Bioadsorption of Multiple Heavy Metal Ions by *Rhizophora Apiculate sp.* and *Elaesis Guineensis sp.*

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ABSTRACT

Heavy metal ions contamination has become more serious which is caused by the releasing of toxic water from industrial area and landfill that are very harmful to all living organism especially human and can even cause death if contaminated in small amount of heavy metal concentration. Currently, peoples are using classic method namely electrochemical treatment, chemical oxidation/reduction, chemical precipitation and reverse osmosis to eliminate the metal ions from toxic water. Unfortunately, these methods are costly and not environmentally friendly as compared to bioadsorption method, where agricultural waste is used as biosorbent to remove heavy metals. Two types of agricultural waste used in this research namely oil palm mesocarp fiber (Elaesis guineensis sp.) (OPMF) and mangrove bark (Rhizophora apiculate sp.) (MB) biomass. Through chemical treatment, the removal efficiency was found to improve. The removal efficiency is examined based on four specification namely dosage, of biosorbent to adsorb four types of metals ion explicitly nickel, lead, copper, and chromium. The research has found that the removal efficiency of MB was lower than OPMF; whereas, the multiple metals ions removal efficiency decreased in the order of Pb2+ > Cu2+ > Ni2+ > Cr2+.

Keywords: *multiple heavy metals ion, mangrove bark, oil palm mesocarp fiber, bioadsorption, biosorbent*

INTRODUCTION

Ecosystem problems precisely metals ion pollution has brought an awareness among researchers toward the hazardous metal ions that have a poisonous characteristic which will lead to health threat to living organism especially human where it can cause organs failure, cancer and some chronic disease [1-3]. Lead (Pb), nickel (Ni), copper (Cu) and chromium (Cr) are some of toxic metals that are found to contribute to toxic metal pollution. Most of toxic metals were generally made from industrial waste namely metallurgical processes, mining, electroplating catalytic process, fertilizers and plastic manufacturing [1, 4]. Besides, certain industries such as ceramic, alloy or steel industries [5], pigment and Cadmium/Nickel battery production can also become the source of toxic metals [2]. Apart from that, toxic metals can also be originated form the activities namely porcelain enamelling, mineral processing, fossil fuel ingesting, aircraft industries and factory work [6]. In order to clean the water sources from heavy metal pollution, several kinds of treatment process have been employed such as adsorption process, chemically reaction and biological process [7-9].

Mangrove bark (*Rhizophora Apiculata sp.*) and oil palm mesocarp fiber (*Elaesis guineensis sp.*) have been shown to have higher capability in removing various toxic metals from industrial water [10-12]. Mangrove bark is a low-cost biosorbent because it is readily available as agricultural waste and thus can become an eco-friendly biosorbent [13]. In addition to that, it can also support to resolve the waste management of agricultural waste which come from debarking of mangrove logs from the making of charcoal [14, 15]. The presence of tannins in the cell walls can remove metal ions effectively from waste water due to the presence of several functional groups namely carboxylic, phenolic groups and phenolic hydroxyls [14, 15]. Apart from tannins, the existence of cellulose and lignocellulose can also accommodate a great number of hydroxyl group that give applicable ability in removing metal ions such as copper, zinc, cadmium and lead [10]. Likewise, OPMF as biosorbent has also been found to remove four kind metal ions namely nickel and lead [16], chromium and cadmium [2].

The heavy metals bioadsorption process employ several mechanism during metals diffusion and adsorption. The process largely depends on the types of biomass used, which in turn to include physical forces and entrapment of the capillaries filament as well as the polysaccharide structure [17-20]. Metals bioadsorption can be divided into two type of methods namely [7] adsorption via reaction amongst metal ions and active site of functional groups. The second type can be further divided into two different type of processes namely passive and active bioadsorption. Passive bioadsorption involves changeable adsorption-desorption process of metal ion which involve rapid independent movement through interaction of metal ions binding mechanism. The active bioadsorption on the other hand takes place after the diffusion mechanism involving the movement of metal ions on the biomass surface [7].

According to Nascimento *et al.* [10], chemical treatment is the chemical alteration of bioadsorbent through polymerisation and functionalisation processes involving amide, amine and carboxylic groups. The bioadsorption efficiency is considered to be improved once the chemical treatment is completed because of the multiply in number of active sites. In this study, the objective was to enhance the multiple heavy metal ions adsorption by using chemically treated bioadsorbent of MB and OPMF. Several parameters were investigated namely bioadsorbent dosage, reaction time, initial concentration, and initial pH.

