Papaya Seeds as A Low-Cost Sorbent for Removing Cr(VI) from The Aqueous Solution

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Abstract. The presence of chromium (VI) contaminants and their toxicity in aqueous streams important environmental problems. Adsorption is one of the effective techniques that can be used for removing metal from wastewater. This research was initiated by preparing sorbent from papaya seeds and determining its functional group contents by using FT-IR. The adsorption process was carried out in a batch method. The study of adsorption aspects involved the pH, initial Cr (VI) concentration and contact time between Cr (VI) and sorbent. FT IR analysis results showed that the main functional groups are carbonyl, hydroxyl, and carboxylic. It was also found that the effective pH for Cr (VI) uptake is 2.0 and increasing contact time would increase the Cr (VI) uptake. In addition, the equilibrium was reached after 40 minutes interaction and the increase of initial chromium (VI) concentration would increase the sorbent uptake percentage. All these results indicated that papaya seed is a potential sorbent for removing Cr (VI) from aqueous solutions.

1. Introduction

Chromium is an element which naturally found at low concentrations in rocks, animals, plants, soil, volcanic dust and gases. Chromium is available in the aquatic environment as both Cr (III) and Cr(VI) states, and the most toxic is Cr(VI). The presence of Cr (VI) contaminant in the water bodies is from many industrial processes such as tanning factories, electroplating, metal processing, paint manufacturing, steel fabrication and agricultural runoff [1], [2].

Uncontrolled accumulation of chromium will be harmful to the environment and living organisms. This is due to living organisms, including microorganisms, as well as sea animals can absorb heavy metals. Through the food chain, chromium can be deposited in a living body part which at a certain amount can be toxic. The impact of excessive chromium in the body will be occurred in the skin, respiratory tract, kidneys, and liver.

Heavy metals waste that harm the environment needs to be processed in a certain method in order to make it safe for the environment. Basically, waste treatment can be performed by chemical, biological or physical methods. The common chemical separation methode of heavy metals is by adding certain chemicals such that precipitations of hydroxides at high pH is formed. However, this method is expensive and risky which can emerge secondary pollution caused by the excess of alkaline. Meanwhile the adsorption processing in physical method is by using activated carbon or absorption using a membrane. This method also requires a high cost.

Another method of waste treatment containing heavy metals is by using biological materials as adsorbent. The process is defined as biosorption. Biosorption demonstrates the ability of biomass to bind heavy metals of the solution through metabolic steps or chemical-physics [3], and it includes the removal of toxins from hazardous materials [4]. This method can be done on the spot, so it does not need a waste removal process. The other advantages in the use of biosorbent are abundant raw materials, low cost, efficient, minimum of sludge formation, and the absence of additional nutrients and the regeneration [3]. Therefore, the use of biosorption in waste water treatment has been proven as quite promising method [5]. Previous research showed that waste materials as multhani matti, mango bark dust, chalk powder, etc are proven to remove Cr(VI) [6].

Papaya is one of commonly plant in Indonesia, and bears fruit all of the years. Papaya is widely used not only for its fruit, leaves, but also its seeds. Papaya's seed have been used as traditional medicine for anthelmintic, diarrhea, cold, etc. However, in general, papaya's seeds are underutilized or directly disposed as a waste.

The main characteristics of papaya's seed can be used to reduce or mitigate the metal as the result of chemical composition. The main component of papaya's seeds is lignin and cellulose, included polar functional groups of lignin, such as alcohols, aldehydes, ketones, carboxylic acid, phenol, and ether. These groups are able to bind metal ions by donating an electron pair to form complexes with metal ions in solution [7]. This research was designed to study the removal of Cr(VI) ions from aqueous solution by low cost adsorbent, i.e papaya seeds which is explored under batch condition.

2. Method

Potassium dichromate ($K_2Cr_2O_7$) AR grade was used for the preparation of Cr (VI) standard solutions stock in distilled water. For pH adjustment throughout the experiment, 0.1 M hydrochloric acid (HCl) and/or 0.1 M sodium hydroxide (NaOH) were added.

