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Research Article

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Comparison of Indonesian medicinal herbal red betel and green betel leaves for the removal of lead from aqueous solution

I. Nyoman Ehrich Lister[1], Siffa Fauziah[2], Rahmiana Zein[2], Yunazar Manjang[2] and Edison Munaf[2]*

[1]*Department of Physiology, Faculty of Medicine, the University of Prima Indonesia, Medan, North Sumatra, Indonesia*
[2]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Padng, West Sumatra, Indonesia*

ABSTRACT

Bisorption of lead by using red betle (Piper crocatum) and and green betle (Piper betle) leaves had been studied through batch method. The effect of pH, initial concentration, bisorbent dosage and contact time were investigated to find the best condition in order to achieve the optimum biosorption capacity. Isotherm Langmuir and Isotherm Freundlich model were used to check conformity of adsorption process. Morphological change and functional groups that involve during the biosorption process were observed by Scanning Electron Microscope and Fourier Transform Infra Red Spectrosopy, respectively. Batch studies indicate that the optimum biosorption capacity was achieved at pH 4, initial concentration 1,800 mg/L and adsorbent dosage 0.1 g for both biosorbents. Whereas contact time achieved optimum value at 120 minutes and 15 minutes for Piper crocatum and Piper betle leaves, respectively. SEM's images showed that significant difference before and after Pb(II) ion uptake binding into the surface of biosorbent. FTIR analysis indicated functional group of OH stretching, C=O carbonyl that play a role in adsorption due to wavelength shifted. Both of these biosorbents fit to isotherm Langmuir model based on the value of R^2 *0.9576 and 0.9959 for Piper crocatum leaf and Piper betle leaf. Piper crocatum leaf give the best adsorption process to remove Pb(II) ion from aqueous solution with removal percentage 92.65 %.*

Keywords: Biosorption, lead, *Piper crocatum*, *Piper betle*, FTIR, SEM

INTRODUCTION

Development of industrialization produce large quantities of wastewater containing heavy metals such as cadmium, tin, mrcury and lead. Heavy metals can be bioaccumulated and enter in to human beings through the food chain and can cause several health problems [1]. It is well known that some metals are harmful to life, such as antimony, chromium, copper, lead, manganese, mercury, cadmium, etc., they are significantly toxic to human beings and ecological environments [2].

There are several methods that can be used to remove heavy metals from indstrial and domestic wastewater. Biosorption is one of most common method which is used to remove heavy metals ion on solution [3]. The advantages of biosorption are an efficient, potential, low-cost effective way of removing toxic and heavy metals from industrial effluents with comparing the other alternative methods [4].

Recent biosorption experiments have focused attention on waste materials as biosorbent for both heavy metals and dyes such as *Psidium guajava leaves* [4], langsat fruit peel [5], *Nypa fruticans Merr* shell [6], rambutan seeds [7], *Annona muricata* L seeds [8], durian fruit seeds [9], sugar palm fruit seeds [10], microalga *Scenedesmus dimorphus*

[11] and a few medical plants for example *Moringa oleifera* leaves [12], *Tridax procumbens* [13], *Oscimum sanctum Linn* (Tulsi) [14] and etc.

Piper crocatum and *Piper betle* are well-known as medical plants. *Piper* leaves contains organic compounds such as polyphenols, flavonoids, tannin, alkaloids, and essential oils [15]. *Piper crocatum* leaves is widely used to cure various diseases such as diabetes, hepatitis, kidney failure, stroke, hypertension and etc [16]. On the other hand, *Piper betle* is used to treat alcoholism, bronchitis, asthma, leprosy and dyspepsia [17].

Althogh the *piper crocatum* and *piper betle* leaves are widely used as a traditional medicinal, scarcely any authors describe this plant as material to remove toxic metals from aqueous solution as well as from human organs.

The present research focused on the use of *Piper crocatum* leaves and *Piper betle* leaves as biosorbent to remove Pb(II) ion from aqueous solution

EXPERIMENTAL SECTION

Chemical and Apparatus

All reagents used are analytical grade and obtained from E.Merck (Darmstad, Germany). The apparatus used are analytical balance (Kern & Sohn GmbH), crusher (Fritsch, Germany), pH meter (Metrohm), shaker (Edmun Buhler 7400 Tubingen), FTIR (Unican Mattson Mod 7000 FTIR), SEM (Hitachi S-3400).

