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A STUDY ON ADSORPTION OF CADMIUM BY USING CHEMICALLY MODIFIED *SALVINIA*

(Kajian Penjerapan Kadmium Dengan Menggunakan *Salvinia* Yang Diubah Suai Secara Kimia)

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Abstract

Salvinia was collected at the Tasik Melati, Perlis, Malaysia and it was modified using citric acid to increase the performance in removing heavy metals from standard heavy metal solution. Fourier Transform Infrared (FTIR) and Field Emission Scanning Electron Microscope (FESEM) were used to characterize *Salvinia* before and after chemical modification. Cadmium (Cd^{2+}**)** removal studies were carried out by using modified *Salvinia* and the effect of various parameters such as contact time, initial heavy metal concentration and biosorbent dosage were studied. The adsorption study was investigated by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine the remaining of heavy metal concentration from the standard Cd^{2+} solution. From the study, FTIR analysis was shown the increasing of intensity on hydroxyl group after modification. A clear and smooth surface morphology of *Salvinia* after treatment were observed by using FESEM. The adsorption of cadmium was increased as contact time and biosorbent dosage increased. In contrast, the percent of adsorption was slightly decreased when initial concentration of Cd^{2+} increased.

Keywords: *Salvinia*, biosorbent, citric acid, cadmium and adsorption

Abstrak

Salvinia diambil di Tasik Melati, Perlis, Malaysia dan diubah suai menggunakan asid sitrik untuk meningkatkan kebolehan dalam membuang cadmium daripada larutan Cd^{2+}. Fourier Transform Infrared (FTIR) dan Field Emission Scanning Electron Microscope (FESEM) telah digunakan untuk mencirikan *Salvinia* sebelum dan selepas pengubahsuaian secara kimia. Kajian pengambilan Cd^{2+} telah dijalankan dengan menggunakan *Salvinia* yang telah diubah suai dan kesan terhadap pelbagai parameter seperti masa sentuhan, kepekatan awal Cd^{2+} dan dos dikaji. Kajian penjerapan telah disiasat dengan menggunakan Inductively Coupled Plasma Mass Spectrometry (ICP-MS) untuk menentukan pengambilan Cd^{2+}dari larutan Cd^{2+}. Analisis FTIR telah menunjukkan peningkatan intensiti pada kumpulan hidroksil selepas pengubahsuaian. Satu permukaan yang jelas dan licin pada *Salvinia* selepas rawatan telah diperhatikan dengan menggunakan FESEM. Penjerapan Cd^{2+} telah meningkat apabila masa sentuhan dan dos meningkat. Sebaliknya, peratus penjerapan telah sedikit menurun apabila kepekatan awal larutan Cd^{2+}meningkat.

Kata kunci: *Salvinia,* biosorben, asid sitrik, cadmium dan penjerapan

Introduction

Water pollution can be defined as the introduction of unwanted substances into fresh or ocean waters which changes the quality of water. The growth of the industries such as metallurgy, paper, electronic and food was caused increasing of water pollution level [1]. All these industry produced various types of pollutants such as heavy metals (Cr, Fe, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb, Zn and Al) and being drain away into the rivers as a final outlet.

Cadmium is an element naturally presence in the earth and also come from electroplating, smelting, alloy manufacturing, plastic, mining and refining industries [2]. It is high toxicity and easily accumulates in the environment [3]. The presence of excess cadmium was result in damaging the human health by accumulating in food chain as well as bringing up harmful effects to the flora and fauna [4]. Due to all these adverse effect, cadmium is necessary to be removed from water system especially drinking water.

Conventional technique such as chemical precipitation, adsorption, electrolysis, ion exchange and reversed osmosis are widely applied previously to remove high concentration of heavy metals [3, 5, 6]. However, these conventional techniques are comparatively high cost to remove heavy metals at low concentration [7]. Therefore, an alternative technique like biosorbent was recommended.

Biosorbent is a biomaterial used to attract metal ions from the polluted area such as water bodies. This process is based on the affinity between biosorbent and the sorbate. This alternative technique has low cost, environmental friendly, high efficiency to remove heavy metals, easy to handle and gaining interest due to relative abundance [8].

