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Removal of Cu(II) from aqueous solutions using shell and seed of kelengkengfruits (*Euphoria longan* Lour)

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ABSTRACT

The ability of shell and seed of Kelengkeng fruit(Euphoria longan Lour)to remove Cu(II) ion from aqueous solution were investigated. The experiment were carried out by column method. Several parameter such as the solution of pH, initial concentrations, particle size and flow rate were studied. The optimum condition for adsorption of Cu(II) were at pH 3, concentration 400 mg/L, biosorben dose 0,5 g, and particle size250 µm with adsorption capacity 3,734 mg/g for seed and 7,513 mg/ for shell, respectively.

Keywords : Biosorption column method, shell and seed kelengkeng fruit (*Euphoria longan*Lour), Cu.

INTRODUCTION

Copper is known to be a hazardous heavy metal introduced into the water from many industries such as mining, smelting, electroplating, electrolysis, electric bonds/circuits manufacturing industries as well agriculture sector including fertilizers, pesticides. etc. Although copper is an essential trace element required by living beings for it's role in entryne synthesis, tissues and bones development. It is potentially toxic and carcinogenic with excessive ingestion [1]. Several decade due to heavy metal contamination in aquatic environment have increased the awareness about the heavy metal toxicity. Removal of copper Cu(II) from waste water is crucial and it toxicity for human being is at level of 100-500 mg per day. The word health organization in 2006 recommended 2,0 mg/l as the maximum acceptable concentration of copper in drinking water [2]. Several treatment methods are used to remove there pollutants from wastewater, such as precipitation, ion-exchange, evaporation, oxidation and membrane filtration,[3].

The biosorption considerable a mount of attention as an alternative process to traditional methods a heavy metal removal from contaminated water. Several biosorbenthas interact effectively with toxic metals caused has various functional groups such as hydroxyl, carboxyl, carbonyl, amine to make the metal complexes [4]. Since the agriculture by product was used as biosorbent for heavy metals as low cost sorption method, it was affective for removal of heavy metals such as Acidosasa edulis shoot shell, *Garcinia mangostana*L. fruit shell, *Arengapinnata* Merr fruit shell, papaya seed, alomond shell, water melon shell, pomegranate, akke apple seed, banana, lemon and orange cortex, peanut shell, tomato waste, durian(*Duriozibethinus*) seed[1, 4, 5, 6, 7, 8, 9, 10, 11, 12].

The aim of this research are to evaluate the adsorption performance of kelengkeng seed and shell for removal of Cu(II) from aqueous solutions with column method.

MATERIAL AND METHODS

Chemicals and Apparatus: The chemicals used were the standard solution of $CuSO_4$(1000 mg/L)from E-merck and HNO_3 65 %. The following apparatus was used: Colomn glass size (1 id x 15) cm, Atomic Absorption Spectrophotometer (AAS, varian AA240, America), SEM-EDX (Hitachi, S3400N), FTIR (Perkin elmer, Frountier)

Preparation of biosorbent : Kelengkeng were collected from the market of Padang city. Kelengkeng were wasted with deionized water, air-dried for 7 days and ground using crusher, with particle size various 106-425µm. The kelengkengshell and seed in a solution of 0,01 M HNO_3 for 2 h with 20 g biomass in excess of 80 ml HNO_3 0,01 M, followed by washing thoroughly with deionized water and then air-dried. The biosorbent was dried and ready to used.

Biosorption studies: The adsorption experiments were studied by using column method. In the column glass was entered(0,1-0,5) g of powder of Kelengkengshell and seed then flowing 10 ml of solution Cu(II) concentration (40-600) mg/L with pH (2-6),and particle size (106-425) µm. The concentrations of Cu(II) in the filtrate was measured by Atomic Absorption Spectrophotometer. To determine the amount of Cu(II) adsorbed by Kelengkengshell and seed, the formula used is:

$$Qe = \frac{C_o - C_e}{M} \times V \ldots.. (1)$$

where C_o is the initial concentration of metal ions (mg/L), C_e, final concentration at equilibrium state (mg/L), m, biosorbent mass(g) and v is volume solution (L).

