Sugar palm *Arenga pinnata Merr* (Magnoliophyta) fruit shell as biomaterial to remove Cr(III), Cr(VI), Cd(II) and Zn(II) from aqueous solution

Rahmiana Zein, Dian Arrisujaya Hidayat, Mega Elfia, Nazris Nazarudin and Edison Munaf

ABSTRACT

The removal of toxic heavy metals Cr(III), Cr(VI), Cd(II) and Zn(II) from aqueous solution by sugar palm (*Arenga pinnata*) fruit shell has been examined. Adsorption factors consisted of solution of pH, mass of biosorbent as well as initial metal concentration. The Langmuir isotherm was used to study the adsorption mechanism. Moreover, characterization of sugar palm fruit shell was investigated using Fourier transform infrared spectroscopy and surface morphology was checked using scanning electron microscope. The removal percentage at maximum conditions were: 0.28, 0.52, 0.43 and 0.58 mg g^{-1} for Cr(III), Cr(VI), Cd(II) and Zn(II), respectively. Desorption study was carried out by using nitric acid at a range of pH 1–4. This work shows that the performance of biosorption of metals by *A. pinnata* has many advantages, such as good removal and deremoval efficiencies.

Key words | aqueous solution, *Arenga pinnata*, biosorption, Fourier transform infrared spectroscopy, scanning electron microscope, toxic metals

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INTRODUCTION

Heavy metal pollution is a threat to human health, animals and the ecosystem, mainly caused by rapid industrial and technology activities and their consequences and poses a serious environmental problem (Munaf & Takeuchi 1994). Various toxic metal ions present in industrial effluent are a major source of pollution to the environment (Demirbas 2008; Volesky 2009). Physicochemical treatment technologies such as precipitation, coagulation, ion exchange, electrodialysis, reverse osmosis, chemical oxidation, membrane processing, ion exchange and adsorption onto activated carbon are available for the removal of heavy metals from liquid effluents (Ahmad *et al.* 2005; Aguado *et al.* 2009; Ali 2010; Cao *et al.* 2010). The major disadvantages of these conventional treatment methods are high capital investment for chemical purposes, reoccurring expenses and incomplete metal removal (Enzminger *et al.* 1987; Silva *et al.* 2004; Naik *et al.* 2012). Membranes applied for microfiltration are susceptible to fouling due to formation of biological slimes and this poses a significant problem for continuous use of the technology.

Recently, research has focused on biosorption technology. This utilizes the ability of agricultural byproducts to accumulate heavy metals from waste streams and has received much attention (Munaf & Zein 1997; Tien 2002; Wang & Chen 2009; Zein *et al.* 2011).

Biosorption is a term that describes the removal of heavy metals by the passive binding to non-living biomas from an aqueous solution (Volesky 1990). Researchers have used different kinds of biological and/or agricultural byproduct material for the removal of metal ions such as brown algae (Davis *et al.* 2003), marine macrophytes (Pennesi *et al.* 2012a, b) and lichen (Sari & Tuzen 2010). *Arenga pinnata* has high economic value, and almost all parts of the plant including stem, leaf, palm blossom, fibre, root and fruit are useful to human life. Leaves are used for rough brooms and woven into coarse baskets, fibre is used

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as an organic roof material and bark for barriers, flooring, furniture and tool handles. The sweet sap is used as a favourite drink such as vinegar and sugar. Moreover, the fruit of *A. pinnata* (Figure 1(a)) can be processed for making pickles, juices, desserts, for canned foods, and also cooked for making traditional sugary syrup (Ishak *et al.* 2012). Scattered almost all over parts of Indonesia, especially in Papua, Maluku, West Sumatra, West Java, Central Java, Banten, Sulawesi, Bengkulu and Nangroe Aceh Darussalam province, the total production of sugar palm fruit is approximately ten thousand tons per year. Most of the *A. pinnata* shells (Figure 1(b)) are removed as waste. To the best of our knowledge, there is no literature describing the function of sugar palm fruit shells as biosorbent for the removal of toxic metals from aqueous solution. Since the material contains functional groups which have the capability to adsorb metals ions, the present research studies the capability of *A. pinnata* fruit shell as biosorption material for Cr(III), Cr(VI), Cd(II) and Zn(II) ions.

