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Research Article

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Removal of Mn (II) ions from aqueous solution by adsorption using *Terminalia catappa* fruit powder

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ABSTRACT

The removal of Mn (II) ions by adsorption using biomass derived from Terminalia catappa fruit powder was studied in a batch system. The influence factor such as pH, initial concentrations, biosorbent dosage and contact time were also studied. Result showed that optimum pH for adsorption was 6, optimum contact time was 15 minutes and initial concentration of Mn (II) was 6900 mg/L. The effect of biosorbent dosage for Mn (II) ions removal and adsorption capacity also investigated. The optimum amount of T. catappa fruit powder biomass to remove Mn (II) ions was 1 g, and able to remove Mn (II) ions up to 75.22%. The biosorption data were fitted to Langmuir isotherm with R^2 *= 0.9810. Characterization of T. catappa fruit powder biomass was analyzed using Fourier Transform Infra Red (FT-IR) spectroscopy and active functional group that might be involved in adsorption were –NH stretching and carbonyl groups. The surface analysis before and after adsorption was analyzed using Scanning Electron Microscope (SEM). This research indicated that the adsorbent has a great potential to remove Mn (II) from aqeous media contributing to an eco friendly technology for efficient bioremediation*

Keywords: Biosorption, Terminalia catappa, adsorbent, Mn (II) ion, batch system

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INTRODUCTION

The inorganic pollutants such as heavy metal ions that present in the ecosystem may cause a major environmental problem. Not only contaminate the earth's water such as seas, lakes, ponds and reservoirs, but can also contaminate the underground water [1]. The heavy metal contamination may pose a significant danger to human health due to their non biodegradability and persistence, so it can accumulate in the environment element such as food chain, and may pose a significant danger for human health [2].

Manganese is the second most abundant metal in nature and has variety of applications in ceramics, dry battery cells, and many alloys. They also an essential micronutrients for organisms and plants. But they become toxic if they exist at higher levels [3]. Exposure to manganese could causes neurotoxicity [4], low hemoglobin levels [5] and accumulation in gastrointestinal [6]. However, extensive research has been conducted on the discharge of metal ion that contained in industrial effluent due to the presence and accumulation of toxic effect on living species [7].

Conventional processes such for metal ions removal include chemical precipitation, ion exchange, reverse osmosis *etc*, have several disadvantages such as required high processing cost and could generate secondary toxic waste products [8] and also ineffective especially when the heavy metals ions are present in high concentration [9]. Biosorption is a fast and reversible reaction of the heavy metals with biomass [9]. Several agricultural waste materials have been studied and developed for the effective removal of heavy metals like coffee husk [10], rice straw [11], banana peel [12], apple wastes [13], cocoa shell [14] and grape stalks [15].

Tropical almond (*Terminalia catappa*) is a large, spreading tree distributed throughout the tropics in coastal environment. The dried leaves usually used for fish pathogens treatment, as an alternative antibiotic [16]. The leaves have antioxidant as well as anticlastogenic properties, and various extract of leaves and bark of *T. catappa* have been reported to be anti cancer, anti HIV transcriptase [17] and hepatoprotective [18].

In this study, the potential of *T. catappa* fruit as biosorbents for the removal of Mn(II) from aqueous solution was investigated. The factor of pH solution, contact time, biosorbent dosage, initial metal concentration was studied. The equilibrium adsorption data were fitted with Freundlich and Langmuir isotherm models. Scanning Electron Microscope (SEM) and Fourier Transform Infra Red (FTIR) spectrometer were used to analyzed the surfaced of biosorbent and functional groups which involved in adsorption.

EXPERIMENTAL SECTION

Chemical and Apparatus

The biosorption experiments were conducted by using stock standar solution (1000 mg/L) of $MnCl_2$, HNO_3 65%, CH_3COOH 0,1 M and CH3COONa 0,1 M, NH_4Cl 0,1 M, NH_4OH 0,1 M and NaOH solution. All reagents used are analytical grade and obtained from E. Marck (Darmstad, Germany). The apparatus used are siever 180 μm, 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 (Unican Mattson Mod 700 using KBr pellets), grinder (Christy Hunt), Scanning Electron Microscope (SEM SU 3500).

