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Removal of Cadmium (II) and Copper (II) from Aqueous Solution by Using Langsat Fruit (*Lansium domesticum* Corr) Seed.

Dilla Wahyuni, Firda Furqani, Ayu Widya Astuti, Khoiriah, Indrawati, Rahmiana Zein, and Edison Munaf*

Laboratory of Analytical Environmental Chemistry, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Padang 25163, Indonesia.

ABSTRACT

Research about biosorption of Cd(II) and Cu(II) ions by langsat fruit (*Lansium domesticum* Corr) fseed has been investigated through batch experiment. Based on the experiment optimum condition adsorption metal ions Cd(II) and Cu(II) was pH 4 for Cu(II) and 6 for Cd(II), respectively. Biosorben dosage 0.1 g, initial concentration of metal ion solution 120 mg/L, contact time 6 min., and biosorben temperature 40°C with maximum adsorption capacity 5.7186 and 4,9950 mg/g for Cd(II) and Cu(II) ions, respectively . The Isotherm data for this adsorption well to Langmuir equation with R^2 0.8910 for Cd(II) and 0.9996 for Cu(II). Desorption studies of Cd (II) and Cd(II) ions with HNO₃ 0.1 M were conducted to avoid the disposal of metal contaminated solid waste and to explore the possibility of reuse of langsat seed as well as the recovery of the Cd (II) and Cu(II) and The total desorption for Cd (II) was 47,47 % and Cu(II) was 81,67 %. Characterization of langsat seed was evaluated using Fourier Transform Infrared (FT-IR) spectroscopy, estimated the active functional group was -OH and C=O. Measuring of metal ion concentration evaluated using Atomic Adsorption Spectroscopy (AAS). This research show that langsat seed could be employed as an efficient adsorbent for removal heavy metal ion Cd(II) and Cu(II).

Keywords: Biosorption, *Lansium Domesticum* Corr seed, Isotherm biosorption.

*Corresponding author

INTRODUCTION

The increased industrial activities, indiscriminate use of organic and inorganic fertilizers and pesticides, and disposal of industrial effluents enhance the possibility of pollution and toxicity of heavy metals in environment. Due to their extended persistence in biological systems and tendency to bioaccumulate, the contamination of water by toxic heavy metals is a worldwide environmental hazard [1,2].

Copper pollution arises from copper mining and smelting, brass manufacture, electroplating industries and excessive use of Cu-based agri-chemicals. Copper along with arsenic and mercury, is recognized as the highest relative mammalian toxic [3] and continued inhalation of copper containing sprays is linked with an increase in lung cancer among exposed workers [4]. Copper sulphate is used widely as an algicide in ornamental ponds and even in water supply reservoirs, which are affected by blooms of blue-green alga [5]. Maximum acceptable copper concentration in drinking water is less than $3000\mu\text{g}/\text{dm}^3$ [6,7]. Cadmium is introduced into water bodies from smelting, metal plating, cadmium-nickel batteries, phosphate fertilisers, mining, pigments, stabilizers, alloy industries and sewage sludge. The harmful effects of cadmium include number of acute and chronic disorders such as, renal damage, emphysema, hypertension and testicular atrophy [8]. Hence, removal of copper and cadmium from water and wastewater assumes importance.

Various processes of heavy metals elimination are used, such as precipitation, electro precipitation, electro coagulation, cementing and separation by membrane, the solvent extraction and the exchange of ions on resins [9]. However, these processes are not economical enough for wastewater treatment. Strict environmental protection legislation and public environmental concerns lead the global search for novel and low-cost techniques to remove heavy metals from industrial wastewater [10]. So, recent research is directed to developing cost-effective technologies for the removal of metal ions from aqueous solutions. Adsorption is considered quite attractive in terms of its efficiency of removal from dilute solutions. Although, the use of common materials, activated carbon [11], chitosan [12], zeolite, clay is still very popular due to the high adsorption capacity, but there are expensive, too. Thus, there is a growing demand to find relatively efficient, low-cost and easily available adsorbents for the adsorption of cadmium and copper, particularly if the adsorbents are the wastes. The researchers were oriented towards no expensive adsorbents which are the vegetable wastes or agricultural byproduct.