METHODOLOGY

Bioadsorbent Preparation

The mangrove log was acquired from Santubong Wetland Mangrove National Park, Kuching Sarawak. The debarked mangrove barks were dried out in the laboratory stove after being washed to remove any impurities at 60°C for overnight. It was then crushed into fine particles by using laboratory heavy-duty blender and partition sieved into 250-300 micrometre size. Then, the sorbent was washed repeatedly by deionised water (DI) in order to remove any dust and impurities of MB. It was then filtered out using filter paper (Whatman 41) and the small particles of MB was chemically treated by using 37% of formaldehyde and 0.1M of sodium hydroxide (NaOH) (1:4, v/v) at 50°C for two hours. This is important to immobilise the water soluble component inside the MB. Then, it was washed thoroughly and repeatedly by deionised water to remove any excessive of formaldehyde and NaOH. The chemically treated MB was kept in the container after being oven-dried overnight at 60°C.

The oil palm fruit bunch was acquired from Ensengei Palm Oil Mill, Sdn. Bhd., Kota Samarahan. Fresh material of oil palm mesocarp fiber (OPMF) was taken out from fruit bunch and soaked in the boiled deionised water mixed with liquid detergent for defatting the fibers. After five hours of soaking, OPMF was washed with boiled deionised water to remove all debris. After dried for overnight at 60°C, OPMF was pulverised into smallest particles and sieved into 250-300 micrometre size. This is crucial because according to Kalam *et al.,* [21], the affinity of accumulation were directly depended on the surface area of the particles where smaller particles will have higher surface energy and Van der Waal forces [21]. For chemical modification, OPMF was treated with excesses 0.3M of nitric acid (HNO_3) solution for five hours and washed entirely using deionised water. Then, it was filtered out using filter paper (Whatman 41) and dried in the oven for overnight. The dried OPMF was kept in dried container for further use. The chemical treatment using 0.3M nitric acid (HNO_3) is very crucial to eliminate debris and any soluble material for it can react with metal ion during the bioadsorption of heavy metal ions [16].

Bioadsorbent Characterisation

The physical characterisation of MB and OPMF surfaces were analysed using Fourier Transform Infrared Spectroscopy (FTIR). The FTIR analysis was important to recognise the functional groups that exist in MB and OPMF. IR absorbance data were obtained for wavenumbers in the range of 650–4000cm^{-1}. Both bioadsorbent of MB and OPMF were analysed with a Bio-RadFTS-3500 ARX FTIR spectrophotometer for before and after the metals ion bioadsorption process.

Preparation of Metal Standard Solution

Multiple standard stock solutions were prepared through dilution of standard stock solutions in 1000 mg/L which include chromium, lead, nickel and copper metal ions solution with deionised water using 1000ml of volumetric flask.

Bioadsorption Analysis

Bioadsorption experiments were carried out by agitating each bioadsorbent of MB or OPMF together with 50 mL of initial concentration consist of multiple elements standard solution (Ni, Cu, Cr and Pb). The experiment also were done under three types of parameters namely reaction time, initial metals concentration and bioadsorbent dosage. The set of experiments was performed to determine the effect of bioadsorbent dosage (0.1, 0.3 and 0.5 gram) with other constant values of parameters includes 10mg/L for 60 minutes.

After each of experiment conducted, by using filter paper (Whatman 41) the sample metals solution were filtered out to separate the metals solution with bioadsorbent. The filtered metals solution and blank standard solution were analysed using atomic adsorption spectroscopy (AAS) Shimazu AA-7000 in order to detect metal concentrations of chromium, lead, nickel and copper before and after the bioadsorption test. The adsorption efficiency of multiple metal ions were calculated using as following equation (1):

$$Q_e = \frac{C_i - C_f}{C_i} x100 \qquad (1)$$

where C_i and C_f is initial and final concentration of multiple heavy metal ions, respectively.

RESULT AND DISCUSSION

Biosorbent Characterisation

The FTIR spectra of MB and OPMF before and after adsorption analysis are shown in the Figure of 1(a) and (b), respectively.

