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Research Article

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Comparizon of *Muntingia calabura* L. and *Andrographis paniculata* leaves on sorption of Zn(II) ions in wastewater

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ABSTRACT

The ability of Muntingia calabura L. and Andrographis paniculata leavesto remove Zn(II) ions in wastewater on some parameter test such aseffect of pH solution, initial metal concentration, contact time and biosorbent mass were studied. The optimum conditions forMuntingia Calabura L leaveswere obtained at pH 4, initial concentration of Zn(II) Ion is 750 mg/L for 30 minand 0.1 g of biosorbent mass, while Andrographis paniculata leavesobtained at pH 6, initial concentration of Zn(II) Ion is2400 mg/L for 15 min and 0.1 g of biosorbent mass. Isoterm adsorpstion found for Muntingia calabura L. and Andrographis paniculata leaves were Freundlich and Langmuir respectively. Based on this research, the ability ofAndrographis paniculata is better than Muntingia calabura L. leaves on removing Zn(II) ions. Metal ion concentrations were measured by using Atomic Absorption Spectroscopy (AAS). Maximum adsorption capacity of Zn(II) by using Andrographis paniculata and Muntingia calabura Lleaves were 71.66 mg/L and 27.6350 respectivelywhile the morfology surface of biomaterialwere performed using Scanning Electron Micrograph (SEM) and Fourier Transform Infra Red pectroscopy (FT-IR) were used to describe theinteraction of Zn(II) ions with the funtional groups of biosorbents to the formation of discrete aggregates on the biosorbents surface.

Keywords: Biosorption, Zn(II), *Andrographis paniculata* leaves, *Muntingia calabura L.* leaves, adsorption isotherm.

INTRODUCTION

Development of industrialization produce large quantities of wastewater containing heavy metals especially Zn(II) Ion. Heavy metals are not hazardous at lower concentration however, at higher concentration they can bioaccumulate and enter to human beings through the food chain and can cause several health problem[1,2]. Heavy metal ions are released into the environment from various sources, various methods, such as precipitation, adsorption, evaporation, reverse osmosis, and ion exchange, has been used to reduce the levels of pollutants from water or wastewater, each method has some limitations [3,4,5,6,7].

In recent years, the adsorption technique has proven to be an effective alternative method to reduce the concentration of heavy metals in wastewater and water body [8]. In this research, the adsorption of Zn(II) ions by using *Muntingia calabura* and *Andrographis paniculata* leaveswere done. *Muntingia calabura* L have a shade leaves has chemical compounds such as saponins and flavonoids which acts as antioxidants. The dried leaves of *Muntingia calabura* extracted by ethyl acetate, report quinone reductase activity in cell culture test and has a significant antidiabetic activity [9,10].

Andrographis paniculata leaves known as a medicinal plant because its contains the main constituen of diterpenoid, flavonoids and polyphenols that are useful as anti-infective, anti-atherosclerosis, and anti-inflammatory [11]. Biomaterial that has been used to adsorb heavy metal ions are the rind biwa, leather palm fruit [12], soursop seeds [13], olive seeds [14], mangosteen skin [15] and others.

EXPERIMENTAL SECTION

Chemicals and Equipments

All chemical used in this experiment namely $ZnSO_4.7H_2O$, HNO_3, NaOH, HCl, CH_3COOH, CH_3COONa, NH_4OH and NH_4Cl are analytical grade and obtained from E-Merck (Germany). Distilled water were obtained from laboratory made. A cruiser, Mortal grinding, pH meters, analytical balance, rotary shaker, AAS (spectraAA-240 VARIANT), Oven, FTIR (NICOLET is10), SEM were used in this experiment. Herbal plant of *Mutingia calabura*L. and *Andrographis paniculata* leaves were collected from home garden in Padang City, West Sumatra,Indonesia.

Preparation of Biosorbent

Biosorbentleaves were washed by running water, cut into small pieces, then dried at room temperature. The dried leaves were crushed to a powder using a cruiser. The powder were soaked with a solution of 0.01 mol/L HNO_3 for three hours, filtered and then rinsed with distilled water until neutral. The biosorbent were dried and ready to be used.

Batch Adsorption

Biosorbent was entered into 10 mL solution containing metal ions, and stirred using a shaker for several min. The experiments were conducted by varying pH solution, initial concentration, contact time and biosorbent mass.

Data Analysis

To determine the amount of metal ions adsorbed, the formula used is:

$$Q = \frac{C_o - C_e}{m} \text{ x } v$$

Where "Co" and "Ce" are initial and equilibrium of metal concentration in solutions (mg/L), respectively; "V" is the volume solution (L); and "m" is the amount of biosorbent (g).