The measurement of Cr (VI) concentration using ultraviolet-visible spectrophotometer (UV-vis) by Diphenyl Carbazide (DPC) method and pH solution was adjusted at 1.5. The absorbance was measured in the UV – visible spectrophotometer at 540 nm. The reagent blank was also measured by the same procedure. A calibration curve was prepared for Cr (VI) standard solutions and absorbance. The sample concentration was determined by calibration curve. The percentage uptake of Cr(VI) was calculated according to the following equation:

$$\text{Uptake}\,\% = \frac{[C_0 - C_t]}{C_0} x100\%$$

Where C_0 is the initial concentration and C_t is the concentration at t time.

Papaya seeds were taken from the local papaya fruit. Papaya seeds were washed several times to remove dirt and other impurities, and then boiled for 8 hours to remove the gelatin aryl transparent, and finally washed with deionized water. The clean papaya seeds were dried in the oven at a temperature of 60°C for 48 hours to remove moisture content. Dried seeds were crushed and sieved to obtain the same surface area. The functional groups in papaya seeds were determined by FTIR.

Adsorption process was carried out using batch method. The study of pH effect on the adsorption of Cr (VI) was performed by interacting 100 mg of adsorbent with 20 mL of 50 mg/L solution of Cr (VI) at various pH (4-8) at room temperature and stirred with a magnetic stirrer for 30 minutes. The samples were filtered using Whatman filter paper No. 42. Supernatant was determined by UV – visible spectrophotometer at 540 nm. Control experiments without sorbent was carried out to ascertain that the sorption was due to the sorbent and not the wall of the container.

To study the contact time effect, 100 mg of adsorbent was interacted with 20 mL of 50 mg/L solution of Cr (VI) at optimum pH. The mixture was stirred with a magnetic stirrer with a time variation of 10, 20, 30, 40, 50, and 60 minutes. The samples were filtered using Whatman filter paper No. 42. Supernatant was determined by UV – visible spectrophotometer at 540 nm.

To study the effect of initial concentration, 100 mg of adsorbent was interacted with 20 mL of Cr (VI) various concentrations of 10, 20, 30, 40, 50, 60 mg/L. System solution of pH was adjusted to pH optimum with interaction time 40 minutes. The samples were treated in the same method as studying the effect of contact time.

3. Results and Discussion

3.1. Functional Groups Analysis of Adsorbent of Papaya Seeds.

To determine the functional groups in papaya seeds, FT IR analysis was employed. The results are shown in Figure 1.

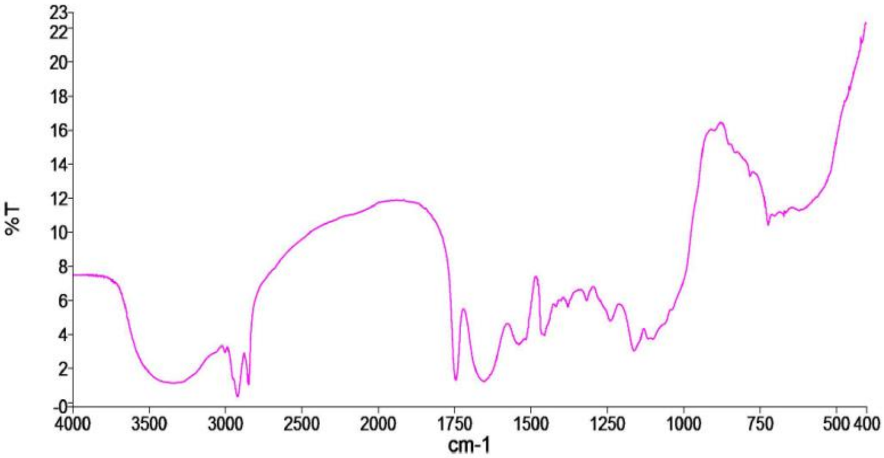

Figure 1. IR Spectra Adsorbent of Papaya Seeds.

Fig. 1 shows hydroxyl group (alcohol) which is indicated by the shape of the wider spectra in wave number of 3350.0 cm-1 (as an O-H stretching vibration). Sharp spectra at wave number 1746 cm-1 indicates the presence of carbonyl groups. The evidence of the aldehyde group, in addition to the carbonyl group, was also supported the C-H bond at wave number 2854 cm-1. The existence of carbonyl groups and hydroxyl groups indicated the presence of a carboxylic acid.

