Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(9S):1-8

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Biosorption of cadmium (II) ions from aqueous solution by cassava (*Manihot utilissima*) leaves

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ABSTRACT

In this study, the ability of cassava (Manihot utilissima) leaves for Cd (II) removal was investigated. The effects of pH, biosorbent dosage, contact time, initial Cd (II) concentrations were also studied. The result showed that the adsorption process was strongly dependent on initial concentration and biosorbent dosage. The optimum pH value was 6, contact time 90 minutes, initial concentration 500 mg/L and biosorbent dosage was 0.1 g. The biosorption data were fitted to Langmuir isotherm with R^2 = 0.9945. The spectroscopy analyses showed that the functional groups of –OH, C=O and –C=C- might be involved in adsorption. The Cd (II) ion concentrations were determined by the use of Atomic Absorption Spectroscopy (AAS). The analysis of biosorbent surface before and after adsorption was confirmed by the use of Scanning Electron Microscope (SEM). It was concluded that Manihot utilissima leaves could potentially used as a biosorbent for Cd(II) in aqueous solution

Keywords: Biosorption, *Manihot utilissima* leaves, isotherm biosorption, ion Cd (II)

INTRODUCTION

The increasing of development and industrialization has placed stress on the natural resources, resulted in the pollution of environment through discharge of wastes from industrial units. This effluent interferes with intended use of water when level of pollutants in water is exceeding the allowable limits [1]. Most of the industrial waste contains heavy metals with certain concentration. So, the presence of heavy metals in water and wastewater in increasing due to the industrial development disposal in the sewerage or in the water bodies [2]. Heavy metals are a sanitary and ecological threat, highly toxic, have carcinogenic properties, and recalcitrant even at very low concentrations and they can pollute drinking water resources [3].

Unlike organic pollutants, biodegradation of heavy metals is not possible because metals as elements cannot be mineralized to non toxic compound such as H_2O and CO2. Heavy metals can be extremely toxic as they damage nerves, the bones, liver and even block the functional groups of vital enzymes [4].

Cadmium (Cd) is known for high toxicity properties to all biota and high mobility in the terrestrial environment. Cadmium is a wide spread heavy metals and released in environment by power stations, heating systems, metal industries, incinerations, cement factories and as a byproduct of phosphate fertilizers. Cadmium has a great solubility in soil and water, and it is known that the level of cadmium in the soil appears to be increasing over the years [5]. There are many efforts have been made to relieve cadmium contamination such as on exchange, chemical precipitation and membrane technologies, all showing significant disadvantage and low efficiency. The biosorption method is a promising technology for remediation of contaminated wastewater metal solutions [6]. The advantages of biosorption is an efficient, potential and cost effective way of removing toxic and heavy metals from industrial effluents with comparing the other alternative methods [7].

In recent year numerous low cost natural materials have been proposed as potential adsorbents. These include corn stalkes [8], orange rind [9], neem leaves powder [10], microalgae [11], macrofungus [12] and rice husk [13]. In this research adsorbent prepared form cassava (*Manihot utilissima*) leaves was used for treatment of cadmium in aqueous solution. Effect of operating conditions like pH, initial concentration, biosorbent dosage, and contact time were investigated. The equilibrium adsorption were fitted with Freundilich and Langmuir isotherm models, Scanning Electron Microscope (SEM) and Fourier Transform Infra Red (FTIR) spectroscopy were used to analyzed the structural of biosorbent and the functional groups which involved in adsorption process.

EXPERIMENTAL SECTION

Chemical and Apparatus

The reagents used in the experiments are $(CH_3COO)_2Cd.2H_2O$, NaOH, HNO_3, CH_3COONa, CH_3COOH, NH_4OH, NH_4Cl, H_3PO_4, KH_2PO_4 and K_2HPO_4. All reagents used are analytical grade and obtained from E. Merck (Darmstad, Germany). The apparatus used are analytical balance (Kern & Sohn GmbH), Rotary shaker (Edmund Buhler 7400 tubingen), pH meter (Lovibond Senso Direct), Atomic Absorption Spectroscopy (AAS Variant Spectra AA 240 spectrometer), Fourier Transform Infra Red (Thermo Scientific Nicolet IS10 using KBr), Scanning Electron Microscope (Hitachi Model S-3400N).

Samples Preparation and Biosorption Studies

Cassava (*Manihot utilissima*) leaves were collected from home garden in Medan, washed, wind dried then milled by crusher and 30 g of powder was soaked into 120 mL HNO_3 0.01 M for 2 hours. The leaves powder was rinsed by distilled water, wind dried and biosorbent is ready to be used. The effect of pH, initial concentration of metal ions, dosage of biosorbent and contact time were investigated. Characterization was carried out by using FTIR and SEM.

