Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(9S):81-88

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

The removal of Cr(VI) with *Dimocarpus longan* as a low cost biosorbent

Florenly[a], Refi Ikhtiari[a], Hermansyah Aziz[b], Syafrizayanti[b] and Rahmiana Zein[c*]

[a]*Faculty of Dentistry, University of Prima Indonesia, Medan, Indonesia*
[b]*Department of Chemistry, Faculty of Mathematics and Natural Science, Andalas University, Padang, Indonesia*
[c]*Laboratory of Environmental Chemistry, Faculty of Mathematics and Natural Science, Andalas University, Padang, Indonesia*

ABSTRACT

Dimocarpus longan has been proposed to be a low cost biosorbent. The adsorption ability of its seed and skin to remove the Cr (VI) in aqueous solution has been investigated in a batch method. Longan`s seed showed better ability compared to longan`s skin at any experimental condition. Adsorption capacity showed the optimum values at pH 3, initial concentration 300 mg/L, biosorbent dose 0.25 g and contact time 15 min. Langmuir and Freundlich models have the value of R2 = 0.5408 and 0.8976. Results showed that Freundlich model was better than Langmuir, proposed a multilayer biosorption ofCr (VI). FTIR showed strecthing vibration of hydroxil groups, sp^3 alkanes, carbonyl groups, alkanes, and bending of primary amines. Both of the biosorbent also showed the stretching vibration of symmetric nitro compounds which supported by other peaks in the fingerprint area. SEM observation showed the surface of Dimocarpus longan has pores, granules and fibers. Typical morphological damages found after biosorption. Based on Isotherm models, FTIR and SEM images, we suggested a physico-chemical pathway could describe the metal sorption mechanism.

Keywords: Removal of Cr (VI), *Dimocarpus longan*, Isotherm adsorption, FTIR, SEM.

INTRODUCTION

Heavy metal pollution is now being considered as a worldwide environmental concern. Heavy metalsare persistent and readily accumulate to toxic levels by finding their way to water bodies through waste waters [1-2]. Instead of environmental impact, the toxic hexavalent Cr (VI) could be exposed to human through inhalation, ingestion, and skin permeation of workers in leather tanning, pigment production and stainless steel welding industries [3]. Several studies reported that Cr (VI) exposure could induce health problems such as headache, nausea, severe diarrhea, vomiting, epigastric pain, hemorrhage, carcinogenic and has an adverse potential to modify the DNA transcription process [4-7]. Furthermore, Cr (VI) has been widely used in orthodontic appliances. Most of the orthodontic products such as bracket and archwires were made of stainless steel containing 8-12 % nickel (Ni), 17-22% chromium (Cr) and various proportions of manganese (Mn), copper (Cu), titanium (Ti) and iron (Fe) [8]. Since the orthodontic materials interact continuously with physiological fluid inside of mouth, degradedmaterials might released from brackets or archwires,through emission of electro-galvanic currents,with saliva acting as the medium for continuous erosion. This condition may lead to toxic effect on the surrounding oral tissues[9 -14].

Recently, several methods for the removal of heavy metals from aqueous solution have been established e.g. chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis, evaporative recovery and solvent extraction. Although, biosorption process is still retain few advantages over other techniques mentioned above due to its selectivity, cheap, eco-friendly and effective eventhough at very low concentrations [15-19]. Biosorption process may involved chemisorption, complexation, adsorption – complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption [20-22].This study reported the seed and skin of

Dimocarpus longan as a low cost biosorbant due to its abundant availability as waste material for sequestering the Cr (VI) ionsfrom aqueous solution.

EXPERIMENTAL SECTION

Chemicals and Equipments

All chemicals used are analytical grade and obtained from E-Merck (Germany). Distilated water obtained from laboratory made. A cruiser (Fritch, Germany), pH meter (Metrohm), analytical balance (Kern & Sohn, GmbH), rotary shaker (Edmun Buhler 7400 Tubingen), AAS (spectra AA 240-Variant), UV-Vis (Thermo Insight), FTIR (Nicolet iS10 with KBr) and SEM (Hitachi S-3400N) were used in this experiment.

Preparation of Biosorbent

The *longan`s* seeds and skin were collected from home garden in Padang city, West Sumatra, Indonesia.After washed, *longan`s* fruit was then separated between seeds and skin. Then dried at room temperature and treated by a cruiser to form powder. The powder was sieved to 450 µm and soaked with 0.01 mol/L HNO_3 for two hours, filtered and rinsed with distilled water until neutral. Finally, the biosorbent were dried and ready to be used.

Batch Adsorption

Powder of seed and skin of biosorbent were soaked with 10 mL solution containing Cr (VI) ions and stirred at 100 rpm for several minutes. Variations of pH solution, initial concentration, contact time, biosorbent mass and heating temperature of biosorbent were conducted during experiment.