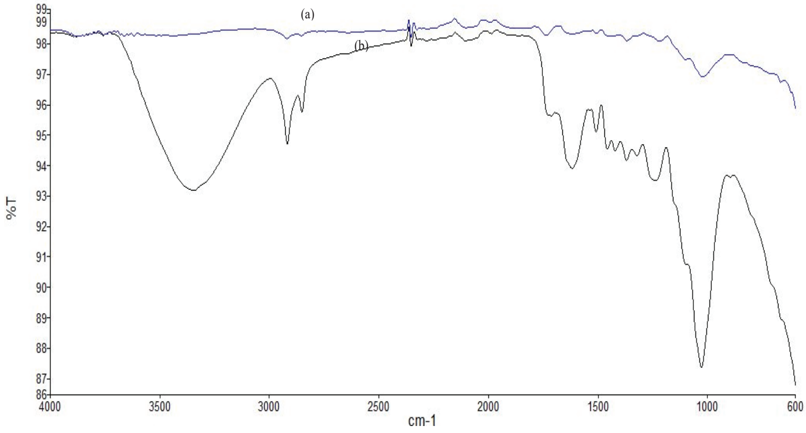

Figure 1(a): FTIR of MB (a) after bioadsorption (b) before bioadsorption

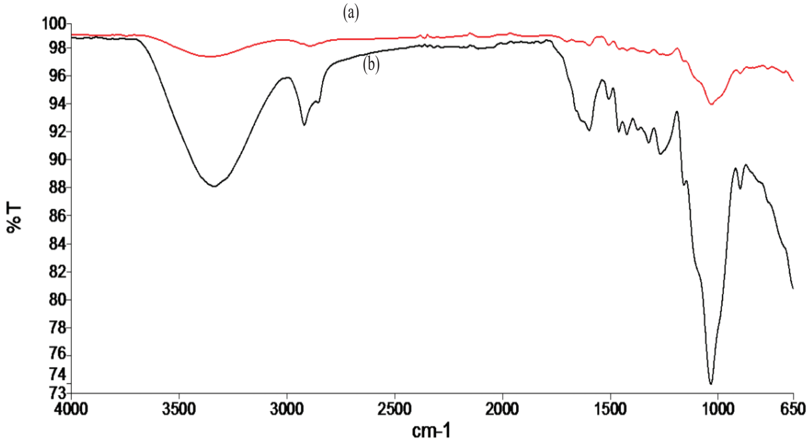

Figure 1(b): FTIR of OPMF (a) after bioadsorption (b) before bioadsorption

There are significant similarities between the vibrational peak of both MB and OPMF that represent the complex functional group of bioadsorbent. For example, the band at the range of 3500–3200 cm^{-1}, 3000–2900 cm^{-1}, 1740–1730 cm^{-1}, 1650–1550 cm^{-1}, 1550–1450 cm^{-1}, 1300–1200 cm^{-1} and 1100–1000cm^{-1} represent the alcohol, alkane, carbonyl, alkene, aromatic ring [22], amine and phenolic hydroxyl group, respectively [14]. After the bioadsorption process, the spectra of both MB and OPMF collapsed due to the reaction of metal ions with the functional groups which give rise to formation of new compounds. The functional groups can behave as ligand which can experience chelation mechanism with the metal ions to form a complex. The chelation mechanism leads to coordination of metal ion to the ligands having donor atoms namely O, N, S and P [23].

Effect of Bioadsorbent Dosage

The dosage is an important parameter in order to find the optimum quantity of bioadsorbent that can be used during the experimentation under constant initial metals concentration of 10 mg/L which were agitated at 200 rpm for 60 minutes. Under dosage as parameter, several sets of dosage were carried out to find the optimum dosage namely 0.1, 0.3 and 0.5 gram for both types of samples; i.e. MB and OPMF.

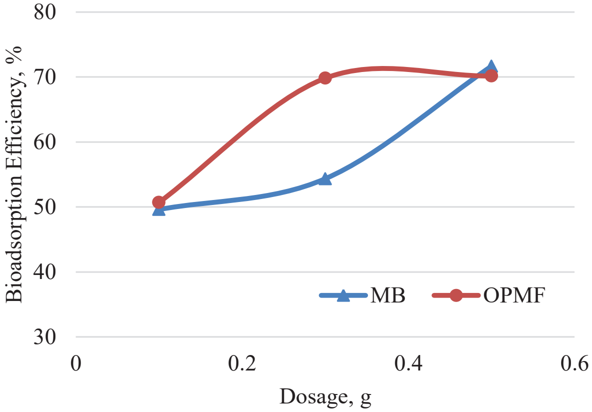

Figure 2(a): The removal of copper metal ion for both MB and OPMF under constant parameter of 10mg/L initial concentration, agitate speed at 200rpm for 60 minutes.

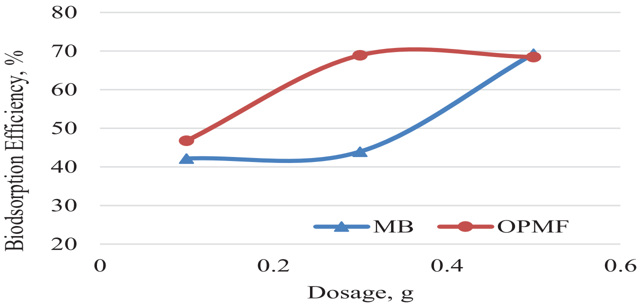

Figure 2(b): The removal of chromium metal ion for both MB and OPMF under constant parameter of 10mg/L initial concentration, agitate speed at 200rpm for 60 minutes