Samples Preparation and Biosorption Studies

T. catappa were collected from home garden in Padang, then washed, and wind dried on a filter paper. *T. catappa* fruit that have been dried then crushed using blender, and then sieved with siever with size 3.2 μm. About 20 gram of samples was soaked with 80 ml HNO_3 for 2 hours. Then the fruit powder was rinsed by distilled water and dried. The effect of pH, initial concentration of metal ions, biosorbent dosage and contact time were investigated. The characterization of biosorbent surface and functional groups was conducted using SEM and FTIR.

RESULTS AND DISCUSSION

Effect of pH

In the biosorption, pH of solution has been found to be the most important factor. The pH solution affects the speciation of metal ions and also the charge on the sorption sites [7]. pH is also affects the solubility of metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction [19]. The result was shown in Fig.1.

The optimum pH for adsorption capacity of *T. catappa* was achieved at pH 6 with adsorption capacity 0,9334 mg/g. The same result was reported by Nazaruddin *et al* in 2014 [7] where the optimum condition of *Nypa fruticans* Merr shell was on pH 6 for adosorption of Cu(II), Pb(II), and Zn(II). The similar result was also reported by Li *et al* (2011) where the optimum pH for biosorption using red alga (*Palmaria palmata*) was in the range 5-6 [20].

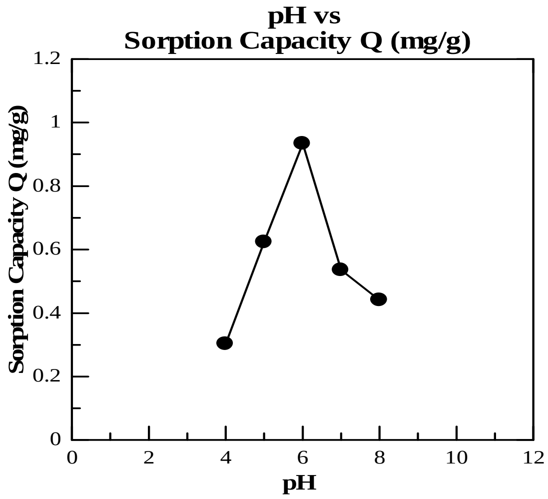


Figure 1. Effect of pH on adsorption of Mn (II) using *T. catappa* initial concentration 30 mg/L; stirrer speed 100 rpm; contact time 15 min; biosorbent dose *T. catappa* 0.25g

Effect of initial concentration

The effect of initial concentration of Mn (II) on adsorption capacity using *T. catappa* flesh powder was shown in Fig.2. It can be observed in constant pH, the increase of initial concentration of Mn (II), increased the sorption of Mn (II) by biosorbent, the decreased. The optimum of initial concentration of Mn (II) adsorption was found at 6900 mg/L. Increasing the initial metal concentration results in an increase in the biosorption capacity because it provides a driving force to overcome mass transfer resistance between the biosorbent and biosorption medium [21]. The adsorption capacity decreased after concentration 6900 mg/L. This may be due to the lack of available active sites required for the high concentration of Mn(II) [22].

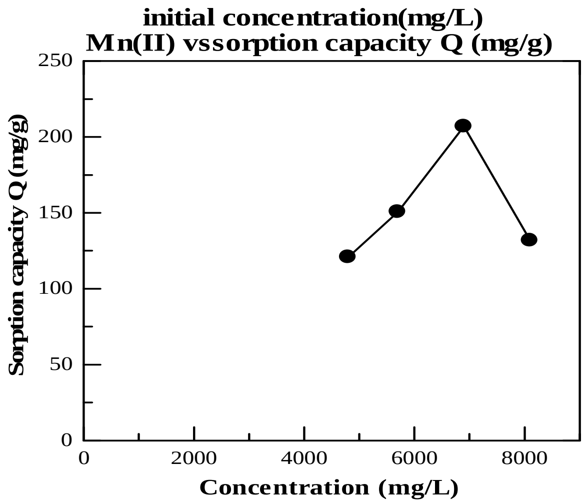


Figure 2. Effect of initial concentration on adsorption of Mn(II) with pH 6; 0.25 g biosorbent dose 0.25 g; contact time 15 min with stirrer speed 100

Effect of biosorbent dose

The effect of biosorbent dose of *T. catappa* flesh powder on adsorption capacity was shown in Fig.3