Previously, *Salvinia* was used as activated carbon to remove chromium (VI) [9]. In this study, *Salvinia* was used as potential biosorbent to remove Cd^{2+}. It was chemically modified with sodium chloride and citric acid in order to increase the performance of biosorbent to remove cadmium from solution. The adsorption process was investigated as function of biosorbent dosage, contact time and initial concentration of Cd^{2+} solution. Furthermore, characteristic of *Salvinia* before and after modification was studied using FTIR and FESEM analysis.

Materials and Methods

Preparation of biomaterial

Salvinia was collected in the Tasik Melati, Perlis and washed with distilled water to remove dirt. Then, it was oven dried for 24 hours at 60^{o}C. The dried *Salvinia* was grounded and sieved between 150-250 μm sizes. Then, it was stored in the desiccators for further analysis.

Chemically modification of biomaterial

Pre-treatment of biomaterial; The dried *Salvinia* was treating with 1 g/L of sodium chloride (NaCl) for 4 hours. Then, washed with deionized water until neutral (pH 6.9-7.1) and dried at 70^{o}C for 24 hours in a drying oven. The function of pretreatment with NaCl is to remove the pectin and waxy [10]. The modified *Salvinia* (mS) was stored in desiccators before undergo modification using citric acid.

Citric acid; 10g of mS was mixed in 100 mL of citric acid to activate the binding site of biomaterial for heavy metals bind [6, 8, 11]. After that, the modified *Salvinia*-citric acid labeled as (mS-CA) was placed in oven overnight at 60^{o}C. After completely dried, the excess citric acid was washed in buncher funnel by using distilled water until citric acid excess is completely removed. Then, mS-CA was dried overnight at 60^{o}C again. The final product (biosorbent) was stored in desiccators for the further used. In this study, citric acid acts as chelating agent which is encourages cadmium to bind on the biomaterial. Thus, the adsorption capacity of the biomaterial is expected to be increased.

Characterization of biosorbent

FTIR was used to verify the chemistry bond and the vibration frequency changes of the functional groups in the biosorbents. FESEM used to observe the morphology of the *Salvinia* before and after modification.

Cd^{2+} standard solution

Cd^{2+} standard solutions were prepared at desired concentration. The pH range of the solution is in between 3-6 and it was adjusted by adding sodium hydroxide (NaOH) or hydrochloric acid (HCl).

Adsorption study

Cd^{2+} solution was mixed with biosorbent and the adsorption capacity of Cd^{2+} was studied. The variables was used in this study are contact time, initial heavy metal concentration and biosorbent dosage. The concentration of Cd^{2+} before and after adsorption was measured by using ICP-MS. The uptake capacity of Cd^{2+} was calculated by using equation (1) and (2) below:

$$\text{Uptake capacity} = Ci - Cf \qquad (1)$$

$$\text{Adsorption (\%)} = [(Ci - Cf)/Ci] \times 100 \qquad (2)$$

where Ci (mg/L) and Cf (mg/L) are the initial and final Cd^{2+} concentrations.

Results and Discussion

Characterization of biosorbent

Fourier Transform Infrared (FTIR) analysis

The FTIR spectra of the *Salvinia* samples are shown in the Figure 1 and the characteristic bands of functional groups were obtained. FTIR spectra of raw material, mS and mS-CA showed the presence of characteristic adsorption bands of hydroxyl groups (-OH), amines ($-NH_2$), carboxyl groups (COOH), carbonyl groups (C=O) and alkyl groups (C-H) [12].

From the Figure 1, hydroxyl and amine groups were appeared for all sample of *Salvinia*. mS-CA showed a broad peak and high intensity of hydroxyl and amine group at 3355.42 cm^{-1} compared to raw material and mS. It is due to the reaction of citric acid on the biomaterial [6]. Citric acid treatment was encouraged more –OH group presence and the ability to metal ions to attach is high [13]. The $-CH_2$ peak are appeared in the spectrum at 2919.29-2915 cm^{-1} for the all samples and mS-CA was showed high intensity of absorption compared to others. In contrast, the figure 1 showed mS have a strong stretching of carboxyl group and carbonyl group with 1617.35 cm^{-1} and 1041.63 cm^{-1}. The functional groups suggested here were agreed with those reported in other studies on infrared spectra of biomaterial [6, 11, 12, 14].