Data Analysis

The amount of Cr (VI) ion which adsorbed by *longan`s* seed and skin powder were calculated by:

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

Where $\mathbf{c_o}$ is the initial concentration of metal ions (mg/L), $\mathbf{c_e}$is final concentration at equilibrium state (mg/L), **m** is biosorbent mass (g) and ***v***is volume solution (L).

RESULTS AND DISCUSSION

Effect of pH solution

The pH value influences the dissociation site on the surface of the biosorbent and the solution chemistry of the heavy metals, e.g., hydrolysis, complexation by organic and/or inorganic ligands,redox reactions, and precipitation, as well as the speciation and biosorption availability for heavy metals [23-24].The results in the Figure 1 showed that *longan`s* seed has better adsorption ability compared to *longan`s* skin at the same pH condition. The optimum adsorption capacity for both seed and skin has reached at pH 3. The lower acid condition was suitable for biosorption of heavy metal ions due to the increasing of electrostatic interaction on the surface and sorption of positively charged Cr (VI) ions [25].Interestingly, the *longan`s* skin was ineffective at pH 6 when the *longan`s* seed reached the minimum values at pH 7. This result suggested that *longan`s* seed could be used as biosorbent at broader pH condition compared to *longan`s* skin. The optimum pH condition at 3 wasapplied in the allfurther experiments to explore the effects of other variables.

Effect of Initial Concentration

Ion sorption of Cr (VI) on to *longan`s* seed and skin was investigated at different concentration ranging from 30 mg/L to 400 mg/L as shown in Figure 2. The adsorption capacity increased as well as concentration of Cr (VI) up to 300 mg/L. Figure 2 also supported the data that *longan`s* seed having better sorption capacity when compared to *longan`s* skin at a given initial concentration 300 mg/L. The adsorption capacity will increase until the number of active site is equal with the number of Cr (VI) ion, then equilibrium condition will be reached [26]. The increase in the biosorbent's loading capacity as a function of metal ion concentration was considered due to a high driving force for mass transfer [27].

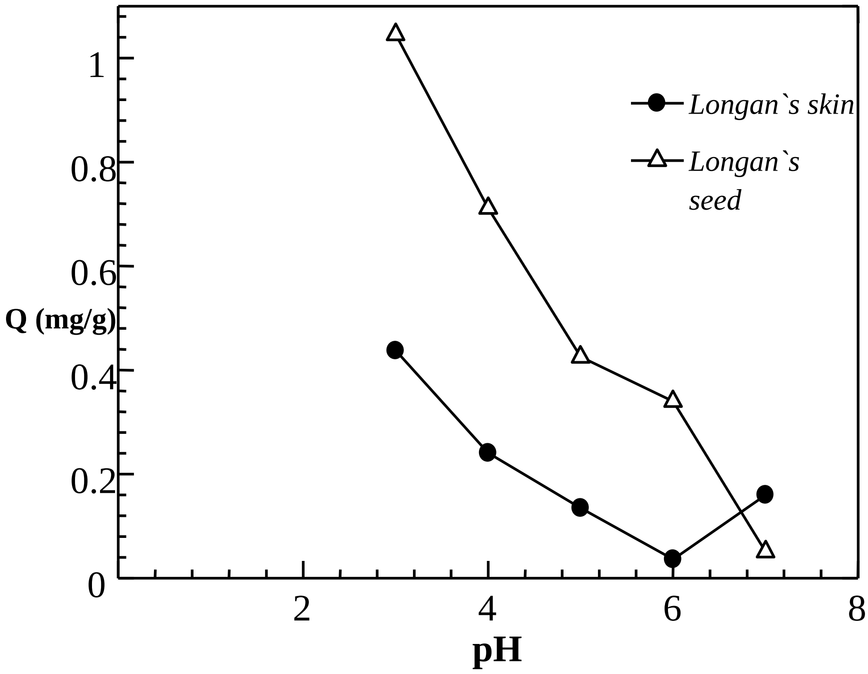


Figure 1. Effect of pH on Adsorption Capacity (Q)

