Removal of Copper(II) Ions in Aqueous Solutions Using Tannin-Rich Plants as Natural Bio-Adsorbents

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Abstract. In this study, the purpose of our interest is to investigate the adsorption behavior of copper (II) ions in aqueous solution using some tannin-rich plants as natural bio-adsorbents such as mangosteen peels (Garcinia mangostana L.), cassava leaves (Manihot esculenta Crantz) and Thai copper pod leaves (Senna siamea (Lam.)) as powder form in different dosage of adsorbent plant materials. The adsorption capacities at different pH of solution and contact time were performed. All the experiments in this study were chosen at room temperature by batch technique. From the experimental results showed that cassava leaves gave better adsorbent properties than mangosteen peels and Thai copper pod leaves. The increasing dosage of all adsorbents and contact time have been found to increase adsorption capacities. In this respect, the adsorption capacities depend crucially on the adsorbents and contact time. The optimum pH of copper (II) ions adsorption was pH 4. According to this work, it was observed that bio-adsorbent materials from tannin-rich plants could be used to remove copper (II) ions from aqueous solutions.

1. Introduction
One of the most important environmental problem issues is the presence of heavy metals contaminated in water, because heavy metals are not biodegradable [1]. The increasing heavy metals usage in industrial activities has caused the existence of them in water [2]. The heavy metals often found from industrial effluent are copper. Copper is a transition metal which belongs to period 4 and group IB of the periodic table [3]. Some toxic of copper in the body has a potentially damaging protein, lipid and DNA [4]. The excess copper compound in the body may affects on aging, mental illness and Alzheimer’s diseases [5]. Removal of metal ions from wastewater in an effective manner has become an important issue. Adsorption technology has recently become a real alternative to traditional wastewater treatment due to its relatively simplicity and efficiency. Nowadays, agricultural materials are receiving as adsorbents for the removal of pollution from water. Different bio-adsorbents are developed from agro-wastes and used for heavy metals removal. One class of such materials is that of the tannins, a term which covers many families of chemical compounds. Tannins are large and complex molecules, weak acid and astringent taste, which they can be found in various parts of some plants. Tannins are divided in two types. One is the condensed tannin that is found in the bark and cores of the plants. The other is the hydrolysable tannin that can be found in leaves and sheath [6]. Tannins have shown to be potential alternative for the removal of heavy metal ions from aqueous solution, especially lead, iron, chromium and copper. Tannins exhibit extremely high metal ion chelating ability because metal ions can generate highly reactive phenolic hydroxyls of tannins molecules [7]. Mangosteen peels, cassava leaves and Thai copper pod leaves are agricultural waste materials, low cost and high amount of tannins, which they can be used as bio-adsorbents [8, 9].
The purpose of research was to studies the bio-adsorption of copper (II) ions from aqueous solution. We have selected three tannin-rich plants sources such as mangosteen peels, cassava leaves, Thai copper pod leaves as bio-adsorbents. The influences of adsorbent doses, contact time, and pH were studied in batch experiments at room temperature for selected the best bio-adsorbent materials and the most removable metals of optimum adsorption condition.

2. Materials and Methods

2.1. Preparation of adsorbent materials
Three types of agricultural waste materials have been employed to use as bio-adsorbent materials in order to remove copper (II) ions from aqueous solution. Firstly, the bio-adsorbents, such as mangosteen peels, cassava leaves and Thai copper pod leaves, were washed with distilled water in order to remove the impurities and leave to dry at room temperature. Then, they were cut into small pieces and dried in hot airoven at 70°C for 6 hours. After that, the dried bio-adsorbents were ground into powder by electrical blender in order to obtain small particle size.

2.2. Preparation of copper (II) ions in aqueous solutions
In general, copper (II) ions was used as the adsorbate. For this work, we compared different five concentrations in order to detect the adsorption capacities for analytical standard calibration curve. Firstly, clear stock solutions of 1 mol/L copper (II) ions solution was prepared by dissolving 249.28 g of copper (II) sulphate pentahydrate (CuSO$_4$·5H$_2$O) in 1L of distilled water. Then, clear stock solutions of 1 mol/L copper (II) ions solution was diluted with distilled water in concentration of copper (II) ions in aqueous solutions as 0.02, 0.04, 0.06, 0.08 and 0.10 mol/L, respectively.

2.3. Methods

2.3.1. Preparation of standard calibration curve. This experiment was used different five concentrations of copper (II) ions in aqueous solutions to make a series of calibration standard solution such as 0.02, 0.04, 0.06, 0.08 and 0.10 mol/L. The absorbances of these standards were measured to create a calibration curve by spectrophotometry method. The maximum wavelength of copper (II) ions solutions have been detected at 822 nm.

2.3.2. Investigation of adsorbents dosage. The various dosage each of different bio-adsorbents, such as 0.5, 1.0, 1.5 and 2.0 g, were added 10 ml of 0.10 mol/L copper (II) ions in aqueous solution at room temperature.

2.3.3. Investigation of pH. The various of pH were chosen to use around 2-5. These experiments were combined with 2 g of each bio-adsorbents and 10 ml of 0.10 mol/L copper (II) ions in aqueous solution. The pH of the solution was adjusted by using 0.10 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide.