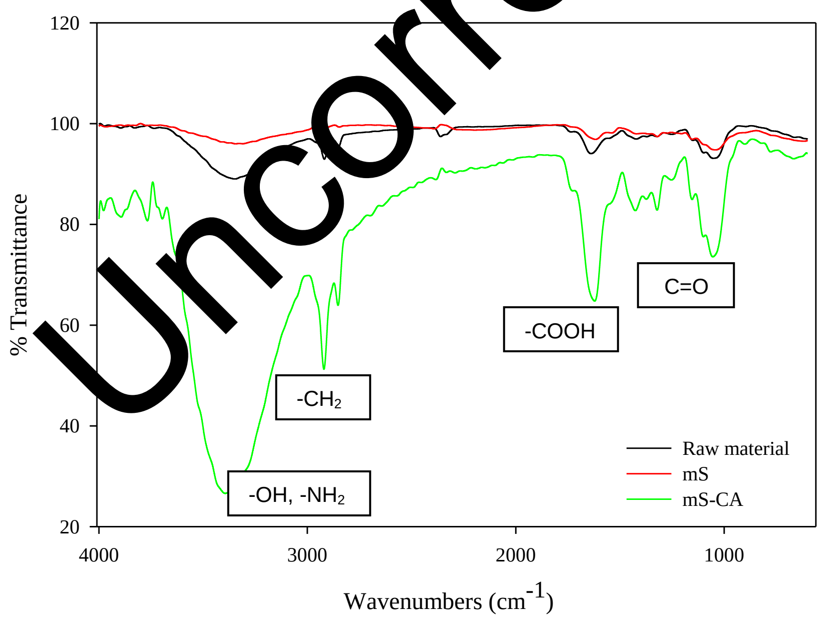

Figure 1: FTIR analysis of raw material, mS and mS-CA

Field Emission Scanning Electron Microscope (FESEM)

In this study, FESEM is used to observe the changes in morphological of *Salvinia* before and after modification with citric acid. From the FESEM, it can be seen that there are the changes of *Salvinia* before and after chemical treatment. Figure 2 (a) showed that the surface of *Salvinia* look alike covered by lignin. After pretreatment with NaOH, the surface of *Salvinia* becomes smooth as shown as in Figure 2 (b). Figure 2 (c) was showed that the changes in morphological after citric treatment. The surface of *Salvinia* becomes clear and the pores structure could be seen in the FESEM at 5000x magnification.

