas, it was reasonable to assume that most of the ester groups had been converted to carboxylic and alcoholic groups. The FTIR spectroscopic analysis indicated broad bands at 3437–3511  $\text{cm}^{-1}$ , representing bonded –OH and –NH groups. The bands observed at about 2930  $\text{cm}^{-1}$  could be assigned to the –CH stretch. The spectral analysis before and after dyes extracted indicated that the –NH was also involved in metal biosorption. There were clear band shifts and intensity decrease of the –NH band at 1516–1535  $\text{cm}^{-1}$ . The change in the intensity of the bands at 3370–3410  $\text{cm}^{-1}$  also suggested changes in the amino groups present in the mangosteen shells. The bands at about 1250  $\text{cm}^{-1}$ , representing –SO<sub>3</sub> stretching, could be observed in the FTIR spectrum of both un-extracted and extracted dyes mangosteen shells. Since these peaks presented approximately the same frequency before and after metal binding, it is likely that –SO<sub>3</sub>, mainly present in sulfonic acids of polysaccharides, such as fucoidan.

#### 3.2. Effect of particle size of mangosteen shells

The ion-exchange capacities much depends on the surface activity, in particular specific surface area available for solute–surface interaction, which is accessible to solute. Consequently, it is expected that the ion-exchange capacity increase with increasing surface area of adsorbent. The rate of exchange is generally controlled by the rate of ion diffusion within the particle and this is related to the size of particles. In the previous experiment we found that porous silica gel having a small pore size, i.e. 3 nm with the specific surface area 704  $\text{m}^2/\text{g}$ , gave the best resolution for the

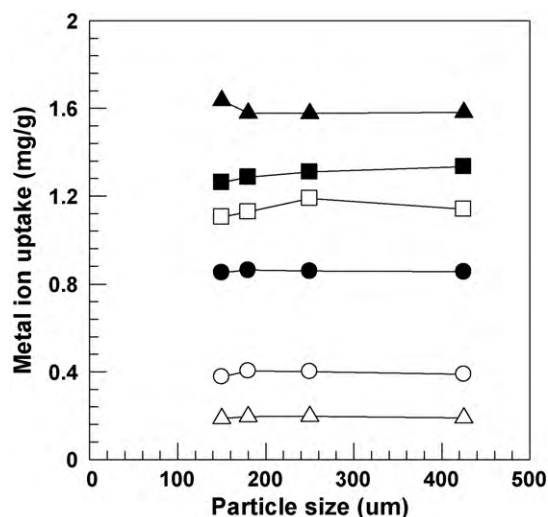


Fig. 3. Effect of particle size of mangosteen shell on lead (●), cadmium (■) and cobalt (▲) adsorption by un-extracted dyes mangosteen shell (close) and extracted dyes mangosteen shell (open).

separation of cations [19]. As mangosteen shell contain many functional groups such as hydroxyl, amino, ester, carboxyl and ether, it was assumed that the ion-exchanged much depends that functional groups. The effect of particle size on the sorption capacities has been carried out by using various sizes viz., 150, 180, 250 and 425  $\mu\text{m}$ . The result is shown in Fig. 3. From the figure it seen, that for all metal ions examined, the increase of particle size will decrease the uptake of metal ions investigated, namely Pb(II), Cd(II) and Co(II). However, metal uptake of Co(II) for un-extracted was higher compared with Cd(II) and Pb(II), i.e. ca 1.6 mg/g, 1.3 mg/g and 0.83 mg/g, respectively. While for extracted material, metals uptake of Cd(II) was higher then Pb(II) and Co(II), respectively. Furthermore for all metal ions investigated, the Pb(II), Cd(II) and Co(II) uptake by un-extracted yields of mangosteen shell was higher when comparing with sorption of metal ions by using extracted dyes of mangosteen shell, namely decreased from 0.82 to 0.39 mg/g for Pb(II), 1.24–0.18 mg/g for Cd(II) and 1.54 mg/g for Co(II), respectively. Therefore for the next experiment 150  $\mu\text{m}$  of particle size has been selected.