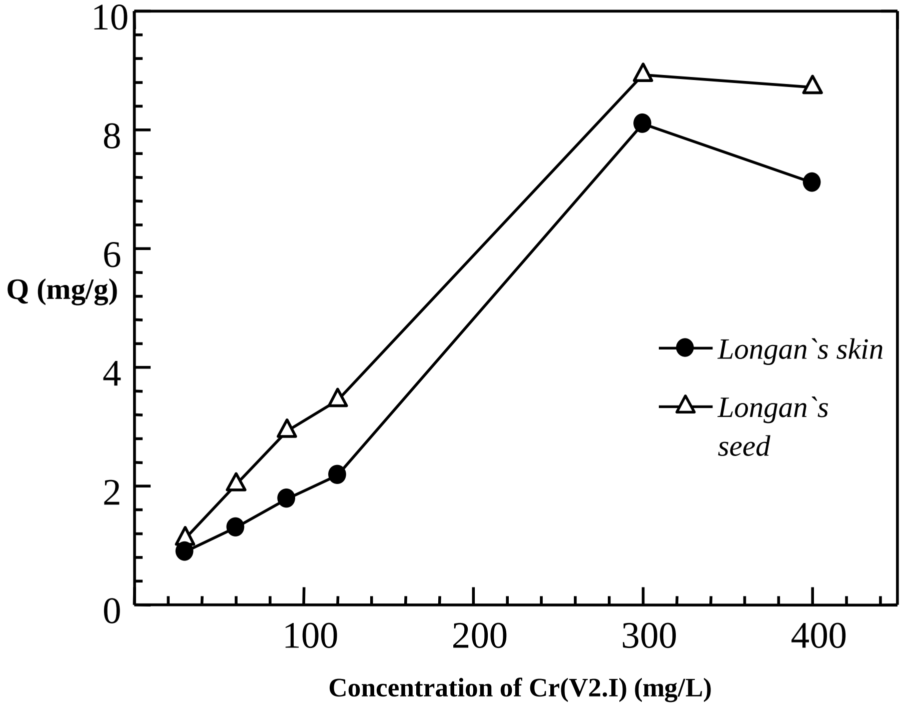


Figure 2. Effect of Initial Concentration on Adsorption Capacity (Q)

Effect of Contact Time

The adsorption of Cr (VI) ions have been investigated in range of 15 min to 120 min as shown in Figure 3. Results indicated that optimum adsorption was at 15 min of contact time. In case of *longan*`s seed, slight increase of adsorption were observed after 45 min. These result suggested the ability of *longan*`s seed to adsorpt the Cr (VI) was better than *longan`s* skin.Further, the adsorption capacity of *longan`s* skin tend to decrease until 120 min.

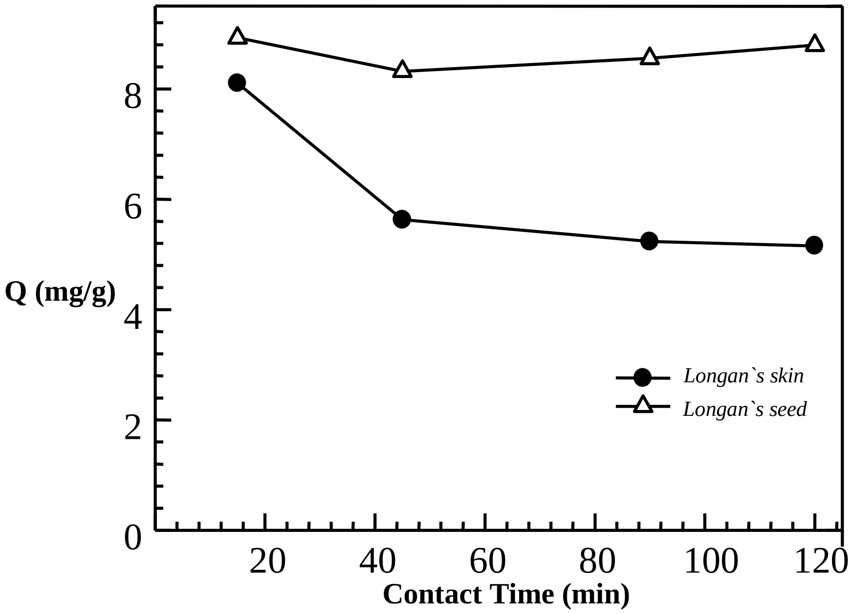


Figure 3. Effect of Contact Time Vs Adsorption Capacity (Q)

Effect of Biosorbent Dosage

The adsorption capacity for a given initial concentration was fully depend on biosorbent dosage. The variation of biosorbent dosage ranged from 0.1 to 1.0 g have been investigated. The results in Figure 4.a and 4.b showed that the optimum dose was achieved at 0.25 g for both type of biosorbent. The percent removal of *longan*`s seed and skin at optimum dosage were 74.36 % and 67.52 % respectively.Interestingly, the adsorption capacity and percent removal of Cr (VI) ions were significantly decreased at 0.5 g. In case of percent removal, it may slightly increased at biosorbent dosage > 0.5 g for both type of biosorbent. Furthermore this result may suggest that addition of biosorbent was relativelyineffective at higher dose due to the powder formed of biosorbent may caused saturation and particle interaction such as aggregation [27-28].