Leaves Preparation and Biosorption Studies

Piper crocatum leaves and *Piper betle* L leaves are collected from home garden at Padang city,West Sumatra, Indonesia. The leaves were washed with destilated water and dried at room temperature. Then the both leaves were milled by crusher and the powder was soaked into HNO_3 0.1 mol/L for 2 hours. Furthermore, the leave powder was rinsed by distilled water and dried. Biosorbent is ready to used.

Bisorption assays were conducted on various pH, concentration, biosorbent dosagee and contact time. Characterization was carried out by using FTIR and SEM.

RESULTS AND DISCUSSION

Effect of pH on biosorption of Pb(II) ion

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions,concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction [18]. The pH optimization study was conducted within pH range 3-8. The adsorption capacity of *Piper crocatum* and *piper betle* leave dramatically decrease as pH increase. At lower pH, association between adsorbent surface and hydronium ions occurs causing repulsive force between the metal ion and biosorbent surface. As the pH increase concentration of hydronium in solution decrease and affect the surface charge of biosorbent causing attractive force between biosorbent and metal ion [3,5,19]. The results can be shown in **Fig. 1**.

The pH optimum adsorption capacity of *Piper crocatum* leaves and *Piper betle leaves* were achieved at pH 4 for both biosorbent, with adsorption capacity 2.9465 mg/g and 1.1879 mg/g, respectively. Shananaz et al [1] investigated the optimum adsorption of lead at pH 4.5, Khoriah et al,at pH 5 [5], and Vanida et al. investigated the adsorption of lead(II) at pH 4 [19].

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

Effect of initial concentration of Pb(II) ion was conducted at various concentration ranging from 600 to 3,000 mg/L at pH 4. Figure 2 shows that maximum adsorption capacity of *Piper crocatum* leaves and *Piper betle* leaves were 88.45 mg/g and 61.08 mg/g, respectively achieved at concentration of Pb(II) 1800 mg/L. Biosorption capacity increased as concentration increased and decreased. This this may caused due to the increased in electrostatic interactions (related to covalent interactions) involving sites of progressively lower affinity for metal ions. Therefore, more metals ions were left un-adsorbed in solution at higher concentration levels [5].

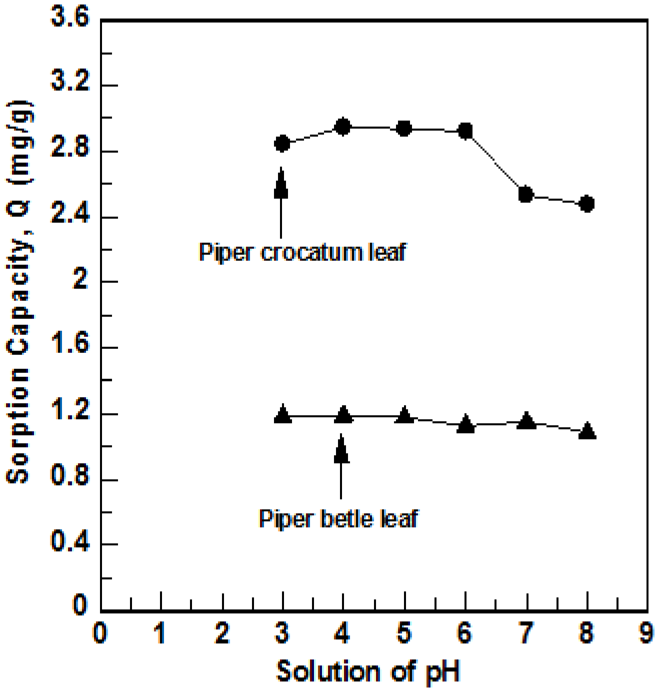


Fig. 1 Effect of pH on Pb(II) adsorption, initial concetration 30 mg/l; stirrer speed 100 rpm; contact time 15 min; biosorbent dose Piper crocatum leaf 0.1 g; Piper betle leaf 0.25 g.