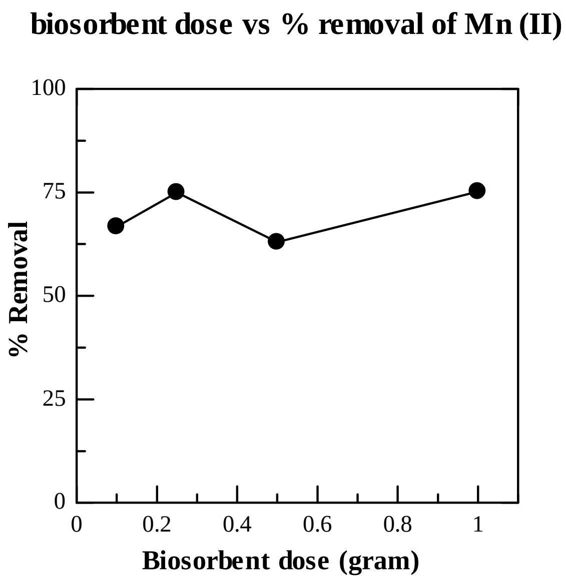


Figure 3. Effect of biosorbent dose of *T. catappa* on removal percentage at contact time 15 min; stirrer speed 100 rpm; pH 6

The study of the effect of biosorbent dose in necessary and very useful in order to find out the optimum amount of *T. catappa* flesh powder required to remove Mn (II) ions. As revealed in Fig.3 the optimum removal percentage was 75.22% and reach at biosorbent dose 1 g. The effect of biosorbent dose on sorption capacity of *T. catappa* was shown in Fig.4. The optimum sorption capacity was 460.18 mg/g with biosorbent dose 0.1 g. For a fixed metal initial concentration, increasing the adsorbent dose provides greater surface area and availability of more active sites, thus leading to the enhancement of metal ion uptake [23].

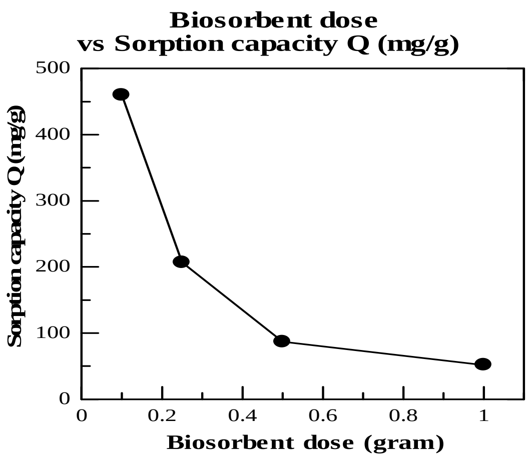


Figure 4. Effect of biosorbent dose against sorption capacity

Fourier Transform Infra Red Spectroscopy (FTIR)

The FTIR spectra of *T. catappa* flesh powder before and after adsorption was shown in Fig. 5**.**