MATERIALS AND METHODS

Treatment of sugar palm (*A. pinnata*) fruit shells

A. pinnata fruit shell, a byproduct of sugar palm fruit, was collected from the central production of sugar palm in Batusangkar district, West Sumatra Province, Indonesia. The epicarp (shell) of *A. pinnata* fruit was separated from the fruit and the shell was extensively washed with doubly distilled water to remove dirt and sand and other particulate material from the surface. After that it was dried at room temperature. Dried fruit shells were cut, ground in a pestle and mortar to make a powder (Figure 1(c)) and sieved to a particle diameter $\leq 250\ \mu m$. The biosorbent was stored in a bottle for use as a sorbent. The biosorbent was soaked with 0.1 mol l^{-1} nitric acid for around 4 hours and then filtered. Finally, it was washed with ultra-pure water until neutral, dried at room temperature and stored in a bottle for use as a sorbent.

In order to identify the active sites of shell investigated as well as the change in chemical bonding after contact with heavy metal ions, these samples were characterized using Fourier transform infrared (FTIR) spectroscopy. The surface morphology of sugar palm fruit shell of untreated and Cr loaded *A. pinnata* fruit shell was examined using scanning electron microscopy (SEM).

(a)
(b)
(c)

Figure 1 | Sugar palm (*A. pinnata* Merr) fruit (a), dried shell of fruit (b) and powder of the dried shell (c).

Chemicals and apparatus

All reagents used were of analytical grade and obtained from Merck (Darmstad, Germany). The following apparatus was used: screener Octagon 200 (Endcots, London, UK) the Inspect F50, FEI Co., USA, an analytical balance (AA-200, Denver Instrument Company), a shaker (Haake SWB 20), FTIR spectrocopy (model 460 plus, Jasco, Japan), SEM (model 460 plus, Jasco) and atomic absorption spectrometer (AAS, Raylight WFX-320, BRAIC, China). Cr(III), Cr(VI), Cd(II) and Zn(II) working standard solution was prepared from 1,000 mg l^{-1} stock standard solution.

Removal studies

Dried sugar palm fruit shell was soaked with 0.1 mol l^{-1} nitric acid for around 4 hours, and then filtered and finally washed with ultra pure water until neutral and dried at room temperature. Working standard solution was prepared from a 1,000 mg l^{-1} stock standard solution of Cr(III), Cr(VI), Cd(II) and Zn(II). Sorption capacity of *A. pinnata* fruit shell was investigated at various solutions of pH, mass of biosorbent, initial concentration under dynamic flow mode using a glass column (25 length × 1 cm I.D.) with the flow rate 2.0 ml min^{-1}. The pH of solutions was adjusted to the required value (range: 2–6) by adding buffer solution at the indicated pH solution. The initial and final concentrations after the column were measured by atomic absorption spectrophotometric method.

FTIR analysis

FTIR spectral analysis of powdered *A. pinnata* fruit shell was done before and after Cr(III) was loaded to determine the functional groups involved in the biosorption process of heavy metals. The surface morphology was measured by SEM.

Desorption studies

Desorption experiments were done using different concentrations of nitric acid to remove the adsorbed metal ions from *A. pinnata* fruit shell biosorbent.

RESULTS AND DISCUSSION

Characteristics of *A. pinnata* fruit shell

The infrared spectral analysis was carried out to determine the type of functional group involved in the biosorption process. The results are shown in Figure 2. FTIR spectra of unloaded biosorbent and Cr(III) loaded biosorbent were recorded in the wave number range 4,000–400 cm^{-1}. As shown in Figure 2(a), the spectra display several vibrational bands, indicating the complex nature of the biosorbent examined. A characteristic strong and broad peak at 3,420–3,400 cm^{-1} indicated the O-H and N-H groups stretching vibration of hydroxyl and amide groups in biosorbent (Guo *et al.* 2012). The hydroxyl groups present in biosorbent are effective binding sites for metal ions. The peaks observed at 2,950–2,928 cm^{-1} can be assigned to the stretching band of C-H group. The distinct peaks observed at 1,650–1,630 cm^{-1} characterize the stretching vibration of carbonyl groups from aldehydes and ketones. The band observed at 1,103 cm^{-1} was attributed to the stretching vibration of alcohol and carboxylic acids assigned to C-O. The stretching at 3,400 cm^{-1} (Figure 2(a)) shifted to 3,420 cm^{-1} (Figure 2(b)) after Cr(III) biosorption, indicating the involvement of free hydroxyl groups in Cr(III) biosorption. A change in intensity and shift in position of the peaks could be observed in FTIR spectra after Cr(III) adsorption by *A. pinnata* fruit shell. The enhancement of the intensity at all the peaks indicates the