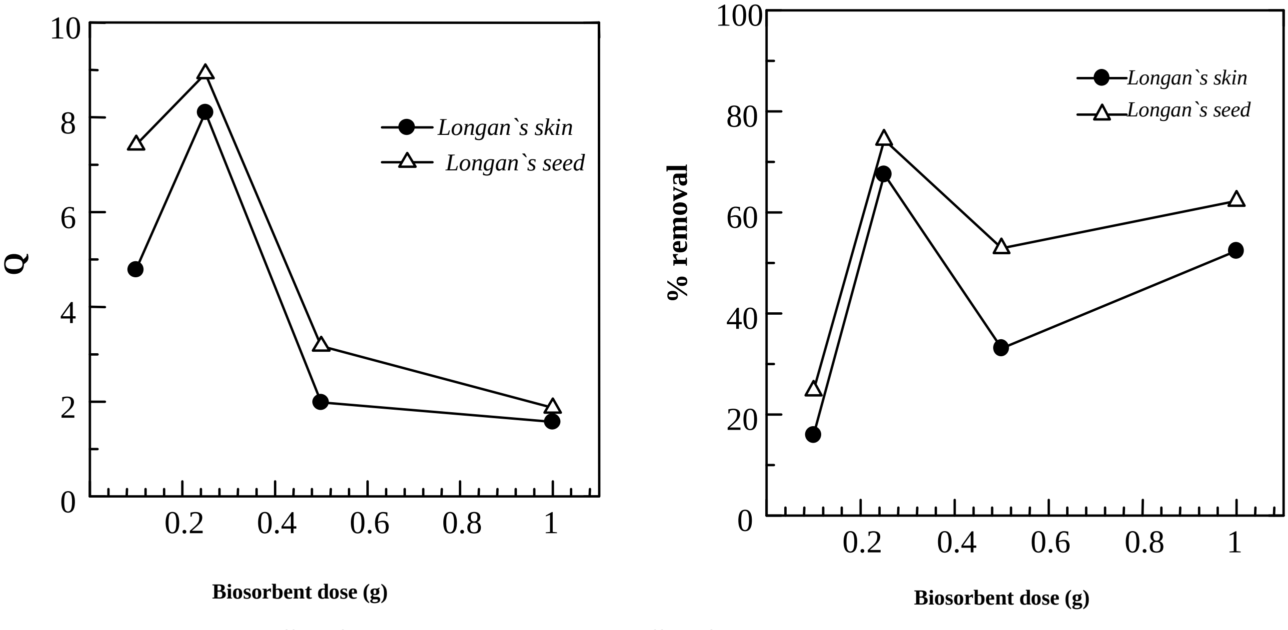


Figure 4. Effect of Biosorbent dose Vs (Q) (a) and Effect of Biosorbent dose Vs % Removal (b)

Adsorption Isotherm

The adsorption process of Cr (VI) ions between solid phase and liquid phase as well as the interaction between Cr (VI) ions with biosorbent will be described with adsorption isotherm models [29]. The adsorption of Cr (VI) ions by *longan`s* seed and skin tend to follow the Freundlich Isotherm model as shown in Figure 5.a and 5.b. The determination coefficient for Cr (VI) ions of *longan`s* seed and skin are 0.9674 and 0.8976 respectively. This results indicated that adsorption process occurred in a multilayer which proposed a physical adsorption mechanism [21,25].