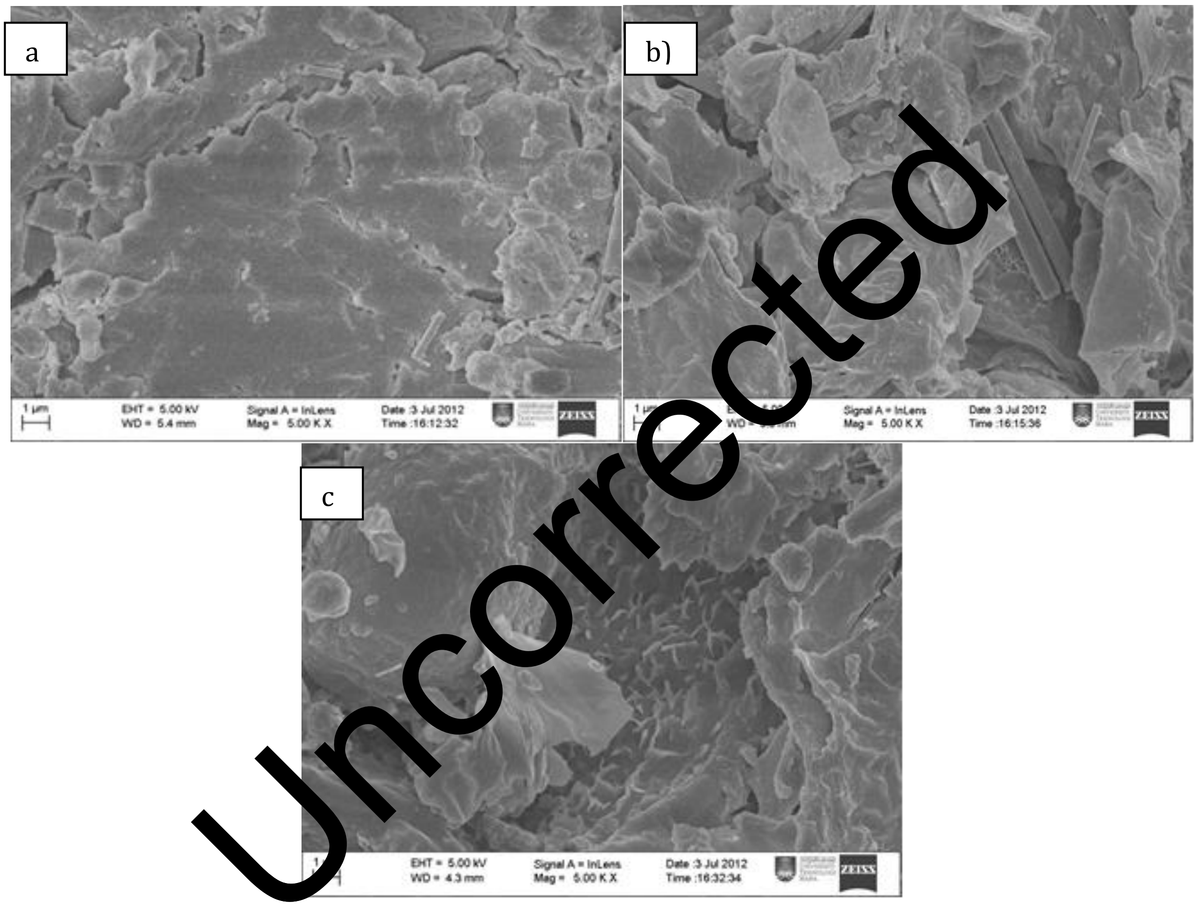

Figure 2: Field Emission Scanning Electron Microscopy of *Salvinia* (a) raw material (b) mS (c) mS-CA

Absorption towards biosorbent

Contact time

The study on contact time was performed in order to determine the maximum adsorption of Cd^{2+} by biosorbent and Figure 3 was present the percent of adsorption against contact time. From the graph, it can be seen that the adsorption rate of Cd^{2+} increase with the time for mS and mS-CA. The graph also shown the adsorption of mS-CA is greater than mS. From 30 minutes to 90 minutes of contact time, adsorption of mS-CA gradually increased and it is maintain for 30 minutes. After 120 minutes contact time, the adsorption of Cd^{2+} increased until 150 minutes and after 150 to 180 minutes there is no adsorption of Cd^{2+} recorded. Besides that, mS also showed increasing in removing Cd^{2+} in heavy metal solution. After 150 minutes contact time of adsorbent, the removing of Cd^{2+} reached equilibrium until contact time end. mS-CA showed higher adsorption capacity due to the adsorption site are open to Cd^{2+} interact [6]. Here, citric acid was played their function to activate the site to metal ion to attach on the adsorbent [6, 13].

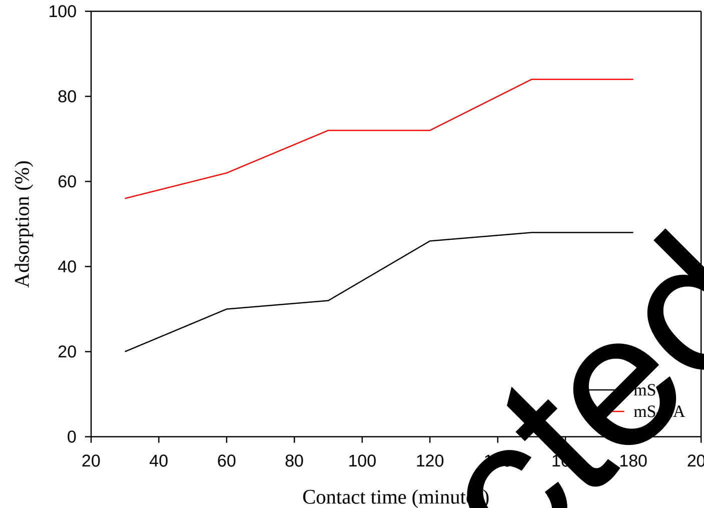

Figure 3: Effect of contacting time on Cd^{2+} adsorption (1.0g adsorbent and 10mL of 0.5 ppb heavy metal solution)

Biosorbent dosage

Biosorbent dosage is also an important factor for adsorption of metal ion. The effect of biosorbent dosage of Cd^{2+} was studied by using the different dosage of adsorbent between 0.1g to 1.0g. Figure 4 was showed the adsorption of Cd^{2+} increased as dosage increased and the adsorption of Cd^{2+} by mS-CA is higher compared to mS. The removal of Cd^{2+} from the solution gradually increased when more treated adsorbent was introduced. Figure 4 was showed 1g of mS-CA was removed 0.47ppb (about 98%) of 0.5ppb heavy metal solution. This is due to the greater availability of adsorbent to bind the metal ions and raise the efficiency of metal ions removal [15]. In contrast, the adsorption capacity of mS decreased when 1g of adsorbent used and it was observed in this study. According to Karthikeyan *et. al.*(2007) [16], a partial aggregation of biomaterial at higher adsorbent dose would lead to decrease of biosorption efficiency due to the reduction of effective surface area for biosorption process [16].