#### 3.3. Effect of solution of pH on metal ion uptake

Fig. 4 shows the metal ions uptake in the solutions of lead nitrate, cadmium nitrate and cobalt nitrate, as a function of pH. In the experimental system (maximum concentration 2.0 mg/l), Pb<sup>2+</sup> remains the dominant species below pH 5.5. Beyond this pH, solid lead hydroxide is thermodynamically the most stable phase. In addition, the effect of sodium and nitrate ions (present from pH adjustment during the sorption experiments) on the metal speciation was negligible. The same methods were applied to determine the metal speciation for the other 2 metal ion solutions at a concentration of 2.0 mg/l. For instance, it was found that Cd remains as the dominant species in the copper nitrate system if the pH is maintained below 5.5. In the systems with cobalt nitrate, the metallic ions are the dominant species below pH 6.0. It is well documented that solution pH is an important parameter that affects the biosorption of heavy metal ions [20,21]. Fig. 4 shows the biosorption of lead, cadmium and cobalt by un-extracted dyes mangosteen shell and extracted dyes mangosteen shell. It can be seen that higher pH led to higher metal uptake. Un-extracted dyes mangosteen shell showed better biosorption performance than extracted dyes in the removal of all three metal ions.

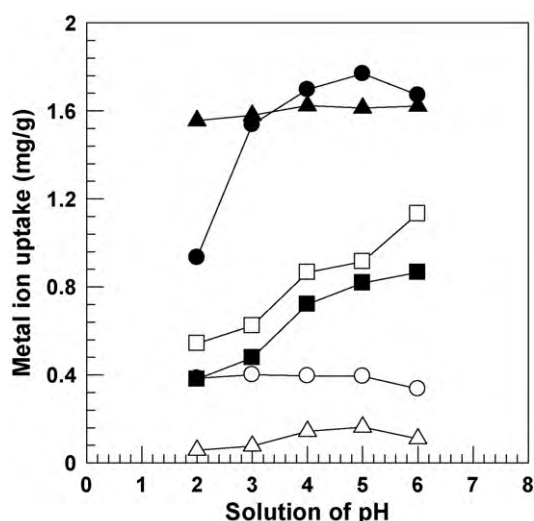


Fig. 4. Effect of solution of pH on lead (●), cadmium (■) and cobalt (▲) adsorption by un-extracted dyes mangosteen shell (close) and extracted dyes mangosteen shell (open).

The uptake capacities generally demonstrated a similar trend where an increase was distinctly manifested at the lower pH range (e.g., from pH 2.0 to 5.0), with the effect leveling off at a higher pH. In the case of cadmium ions, where increasing uptake occurred beyond pH 4.0, this phenomenon may be attributed to the precipitation of insoluble cadmium species (see Fig. 4). Extracted dyes mangosteen showed distinctly lower uptake capacities. The dependence of metal uptake on pH is related to both the surface functional groups on the cell walls of the mangosteen shell and the metal chemistry in solution. As the metals are present in their ionic state at a low pH (e.g.,  $\text{pH} < 4.0$ ), the sharp increase in metal sorption from pH 2 to 4.0 cannot be explained by the change in metal speciation. This implies that the functional groups on the cell wall and its ionic state at these pHs determine the extent of biosorption. The positively charged hydrogen ions may also compete with metal ions for binding on the ligands on the cell wall. At lower pH, the higher concentration of the hydrogen ions effectively leads to fewer ligands being available for the binding of the metal ions. Increased pH (i.e. fewer  $\text{H}^+$  ions) results in more ligands being available for metal ion binding, and hence biosorption is enhanced. The typical dependence of metal uptake on pH suggests that the weak acidic carboxyl groups  $\text{R-COO}^-$  (apparent  $\text{pK}_a$  in the range of 3.5–5.0) of mangosteen shell constituents as the probable biosorption sites. A good correlation between the degree of blocking of  $\text{-COO}^-$  groups by esterification in brown showed and the corresponding decrease in metal uptake has been reported [22].

### 3.4. Effect of contact time on metal ion uptake

Fig. 5 shows that the biosorption process of heavy metal by mangosteen completes rapidly. The biosorption of metal ions investigated, namely  $\text{Pb(II)}$ ,  $\text{Cd(II)}$  and  $\text{Co(II)}$  complete within 30 min. On the other hand, Kapoor and Viraraghavan [23] reported that the biosorption of metals such as copper, zinc, lead and uranium by nongrowing cells of *S. cerevisiae* reaches equilibrium within several hours. Moreover, the biosorption of Pu, Am and Ce with immobilized cells of *S. cerevisiae* reached equilibrium within 60 min. Generally speaking, the biosorption capacity and the removal efficiency of metal ions by mangosteen shell became higher with prolonging the contact time up to 120 min. The result showed that a 30 min sorption period was the best option to ensure the metal removal from solution and good recovery from biosorbent. There-

