Alkali Lignin from Talahib Grass (*Saccharum spontaneum L.*) as An Adsorbent for Chromium (III) and Phenolphthalein: Analysis of the Adsorption Kinetics and Mechanism

Kevinilo P. Marquez* and Rufus Mart Caesar R. Ramos

Institute of Chemistry, University of the Philippines Los Baños, Brgy. Batong Malake, Los Baños, Laguna 4031

ABSTRACT

The study aims to quantitatively assess the capability of lignin extracted from *Saccharum spontaneum* L. (talahib grass) as an adsorbent of chromium (III) and phenolphthalein in aqueous solution through kinetic methods. Results show that using lignin as an adsorbent, the percentage removal for both chromium (III) and phenolphthalein in aqueous solution are 31.70% and 74.98%, respectively, based on the optimum exposure time of the adsorbent, which is 6.5 hours for chromium (III) and 60 minutes for phenolphthalein. Results from the mechanistic analysis show that a pseudo-second order adsorption kinetic model fits better than a pseudo-first order model for both substrates. Also, among the six selected adsorption isotherm models used in this study, the Flory-Huggins isotherm can best predict the properties of the adsorption process of both phenolphthalein and chromium (III) at equilibrium. Further improvement of the extracted lignin through various physical and chemical modifications may improve its ability to remove the contaminants.

Keywords: Adsorption, Lignin, Adsorption Isotherms, Adsorption Kinetics

*Author to whom correspondence should be addressed; email: kgperez3@up.edu.ph

INTRODUCTION

Wastewater Pollution. Water pollution is a threat facing freshwater reserves available for consumption by organisms. Wastewater produced from anthropogenic processes usually seep to the freshwater sources making it hazardous. The Philippines' surface waters face the same threat on its aquatic biota. As an example, river systems in Meycauayan, Bocaue, and Marilao in Bulacan had high concentrations of chromium, lead, and cadmium coming from tanneries and electroplating industries (Greenpeace, 2007). With the growing economy of the Philippines, high demand of such products lead to the increase of manufacture rate, which then increases the volume of hazardous wastewater. Hazardous wastes produced by companies and communities are seldom treated due to lack of proper waste management facility in the country and is usually stored offsite or just diluted using a large body of water (Greenpeace, 2007). Minimizing the concentration of toxic substances (heavy metals, organic effluents, agricultural by-products, inorganic acids) in wastewater and freshwater sources is a crucial step to prevent destruction of the aquatic ecosystem. Common techniques employed to reduce concentration of heavy metals and organic effluents include chemical precipitation, membrane filtration, ion exchange, and adsorption on activated carbon. New treatment methods are currently being developed to reduce the high operational cost of the aforementioned procedures. These methods include adsorption on waste slurry, fly ash, lignite, pine bark, peat, and lignin (Guo, Zhang, & Shan, 2008; Carrott & Carrott, 2007).

Since the abovementioned industries produce large amounts of heavy metal and dye-contaminated wastes, there needs to be a remediation process where the necessary materials are easily sourced, environmentally sustainable, and can significantly reduce the concentration of contaminants. The key for development of more efficient adsorption methods is to generate an adsorbing material with the abovementioned characteristics for desirable results.

Lignin and Its Potential as an Adsorbent for Heavy Metals and Dye in Wastewater. Lignin is the second most abundant natural polymer in the world after cellulose; it is usually concentrated in the middle lamella of the plant and bound with cellulose and hemicellulose. Usually, lignin is deposited in cell walls of specialized plant cells, which undergo secondary cell wall biosynthesis (Chen, 2014; Li, 2011). A complex heteropolymer, lignin is composed of three monomeric units, *p*-coumaryl alcohol, sinapyl alcohol, and coniferyl alcohol, which vary in degree of methoxylation at the *–ortho, –meta,* and *–para* positions. The different monomeric structures and their possible linkages are shown in Figure 1.

Currently, the most popular method for utilizing lignin is its conversion to activated carbon, which is then used for various inorganic and organic decontamination processes in aqueous solution, due to its high performance as an adsorbent (Babel and Kurniawan, 2004). Lignin is an organic material made up of various several phenylpropane monomers, forming a complex, rigid structure (Brebu & Vasile, 2010). The structure of lignin is very specific to the species, which means that different species have different relative compositions of the different phenylpropane monomers.
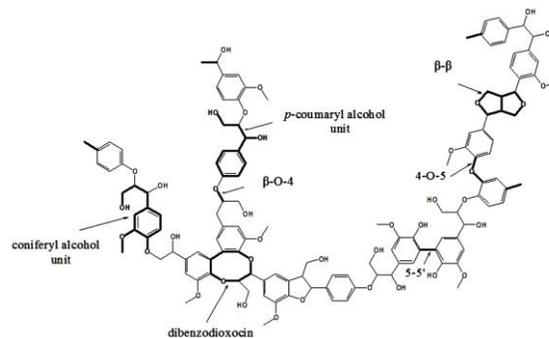
Figure 1. Representative Structure of the Softwood Lignin, with the linkages and

building units Highlighted for emphasis (from Chen, 2015)

Currently, the most popular method for utilizing lignin is its conversion to activated carbon, which is then used for various inorganic and organic decontamination processes in aqueous solution, due to its high performance as an adsorbent (Babel and Kurniawan, 2004). Lignin is an organic material made up of various several phenylpropane monomers, forming a complex, rigid structure (Brebu & Vasile, 2010). The structure of lignin is very specific to the species, which means that different species have different relative compositions of the different phenylpropane monomers.