RESULTS AND DISCUSSION

Effect of pH on Biosorption of Cd (II) ion

Several studies have shown that in metal biosorption by biosorbent, pH is an important factor, and there is an observed relationship between biosorption of metal and the magnitude of negative charge on the surface of biosorbent which is related to the surface functional groups [14]. pH affects the solubility of the metal ions, concentration of the counter ions of the functional groups of the adsorbent and ionization degree of the adsorbate [15]. The effect of pH on biosorption of Cd (II) ion by cassava (*Manihot utilissima*) leaves powder shown in Fig.1

From Fig.1, the pH optimum adsorption capacity of cassava (*Manihot utilisima*) leaves powder was achieved at pH 6 with adsorption capacity 1.1372 mg/g. The minimum biosorption at low pH is due to the fact that high concentration and high mobility of H^+ ions, the hydrogens ions are preferentially adsorbed rather than metal ions [16]. The similar result was reported by Serencam et al [17] with optimum pH for biosorption of Cd (II) using *Morus alba* L. at pH 6. Awwad and Salem [18] reported that the optimum pH for biosorption of Cd (II) using loquat (*Eriobotrya japonica*) leaves was achieved at pH 6.

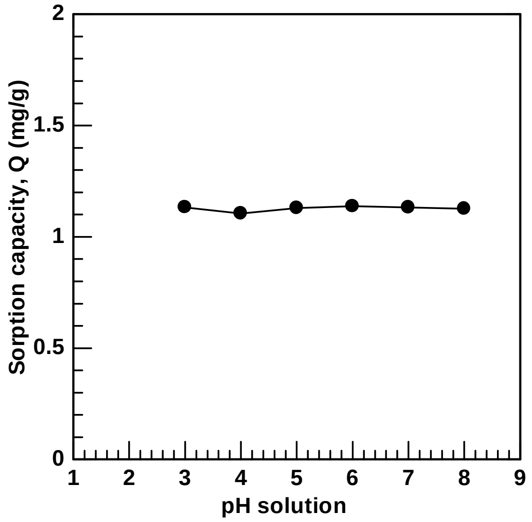


Figure 1. Effect of pH on Cd biosorption by cassava (*Manihot utilissima*) leaves powder; biosorbent dose 0.25 g; contact time 15 min; stirrer speed 100 rpm

Effect of initial concentration on biosorption of Cd (II) ion

Effect of initial concentration of Cd (II) from 30 mg/L – 120 mg/L on the removal of cadmium (II) ions from aqueous solutions at adsorbent dose 0.25 g and optimum pH, with contact time 15 minutes and stirrer speed 100 rpm was studied. The result was shown in Fig.2

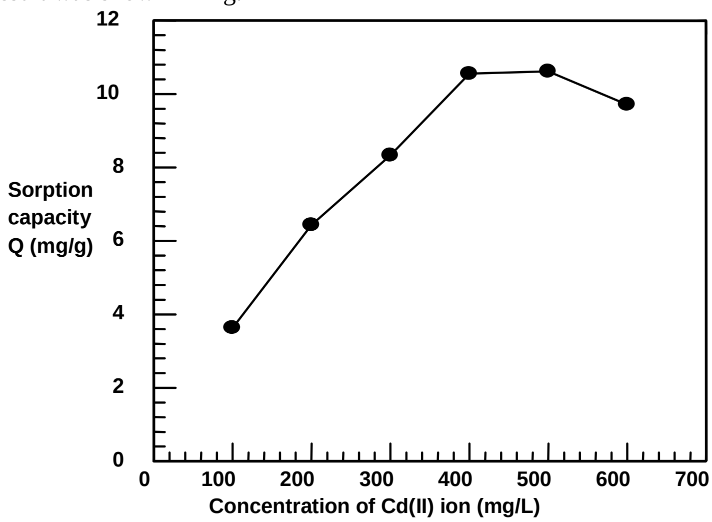


Figure 2. Effect of initial concentration on Cd (II) adsorption; pH 6;stirrer speed 100 rpm; contact time 15 min, biosorbent dose 0,25 g

Fig.2 shows the maximum sorption capacity (Q) of cassava (*Manihot utilissima*) leaves was 10.616 mg/g, achieved at concentration of Cd (II) at 500 mg/L. Fig.2 shows that the metal uptake increase and as the concentration of Cd (II) increase to 500 mg/L then decreased. The decreased of sorption capacity at higher concentration of Cd (II) may be attributed by the lack of sufficient surface area to accommodate much more metal available in the solution [18].