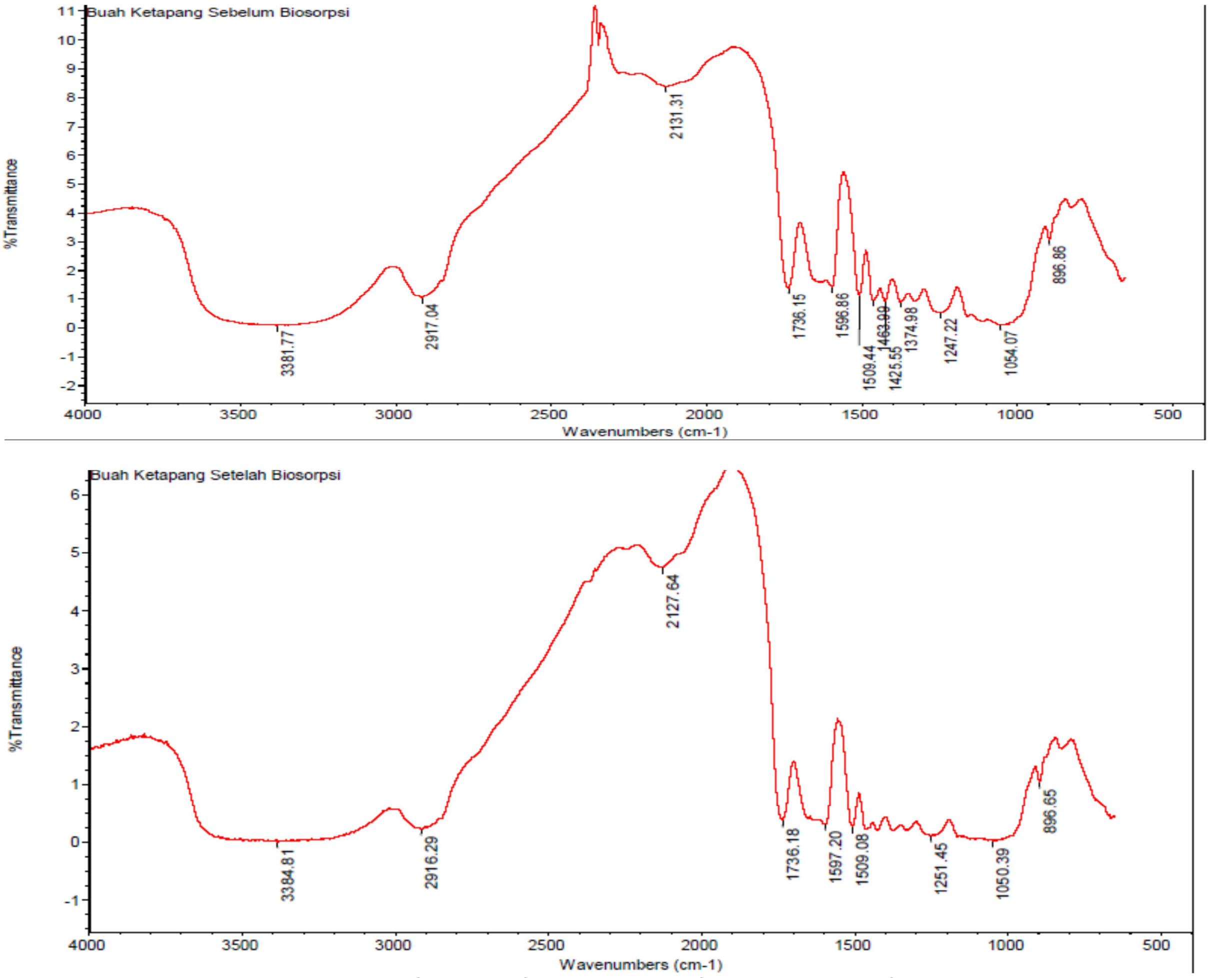
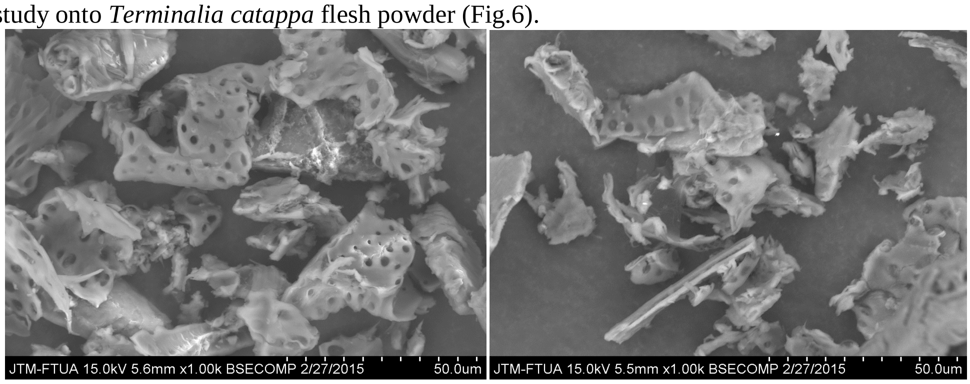


Figure 5. FTIR spectra of *T. catappa* flesh powder; (a) before adsorption; (b) after adsorption

The sorption pattern of metal ions onto plant biomass is attributable to the active functional groups and chemical bonds between them [24]. FTIR analysis is very important to estimate functional groups of biosorbent that might involved in the interaction with metal ions. FTIR analysis in range of 500 cm^{-1} to 4000 cm^{-1} shows the presence of N-H stretch at 3381 cm^{-1}, C=O stretch at 1736.18 and N-H bend at 1597.20 cm^{-1}. The N-H and carbonyl groups are considered as important sorption sites.

SEM analysis

In order to investigate the textural structure of the biosorbent, SEM micrograph was taken before and after adsorption study onto *Terminalia catappa* flesh powder (Fig.6).



(a) **(b)**

SEM micrograph of unloaded biosorbent indicates smooth uniform microporous structure of surface which indicate that *T. catappa* have some good characteristic to be employed as natural adsorbent for metal ions uptake. The structure becomes rough after biosorption indicating the modification of the adsorbent.