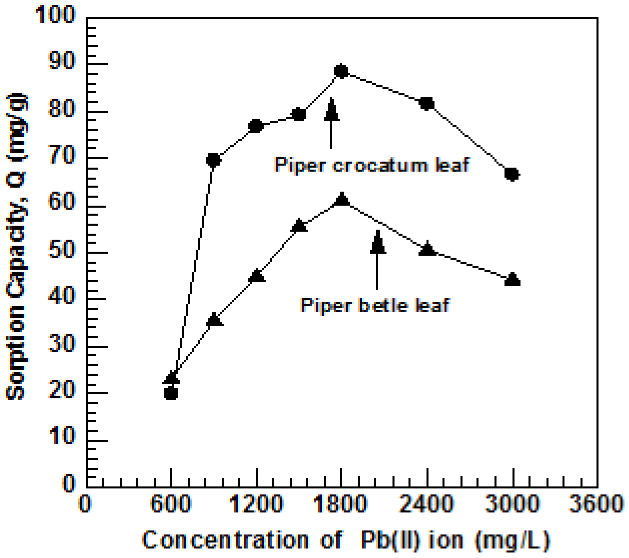


Fig. 2 Effect of concentration on Pb(II) adsorption, pH 4; stirrer speed 100 rpm; contact time 15 min; biosorben dose Piper Crocatum leaf 0.1 g; Piper betle leaf 0.25 g.

Effect of adsorbent dosage on biosorption of Pb(II) ion

Varying dosages of *Piper crocatum* leaves and *Piper betle* ranging 0.1-1 g at pH 4 and intial concentration of Pb(II) were investigated and found that at Pb(II) ion 1,800 mg/L shown that Pb(II) uptake by leaves at maximum value of 0.1 g with biosorption capacity 88.45 mg/g and 166.77 mg/g, respectively. The results are shon in Fig. 3. The larger the surface area, the larger the amount of metal ion adsorbed. This appears to be due to the increase in the available binding sites in the biomass for the complexation of the heavy metals [3]. Adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose [8]. Similar report were given in various studies [1,5,19].

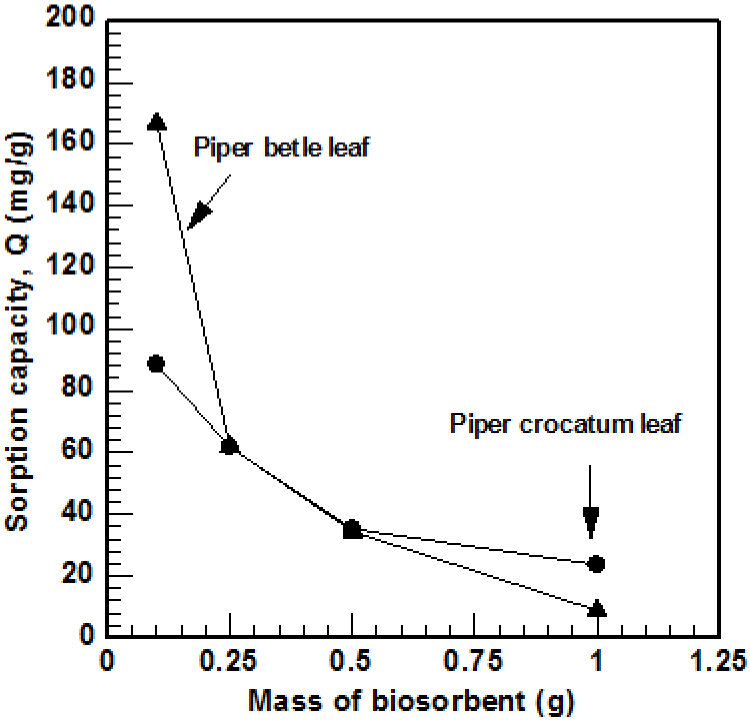


Fig. 3 Effect of biosorbent dose on Pb(II) adsorption, pH 4; stirrer speed 100 rpm; initial concentration 1800 mg/L; contact time 15 min.

Effect of contact time on adsorption of Pb(II) ion

The effect of contact time was carried out with ranging time 15-120 minutes. As shown in Fig. 4 the Pb(II) ion uptake on *Piper crocatum* gradually increased as time goes by to attain equilibrium after 120 minutes. Whereas Pb(II) uptake on *Piper betle* dramatically decrease as effect of contact time with maximum adsorption capacity achieved at 15 minutes. Nazris et al reported contact time for biosorption Pb(II) ion is 6 minutes [6], Adelaja et al achieved the highest adsorption of Pb(II) at the end of 180 minutes.