RESULTS AND DISCUSSION

Effect of pH solution

pH is an important parameter in the adsorption process of Zn(II) ions by biomaterials. The effect of pH solution were studied in range of 3 to 8.**Fig. 1** showsthat at pH 3 the adsorption capacity of both metal ions is low, it is due to the presence of H_3O^+ ions in solution. At higher pH solutionthe competition for metal ion in active site with H_3O^+ decreases, so the adsorption capacity increases [16]. Adsorption capacity of Zn(II) Ions increased at pH 3 to pH 4. The optimum adsorption capacity ofZn(II) ions occur at pH 4for*Muntingiacalabura* Leaves and pH 6 for *Andrographis paniculata* leaves. At pH 5 to 7 the adsorption capacity of Zn(II)ions reduced. However, at pH 8 both adsorption capacity of metal ion increased. This is because the metal ions has been settled before contacted with biosorbent.

Effect of Initial Metal Concentration

The initial concentration of metal ions were studied to determine the ability of the active site of biosorbentto bind metal ions [17]. The amount of metal ions adsorbed by *Mutingia calabura* L. leaves increased with the increasing of metal concentrations. However, capacity is reduced when high concentrations is reached due to the active site that already bonded by metal ions, this causing the saturation and there are no more active site of biosorbentremains to bind other metal ions. In this case the equilibrium between the metal ions adsorbed by biosorbent achieved. **Fig.2** shows that the optimum adsorption capacity of Zn(II) ions were found when the concentration is 750 mg/L with *Muntingiacalabura*L. and 2400 mg/L with *Andrographis paniculata* Leaves.

Effect of Contact Time

Fig. 3 shows that the contact time for the adsorption process of Zn(II) ions reach the optimum value after 30 min contact time with *Muntingiacalabura*L and 15 min contact time with *Andrographis paniculata* Leaves. After 30 min the equilibrium between the amount of metal ions remain in the solution and the amount of metal ions bound to biosorbent is reached. Longer time caused Zn(II) ions which has been bound to the active site becomes loose back and caused the adsorption capacity decreased.

Effect of biosorbent mass

Fig.4 showsthe optimum biosorbent mass for both biomaterialwere found to be 0.1 g. The amount of adsorbent used represents the potential of biosorbent in removing ions on the initial concentration given [18]. The metal ion adsorption capacity is inversely proportional to the mass of biosorbent used. Increased of biosorbent mass resulting decline in metal ion adsorption capacity. A specific area can be defined as a part of total area available for biosorption [19].

Adsorption isotherms

Equilibrium relationship between adsorbent and adsorbate can be explained by adsorption isotherms [20]. Determination of equilibrium parameters provide important information that allows advance adsorption design of the system [21]. Biosorption isotherms are characterized by certain parameters, which explain the nature of the surface and biosorbent affinity. It also be used to compare the biosorptive capacity of biosorbent for different pollutants [22] Data trial uptake of Zn(II) ionsfor both biomaterial were analyze by Langmuir and Freundlich isotherm models. Langmuir isotherm models assume a surface with homogeneous binding sites, equivalent energy adsorption, and no interaction between species adsorbed [23]. Freundlich isotherm models assume the adsorption occure on heterogeneous surfaces with interaction between molecules adsorbed, the application of Freundlich equation also indicates that the energy adsorption decreases exponentially at the completion of the adsorption center of adsorbent [24]. **Fig.5 (a),** shows that R^2 value for Zn(II) ions is 0.9560 with *Andrographis paniculata* Leaves and follows Freundlich adsorption models, while**Fig.5 (b)** shows that the isotherm models of Zn(II) ions with *Muntingia calabura* L. gave the determination coefficient value (R^2) of 0.8627 andit can be concluded that it follows Langmuir adsorption models.

Analysis of functional groups by FTIR

FTIR analysis of *Muntingia Calabura L*leaves were shown in **Fig. 6.**The analysis showedions removal mechanism in adsorbent surface, because it provides information about the functional groups present in the structure of the adsorbent [18]. A wavelength of 3422.35 cm^{-1}, shows the presence of hydroxyl (-OH) stretching groups caused by inter-molecular hydrogen bonding compounds such as phenols, alcohols and carboxylic acids.A wavelength of 1654.41 cm^{-1} is a spectrum of C = O groups in amide. At a wavelength of 1227.85 cm^{-1} peak of the cluster C-N amine and C-O stretching of alcohol groups were found. The wavelength of 1037.58 cm^{-1} indicates the C-N bond stretching.Wavelength of 3422.35 cm^{-1}wereshifted to 3423.64 cm^{-1}. Then becomes 3422.11 cm^{-1}. This FTIR spectra can provide information that hydroxylwas involved during the adsorption process of Zn(II) ions.