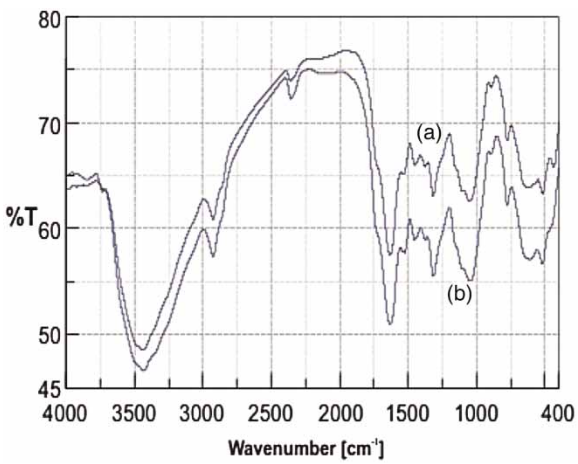

Figure 2 | FTIR spectrum of *A. pinnata* shell powder before (a) and after (b) sorption of Cr(III).

involvement of O-H, C-H and C-O groups in the adsorption process (Andrade *et al.* 2005). From the results shown in Figure 2, it is clear that these functional groups acquire a positive charge when protonated and may interact with the negatively charged metal complex.

Scanning electron microscopy analysis

The SEM is one of the most useful tools for studying the surface morphology of a biosorbent. The SEM images of two different magnifications are shown in Figures 3(a) and 3(b) with magnifications of 100 and 5,000 times, respectively. Clearly depicted are the surface topography and internal structure of *A. pinnata* fruit shell before and after Cr(III) is loaded (Figures 3(c) and 3(d)). The cell surface was a rough, wrinkled and porous structure, making it possible for the biosorption of metal ions onto the shell wall. As can be seen in Figures 3(c) and 3(d), the possible mechanism of adsorption of metal ions on *A. pinnata* fruit shell may be due to physical adsorption and complexation with functional groups and chemical reaction with the surface sites.

Effect of solution of pH on sorption capacity of metal ions

The acidity of the medium affects the competition of the hydrogen ions and metal ions for the active sites on the biosorbent surface. Sorption capacity was analysed over a pH range of 2 to 6. The effect of pH on Cr(III), Cr(VI), Cd(II) and Zn(II) adsorption is presented in Figure 4. The sorption capacities generally demonstrated a similar trend, where an increase of pH solution from 2 to 4 increased the sorption capacity of Cr(III), Cd(II) and Zn(II) as follows: from 0.04 to 0.28 mg g^{-1} for Cr(III), 0.25 to 0.43 mg g^{-1} for Cd(II) and 0.51 to 0.58 mg g^{-1} for Zn(II). Biological materials primarily contain weak acidic and basic funtional groups. It follows the theory of acid–base equilibria, in the pH range from 2 to 4. As the pH increases, the electrostatic repulsion decreases due to the reduction of the positive charge density of protons on the sorption sites. In this range, carboxyl groups are the important groups for the metal sorption. Moreover, sorption capacity of Cr(VI) ion was increased up to pH 3. The negative charge of the carboxyl groups

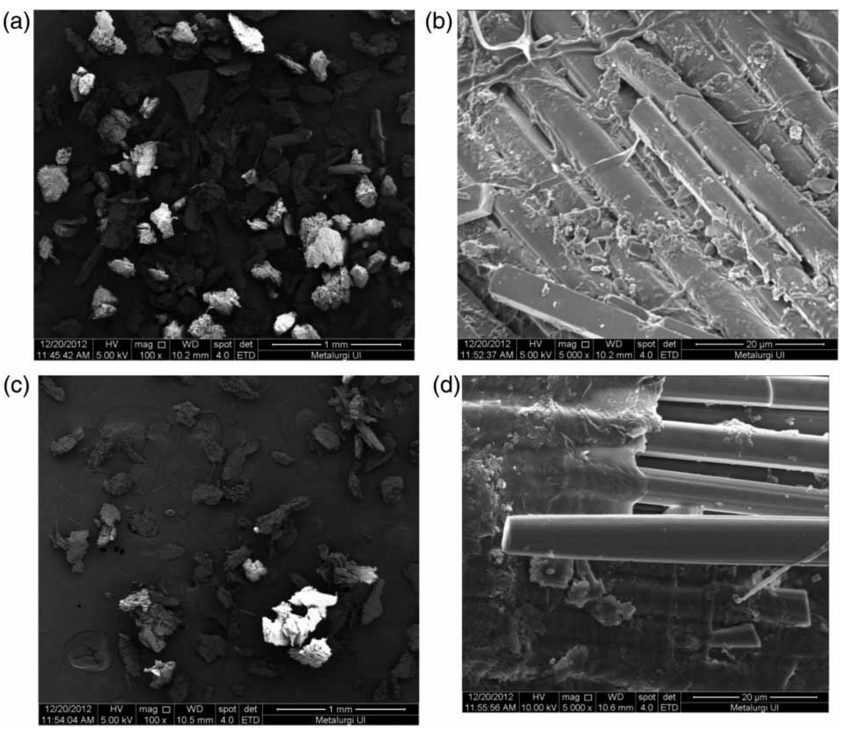

Figure 3 | Scanning electron image of *A. pinnata* sample at the following magnifications: (a) 100×, (b) 5,000×, (c) after loaded Cr 100×, (d) after loaded Cr 5,000×. Scale as indicated in photo.