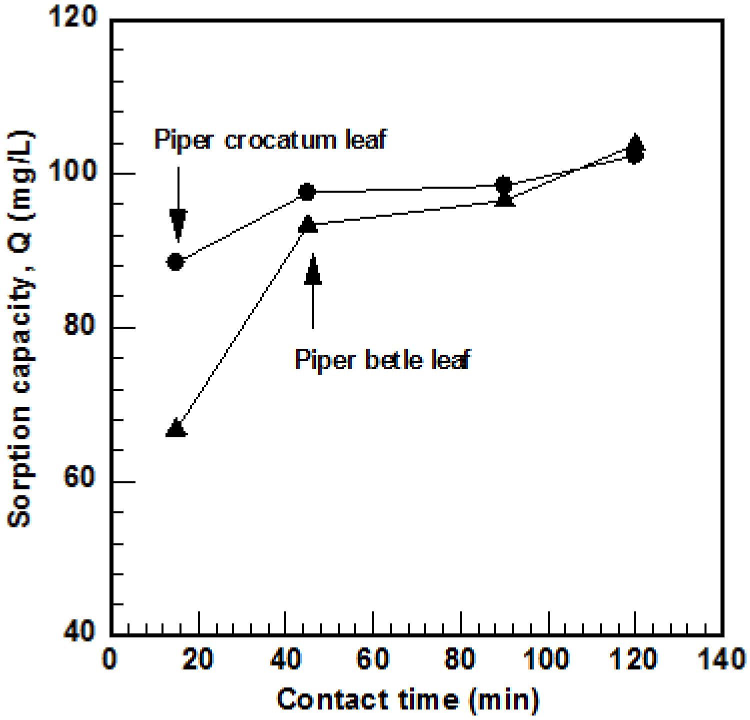


Fig. 4 Effect of contat time on Pb(II) adsorption, pH 4; stirrer speed 100 rpm; intial concentration 1800 mg/L, biosorbent dose Piper crocatum 0.1 g; Piper betle 0.25 g.

Adsorption Isotherm

Langmuir and Freundlich isotherm were used to determine equilibrium of adsorption model. Freundlich isotherm model deals with adsorption at multilayer heterogeneous surface. The Freundlich linear form is given by the following equation [5].

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

Where K_f is a constant related to the adsorption capacity (Freundlich constant) and 1/n is an empirical parameterrelated to the adsorption intensity (which varies with the heterogenity of the material). Values of 1/n and K_f are calculated respectively from the slope and the intercept of plot of log qe vs log Ce, is shown in **Fig. 5**.

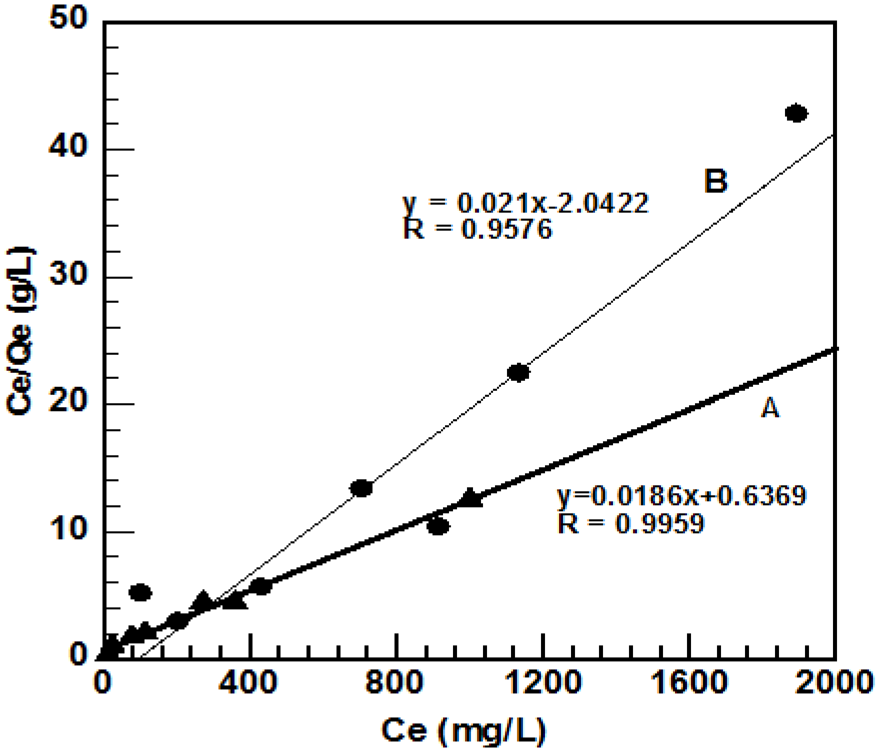


Fig. 5 Langmuir Isotherm of Piper betle (A); Piper crocatum (B).

