Biosorption of Cadmium and Copper Ions from Aqueous Solution using Banana (*Musa paradisiaca*) Shell as Low-Cost Biosorbent

Edi Nasra^{a*}, DesyKurniawati^a, Bahrizal^b

 ^aAnalytical Chemistry Laboratory, Faculty of Mathematics and Sciences, UniversitasNegeri Padang, Jl. Prof. Hamka, Air Tawar Padang 25131, Indonesia
^bInorganic Chemistry Laboratory, Faculty of Mathematics and Sciences, UniversitasNegeri Padang, Jl. Prof. Hamka, Air Tawar Padang 25131, Indonesia

Abstract

The research of Cd (II) and Cu (II) biosorptionin aqueous solution using banana shell powder has been conducted. Optimization of heavy metal adsorption using banana shell as adsorbent with column method has been investigated. The studies include determination of optimum pH and concentration. The result showed that the optimum condition was at pH = 5, concentration 500 mg/L with adsorption capacity 8.3864 mg/g for Cd (II) and pH = 3, concentration 500 mg/L for Cu (II) with adsorption capacity 7.5975 mg/g. This study shows that banana shell waste can be an important low cost biosorbent for Cd (II) and Cu (II) removal.

Keyword: Biosorption, cadmium (II), copper (II), banana (Musa paradisiaca) shell

1. Introduction

Nowadays the pollution of different natural water by heavy metals is a great concern because of the toxic effects on living organisms. Urbanization, industrial development, and heavy traffic lead to contamination of water bodies by heavy metals. [1]

Copper, as one of essential of trace elements used to maintain normal life activities, plays significant rule in many biological processes and systems. However, it is environmental pollutant at high concentration [2,3], and an excess concentration of Cu^{2+} in human body can cause many serious diseases such as Alzheimer's [4], Parkinson's [5] and Mengke's disease [6].

Cadmium is mainly used in Ni-Cd batteries manufacturing, as pigments, stabilizers, fabric coatings, alloys and electronic compounds such as Cadmium Telluride (Cd-Te) as the semiconductor [7,8]. Cadmium is not an essential element for human body. Human can absorb the element of cadmium into the body through breathing or food, while the absorption through the skin is not generally done. The total cadmium absorbed by the body is 2 to 6% of the entire cadmium entering through food [7].

Cases of chronic pollution caused by cadmium poisoning have occurred in Japan along the river Jitsu, known as "itaiitai" (it means screaming because of sudden illness). Patients have great disorders of the kidneys, liver and bone which sometimes lead to death. This pollution arises from industrial waste mining cadmium, zinc and lead [7,8].

Due to its important role, a large number of methods have been developed for quantitative determination of metal ions in aqueous solution. Conventional methods for removing metals from aqueous solution include chemical precipitation [9], chemical oxidation and reduction, ion exchange filtration, electrochemical treatment, reverse osmosis, membrane technologies and evaporation. The major disadvantages with conventional treatment technologies are the production of toxic chemical sludge and its disposal/treatment becomes costly affair and is not eco-friendly.

Therefore, removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner assumes great importance [10-12]. Removal ofCd (II) and Cu(II) from wastewater is crucial and it toxicity for human being is at level of 100-500 mg per day. The World Health Organization in 2006 recommended 2.0 mg/l as the maximum acceptable concentration of copper in drinking water [1,2,7,8].

Thebiosorption has considerable amount of attention as an alternative process to traditional methods and heavy metal removal from contaminated water. Different kind of biomaterials interacts effectively with toxic metals [4]. A long with aforementioned advantages, various functional groups such as hydroxyl, carboxyl, carbonyl, amine in biosorbents have hightaffinity to form metal complexes. Hence, there is a growing demand to find effective, low-cost and locally available biosorbents for the biosorption of heavy metal ions, [10]. 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 product and by products have been reported to be effective in removing toxic metals [14]. Waste Mangostreen shell [14], pomegranate [13], akke apple seed [10], banana, lemon and orange cortex [15], melon seed [16][17], peanut shell [11], tomato waste [18], papaya seed [19] and longan [20].

The main objective of this work was to evaluate the adsorption performance of banana shells for removal of Cd (II) and Cu(II) from single aqueous solutions. The effect of solution pH, initial concentration, particle size, amount of biosorbent dose and flow rate in biosorption with column method. The banana shells were characterized by FTIR spectroscopy to identify chemical bond type in molecules present in banana shells.

2. Method

2.1 Chemicals and apparatus

All reagents used were of analytical grade obtained from Merck (Darmstad, Germany). In present work, the biosorption experiments were conducted by using stock standard solution (1000 mg/L) of $CuSO_4.5H_2O$ and $Cd(NO_3)_2$ from E-merck, HNO₃ 65 %, NH_{3(aq)} 25%. The apparatus used were screener Octagon 200 (Endcots, London, England), analytical balance (AA-200 Denver Instrument Company), shaker (Haake SWB 20), pH meter (Denver Instrument Company), FTIR (Bio-Rad FTS 60), and atomic absorption spectrometer (AAS Alpha-4, Analysis 100, London, England).

2.2 Preparation of biosorbent

Bananashells (Fig. 1) were used a biosorbent for sorption of Cu(II) and Cd(II) from an aqueous solution. Banana was collected from local market of Padang City, West Sumatera Province of Indonesia. Banana shells were washed with deionized water remove dirt, sand, clay and particulate materials from the surface. After washing, they were dried under the sunlight. Dried banana shells were cut, ground using crusher, with various particle size range $105 - 425 \mu m$. The banana shells in a solution of 0,01 M HNO₃ for 2 h with 20 g biomass in excess of 80 ml HNO₃ 0,01 M, followed by washing thoroughly with deionized water and then air-dried. The biosorbent was dried and ready to use.