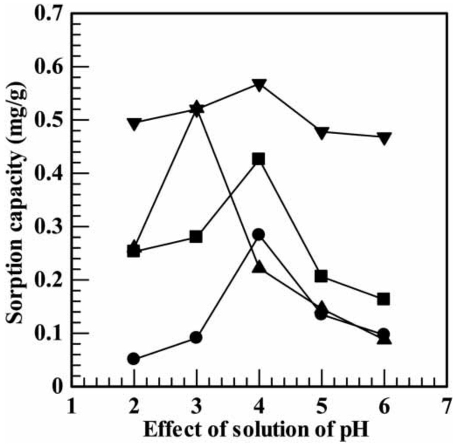

Figure 4 | Effect of solution of pH on sorption capacity of Cr^{+3} (●), Cr^{+6} (▲), Cd^{+2} (■) and Zn^{+2} (▼).

(-COOH) are important for the metal uptake by biological materials (Kok *et al.* 2002). The sorption capacity of metal ions decrease when solution of pH increases from pH 4 for Cr(III), Cd(II) and Zn(II) ion and from pH 3 for Cr (VI) ion. This is because at pH greater than 4 the hydroxy complexes were achieved causing a decrease in adsorption capacity (Cordero *et al.* 2004).

Effect of mass of *A. pinnata* fruit shell powder on sorption capacity of metal ions

Figure 5 shows the effect of amount of *A. pinnata* fruit shell on percentage of metal ions removal. The mass of biosorbent can influence the extent of metal ion uptake from the solution. When each 10 mg l^{-1} of Cr(III), Cr(VI), Cd(II) and Zn(II) flows through different amounts of *A. pinnata* fruit shell (0.5–2 g) at pH 4 and flow rate of solution 2.0 ml min^{-1}, it is observed that the sorption capacity of all metal ions investigated increases with increasing the mass of *A. pinnata* fruit shell on the column. This may be due to the availability of more binding sites present on the biosorbent surface.

Effect of concentration of metal ion solution on sorption capacity

The initial concentration of Cr(III), Cr(VI), Cd(II) and Zn(II) provides the necessary driving force to overcome all mass transfer resistance of metals between the aqueous and solid phases. Figure 6 shows the effect of metal ions concentration on sorption capacity of Cr(III), Cr(VI), Cd(II) and Zn(II) by *A. pinnata* fruit shell. The increase in initial concentration of metal ions investigated from 5 to 100 mg l^{-1} resulted in an increase of sorption capacity: for Cr(III) and Cd(II) ions up to concentration 75 mg l^{-1}, while for Cr(VI) and Zn(II) ions increases up to concentration 100 mg l^{-1}.

The Langmuir adsorption isotherm of metal ions examined in Figure 7 is commonly used for biosorption studies based on metal ion concentrations. The Langmuir isotherm model is obtained under the assumption of totally

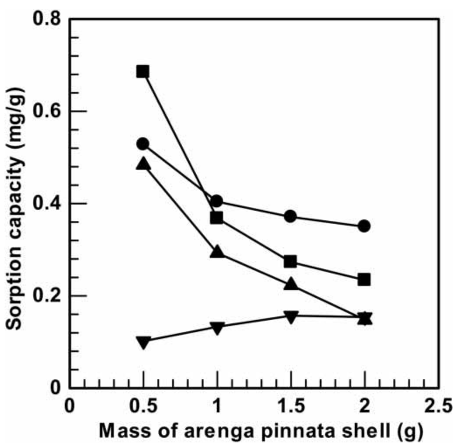

Figure 5 | Effect of mass of *A. pinnata* powder shell on sorption capacity of Cr^{+3} (●), Cr^{+6} (▲), Cd^{+2} (■) and Zn^{+2} (▼).