The Langmuir model represents monolayer sorption on a set of distinct localized sorption sites having the same sorption energies independent of surface coverage with no interaction and no steric hindrance between sorbed molecules and incoming molecules. The sorption data are also subjected to the following linearized form of Langmuir equation [18].

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

Where q_m represent sorption saturation capacity (mmol g^{-1}), indicating a monolayer coverage of sorbent with the sorbate, b elucidate the enthalpy of the sorption (dm^3 mol^{-1}), independent of temperature. Result revealed that the adsorption of Pb(II) from Langmuir isotherm is shown in figure 6.

From graphics of adsorption of Pb(II) fit to Langmuir isotherms model for both Piper croactum and *Piper betle* leaves with the higher value of determination coefficient R^2 = 0.9576 and 0.9959 respectively. This result shown that biosorption of Pb(II) with *Piper crocatum* and Piper betle leaves through chemisorptions process.

Characterization of biosorption

FTIR Analysis

FTIR is an important analytical technique, which detects the vibration characteristics of chemical functional groups existing on the surface of adsorbent. FTIR can give information about functional group that may involve during adsorption process. As shown in **Fig**. **7** and **Fig. 8**, the peak at 3400-3200 cm^{-1} indicate the presence of OH stretching, peak 3000-2850 cm^{-1} show the spectrum of CH stretching and sharp spectrum at 1700-1600 cm^{-1} indicate the presence of C=O group. As observed in both types of adsorbent, there was different wavelength number before and after Pb(II) ion uptake. This indicate that biosorption prosess occur between both *Piper crocatum* and *Piper betle* with Pb(II) ion.

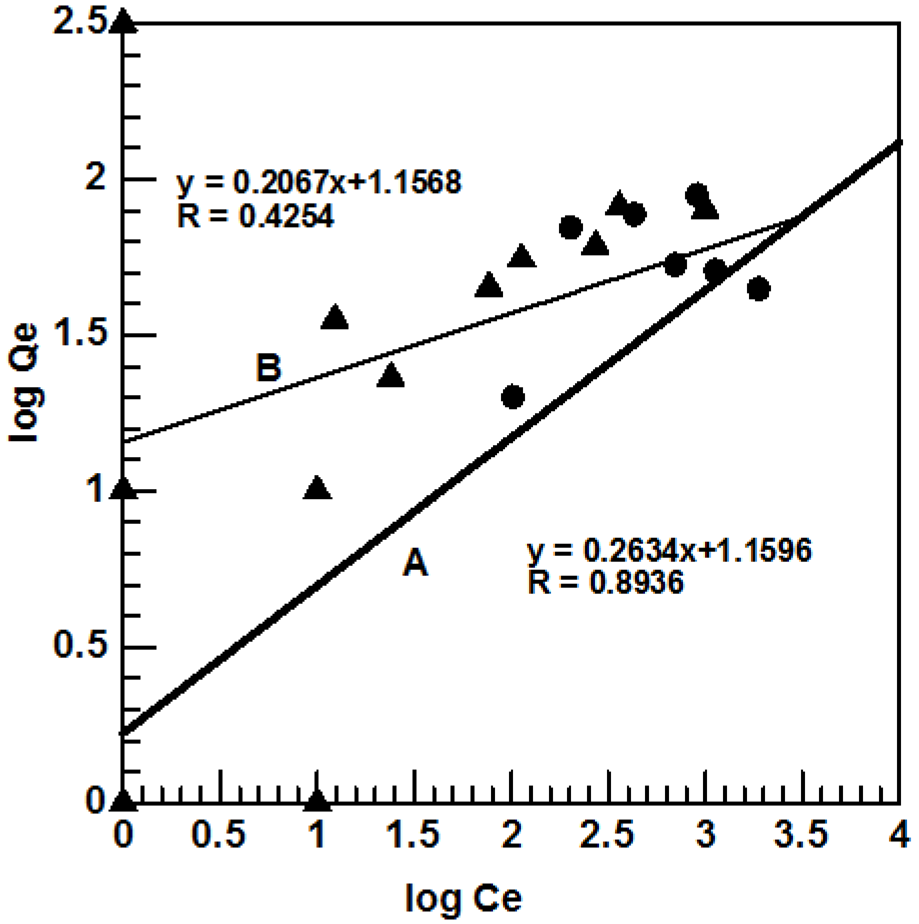


Fig. 6 Freundlich isotherm Piper betle (A); Piper crocatum (B)