Effect of biosorbent dosage on biosorption of Cd (II)

The effect of adsorbent concentration on the removal at equilibrium conditions was studied. The result was shown in Fig.3.

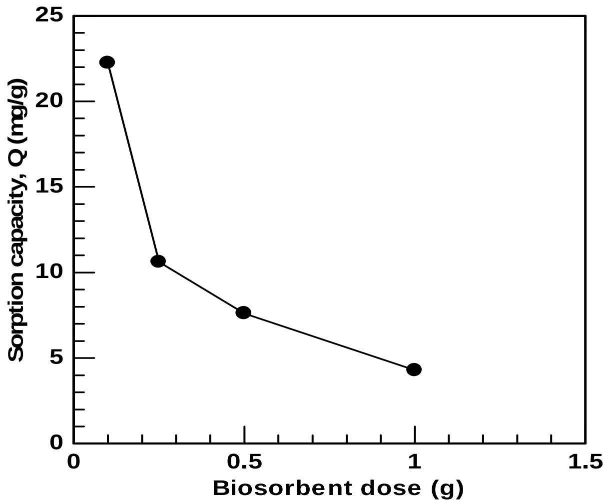


Figure 3. Effect of initial concentration on Cd (II) adsorption; pH 6; stirrer speed 100 rpm; contact time 15 min; initial concentration of Cd (II) 500 mg/L

Fig 3 shows that 0.1 g of cassava *(Manihot utilissima*) leaves shown the maximum adsorption capacity for Cd (II) ions with sorption capacity 22.24 mg/g. The sorption capacity decreased as the biosorbent dose increase. At low biomass dosage, the amount of ions adsorbed per unit adsorbent weight is high. The adsorption capacity is reduced when the biosorbent dosage increases as a result of lower adsorbate to binding site ratio where the ions are distributed onto larger amount of biomass binding sites [19]. Similar report was given in various studies [3,9,20]

Effect of contact time on biosorption of Cd (II) ions

The effect of contact time was investigated with ranging time 15-120 minutes. The result was shown in Fig.4.

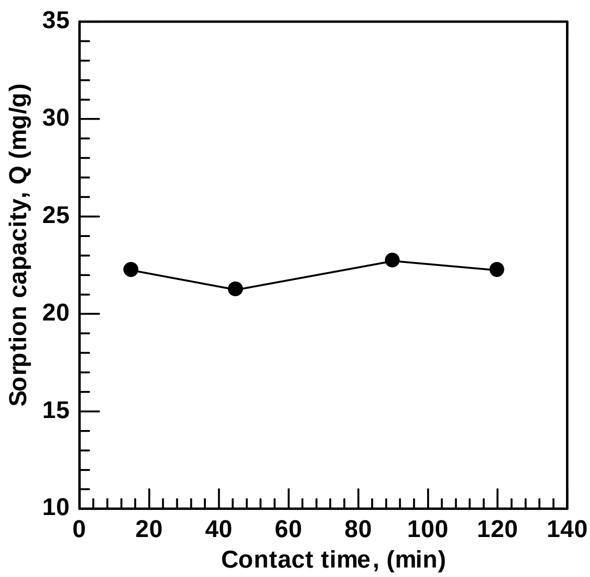


Figure 4. Effect of contact time on Cd (II) adsorption, pH 6; stirrer speed 100 rpm; initial concentration 500 mg/L, biosorbent dose 0.1 g

As shown in Fig.4, the sorption capacity of cassava (*Manihot utilissima*) leaves was gradually increased and reached the optimum at 90 min with sorption capacity 22.72 mg/g. From Fig.3 the plot reveals that the sorption capacity was higher at the beginning. This is probably due to a larger surface area of the biosorbent available at the beginning for the adsorption of cadmium [13]. The metal ions uptake by the biosorbent surface will be rapid initially, and then slowing down as the competition for decreasing availability of active sites intensifies by the metal ions remaining in solution [21].