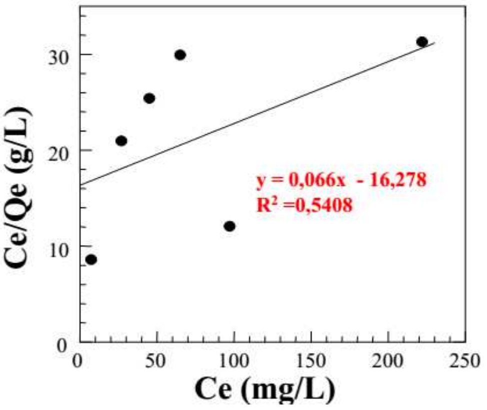


Figure5 (a.1) Adsorption kinetics of *longan`s* skinLangmuir Isotherm

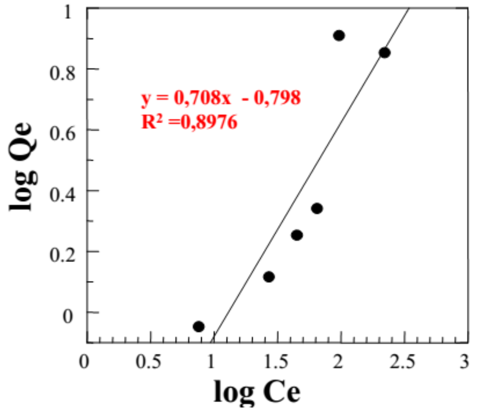


Figure 5 (a.2) Adsorption kinetics of *longan*`sskin Freundlich Isotherm

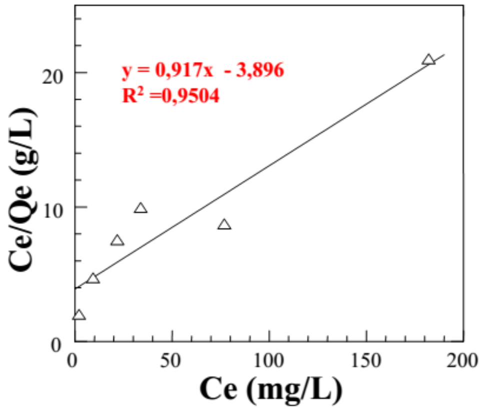


Figure5(b.1)Adsorption kinetics of *longan`s* seed Langmuir Isotherm

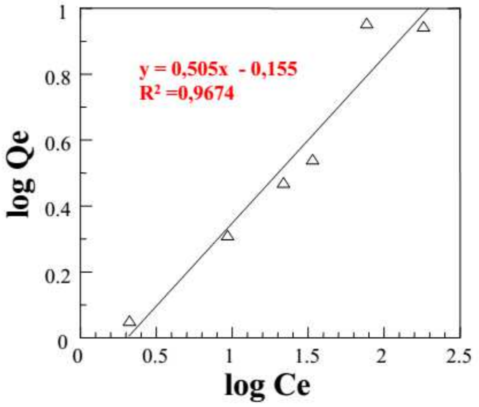
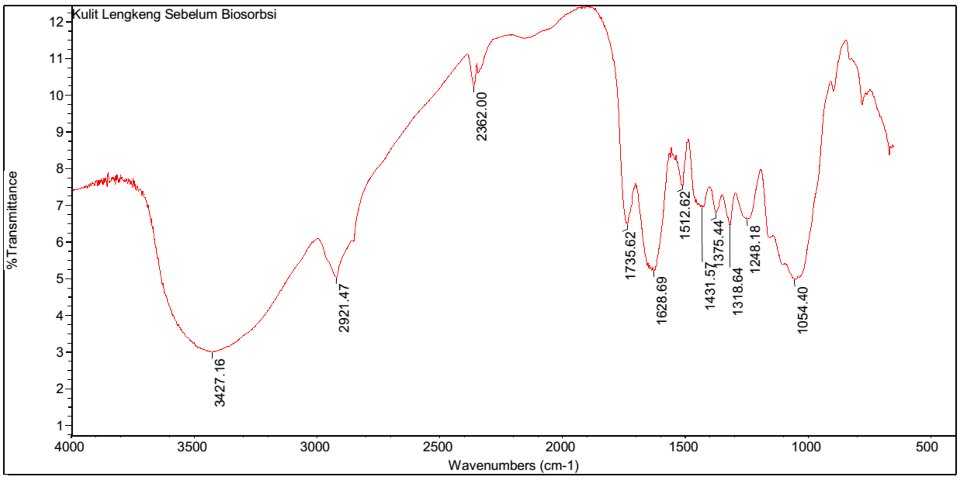