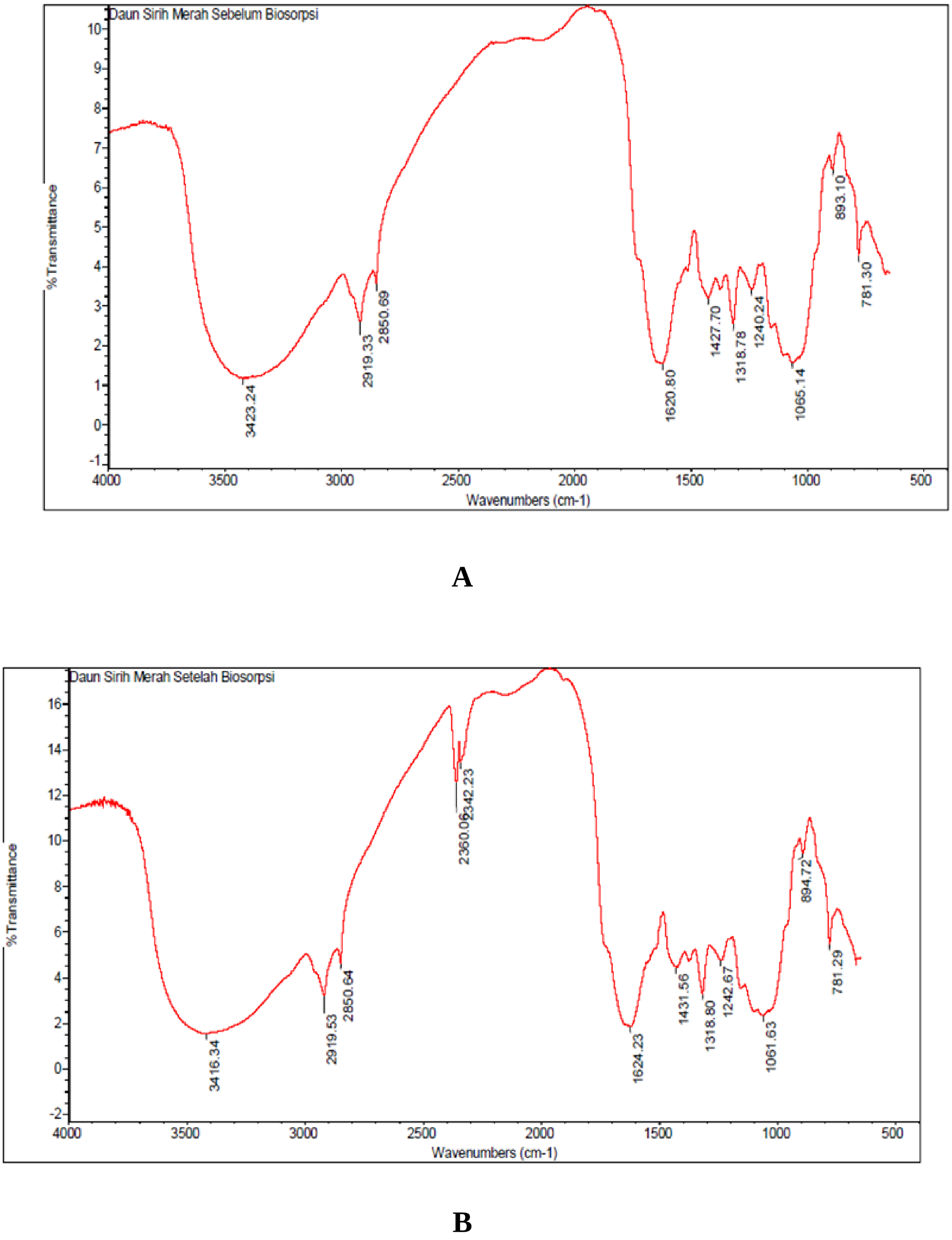