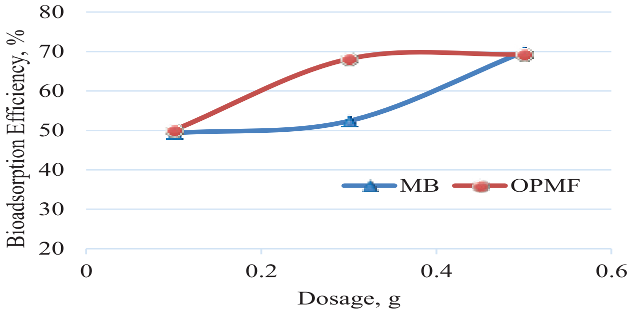

Figure 2(c): The removal of nickel metal ion for both MB and OPMF under constant parameter of 10mg/L initial concentration, agitate speed at 200rpm for 60 minutes

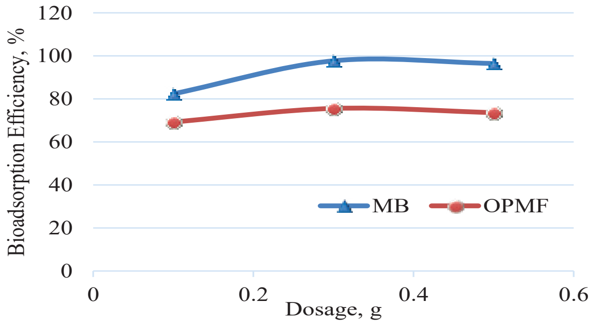

Figure 2(d): The removal of lead metal ion for both MB and OPMF under constant parameter of 10mg/L initial concentration, agitate speed at 200rpm for 60 minutes

Table 1: The effect of dosage parameter

Types of Heavy Metal	Bioadsorbent/Adsorption Efficiency (%)	Biosorbent Dosage(gram)		
		0.1	**0.3**	**0.5**
Chromium	OPMF (%)	42.17	43.96	69.31
	MB (%)	46.77	68.91	68.47
Copper	OPMF (%)	50.69	69.81	70.16
	MB (%)	49.61	54.35	71.67
Nickel	OPMF (%)	50.04	68.14	69.31
	MB (%)	49.31	52.37	69.92
Lead	OPMF (%)	69.30	75.61	73.65
	MB (%)	82.40	97.74	89.91

Table 1 shows the summary of the heavy metal ion bioadsorption of MB and OPMF toward four types of heavy metal ions specifically nickel, lead, copper and chromium. Figure 2(a) shows the bioadsorption efficiency toward copper ions that rapidly increased from dosage of 0.1 to 0.3 gram and 0.3 to 0.5 gram for MB and OPMF, respectively. Generally, the adsorption efficiency of bioadsorbent dosage at 0.3 to 0.5 gram and 0.1 to 0.3 gram of MB and OPMF, respectively marginally increased for all metal ions bioadsorption, excluding the chromium (Figure 2(b)) and lead (Figure 2(d)) ions that showed a decrease in efficiency particularly for MB. Moreover, the bioadsorption for nickel and copper ions as shown in Figure 2(a) and 2(c) indicate similar pattern where MB drastically increase at dosage of 0.5 gram while at dosage 0.3 gram, the efficiency only increased slightly for both metals ions. Meanwhile, OPMF was also observed to significantly increase at dosage of 0.3 gram, and then marginally increased at 0.5 gram dosage.

The present of functional groups on the bioadsorbent surfaces play crucial part in metal ions adsorption and provide the great influence on the metal ions adsorption via providing additional accessibility of active site that lead to the enhancement of the bioadsorption efficiency. The number of functional groups on the bioadsorbent surfaces was directly depended on the amount of dosage. This research findings has a good agreement with Rozaini *et al.,* [14], where the availability of active sites was improved if more amount of dosage was used. However, as shown in Figure 2(d), the lead ions bioadsorption at dosage of 0.3 gram were 97% and 75% for both MB and OPMF, respectively and slightly decreased at 0.5gram dosage. The decrease in lead ions bioadsorption at that particular dosage might be possibly due the inter ions competition on the bioadsorbent surfaces.

CONCLUSION

The capability of MB (*Rhizophora apiculate sp.*) and OPMF (*Elaesis guineensis sp.*) as bioadsorbent for multiple metal ion adsorption namely copper, nickel, lead and chromium and lead was examined. The metal ions bioadsorption thru these bioadsorbent has been established to have high competence in adsorbing various heavy metal ions. Nevertheless, this research demonstrated that the bioadsorbent likewise have high ability in adsorbing various heavy metal ions at once. The results also revealed that, the bioadsorption efficiency of various heavy metal ions was directly depended on the parameters specifically the quantity of dosage used in heavy metal ions bioadsorption. The bioadsorption efficiency is high due to the smallest particles that gives high surface area which about 250-300 micrometer, indicating the accessibility of the active site on MB and OPMF surfaces. This study has shown that MB and OPMF can act as potential bioadsorbent for the various heavy metal ions.

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