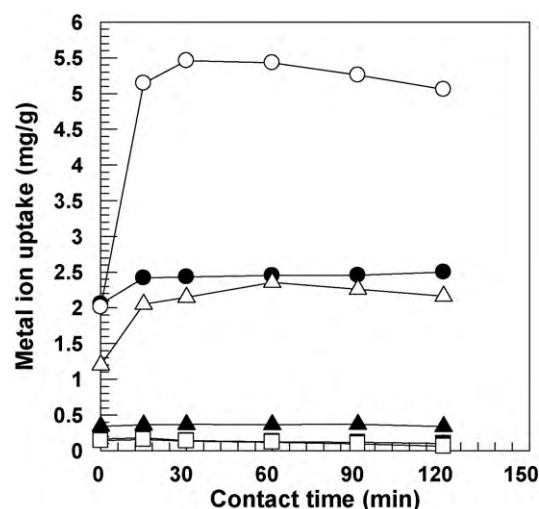


Fig. 5. Effect of contact time between metal ions and biomaterial on lead (●), cadmium (■) and cobalt (▲) adsorption by un-extracted dyes mangosteen shell (close) and extracted dyes mangosteen shell (open).

fore for the further experiment, 30–35 min of contact time between metal ion and adsorbent has been selected.

### 3.5. Effect of initial concentration on metal ion uptake

The initial concentration of  $\text{Pb(II)}$ ,  $\text{Cd(II)}$  and  $\text{Co(II)}$  provides the necessary driving force to overcome all mass-transfer resistance of metals between the aqueous and solid phases. Hence, a higher initial metal concentration will have a benefit effect on the mangosteen shells sorption capacity. Such an effect is clearly shown in Fig. 6. From the figure it seen that the equilibrium sorption capacity seems to increase essentially linearly with an increases in the initial metals concentration up to 50 mg/l for  $\text{Cd(II)}$  ion, 125 mg/l for  $\text{Co(II)}$  ion. On the other hand  $\text{Pb(II)}$  ion reach 250 mg/l by using extracted yields mangosteen shell. The distribution of the solute, i.e.  $\text{Pb(II)}$ ,  $\text{Cd(II)}$  and  $\text{Co(II)}$  metal ions between the liquid phase and solid phase can be described by several mathematical relationships such as the standard Langmuir–Freundlich isotherm model [24,25]. From the experimental data for binding metal ions-mangosteen

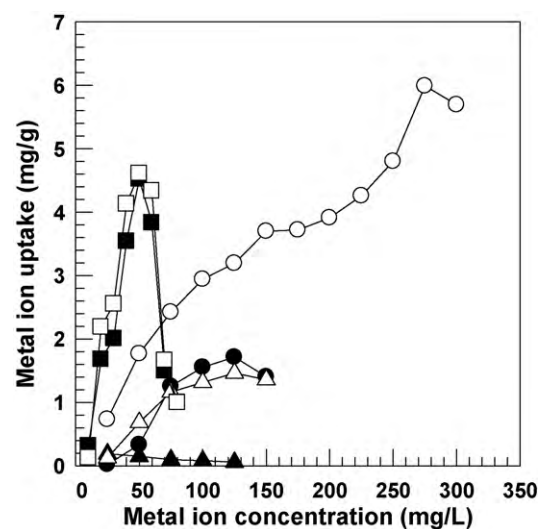


Fig. 6. Effect of concentration of lead (●), cadmium (■) and cobalt (▲) solution on adsorption by un-extracted dyes mangosteen shell (close) and extracted dyes mangosteen shell (open).

shell system, the maximum sorption capacities for metal ion investigated absorb by mangosteen shell is 3.56 mg/g for Pb(II), 3.15 mg/g for Cd(II) and 0.34 mg/g for Co(II).

#### 4. Conclusion

The present experiment could be used for the absorption of heavy metals using low-cost biosorbent such as mangosteen shell, with sorption capacity 3.56 mg/g, 3.15 mg/g and 0.34 mg/g for Pb(II), Cd(II) and Co(II), respectively. We also found that, the Pb(II), Cd(II) and Co(II) uptake by un-extracted yields of mangosteen shell was higher when comparing with sorption of metal ions by using extracted dyes of mangosteen shell, namely decreased from 0.82 to 0.39 mg/g for Pb(II), 1.24 to 0.18 mg/g for Cd(II) and 1.54 mg/g for Co(II), respectively.

#### Acknowledgement

One of the authors (R. Zein) would like to thanks to Directorate General of Higher Education of the Ministry of National Education of the Republic of Indonesia for PAR-B Project grant to write the article.

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