Fig. 1.Banana shells.

2.3 Biosorption studies

The adsorption experiments were studied by using dynamic sorption experiments. Powder of banana shells (biosorbent) was implemented in a set of conical flask containing 10 ml of solution containing Cd (II) and Cu(II). The effects of pH (2-6), initial metal ion concentration (100-500 mg/L), biosorbent dosage (0.2-0.5 g), particle size (106-425 μ m) and flow rate (1-6 ml/min) were studied. The suspension then filtered and metal ion concentrations in the supernatant solution were measured by Atomic Absorption Spectrophotometer. The optimum conditions for the biosorption of Cd (II) and Cu (II) ion were determined. To determine the amount of Cd (II) and Cu(II) adsorbed by banana shells, the formula used is:

$$Qe = \frac{C_o - C_e}{M} \times V$$

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

2.4 Fourier Transform Infrared Spectroscopy analysis

For the IR studies, 5% (w/w) of dried banana shells were pressed to form KBr disc. The FTIR spectra were recorded in the range of 4000-450 cm⁻¹ spectral range using a Bio-Rad FTS 60 instrument. A total of scans were averaged for each sample with resolution of 2 cm⁻¹.

3. Results and Discussion

3.1 Characterization of biosorbentMusa paradisiaca

3.1.1 FTIR Analysis

FTIR is an important analytical technique, which detects the vibration characteristics of chemical functional groups existing on the surface of adsorbent [22]. Furthermore, it provides information on binding mechanism and possible functional groups involved in the interaction with metal ions [23]



Fig. 2.FTIR spectrum of banana shells.

FTIR characterization was carried out to analyze the major functional group which exists in the biomass. The broad and intense peak at 3296.60 cm⁻¹ranging from 3600 to 3200 cm⁻¹, was assigned to the stretching of – OH groups due to interand intra- molecular hydrogen bonding of polymeric compound such as alcohols and carboxylic acid. At 2926.13 cm⁻¹, C-H stretching. The 1600.21 cm⁻¹ (a) peak was a carboxyl stretch in ester.

3.2 Effect of pH solution

The pH of solution had a significant impact on the removal of heavy metals since it determined the surface change of the adsorbent has carboxylate. Fig.3. shows the maximum biosorption of Cu (II) occurred at pH 3 with biosorption capacity mg/g. There was a decrease in biosorption capacity with the pH increase from 3 to 6. Biosorption of metal ions decreased because of increasing of competition with H^+ ion for active biosorption sites at lower pH. Similar results were shown by [21] in the removal of Pb⁺² also got the optimal pH for biosorption as 3. Gupta et al in [21] used bassage, fly ash a sugar industry waste material for the removal of Pb(II), the optimum pH 3.



Fig 3.Effect of pH solution on Cu (II) and Cd (II) adsorption by banana shells.

Fig. 3 shows the metal ions uptake in the solution of cadmium nitrate and copper nitrate, as a function of pH. In the experimental system, Cu^{2+} remains the dominant species below pH 3 and Cd^{2+} belowpH. Beyond this pH, solid cadmium hydroxide and copper hydroxide is thermodynamically the most stabile phase.

3.3 Effect of initial metal ion concentration

The heavy metal ionsbiosorption capacities of banana shells as a function of the initial concentration of Cd (II) and Cu (II) ion within the aqueous solution were studied. The amount of metal ions adsorbed per unit mass of banana shell increased with an increased in initial concentration of Cd (II) and Cu (II) ion. At the lower concentrations, all metal ions present in the solution would interact with the binding sites and thus facilitated 100 % biosorption. At concentrations adsorption, sites took up the available metal ions more quickly. However, at higher concentrations metal need to diffuse to biomass surface by intra-particle diffusion and more hydrolyzed ion will diffuse at slower rate [21]. The maximum biosorption capacity of Cd (II) per gram of banana (*Musa paradisiaca*) shells were calculated at 8.3864 mg or mg/L metal solution and adsorption capacity of Cu (II) were calculated at 7.5975 mg/g banana shells.



Fig. 4.Effect of concentration of Cd (II) and Cu(II) solution on adsorption by banana shells.

3.4 Adsorption isotherm studies

An adsorption isotherm describes the relationship between the amount of adsorbates taken by the adsorbent and the adsorbates concentration remaining in solution. This isotherm was derived from equilibrium constant of the interaction of adsorbate with adsorbent [22]. In this research, the equilibrium data for biosorptionprocess of Cu (II) ions on banana shells evaluated by the Freundlich and Langmuir isotherm models. Fig. 7 described some information related to biosorption processof Cu (II) ions on powder of longanshells and seeds. Fig. 7 shows the comparison between the Langmuir and Freundlich regression coefficients. It was observed that the experimental data fitted the Langmuir isotherm model best. The model Freundlich was far from unity while the Langmuir isotherm model was closer to unity [23].

4. Conclusion

The results demonstrate that banana shells are the effective biosorbents to remove Cd (II) and Cu (II) from aqueous solution. Cd (II) and Cu(II) were removed in column experiments. Biosorption process was affective by pH 3, initial concentration 500 mg/L for Cu (II) with adsorption capacity 7.5975 mg/g banana shells for Cu and pH = 5, initial concentration 500 mg/L with adsorption capacity 8.3864 mg/g banana shells for Cd (II). The equilibrium data fitted well to Langmuir isotherm with $R^2 = 0.9984$. The study revealed that banana biosorbent could be used as adsorbent for the removal of other heavy metals on large scale.

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