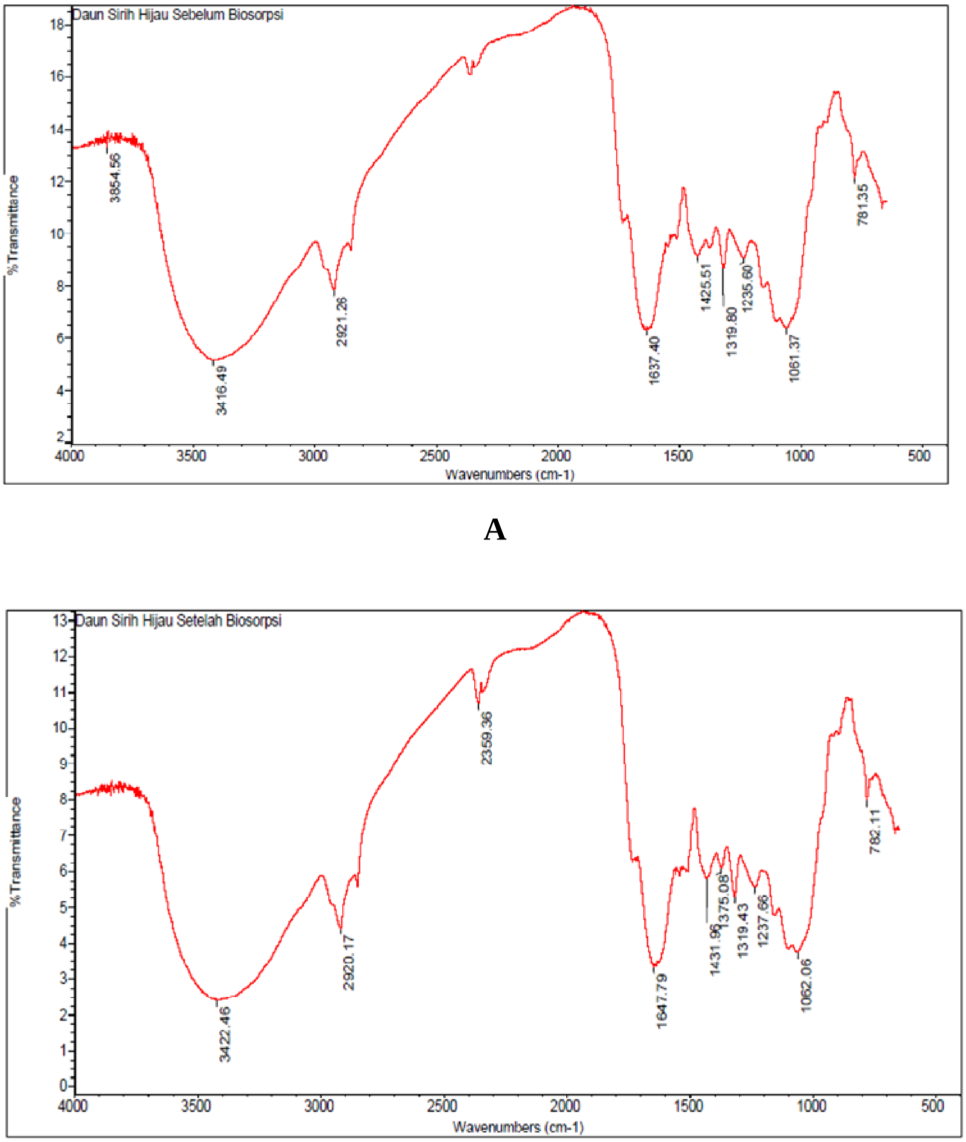