RESULTS AND DISCUSSION

Characterization of Kelengkeng(*Euphoria longan* Lour) Biosorbent

FTIR Analysis :FTIR is an important analytical technique, which detects the vibration characteristics of chemical functional groups existing on the surface of adsorbent. Furthermore, it provides information on binding mechanism and possible functional groups involved in the interaction with metal ions [13,14].The FTIR spectra of kelengkeng seed and shell, before and after metal ion adsorption are shown in Fig.1.

Based on Fig. 1. wave numbers of functional group in the kelengkeng shell and seed were seem, namely -OH stretching, shifting wave number was changed from 3286.05 to 3290.83 cm^{-1} for seed and 3305.10 to 3309.82 cm^{-1} for shell, -CH stretching, shifting wave number was change from 2034.59 to 2170.53 cm^{-1} for seed and 2085.85 to 2169.14 $cm^{-1}$for shell, C=O stretching, shifting wave number was change from 1638.72 to 1637.27 cm^{-1} for seed and 1621.26 to1623.08 $cm^{-1}$for shell, and C-O stretching, shifting wave number was change from 1008.19 to 1010.71 cm^{-1} for seed and 1027.61 for shell 1023.10 cm^{-1}. It can be concluded the four functional groups played a role in the process of metal ion biosorption [15].

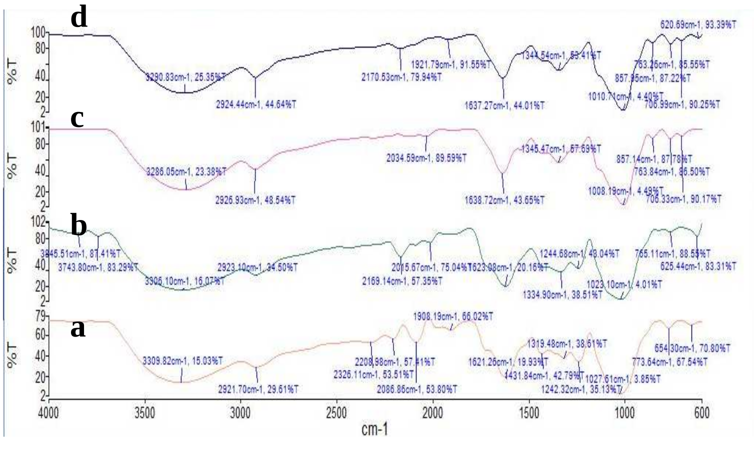

Fig. 1. FTIR spectra of kelengkeng shell before (a), after(b) adsorption of Cu(II), kelengkeng seed before (c), and after (d) adsorption of Cu(II)

Biosorption Studies

Effect of pH solution: The removal of metal ions from aqueous solution by adsorption is related to the pH of solution. The first set of tests, therefore, examines the effect of pH on the effluent concentration.

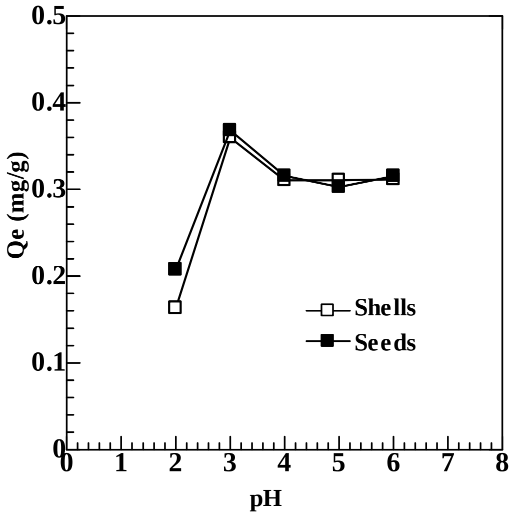

Fig. 2 Effect of pH on Cu(II)biosorption by *Euphoria longan* Lourseed, particle size 150 µm, mass of biosorbent 0,5 g, concentration 20 mg/L