Analysis of SEM

Characterization using SEM was done to see the morphology structure of adsorbent material. Characterization is done at a magnification of 1000x.**Fig.7**shows irregular structure of *Mutingia calabura* leaves and the presence of empty pores.These pores will facilitate the adsorption place of metal ions.

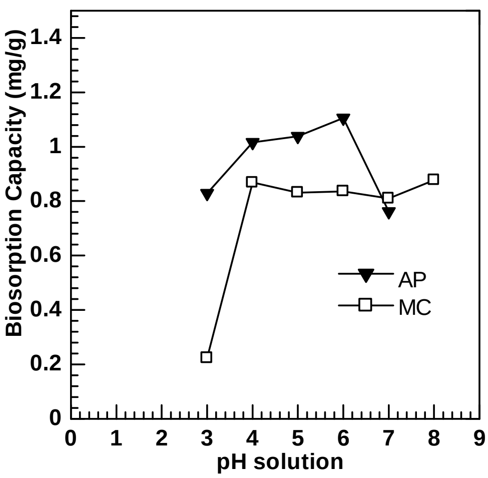


Figure.1. Effect of solution of pH on the biosorption capacity of Zn(II) ions on Muntingia calabura L leaves (□) and *Andrographis paniculata* Leaves (▼). Experimental condition: Initial concentration = 10 mg/L, biosorbent dose = 0.1 g, stirring speed = 200 rpm and contact time = 15 min

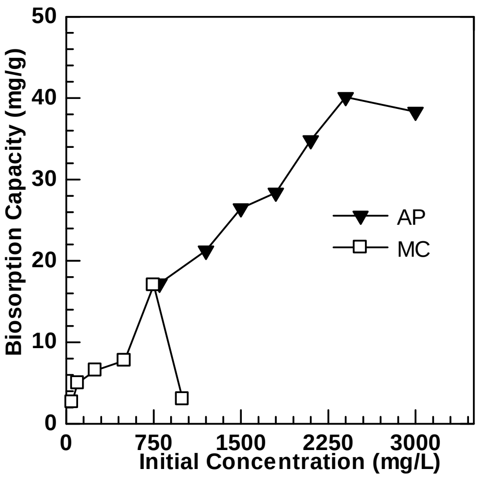


Figure.2. Effect of initial concentration on the biosorption capacity of Zn(II) ion Muntingia calabura L leaves (□) and *Andrographis paniculata* Leaves (▼). Experimental condition: solution of pH = 4 and 6, biosorbent dose = 0.1 g, stirring speed = 200 rpm and contact time = 15 min

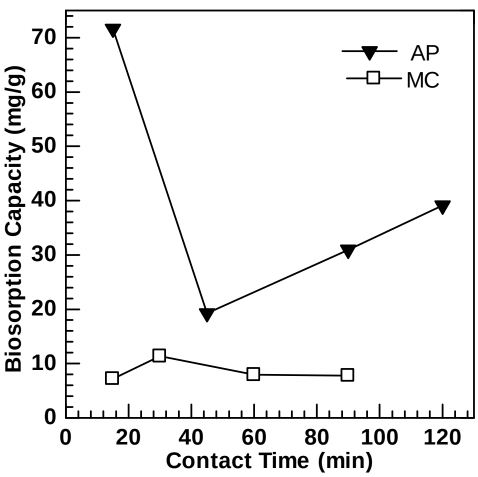


Figure. 3.Effect of contact time on the biosorption capacity of Zn(II) ion on Muntingia calabura L leaves (□) and *Andrographis paniculata* Leaves (▼). Experimental condition: Cd(II) ionconcentration = 750 mg/L and 2400 mg/L, solution of pH solution = 6 and 4, biosorbent dose = 0.1 g and stirring speed = 200 rpm

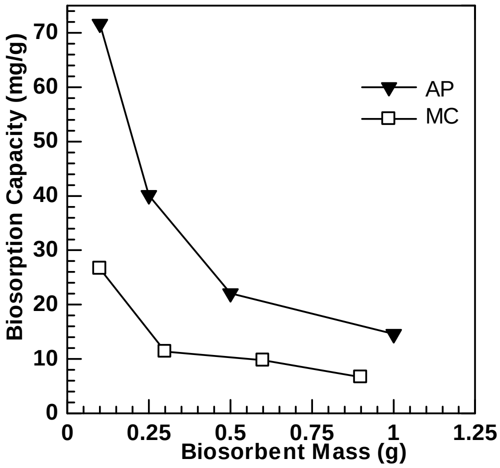


Figure. 4. Effect of adsorbent mass of the metal on the biosorption capacity of Zn(II) ion on Muntingia calabura L leaves (□) and *Andrographis paniculata* Leaves (▼). Experimental condition: Cd(II) ionconcentration = 750 mg/L and 2400 mg/L, solution of pH solution = 6 and 4, and stirring speed = 200 rpm