Figure5(b.2)Adsorption kinetics of *longan`s* seed Freundlich Isotherm

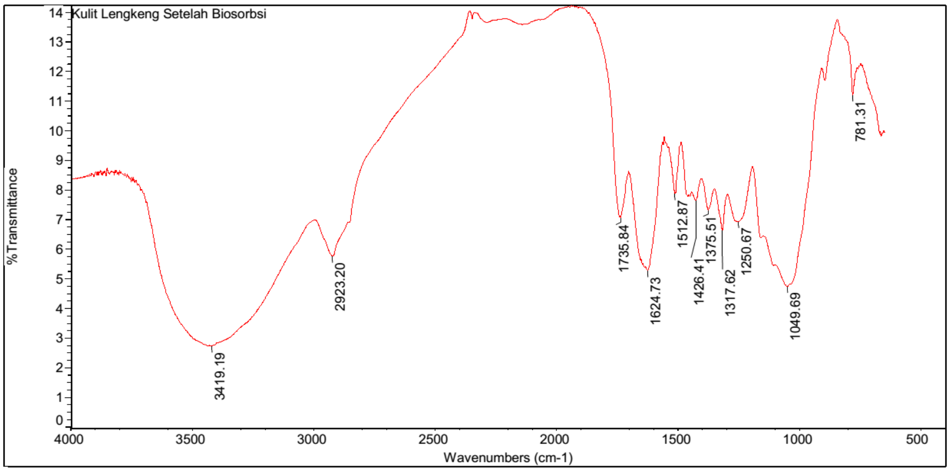
FTIR Analysis

FTIR analysis of *longan`s* seed and skin showed strecthing vibration of –OH ranging at 3500-3200 cm$^{-1}$ which attributed to H bonded of alcohol or phenol as shown in Figure 6 and 7. The *longan*`s seed showed broader band because of the *longan`s* skin contain more watern. Both of biosorbents also showed medium band at 3000-2850 cm$^{-1}$ indicated the stretching vibration of sp$^3$ C–H(alkanes) which assigned to alkanes. Interestingly, some functional groups which might play the role of adsorption have been also detected [22]. The*longan`s* skin has specific stretching vibration of C=O (carbonyl groups) which indicated by sharp/medium band at 1750-1720 cm^{-1} , it may represented the esters, aldehydes and saturated aliphatics. In the other hand, the *longan`s* seed at before adsorption has specific stretching vibration of –C=C– (alkanes) at 1644.16 cm$^{-1}$ . After adsorption, the medium band shift of bending N–H (1$^o$ amines) was indicated by 1626.53 cm$^{-1}$ . The medium band shift of *longan`s* skin after adsorption process was also indicated by the bending of N–H (1^o amines) at 1624.73 cm^{-1}. The *longan`s* seed and skin altogether showed the stretching vibration of N–O (symmetric nitro compounds) which were indicated by medium band at 1550-1390 cm^{-1} , this result also supported by other peaks in the fingerprint area ranging from 1390-1300 cm^{-1}.

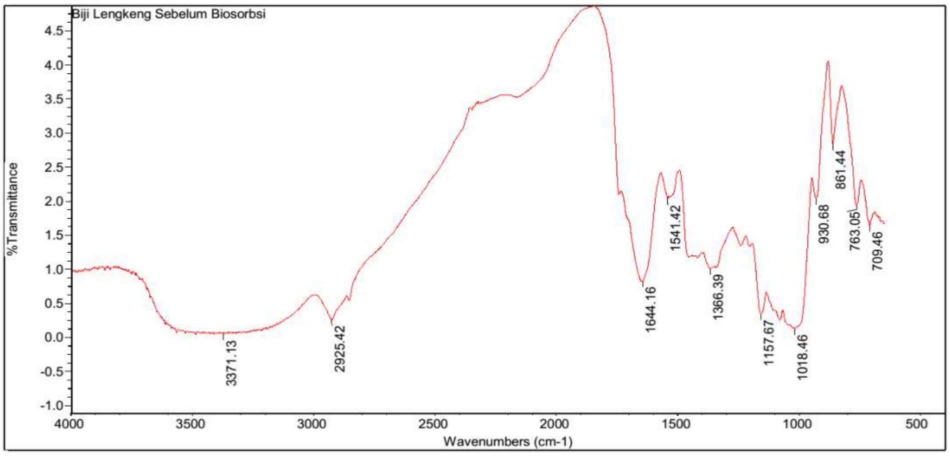
Most of the functional groups involved in the binding process are found in the cell walls. Plant cell walls are generally considered as structures built by cellulose molecules, organized in microfibrils and surrounded by hemicellulosic materials (xylans, mannans, glucomannans, galactans, arabogalactans), lignin and pectin along with small amounts of protein[30-32]. Based on the FTIR data we conclude that chemisorption also take place instead of physical sorption which showed by isotherm models.



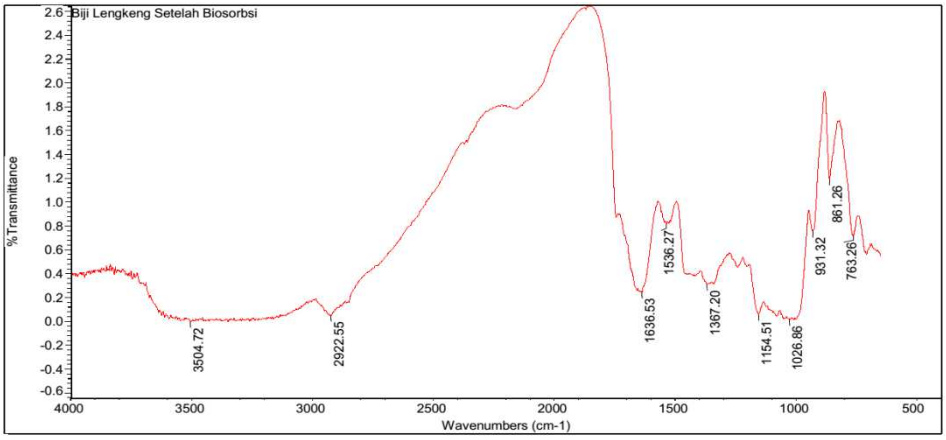
Figure(6.a) FTIR spectra of *longan`s* skin before adsorption
Freundlich Isotherm