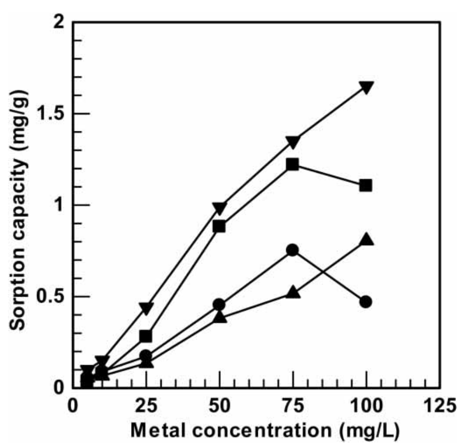

Figure 6 | Effect of concentration of Cr^{+3} (●), Cr^{+6} (▲), Cd^{+2} (■) and Zn^{+2} (▼) solution on sorption capacity by *A. pinnata* powder shell.

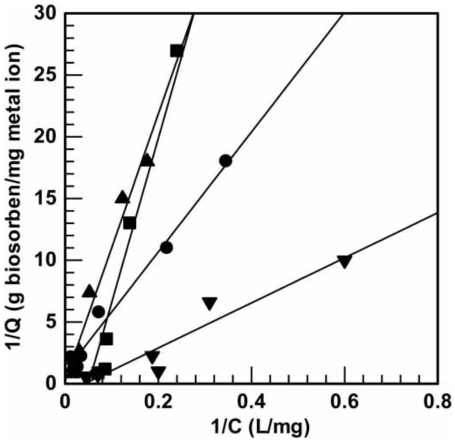

Figure 7 | Langmuir isotherm for biosorption of Cr^{+3} (●), Cr^{+6} (▲), Cd^{+2} (■) and Zn^{+2} (▼) by *A. pinnata* powder shell.

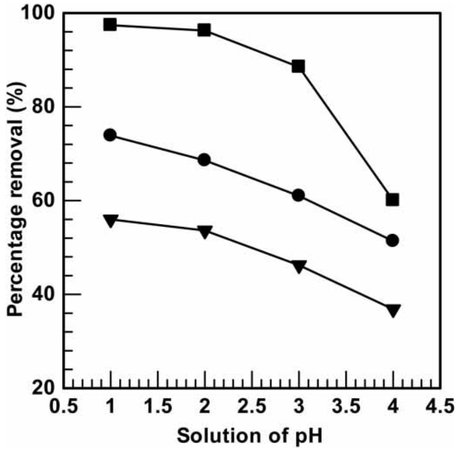

Figure 8 | Effect of solution of pH on regeneration of Cr^{+3} (●), Cd^{+2} (■) and Zn^{+2} (▼) ion sorbed on *A. pinnata* powder shell.

homogeneous adsorption surface, and it can be represented as follows:

$$Q = (Q.bC)/(1 + bC)$$

where Q = uptake of metal ion (mg g^{-1}), C = final concentration at equilibrium (mg l^{-1}) and b = constant related to energy of adsorption (l mg^{-1}). The equation assumes that the surface of biosorbent consists of adsoption sites where metal ions interact only with a site and adsorption process is limited to monolayer (Febrianto *et al.* 2009).

Desorption of Cr(III), Cd(II) and Zn(II) by nitric acid

The results of desorption study of Cr(III), Cd(II) and Zn(II) by the nitric acid solution as eluent is shown in Figure 8. Desorption studies are important to determine the feasibility of regenerating metal ions adsorption in biosorbent and to elucidate the mechanism of biosorption. The study was carried out using 1, 2, 3 and 4 solutions of pH as eluent. From the results shown in Figure 8, it was observed that the desorption efficiencies, i.e., percentage removal of Cr(III), Cd(II) and Zn(II) by *A. pinnata* fruit shell decreased from pH 1 to pH 4. The results indicated that at a lower pH, the *A. pinnata* fruit shell biosorbent was covered by H^+ ions while the coordination spheres of Cr(III), Cd(II) and Zn (II) ions were disrupted, resulting in the release of Cr(III), Cd(II) and Zn(II) ions from biosorbent surface.

CONCLUSIONS

A. pinnata fruit shell effectively removed toxic heavy metals Cr(III), Cr(VI), Cd(II) and Zn(II) from aqueous solution through adsorption couple reduction mechanism. To quantitatively evaluate the removal percentage of the metal ions investigated, some variables such as solution of pH, mass of *A. pinnata* fruit shell, initial concentration and Langmuir isotherm model were examined. The removal percentage at maximum conditions are: 0.28, 0.52, 0.43 and 0.58 mg g^{-1} for Cr(III), Cr(VI, Cd(II) and Zn(II), respectively. The present biomaterial could be used for the removal of toxic metals from aqueous solution. Future work could be carried out to improve the sorption capability, such as using catalytic agents and modifying the functional groups to enhance the sorption capacities.

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