Similar results of research conducted by Saikaew, (2009); Norhafizah et al., (2011), where papaya's seeds contained polar functional groups such as alcohols, aldehydes, ketones, carboxylic acid, phenol, and ether. These groups are able to bind metal ions by donating an electron pair to form complexes with metal ions in solution.

3.2. Effect of pH

This research studied the effect of pH on the ability of Cr (VI) adsorption by papaya seeds. It is known that the degree of acidity (pH) of water has a major influence on the physical and chemical forms of metal compounds in aquatic environments because pH controls the solubility and concentration of metal species. The results are provided in Figure 2.

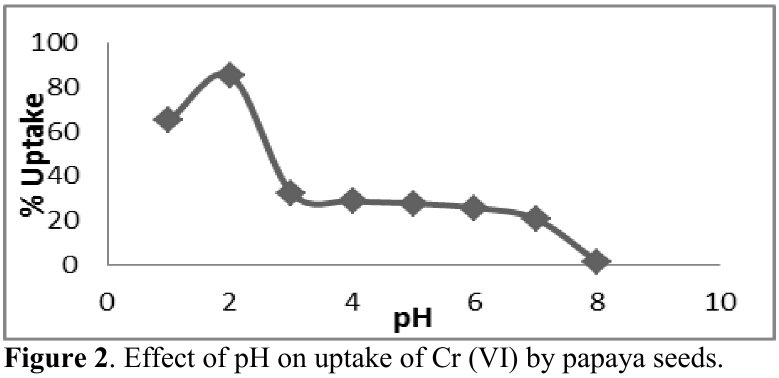

Figure 2. Effect of pH on uptake of Cr (VI) by papaya seeds.

Figure 2 shows that by the increase of pH, the ability of the papaya's seeds adsorbent of to bind metal Cr (VI) is decreasing, and the maximum adsorption occurs at pH 2. In aqueous solutions, pH and concentration are influencing to form Cr(VI) ions. In acidic medium, the predominant form is $HCrO_4^-$ of Cr(VI). As pH increases, $HCrO_4^-$ converts to CrO_4^{2-} and $Cr_2O_7^{2-}$[8]. This trend would weaken the ability of Cr(VI) forming H-bond with oxygen groups. On the other hand, the increase of pH makes the dissociation degree of carboxyl groups increase. As the result, the repulsion between adsorbent and $HCrO_4$- enhances[9].

Due to increase in pH of the system, the degree of protonation of the surface reduces gradually and hence there is a decrease in the adsorption. Similar trend was observed at the removal of Cr (VI) from aqueous solution using carbon-microsilica composite adsorbent [9].

3.3. Effect of Interaction Time

The interaction of functional groups between the solution and the surface of adsorbent influences the adsorption of metal ion [10]. The effect of contact time on the uptake of Cr(VI) metal solution by papaya seeds was depicted in Figure 3:

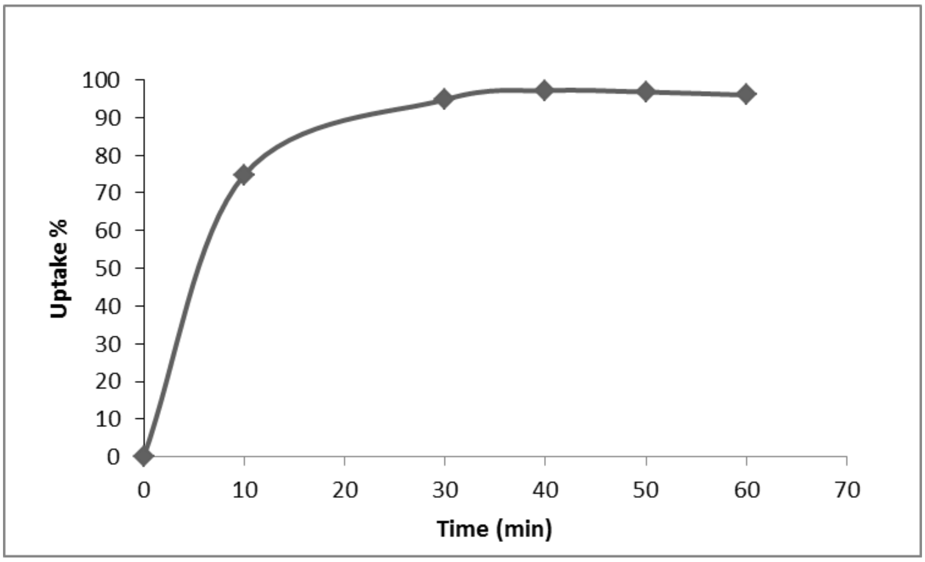

Figure 3. Effect of interaction time on uptake of Cr (VI) by papaya seeds.

Figure 3 shows that as rising of interaction time lead to the amount of absorbed Cr (VI) increases. However, significant increase occurs in 10-30 minute interaction. After 40 minutes of interaction the increase of adsorption is very small. It indicates that the interaction for 40 minutes has reached the equilibrium. Adsorption process with relatively short contact time indicates that the most probable adsorption is chemisorption [10].

3.4. Effect of Initial Concentration

Initial concentration of metal ions influence the metal removal efficiency through factors such as the availability of typical surface functional groups and the ability of surface functional groups to bind metal ions (especially at high concentrations) [11]. The effect of initial concentration on the uptake of Cr(VI) metal solution by papaya seeds is described in Figure 4.

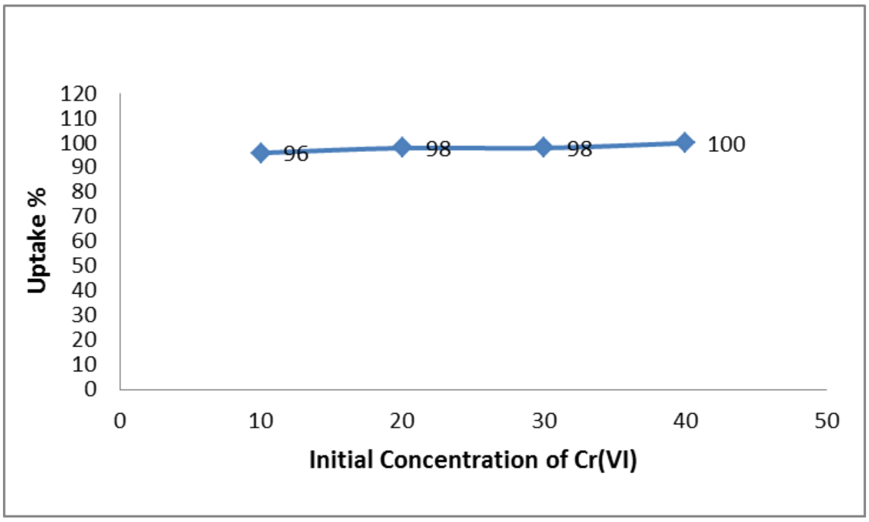

Figure 4. Effect of initial concentration on the uptake of Cr(VI) by papaya seeds.

Figure 4 shows that the uptake percentage of Cr(VI) increases in line with the increase of the concentration in the range of 10 to 40 mg/L. Maximum uptake occurs at initial concentration of Cr(VI) 20 to 40 mg/L. Initial metal concentration can be the strength factor to solve the mass transfer between the surface of adsorbent and the solution [12].

4. Conclusion

The adsorption of Cr (VI) from aqueous solution using papaya seeds as the low-cost adsorbent was investigated in batch process. FT IR analysis of papaya seeds shows that the main functional groups are carbonyl, hydroxyl, and carboxylic. The optimum pH for maximum uptake of Cr (VI) is 2.0 and the increase of contact time will enhance Cr(VI) uptake. The equilibrium was reached after 40 minutes interaction and the increase of initial chromium (VI) concentration would increase the sorbent uptake percentage. All these results indicated that papaya seeds is a potential sorbent for removing Cr (VI) from aqueous solutions.

Acknowledgments

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