Lansium domesticum cv Kokossan (family Meliaceae) is a higher tree, commonly called "kokosan" in Indonesia and widely distributed in Southeast Asian countries [13]. This plant has been reported to produce fruits and contain a bitter seed substance with antifeedant activity [14]. Previous phytochemical studies on *L. domesticum* reported the presence of tetranortriterpenoids [15-16], triterpenoid glycosides [17], onocerandione-type triterpenoids [13] and onocerandiendione-type triterpenoids [16]. These compounds have the ability to bind heavy metals by donating an electron pair to form complexes with the metal ions in solution.

In this study, the potential of *Lansium domesticum* seed waste as biosorbents for the removal of Cu(II), and Cd(II) from aqueous solutions was investigated. The influence of solution pH, contact time, biosorbent dosage, initial metal concentration and temperature on adsorption capacity was studied. The equilibrium adsorption data were fitted with Freundlich and Langmuir isotherm models. Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectrometer (FTIR) were used to understand the adsorption mechanism.

MATERIALS AND METHODS

Preparation of Solution

The biosorption experiments were conducted by using stock standard solution (1000 mg/L) of $\text{Cd}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ in 0.5 M HNO_3 . These solutions were purchased from E. Merck (Germany). Working standard solutions were prepared just before used by the appropriate dilution of the stock solutions. 0.1 mol/L HCl and NaOH were used for pH adjustment.

Preparation of Adsorbent

Lansium domesticum seeds were collected, washed with deionized water, air dried for 3 days, finally ground using a mortar and grinder (Fritsch, Germany). The powder was activated by soaking 20 g biomass in excess of 80

mL HNO₃ 0.01 M for 2 h, followed by washing thoroughly with deionized water and then air-dried. The resulting pale brown powder can be stored for a long time.

Batch Adsorption Experiments

The adsorption experiments were studied by using batch sorption experiments. All the experiments were performed at 25 °C and 200 rpm on a mechanical shaker with 0,5 g of adsorbent in 100 mL conical flask containing 10 mL of Cd (II) and Cu(II) solution. The effect of pH of the solution, contact time, biosorbent dosage, initial concentration and temperature of biosorbent were studied. After adsorption, the mixture was filtered through filter paper. The concentration of Cd (II) and Cu(II) in solution after equilibrium was determined by atomic absorption spectrophotometer (AAS).

The amount of adsorbed metal ions per gram of the biomass (biosorption capacity, Q) was obtained using the following equation:

$$Q = \frac{V(C_0 - C_e)}{m} \quad (1)$$

Where C₀ and C_e were initial and equilibrium metal ions concentration in solutions (mg/L), respectively; V was volume of the solution (L); m was the amount of biomass (g).

Desorption Studies

The desorption studies were carried out with varying concentrations of HNO₃ solution. The sorbent, which was removed from filtration, was transferred into stoppered reagent bottles. To this 10 mL of HNO₃ solution was added. The bottles were shaken at room temperature (25 °C) using a mechanical shaker with 200 rpm. The sorbent was then removed by filtration. The concentrations of copper and cadmium in the aqueous solutions were determined by AAS method.

RESULTS AND DISCUSSION

Characterization of *Lansium Domesticum* Seed

Scanning electron microscopy

The scanning electron microscopic images were used to examine the surface morphologies of langsat seed waste before and after chemical modification [19].

The images are given in Fig. 1. Initially the surface of biosorbent is smooth with uniform microporous structure which becomes rough after biosorption indicating the modification of the adsorbent.

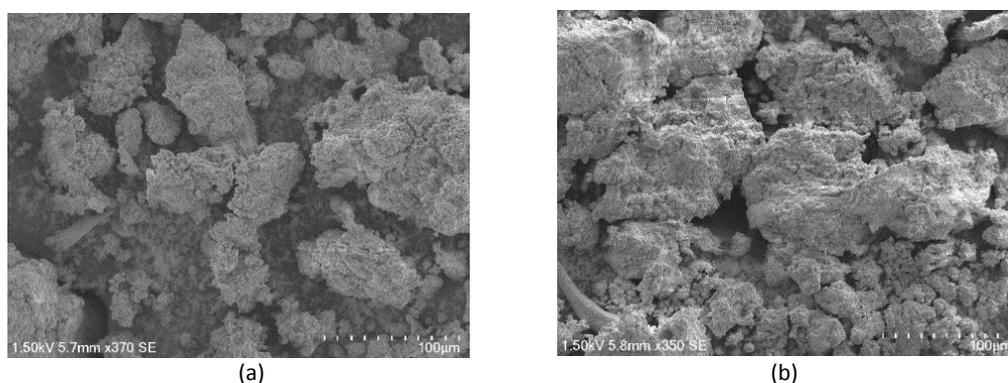


Figure 1: SEM images of Langsat seed (a) before biosorption and (b) after biosorption.