Initial concentration of heavy metal

The initial concentration of Cd^{2+} was varied from 0.5 ppb to 10.0 ppb to evaluate the effect on the adsorption efficiency. From the Figure 5 above, it was observed that the adsorption capacity of Cd^{2+} by mS-CA is greater than mS. However, the percent removal of Cd^{2+} slightly decreased with the initial concentration of solution as shown as in Figure 5. This is because at low heavy metal concentration, the ratio of surface active sites to the total metal ions in the solution is high. Hence, all Cd^{2+} may interact with the mS-CA and it was removed from the heavy metal solution [17]. In contrast, at higher concentration of cadmium ions was provided more cadmium ions for attached on the biosorbent. As a result, the active sites are not sufficient and the saturation in adsorption process was happened. Therefore, it is resulting reduction in percentage removal.

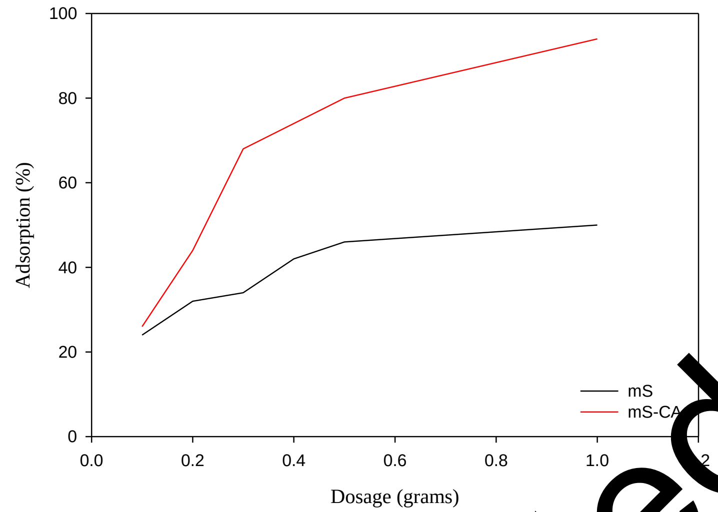

Figure 4: Effect of biosorbent dosage on Cd^{2+} adsorption (180 minutes immersion time and 10mL of 0.5 ppb heavy metal solution)

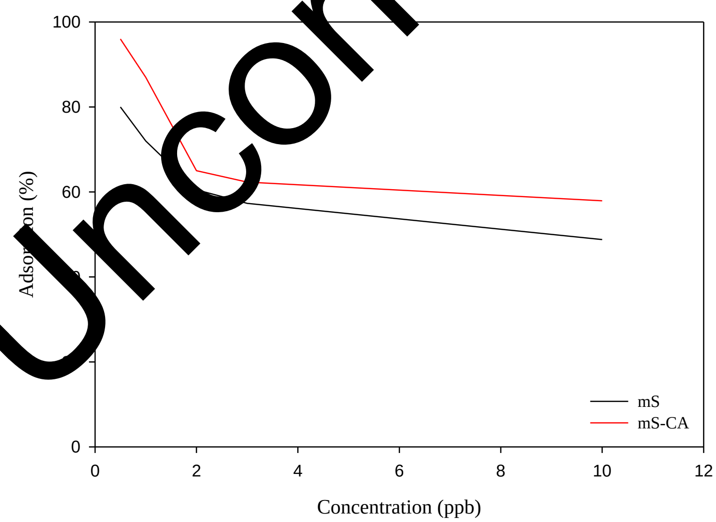

Figure 5: Effect of initial concentration of heavy metal solution on Cd^{2+} adsorption (180 minutes immersion time and 1.0g biosorbent dosage.

Conclusion

As a conclusion, chemical modification of *Salvinia* by citric acid was enhanced the adsorption of Cd^{2+} ions. The uptake capacity of Cd^{2+} was increased by raising the contact time and biosorbent dosage. However, the adsorption of Cd^{2+} was decreased after varying the initial concentration of heavy metal solution.

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