The result is shown in Fig. 2. showed the maximum biosorption of Cu(II) occurred at pH 3 with biosorption capacity 0,3681 mg/g for shell and 0,3598 mg/g for seed. There was a decrease in biosorption capacity with on increase pH from 3 to 6.Biosorption of metal ions decreased because of increasing of competition with H^+ ion for active biosorption sites at lower pH [16].The same research was obtained by Wahyuni [14] using Langsat Fruit (*Lansiumdomesticum*Corr) Seed for removal Cadmium (II) and Copper (II) from the aqueous solution.

Effect of biosorbent dosage: Biosorbent dosage is an important parameter in the biosorption process to evaluate the adsorption capacity of metal ions on the biosorbent. Biosorption of metal ions depends on the type of biosorbentsurface and on the ion forms that metals find in the water solution. This can be explained by the fact that if the mass is more the surface of contact offered to the biosorption of Cu ion is more and hence becomes important in the removal of more adsorbate [17,18].

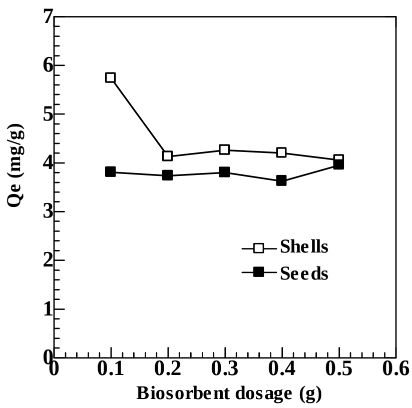

Figure 3. Effect of dose adsorbent on Cu(II)biosorption by *Euphoria Longan* Lour seed and Shell, pH 3, particle size 250 µm, concentration 400 ppm

The mass of biosobent was varied at 0.2, to 0,5gram. Fig.3. showed the optimum biosorbent dosage of Cu(II) ion by kelengkeng (*Euphoria longan* Lour) shell and seed in the aqueous solution. According to Kurniawan*et.al.*,[19] showed that the adsorption capacity decreased with increasing the amount of biomass. The optimum biosorbent dosage for Cu(II) ions found in mass 0.1 gram with biosorption capacity 4,054 mg/g for shell and 3,955 mg/g for seed. In this study used 0.5 gram mass of biosorben dosage for Cu(II) ions.

Effect of initial concentration: The heavy metal ion biosorption capacities of kelengkengseed and shell as a function of the initial concentration of Cu(II) ion within the aqueous solution. Fig. 4.showedthe biosorption capacity of Cu(II) was increased with increasing the concentration of Cu(II) ion solutions. However, at higher concentrations metal need to diffuse to biomass surface by intra particle diffusion and more hydrolyzed ion will diffuse at a slower rate [20]. The maximum biosorption capacity of Cu(II) per mg of kelengkeng (*Euphoria longan* Lour) shell and seed was calculated as 3,9895 g and 3.6700 g metal solution.

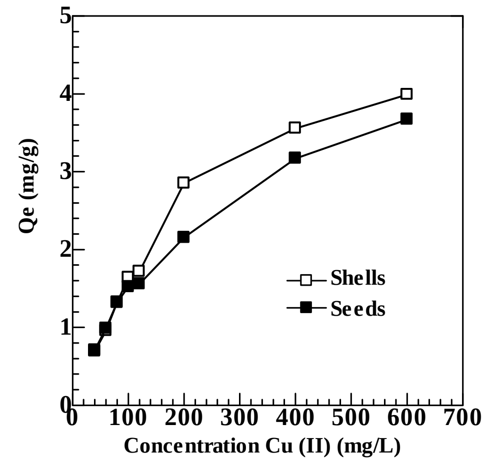

Figure 4. Effect of concentration on Cu(II)biosorption by *Euphoria Longan* Lour seed and Shell, particle size 150 µm, mass of biosorbent 0,5 g, optimum pH 3