Four-transform infrared spectroscopy

FTIR analysis is important to confirm the functional groups present in the biosorbents. Furthermore, it provides information on binding mechanism and possible functional groups involved in the interaction with metal ions. The FTIR spectra of langsat seed, before and after activation and after metal ion adsorption are shown in Fig. 2, as an example. Based on Figure 2(a), a broad and strong band observed at $3390,12\text{ cm}^{-1}$ corresponds to OH group. Absorption bands at the wavenumbers of $2922,61\text{ cm}^{-1}$ can be assigned to alkyl groups. The C=O vibration can be seen at $1646,29\text{ cm}^{-1}$. Absorption bands correspond to OH groups and C=O stretches were found to shift after metal ion adsorption. For example, absorption band related to OH group shifted from $3404,80\text{ cm}^{-1}$ to $3389,93\text{ cm}^{-1}$ following interaction with Cu(II) and Cd(II), respectively. In the case of C=O vibration, the absorption band shifted from $1647,86\text{ cm}^{-1}$ to $1646,98\text{ cm}^{-1}$ after absorption of Cu(II) and Cd(II) respectively.

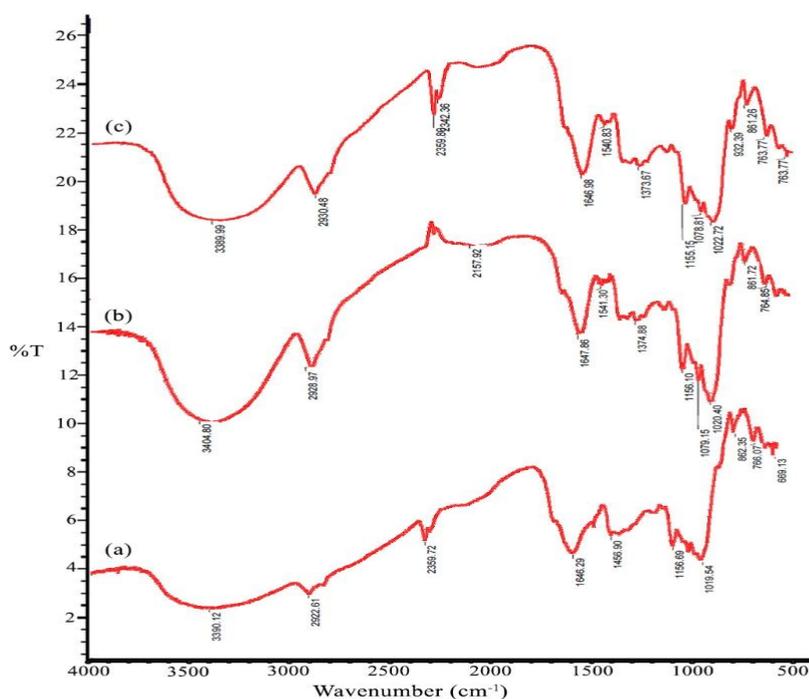


Figure 2: FTIR spectra of langsat seeds before activation (a), after activation (b) and after biosorption (c).

Interaction of langsat seeds with metal ions has also resulted in a shift in wavenumbers of functional groups. This suggests that the binding mechanisms of Cu(II) and Cd(II) to langsat seeds are rather similar. Presumably, the formation of new absorption bands, the change in absorption intensity and the shift in wavenumber of functional groups could be attributed to complexation between metal ions and binding sites of biosorbents. The binding mechanism involved electron pair sharing between electron donor atoms (O and N) and metal ion. FTIR suggests that both hydroxyl and carbonyl groups are indeed the main adsorption sites in langsat seed.

Biosorption Studies

Effect of Solution pH

The removal of metal ions from aqueous solution by adsorption is related to the pH of solution. The first set of tests, therefore, examines the effect of pH on the effluent concentration. The result is shown in Fig.3. The low biosorption capacity at pH values below 4.0 was attributed to hydrogen ions that compete with metal ions on the sorption sites. In other words, at lower pH, due to protonation of the binding sites resulting from a high concentration of protons, the negative charge intensity on the sites is reduced, resulting in the reduction or even inhibition of the binding of metal ions [21-23]. At high pH values, the removal takes place by adsorption as well as precipitation, due to formation of metals hydroxide. This can be explained by the fact that, as the pH of the solution increased the OH ions in the solution increase and form some complexes with

metal ions and precipitate as metals hydroxide [24]. At higher pH concentration of protons decreases and the surface of the adsorbent became negative which increases the adsorption of metal ions. The solubility of metal ions also decrease at higher pH facilitating the adsorption. The further increase of pH results in precipitation of metal ions as hydroxides [25].