Adsorption Isotherm Studies

The equilibrium relationship between adsorbent and adsorbate are best explained by sorption isotherm the biosorption isotherms describe the relationship between the mass of the adsorbed component per biosorbent mass and the concentration of this component in the solution [1]. Langmuir isotherm model is expressed as [25]:

$$\frac{c}{(q)} = \frac{1}{qm.b} + \frac{1}{qm}\ C$$

Where q = mass of solutes adsorbed per mass of adsorbent, c = concentration of adsorbate in solution in equilibrium with the adsorbate, qm and b are constant which are related to sorption capacity and energy of sorbent, obtained by plotting c/q against c. The slope 1/qm while the intercept is 1/qm.b. The Freundlich linear form is given by the following equation [16]:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

Where Kf is Freundlich constant and 1/n is an empirical parameter related to the adsorption intensity. Fig.7 and Fig.8 shows the isotherm model of Langmuir and Freundlich respectively.

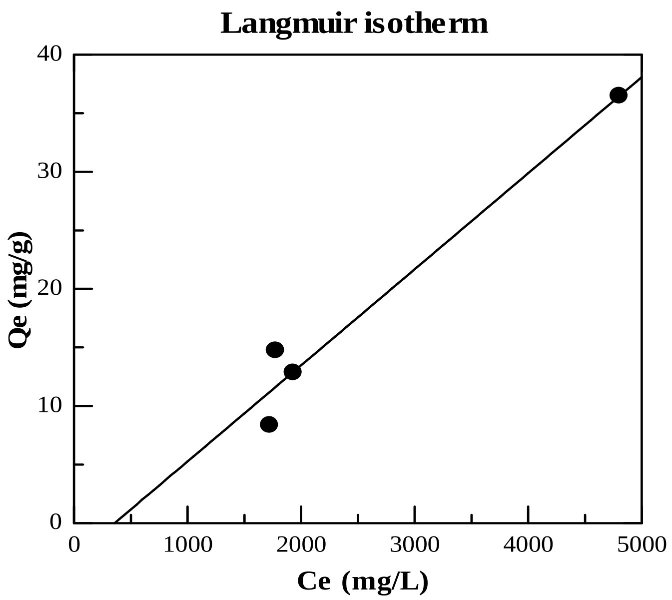


Figure 7. Langmuir isotherm of *T. catappa*

From the Fig.7 and Fig.8 the graphic of adsorption of Mn (II) fit to Langmuir isotherm for *T. catappa* flesh powder with the higher value of R^2 = 0.9810 in Langmuir isotherm. The Langmuir isotherm model assumes a surface with homogenous binding sites, equivalent sorption energies and no interaction between sorbed species [1]. This result shown that biosorption of Mn (II) with *T. catappa* flesh powder leaves through chemisorptions process

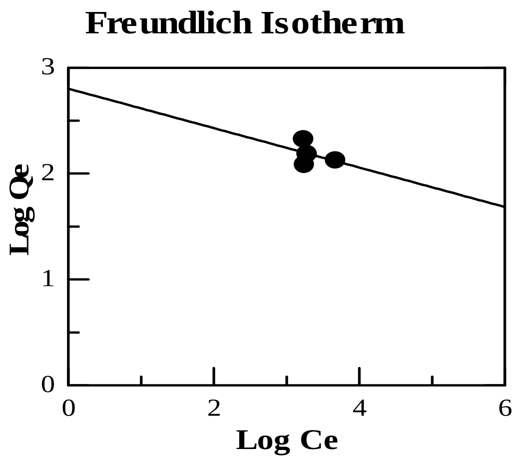


Figure 8. Freundlich isotherm of *T. catappa*

CONCLUSION

This study focused on the biosorption of Mn (II) ions onto *Terminalia catappa* flesh powder as biosorbent in aqueous solutions. The parameters investigated including pH of the solution, contact time, adsorbent dosage and initial concentration. The optimum removal percentage was 79.22 % by 1 g adsorbent. The optimum sorption capacity from the experiment was 460.18 mg/g. The equilibrium adsorption experiments fitted well with Langmuir than Freundlich isotherm models with correlation coefficient R2 equals 0.9810. It can also be concluded that *T. catappa* is an effective and alternative materials for the removal of Mn (II) from wastewater because of its high biosorption capacity, low cost and abundant availability

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