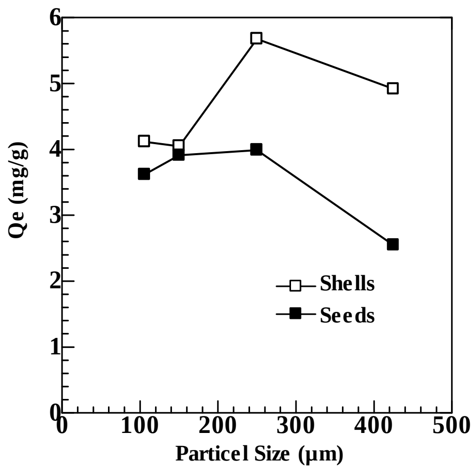

Figure 5. Effect of particle size onCu(II)biosorption by *Euphoria Longan* Lour seed and Shell, mass of biosorbent 0,5 g, concentration 400 ppm, pH 3

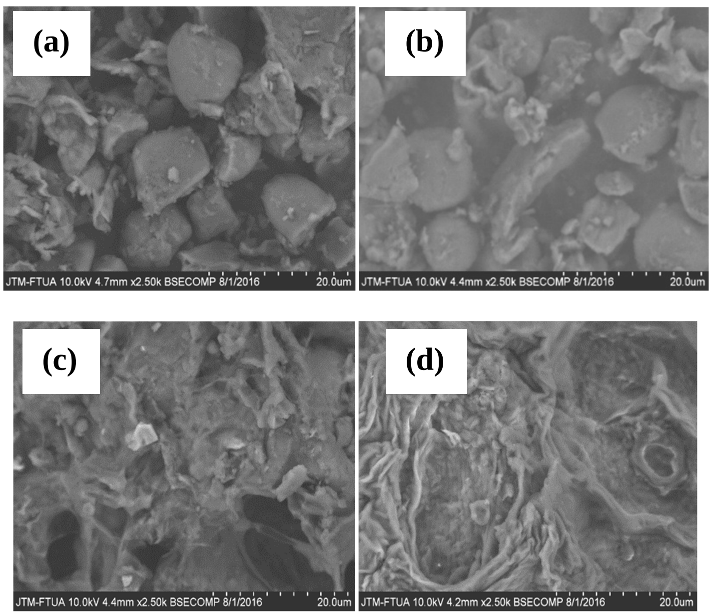

Fig. 6. Scanning Electron Microscope (SEM) Images of Kelengkeng seed and shell with 2500-times magnification seed of kelengkengbefore (a), after(b) adsorption of Cu(II), kelengkeng shell before (c), and after (d) adsorption of Cu(II)

Effect of particle size: The adsorption of Cu(II) ion on kelengkeng (*Euphoria longan*Lour) shell and seed were increased with decreasing of particle size. The particle size was varieted from 106-425µm. Fig. 5. showed that the increasing of particle size from 106-250µm that the biosorption capacity was increased but from 250-425µm the biosorption capacity was decreased, it was caused on a small particle size (106 µm) the mechanism adsorption of Cu(II) by column method was flowing by Van Deemter equation [23]depend on the kind of biosorbent. The optimum biosorption capacity was found 5,6765 mg/g on particle size250 µm.

According to Song *et.al.*, [21] reported that since the biosorption capacity of small size biosorbent showed little increase than the medium and big ones, it is very likely that, in the practical application, the biosorbent in big size would achieve similar performance with the small and medium ones with less cost of pre-treatment.

SEM-EDX Analysis

The scanning electron microscopic images were used to examine the surface morphologies of seed and shell of kelengkeng biosorbent before and after biosorption. The influence of biosorbent morphological was investigated, it was related to the efficiency of adsorption ofmetal ions in the biosorbent particles [15,22].