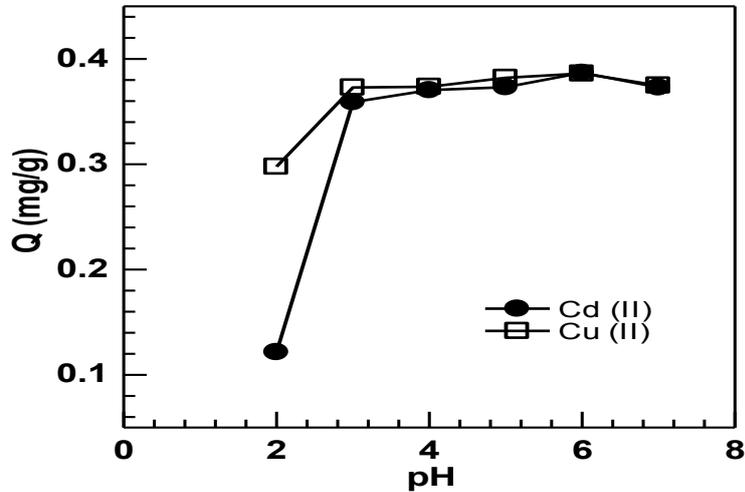


Figure 3: Effect of pH on adsorption of Cu(II) and Cd(II)

Effect of Contact Time

Adsorption kinetics is studied to evaluate the efficiency of adsorption. The effect of contact time on adsorption of Cd (II) and Cu(II) onto langsat seed is shown in Fig. 4. The plot consists of initial rapid adsorption phase and a slower phase where equilibrium uptake was achieved. The initial high rate of adsorption of metal ions is due to free active binding sites on the surface of the adsorbent. As the number of available sites decrease the rate of adsorption of metal ions also decrease [25].

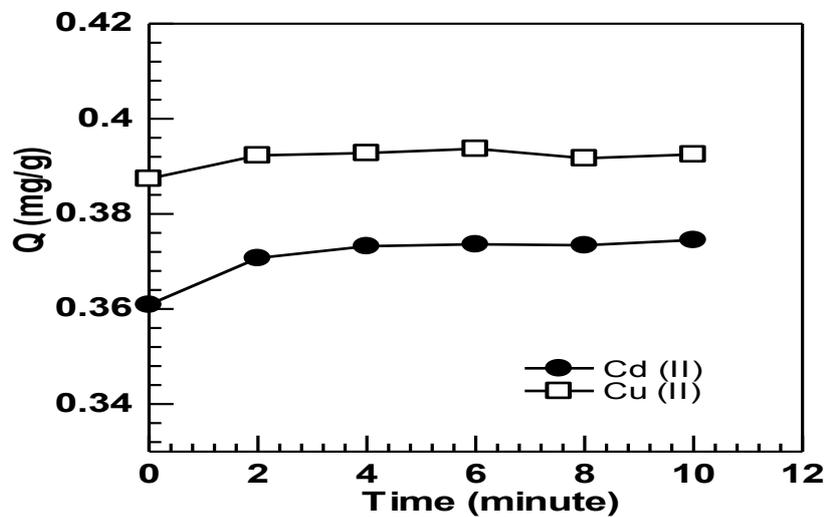


Figure 4: Effect of contact time on adsorption of Cu(II) and Cd(II)

Effect of biosorbent Dosage

The removal efficiency of metals is highly dependent on the quantity of the biosorbent. Several researches reported that the increase in the percentage removal with increase in the sorbent dosage is due to the greater availability of the exchangeable sites or surface area at higher concentration of the biosorbent [26,27]. As revealed in Fig. 5, the biosorption capacity was higher at low dose rates. However, percentage removal increased with increase in biosorbent dose. The reason for this may be the availability of lesser binding sites and these were fully utilized. At the sorbent dosage of 0.5 g , the uptake of the *lansium domesticum* was 0.3761 mg/g for Cd(II) 0.3802 mg/g for Cu(II), clearly lower than at dosage of 0.1 g (1.7459

mg/g for Cd(II) and 1.5431 mg/g for Cu(II)). Similar results were obtained when ectodermis of cactus. The decrease of q_e with increase of biomass concentration might be due to the formation of aggregates between the biomass particles at high biomass concentration, reducing the effective adsorption area [28].