Adsorption Isotherm

Langmuir and Freundlich models were used to determine the adsorption equilibrium between biosorbent and metal ions. The Langmuir model assumes that a monomolecular layer is formed when biosorption take place without interaction between adsorbed molecules and Freundlich isotherm is based on a heteregoneous adsorption due to diversity of adsorption sites, or diverse nature of the metal ions [22]. The Langmuir equation is represented by : Ceq/ Qeq = 1/b Qmax + C_{eq} /Q_{max} ; where Qmax (mg/g) is the maximum amount of metal ion per weight of biosorbent to form a complete monolayer on the surface bound at high Ceq, and b (1/mg) is the Langmuir constant. The Qmax and b can be determined from the linear plot of Ceq/Qeq versus Ceq [12].

The Freundlich isotherm linear equation is expressed by the following equation:

$$\log qe = \mathrm{log k} + \frac{1}{n}.\log Ce$$

Where k is related to adsorption capacity and n is related to intensity of adsorption. The linear plots of two isotherms were presented in Fig.5 and Fig.6.

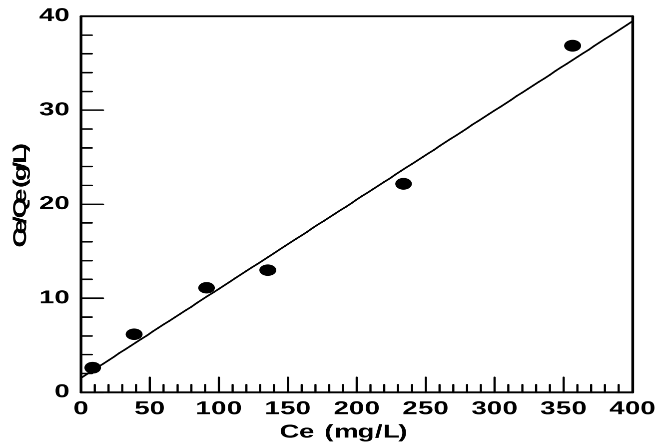


Figure 5. Langmuir isotherm of cassava (*Manihot utilissima*) leaves powder

From the graphics, the biosorption of Cd (II) fit to Langmuir isotherm with value of determination coefficient R2=0.9945. This result shows that the biosorption of Cd (II) with cassava (*Manihot utilissima*) leaves powder through chemisorptions process.

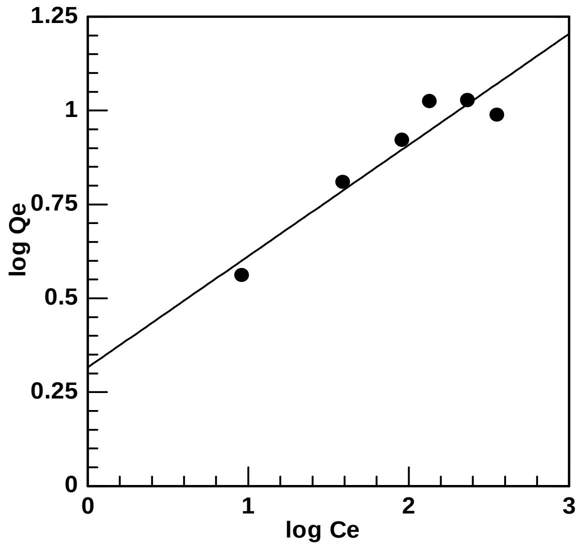


Figure 6. Freundlich isotherm of cassava (*Manihot utilissima*) leaves powder

FTIR Analysis

FTIR analysis allows identification of functional groups of organic compound which might involved in biosorption process. The FTIR spectra of cassava (*Manihot utilissima*) leaves powder before and after biosorption of Cd (II) ions was shown in Fig.7