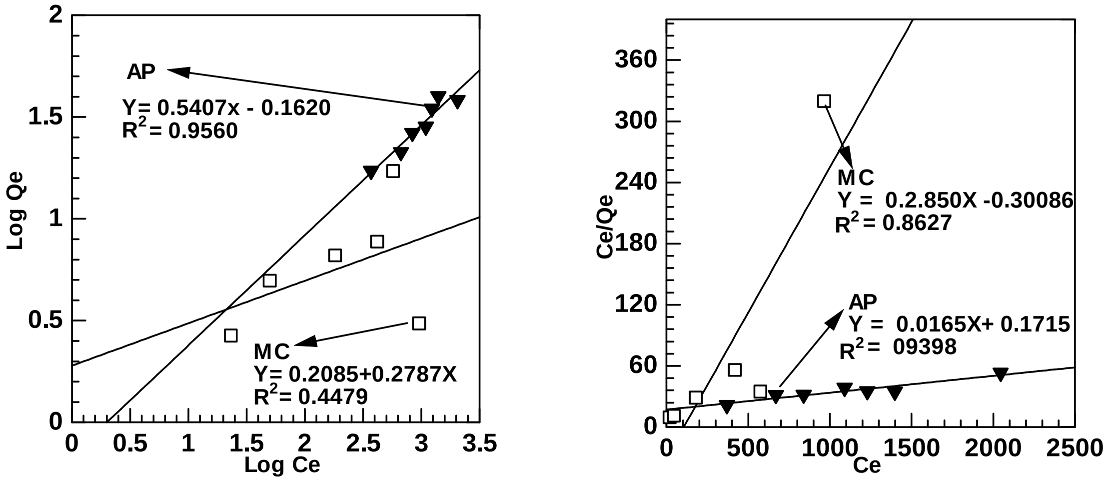
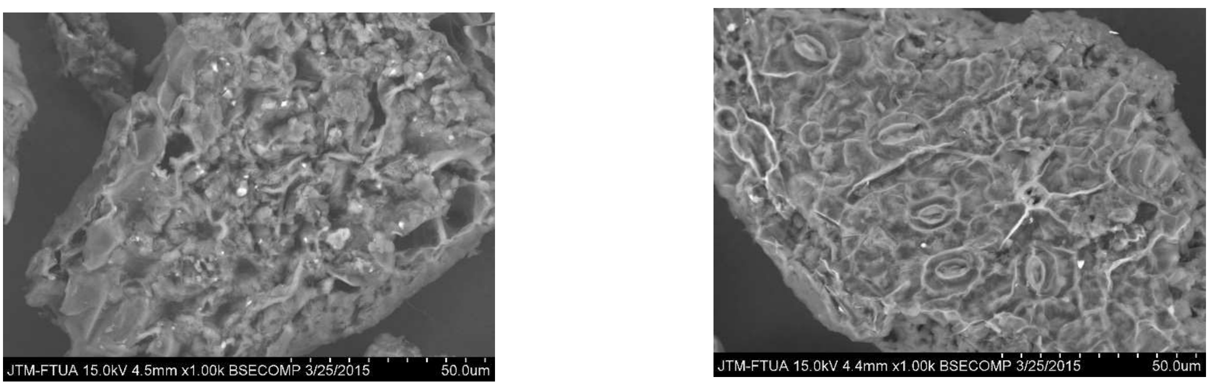


Figure.5. Freundlich (b) Langmuir (a) isotherm models for the adsorption of Zn(II) ions on Muntingia calabura L leaves (□) and *Andrographis paniculata* Leaves (▼)



(a) (b)

Figure.6.Scanning electron microscope of leaves (above) and flesh (below) of *Muntingia Calabura* L (A) and after Zn ion sorption. Magnification 1,000 times

Figure. 7. FTIR Spectrum of Muntingia Calabura leaves powder

CONCLUSION

Based on this research, it can be conclude that, the herbal *Muntingia calabura* L leaves and *Andrographis paniculata* leavescan be used to adsorp Zn(II) ions present in sample either in water and organ sample. Therefore it is a potential herbal plant to adsorp Zn(II) ion present in molecular of animal organ.

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