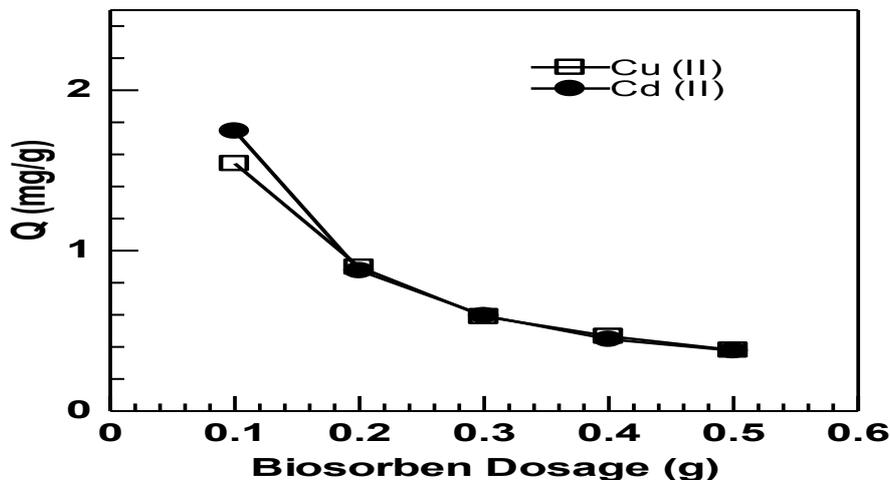


Figure 5: Effect of biosorben dosage on adsorption of Cu(II) and Cd(II)

Effect of initial concentration

Fig. 6 shows that at the constant pH, increasing the initial concentration of Cd and Cu ion solutions from 20-120 mg/L increased the sorption amount of Cd and Cu ions by sorbents. It can be observed that for langsat seeds, the adsorption of Cd (II) and Cu(II) increases linearly with the increase of Cd(II) and Cu(II) concentrations and showing saturation behaviour after 120 mg/L. Considering these results and the Langmuir values could be asserted that Cd(II) and Cu(II) removal was a chemical mechanism. The reduction in the amount adsorbed as affected by modification means that the mercerization may blocks some of the micro-pores making it difficult for the metal ions uptake [29].

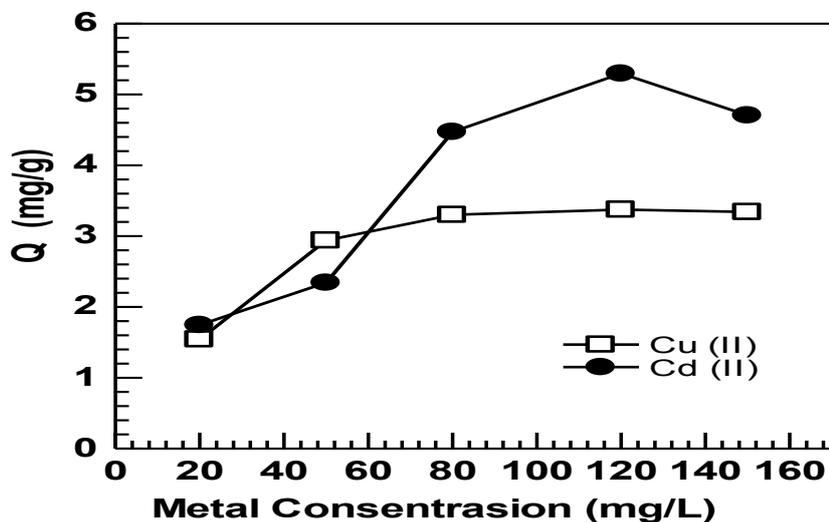


Figure 6: Effect of initial concentration on adsorption of Cu(II) and Cd(II)

Effect of temperature

Fig. 7 show that increasing temperature until 40 °C increased the sorption amount of Cd and Cu ions by sorbents. The high rate of adsorption of metal ions is due to decreasing water in biosorben and the greater availability of the exchangeable sites or surface area at 40 °C. At high temperature, the sorption amount of Cd(II) and Cu(II) decrease. The reason for this may be because the damage in active binding site on the surface when instillation.