Figure(6.b) FTIR spectra of *longan`s* skin after adsorption



Figure(7.a) FTIR spectra of *longan`s* seed before adsorption



Figure(7.b) FTIR spectra of *longan`s* seed after adsorption

SEM Analysis

Scanning Electron Microscopy (SEM)was used to observed the surface morphology of biosorbents before and after adsorption of Cr (VI) ions at 1000 times of magnification as shown in Figure 8. The surface of *longan`s* skin has porous structure and wavy, while the *longan`s* seed has granules and fibers like. There were significant changes to the surface of *longan`s* seed and skin after ions sorption. SEM images showed the destruction of surface morphology due to the interaction of metal ion Cr (VI) with the multilayer surfaces [22].

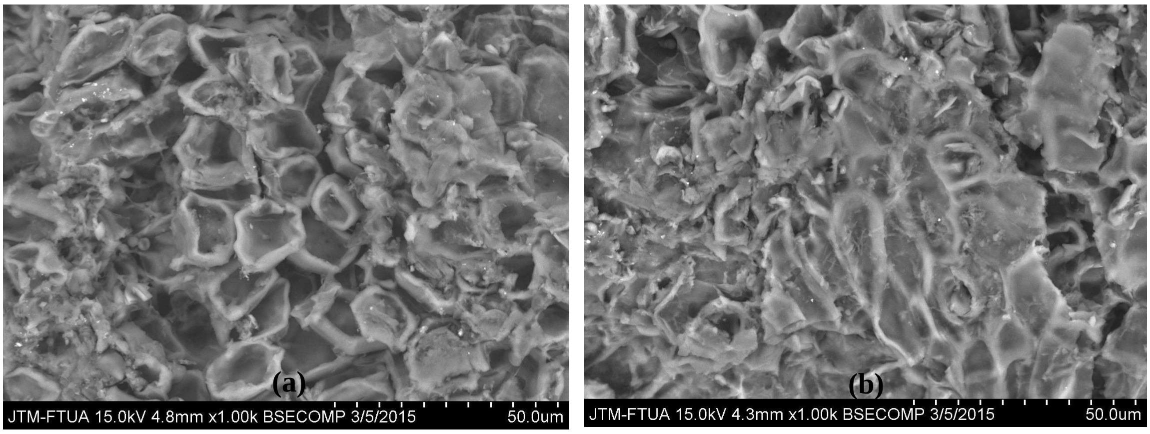
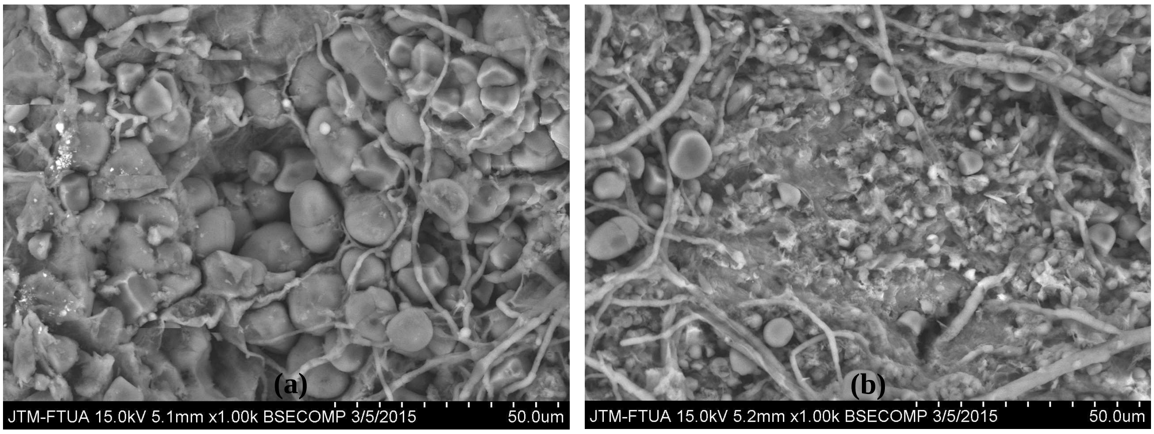


Figure8a. Morphological surface of *longan`s* skin (1000x), (a) before adsorption (b) after adsorption



Figure(8.b) Morphological surface of *longan`s* seed (1000x) (a) before adsorption (b) after adsorption

CONCLUSION

All experimental data showed that *Dimocarpus longan* has potential ability to remove the Cr (VI) ions from contaminated water while optimum condition was achieved at pH 3, initial concentration 300 mg/L, biosorbent dose 0.25 g and contact time 15 min. The number of key functional groups as well as the active sites and multilayer physisorption mechanism may play the role of the adsorption ability. The interaction of metal ion Cr (VI) which caused severe damages has been observed on the morphological surface of biosorbent. Based on this research could be concluded that the abundant availability of *Dimocarpus longan* could be proposed as a low cost biosorbent for removal Cr (VI) ion in aqueous solution.