Fig. 7 FTIR of *Piper crocatum* leaves, (A) before Pb(II) uptake; (B) after Pb(II) uptake



B

Fig. 8 FTIR of *Piper betle* leaves, (A) before Pb(II) uptake; (B) after Pb(II) uptake

SEM Analysis

The SEM analysis was conducted to observe the surface morphology of the biosorbents before and after metal ion uptake. These SEM's images observed at 1000x magnification. As seen at Fig. 9 the both biosorbent have porous on their surface that can be filled by metal ions. And then after metal ions uptake into the surface of both biosorbent the porous was covered by metal ions. These images revealed that the surface of biosorbent dramatically changed after interaction with metal ions.

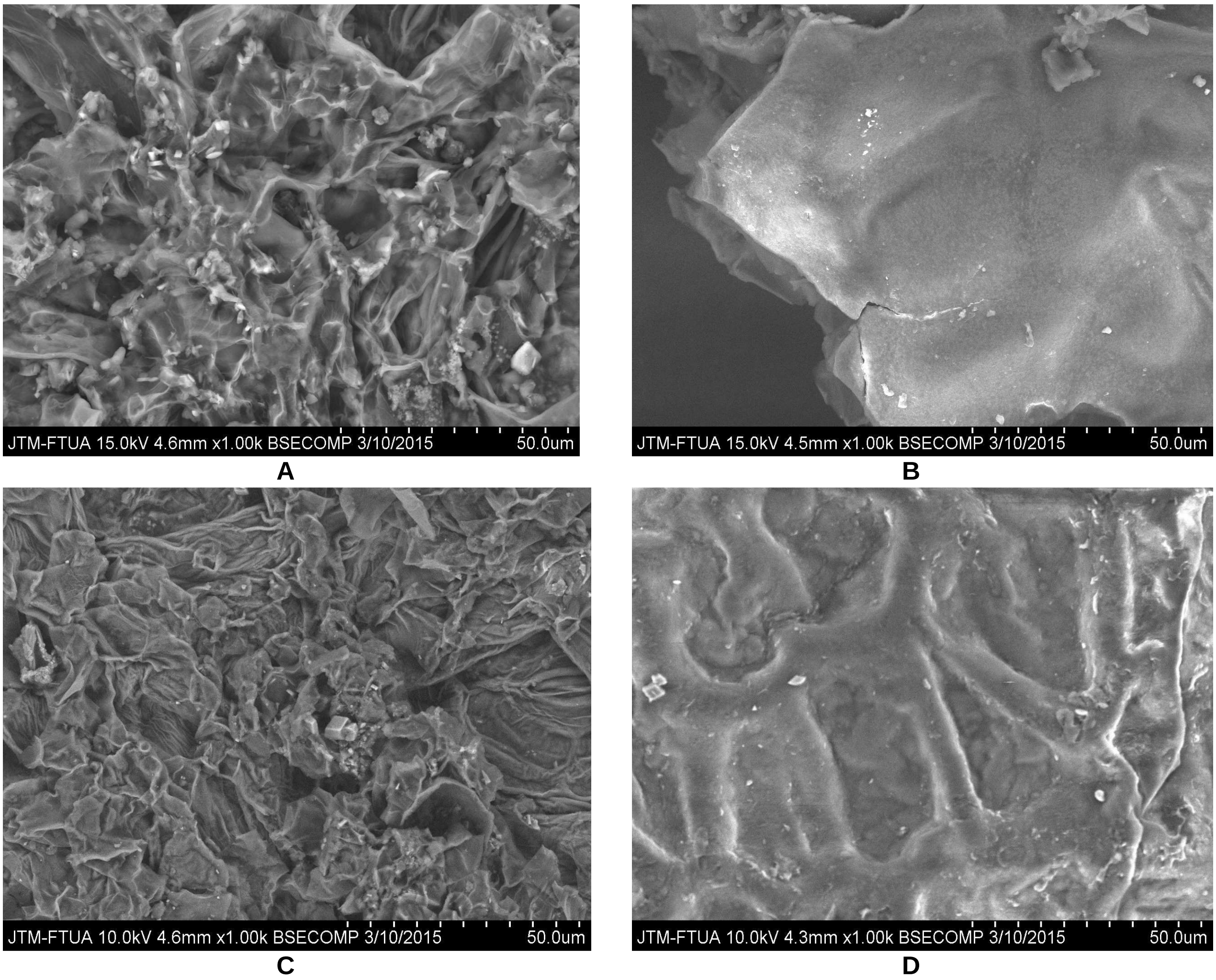


Fig. 9 SEM of *Piper crocatum* leaves (A) before utake; (B) after uptake; *Piper betle* leave (C) before uptake; (D) after uptake

CONCLUSION

Based on the research results, *Piper crocatum* leaves and *Piper betle* leaves can be used as biosorbent for Pb(II) uptake with optimum conditions have similarity. The optimum adsorption capacity was achieved at pH 4, initial concentration 1,800 mg/L and adsorbent dosage 0.1 g for the both biosorbent. Whereas contact time achieved optimum value at 120 minutes and 15 minutes for *Piper crocatum* leaves and *Piper betle* leaves, respectively. Based on the various parameters data, *Piper betle* leaves is the better biosorbent for Pb(II) adsorption with removal percentage 92.65 %.

Langmuir isotherm model is well-described for eliminate Pb(II) ion from aqueous solution by *Piper crocatum* leaves and *Piper betle* leaves. Whereas SEM analysis shown the both biosorbent have capability to remove metal ion due to it pores.

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