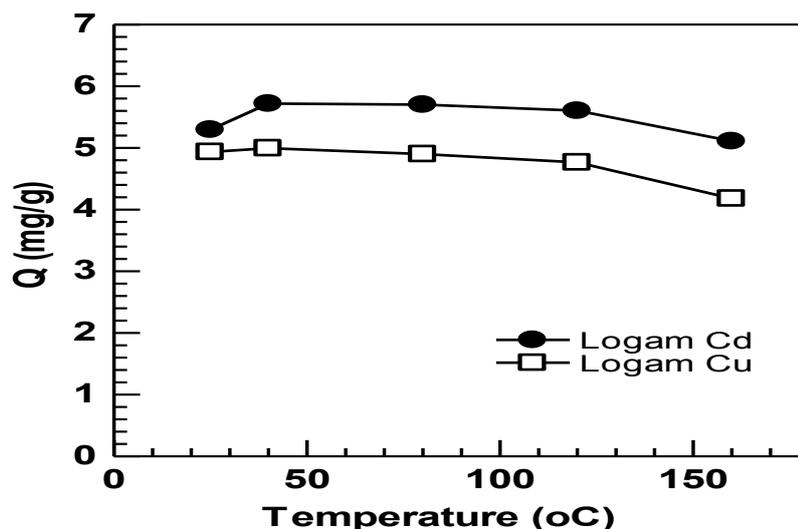


Figure 7: Effect of temperature of biosorbent on adsorption of Cu(II) and Cd(II)

Desorption Study

Desorption studies of Cd^{2+} and Cu^{2+} ions were conducted to avoid the disposal of metal contaminated solid waste and to explore the possibility of reusage of langsat seeds as well as the recovery of the Cd^{2+} and Cu^{2+} ions. HNO_3 as chemical desorbent was chosen to eliminate the high cost of energy usage during thermal desorption. The total desorption for Cd^{2+} metal ions was 47.47% for Cd(II) and 81.67% for Cu(II). The acid solution of 0.1 M HNO_3 has a pH of 1, which allows the Cd^{2+} and Cu^{2+} ions unattached from the surface ligands by the existence of hydrogen ions. The reduction of Cd^{2+} and Cu^{2+} ions uptake by the reduction of pH also proved the phenomena (Fig. 8). The 47.47% of Cd^{2+} and 81.67% of Cu^{2+} ions retained in the langsat seeds was again performed, using the desorption process, several times, to measure the reusability of langsat seeds. The stronger acid solution or using of a complexing agent such as tartaric acid, ethylene diamine, and EDTA should be more effective on the removing and recovery of the Cd^{2+} and Cu^{2+} ions from the used langsat seeds [21].

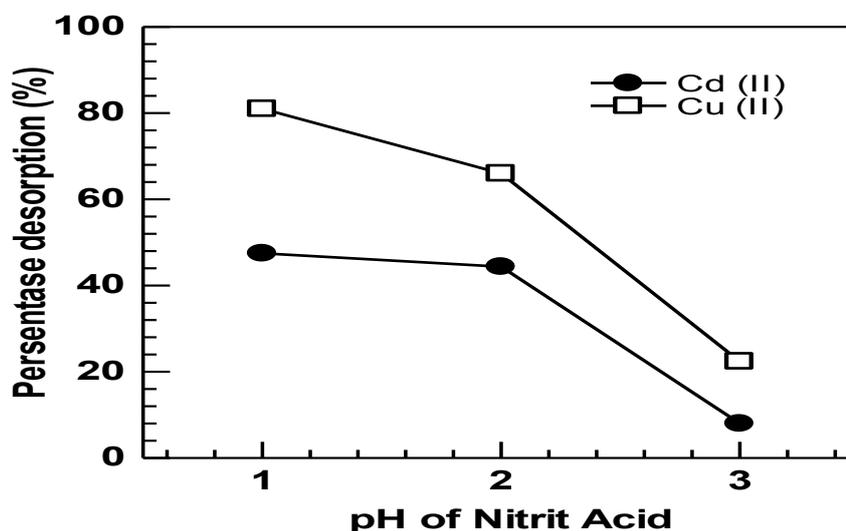


Figure 8: Desorption of biosorbent

Adsorption Isotherm Studies

The Langmuir isotherm model is expressed as [30]:

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

where q = mass of solutes adsorbed per mass of adsorbent, c = concentration of adsorbate in solution in equilibrium with the adsorbate adsorbed, qm and b are constants which are related to sorption capacity and energy of sorben, obtained by plotting c/q against c . The slope is $1/qm$ while the intercept is $1/qm \cdot b$. Fig. 9 show the Langmuir isotherm plots for the adsorption of Cd(II) and Cu(II) using langsat seeds. The Freundlich isotherm model is given by the following equation:

$$q_e = K_f C_e^{1/n}$$

where K_f and n are constants. The linearised form of this equation becomes:

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

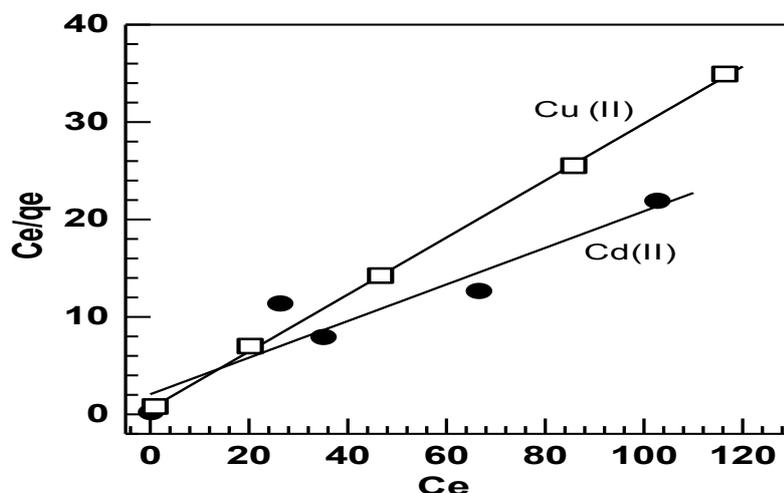


Figure 9: Plot of Langmuir isotherm for Cd(II) and Cu(II) adsorption with lngsat seeds.

By plotting $\log q$ versus $\log C_e$, the constants K_f and n are obtained. The slope $a = 1/n$ while the vertical axis intercept $b = \log K_f$, therefore $n = 1/a$ and $K_f = e^b$. The plot of $\log q$ versus $\log c$ are given in Fig. 10 for the adsorption of Cd(II) and Cu(II) using langsat seed. Table 1 shows the comparison between the Langmuir and Freundlich regression coefficients. It was observed that the experimental data fitted the Langmuir isotherm model best. The model Freundlich was far from unity while the Langmuir isotherm model was closer to unity [11].

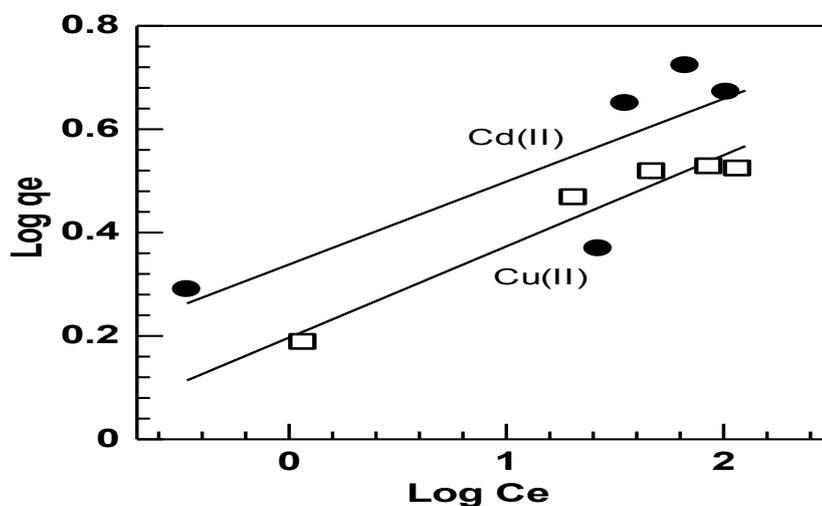


Figure 10: Plot of Freundlich isotherm for Cd(II) and Cu(II) adsorption with langsat seeds.