The images are given in Fig. 6. Initially the surface of biosorbent is rough and not homogeneous (Fig. 6a, c) while the microporous structure was changed after contacted with Cu(II) ion (Fig. 6b, d). EDX analysis was performed to determine the element composition of the biosorbents before and after metal ion adsorption. The metal ion in the biosorbent before contacted has C, O, Ca (Fig 7a,c), but after contacted with Cu(II) seem that ion Cu(II) has at 0.93 and 8.04 keV for shell of lengkeng and at 0.93 keV for seed of lengkeng (Fig. 7c, d). The concentration of carbon and oxygen seem higher its mean from the carbon used in the plate for analysis of element in biosorbent.

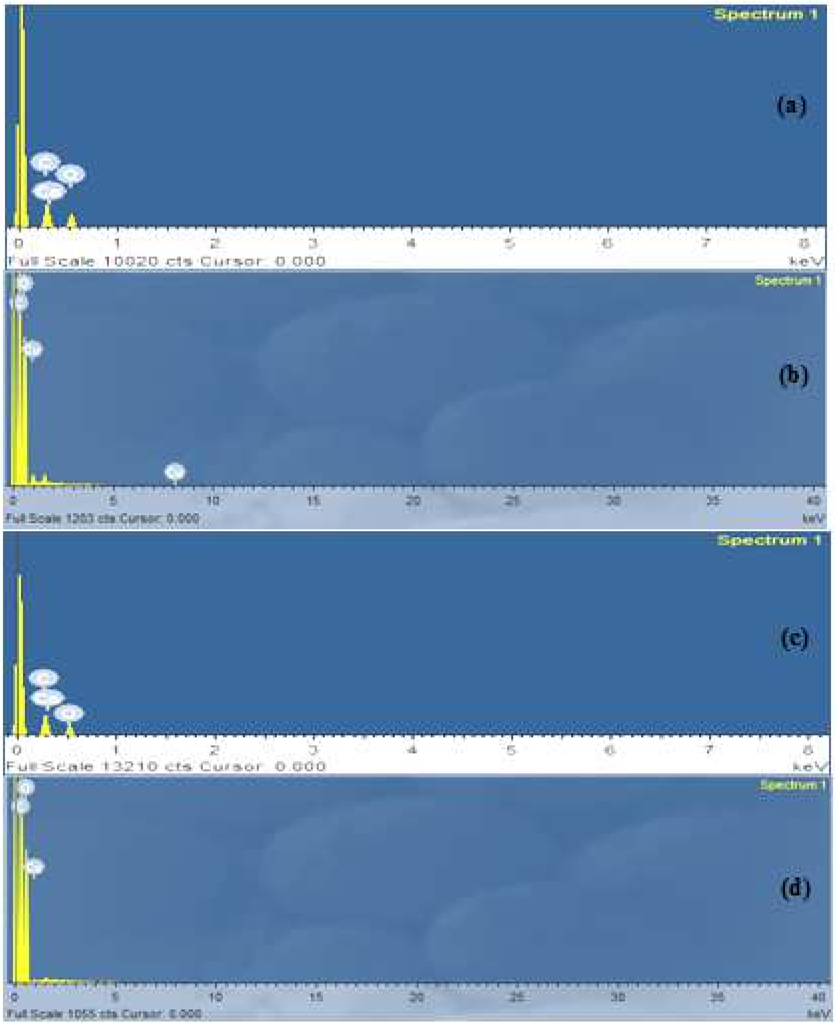

Fig. 7. EDX analysis of Kelengkeng shell of kelengkeng before (a), after(b) adsorption of Cu(II), kelengkeng seed before (c), and after (d) adsorption of Cu(II)

CONCLUSION

The powder of Kelengkeng seed and shell(*Euphoria longan*Lour) could used as biosorbent ofCu(II)ions present in water sample, at the optimum condition for adsorption of Cu(II) were at pH 3, concentration 400 mg/L, biosorben dose 0,5 g, particle size 250 µm with adsorption capacity (qe) 3,734 mg/g for kelengkeng seed and 7,513 mg/g for kelengkeng shell.

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