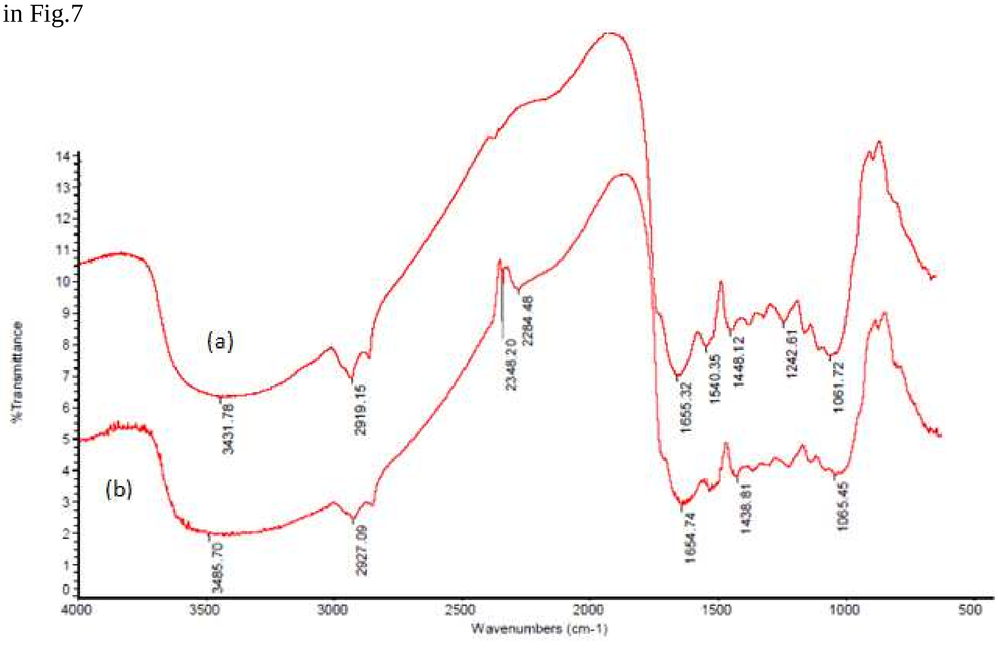
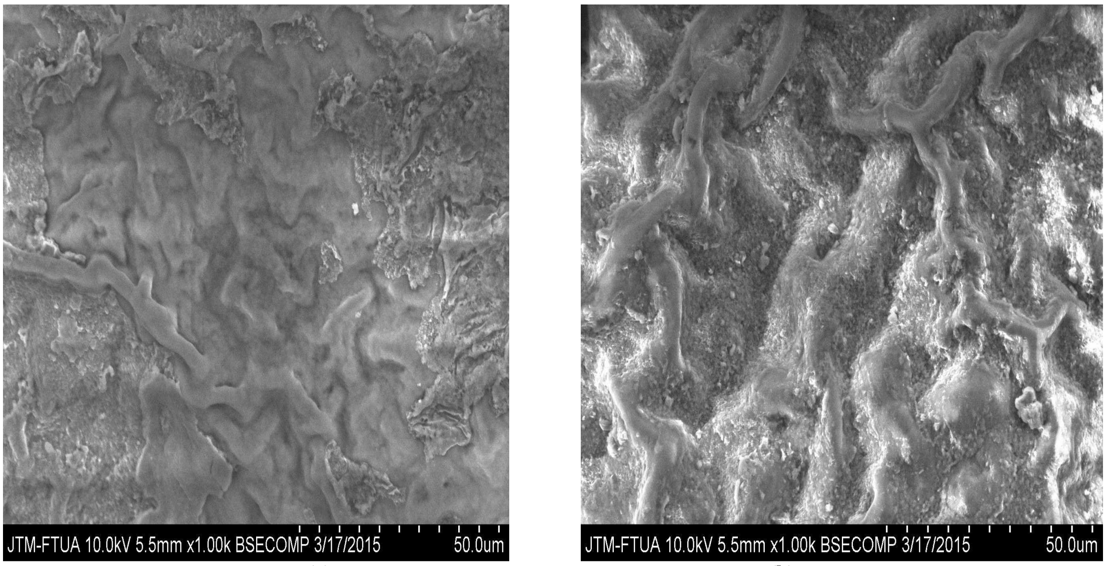


Figure 7. FTIR spectra of cassava (*Manihot utilissima*) leaves; (a) before Cd (II) uptake; (b) after Cd (II) uptake

As shown in Fig.7, the peak at wave number 3485.70 cm^{-1} indicates the presence of O-H stretch. This peak shifted to 3431.78 cm^{-1} after adsorption. This is indicated the formation of a bond between Cd (II) ions and –OH. The peak at 2937.09 cm^{-1} indicates the presence of C-H stretch. This peak shifted to 2919.15 cm^{-1}. The peak at 1654.74 cm^{-1} indicating the presence of –C=C- stretch, and peak at wave number 1064.45 cm^{-1} indicating the presence –C-N.

SEM analysis

Fig.8 shows the SEM image of the cassava (*Manihot utilissima*) leaves powder before and after Cd (II) biosorption. The SEM image analysis was conducted at 1000x magnification. As seen on Fig.8 the surface of cassava (*Manihot utilissima*) leaves powder before Cd (II) uptake seen smooth and have homogenous surface. Generally the surface become rough and irregularly shaped particles dispersed in matrix, predicts feasibility for metal sorption.



(a) **(b)**

Figure 8. SEM image of cassava (*Manihot utilissima*) leaves powder; (a) before adsorption of Cd (II) ions; (b) after adsorption of Cd (II) ions

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