Table 1: A Comparison of the Langmuir and Freundlich Regression Coefficients

Metal	Langmuir Isoterm			Freundlich Isoterm		
	q max (mg/g)	b(L/mg)	R ²	K _F	n	R ²
Cd(II)	5,3220	0,0911	0,891	2,1792	6,2383	0,6613
Cu(II)	3,4176	0,4349	0,9996	1,5736	5,6657	0,9500

CONCLUSIONS

The study indicated that langsat seeds (*Lansium domesticum* Corr) could be used as an effective adsorbent material for the treatment of copper and cadmium-bearing aqueous wastewater. The adsorption of copper and cadmium on langsat seeds is found to be time, concentration, pH, dose, and temperature dependent. The results evidence the capacity of langsat seeds for Cd(II) and Cu(II) metal ions adsorption, with a maximum monolayer adsorption capacity of 5,7186 mg/g for Cd(II) and 4,9950 for Cu(II). The monolayer adsorption capacity (qm) of langsat seeds is comparable to the capacities of other reported agricultural-based adsorbents. The material (*Lansium domesticum* Corr) under consideration is not only economical, but also an agricultural waste product. Hence langsat seeds would be useful for the economic treatment of wastewater containing copper and cadmium metals.

REFERENCES

- [1] D Kratochvil and B Volesky. Trends Biotechnol 1998;16(7):291-300.
- [2] A Babarinde, JO Babalola, J Adegokeetal. J Chem 2013, Article ID 460635.
- [3] HJM Bowen. The Environmental Chemistry of the Elements, Academic Press, London, 1979.
- [4] B Yu, Y Zhang, A Shukla, SS Shukla, KL Dorris. J Hazard Mater 2000;80:33.
- [5] M Doula, A Ioannou, A Dimirkou. Adsorption 2000;6:325.
- [6] SE Manahan. Environmental Chemistry, fifth ed., Lewis, Chelsea, MI, 1991.
- [7] L Murley. Pollution Hand Book, National Society for Clean Air and Environmental Protection, Brighton, 1992
- [8] RL Ramos. Water Sci Technol 1997;35:205.
- [9] Babel S, Kurniawan TA. J Hazard Mater 2003;97:219-243.
- [10] Bailey SE, Olin TJ, Brick RM, Adrian DD. Water Res 1999;33:2469-2479.
- [11] Ijeoma A Chukwu & Elijah T Iyagba. Global Journal of Researches in Engineering Chemical Engineering, 2012;12(3).
- [12] Kyzas GZ, Kostoglou M, Lazaridis NK. Chem Eng J 2009;152:440-448.
- [13] Omar S, et al. J Stored Prod Res 2007;43:92-96.
- [14] Champagne DE, et al. Phytochem 1992;31:377-394.
- [15] Saewan N, Sutherland, JD, Chantrapromma K. Phytochem 2006;67:2288-2293.
- [16] Nishizawa M, Nademoto Y, Sastrapradja S, Shiro M, Hayashi Y. J Org Chem 1985;50:5487-5490.
- [17] Nishizawa M, Nishide H, Hayashi Y. Tetrahedron Lett 1982;23:1349-1350.
- [18] S Glasstone, Text Book of Physical Chemistry, second ed., Macmillan, India, 1981
- [19] Sankaramakrishnan N, and R Sanghi. Carbohy Poly 2006;66:160-167.
- [20] Shriner RL, CKF Hermann, TC Morill, DY Curtin and RC Fuson. The systematic identification of organic compounds. Seventh ed. Wiley, New York. 1998
- [21] Masita MZ, Yaakob DKK. Materials 2013;6:4462-4478.
- [22] M Ali I Al-Hashimi, Manar M Al-Safar. Acta Technica Corviniensis-Bulletin of Engineering.2012
- [23] S Najiah Mohd Yusoff, A Kamari. J Environ Prot 2014;5:289-300.
- [24] Al-Najar JAA. Removal of heavy metals by adsorption using activated carbon and kaolinite, Ph.D. Thesis, University of Technology. 2009
- [25] B Shrestha, P. Homagai MR Pokhrel and KN Ghimire. Nepal J Sci Technol 2012;13(2):109-114.
- [26] Y Gonz'alez Berm'udez, et al. Chem Eng J 2012;183:68-76.
- [27] SR Popuri, A Jammala, KVNS Reddy, and K Abburi. *Electronic J Biotechnol* 2007;3358-367.
- [28] Jose A. Fernandez, M. Angosto, dkk. Biosorption of hexavalent chromium from aqueous medium with opuntia biomass. Hindawi Publishing Corporation, 2014
- [29] ST Song, N Saman, K Johari and HB Mat. Jurnal Teknologi 2013.
- [30] Henderson A.P, Seetohul LN, Dean AK, Russell P, Pruneanu S., Ali Z, Langmuir 2009;25(2):931 -938.