2.3.4. Investigation of contact time. Different contact time on adsorption behavior of copper (II) ions in aqueous solution were used at 30, 60, 90, 120 minutes and 24 hours of 2 g of each bio-adsorbents and added 10 ml of 0.10 mol/L copper (II) ions in aqueous solution at room temperature.

3. Results and discussion
Adsorption method was employed to remove copper (II) ions from aqueous solution, which corresponds to bio-adsorbents dosage, pH and contact time. The results in this work will be discussed in the following section.

3.1. Standard calibration curve of copper (II) ions in aqueous solutions
The calibration curve produced a linear relationship between the absorbance values and concentrations of copper (II) ions in aqueous solution. The standard calibration curve and the equation of copper (II) ions in aqueous solutions are shown in figure 1.

![Figure 1. Standard calibration curve of absorbance values and concentration of copper (II) ions.](image)

### 3.2. Effect of adsorbents dosage

The effect of adsorbents dosage was employed to investigate different dosage of bio-adsorbents from 0.5-2.0 g in 10 ml of 0.10 mol/L copper (II) ions in aqueous solution at normal pH and room temperature. The results have been clearly demonstrated that the percentage removal of copper (II) ions from aqueous solution increased when increasing the adsorbents dosage (figure 2). The percentage removal of copper (II) ions from aqueous solution for calculating is written as:

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\% \text{removal of copper (II) ions from aqueous solution} = \left( \frac{C_i - C_e}{C_i} \right) \times 100
\]

With regard to calculating percentage removal equation, \(C_i\) and \(C_e\) (mol/L) were represent the initial and equilibrium concentrations of copper (II) ions in aqueous solution, respectively [10]. In term of the experimental data, it has been shown that the removal efficiency and specific uptake of copper (II) ions in aqueous solution depend on quantity and sort of the bio-adsorbents. The percentage removal of copper (II) ions in aqueous solution increased when increasing bio-adsorbents dosage. In this respect, the percentage removal of copper (II) ions in wastewater corresponds to surface area of bio-adsorbents [11]. Moreover, tannin rich-plants had high metal binding capacity [7]. The optimum condition of bio-adsorbents dose with contain 0.10 mol/L copper (II) ions in aqueous solution of ratio as 2:10 were chosen for further adsorption experiments.

![Figure 2. Effect of adsorbents dosage on percentage removal of copper (II) ions from aqueous solution.](image)
3.3. Effect of contact time

Effect of contact time was investigated for varying in the range of 30 to 120 minutes and overnight as shown in figure 3. With regard to experimental data, when increasing contact time of bio-adsorbents with 0.1 mol/L of copper (II) ions in aqueous solution, high percentage removal of copper (II) ions from aqueous solution was found. For earlier studies, it was concluded that, the percentage removal of copper (II) ions from aqueous solution clearly confirm that it depends on bio-adsorbents dosage, pH and contact time. The rate of reaction of copper removal was very rapid in 30-120 minutes, thereafter the rate of copper removal constant. The adsorption rate after 120 minutes and equilibrium state because the binding site was shortly become limited and the remaining vacant surface sites were difficult to be occupied by copper (II) ions because of the driving force of mass transfer between the adsorbate and active site surface of bio-adsorbent in aqueous adsorption system decreases with time pass [5].

![Figure 3. Effect of contact time on percentage removal of copper (II) ions from aqueous solution.](image)

3.4. Effect of pH

Effect of different pH was investigated in the range of pH 2 to pH 5 in order to study the effect of percentage removal of copper (II) ions from aqueous solution as shown in figure 4. For the experimental data, it has been demonstrated that the percentage removal of copper (II) ions from aqueous solution in creased when using pH about 2 to 4. Moreover, the adsorption capacities decreased in pH 5. This was exported by considering and adopting some limitations of copper introduces a limiting at pH 5. At higher pH, its precipitation begins in the form of insoluble hydroxide as Cu(OH)\(_2\). Therefore the removal was not complete by adsorption [5, 12]. The maximum adsorption efficiency in pH 4 may be due to the interaction of copper (II) ions with surface functional groups present in the bio-adsorbents.

![Figure 4. Effect of pH on percentage removal of copper (II) ions from aqueous solution.](image)
4. Conclusions
As mentioned earlier, in the case of the batch experimental results was reported that the adsorption behaviour of heavy metal ions was a potentially attractive technique for investigation of removal of heavy metal ions from wastewater. According to this study, it has been demonstrated that tannin-rich plants, such as mangosteen peels, cassava leaves and Thai copper pod leaves, were natural bio-adsorbent materials. The bio-adsorbents were low-cost, easily prepared and high-affinity for heavy metal ions. Based on the experimental data, the optimum conditions with contain 2 g of bio-adsorbents dosage in 10 ml of 0.1 mol/L of copper (II) ions in aqueous solution, the pH of 4, the contact time of 120 minutes were chosen, which correspond to high percentage for removal of copper (II) ions from aqueous solution. With regard to bio-adsorbents, cassava leaves were shown the highest percentage removal of copper (II) ions from aqueous solution. In this respect, cassava leaves could be applied as an alternative low-cost bio-adsorbent for removal of heavy metal ions in wastewater.

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