REFERENCES

[1] K. L. Wasewar; M. Atif; B. Prasad; I. M. Mishra. *Clean*, **2008**, 36, 320 – 329.
[2] H. Aydin; Y. Buluta; C. Yerlikaya. *J. Environ. Manage*, **2008**, 87, 37 – 45.
[3] C. Pellerin; S. Booker. *M.EnViron. Health Persp*. **2000**, 108, A402 - A407.
[4] T. A. Kurniawan et.al.,*Sci. Total Environ*. **2006**, 366, 409 – 426.
[5] T. A. Kurniawan. et.al.,*Chem. Eng. J*. **2006**,118, 83 – 98.
[6] S. Qaiser; A. R. Saleemi; M. M. Ahmad. *Electron. J. Biotechnol*. **2007**,10, 409 – 416.
[7] C. Namasivayam; M. V. Sureshkumar. *Bioresour. Technol*. **2008**, 99, 2218 – 2225.
[8] S. K. Karnam; A. N. Reddy; C. M Manjith. *J. Contemp. Dent. Prac.***2012**, 13 (3), 376 – 381.
[9] R. Codd and P. A. Lay. *J. Am. Chem. Soc*. **2001**, 123, 11799 – 11800.
[10] F. Amini. et.al.,*Euro. J. Ortho.***2012,** 34, 126 – 130.
[11] F. Amini. et.al., *Ortho. Cranio. Res*. **2008**, 11, 51 – 56.
[12] R. Matos de Souza; L. Macedo de Menezes. *Angle Ortho.* **2008**, 78, 345–350.
[13] D. P. Singh et.al. *World. J. Ortho.* **2008**, 9, 196 –202.
[14] T. Eliades; C. Bourauel. *Am. J. Ortho. Dent. Orthopedics*. **2005**, 127, 403 – 412.
[15] M. Isik. *Colloids Surf. B*. **2008**, 62, 97 – 104.
[16] Z. Salem; K. Allia. *Int. J. Chem. Reactor Eng*. **2008**, 6, A10.
[17] M. Dundar; C. Nuhoglu; Y. Nuhoglu. *J. Hazard. Mater*. **2008**,151, 86 – 95.
[18] A. Hammaini et al. *Hydrometallurgy*.**2002**, 67, 109 – 116.
[19] D. Sud; G. Mahajan; M. P. Kaur. *Bioresour. Technol*. **2008**, 99, 6017 – 6027.
[20] A. Demirbas. *J. Hazard. Mater*. **2008,** 157, 220 – 229.
[21] S. O. Lesmana et.al., *Biochem. Eng. J*. **2009**, 44, 19 – 41.
[22] V. O. Arief et.al., *Clean*. **2008**, 36 (12), 937 – 962.
[23] H. L. Wang; C. Chen. *Biotechnol. Adv*. **2006**, 24, 427 – 451.
[24] X. Y. Guo; S. Z. Zhang; X. Q. Shan. *J. Hazard. Mater*. **2008**, 151, 134 – 142.
[25] A.M. Farhan and A.S. Sameen. *Am. J. Environ. Eng*. **2014,** 4 (1), 11 – 17.
[26] Z. Chaidir; D.T. Sagita; R. Zein and E. Munaf. *J. Chem. Pharm. Res.***2015**, 7(1), 589 – 599.
[27] A. Baran et.al., *Bioresour. Technol*. **2007**, 98, 661 – 665.
[28] K. Huang; Y. Xiu and H. Zhu. *Environ. Sci. Pollut. Res*. **2013**, 30, 5930 – 5938.
[29] Khoiriah; F. Furqoni; R. Zein and E. Munaf. *J.Chem. Pharm. Res.***2015**, 7(1), 546 – 555.
[30] T.W. Goodwin; E.I. Mercer; *Introduction to Plant Biochemistry*, Pergamon Press, UK, **1975**.
[31] P. Nobel. *Physicochem. Env. Plant Phys.* Academic Press, New York, **1991**.
[32] S. Al-Asheh; Z. Duvnjak; *J. Hazard. Mater*. **1997**,56, 35 – 51.