Lignin as an adsorbent was studied as an alternative for activated carbon and other wastewater treatments, which have high operational cost (Guo, Zhang, & Shan, 2008). Guo, Zhang, & Shan, 2008, studied the adsorptivity of metal ions (Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+}) on lignin. Lignin has affinity with the metal ions on the following order: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+}$, with metal ion adsorptivity strongly dependent in pH and ionic strength. Phenolic sites of lignin were found to have high affinity to the metal ions. Further studies on metal adsorption on lignin had results indicating high sorption capacity of lignin on metal ions trough ion-exchange mechanism as proven by kinetics studies (Basso, Cerrella, & Cukierman, 2002), (Celik & Demirbas, 2005), and (Christ, Martin, & Christ, 2002). Other adsorptivity studies like adsorption of dyes and metal ions on chitosan-lignin (Nair, Panigrahy, & Vinu, 2014) and pesticide adsorption on lignin (Van Beinum, Beulke, & Brown, 2006) indicate lignin has high sorption capacity even with non-metal species.

The aim of this study is to determine the adsorption properties of lignin towards chromium (III) and phenolphthalein through: (1) determination of the optimum removal percentage of both substrates in aqueous solution, and (2) determination of the mechanism of adsorption through model fitting of the time-dependent adsorption data with selected adsorption isotherms.

EXPERIMENTAL

Materials and Equipment. All reagents purchased from Scharlab Chemicals (Philippines) and were used without further purification. For the analysis equipment, the UV-Visible Spectrophotometer used was a Shimadzu UV-mini 1240 Single beam, while the Atomic Absorption Spectrophotometer was a Varian SpectrAA 55D graphite furnace with a Chromium hollow cathode lamp. Both analyses were performed in the Analytical Services Laboratory, Institute of Chemistry, UPLB. The Saccharum spontaneum L. (Talahib Grass) was collected from Sta. Teresa, Iguig, Cagayan, Philippines. Chromium (III) nitrate was provided by the Institute of Chemistry, UPLB.

Sample Preparation. Ground air-dried stem of Saccharum spontaneum L (Talahib Grass) was sieved through a 0.5 mm screen. The resulting powder was extracted using a cyclohexane-methanol solution (2:1 v:v), in a Soxhlet extraction set-up for 8 hours. The solvent-free sample was then air-dried.

Extraction and Characterization of Alkali Lignin. Three grams of the talahib sample was refluxed in 60.0 mL of 3.53M NaOH solution for 90 minutes. The mixture was allowed to cool for 30 minutes before filtration. The lignin was precipitated in the filtrate with concentrated hydrochloric acid (until pH 2). The mixture after precipitation was heated for 40 minutes at 76°C. The coagulated solid (raw lignin) was recovered through filtration, where it was purified by washing with 15 mL of 10 % NaCl solution, 70% ethanol, and water. The procedure is repeated until the necessary amount of extract is produced.

Isolated lignin was characterized through UV-Vis spectrophotometry with 1.0 M of NaOH solution as the solvent (Xu, et al., 2005). A broad but prominent peak at 282 nm confirms the presence of lignin in the product. Absence of other peaks in the 220-600 nm range ensures purity of the extracted lignin.

Chromium (III) and Phenolphthalein Adsorption. This is a modified procedure of Guo, Zhang, & Shan, 2008 and Nair, Panigrahy, & Vinu, 2014. Isolated alkali -lignin will be used for adsorption.
Ten portions of 250 mg alkali-lignin were weighed. Each portion was then added to ten 25-mL aliquots of 6.0 ppm Chromium (III) nitrate. The resulting solutions were stirred for varying hours (1.0 hour to 10.0 hours, with a 1-hour interval), where the resulting mixtures are filtered. The filtrates were analyzed for chromium using atomic absorption spectroscopy (AAS). The initial and final concentrations of chromium in the samples were determined based on a standard curve.

The same portions of lignin were each added to ten 50-mL aliquots containing 10 mg/L phenolphthalein. The resulting solutions were stirred at varying times (15-150 minutes, with 15 minutes variation). The resulting mixtures were then filtered and adjusted to pH 10 by gradually adding 0.1 M NaOH solution. The alkaline filtrates were then analyzed for phenolphthalein concentration using a UV-Visible spectrophotometer. The initial and final concentrations of phenolphthalein in the samples were determined based on a standard curve.

For both substrates, the adsorption rate kinetics were analyzed using both the pseudo-first order and pseudo-second order analysis, while the properties of adsorption at equilibrium were analyzed through model-fitting using the Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Breunner-Emmett-Teller (BET), Flory-Huggins, and Temkin isotherms.

RESULTS AND DISCUSSION

Extraction and Characterization of Alkali Lignin. The extractions were done in duplicates per day, for a total of 3 days to check for the repeatability of the experimental runs. One-way analysis of variance was employed in the procedure. The ANOVA showed that at 95% confidence level the mean response of 15.19% is within interval limits. Therefore, there is no significant difference between the yields of each daily experiment at 95% confidence level.

The 15.19% yield is also found to be the maximum yield within the range of the

**Table 1.** One-Way ANOVA for the per-day analysis of duplicates.

Groups	Trials	Sum	Average	Variance
Day 1	2	29.7673	14.8837	0.15064
Day 2	2	30.0965	15.0482	0.00011
Day 3	2	31.277	15.6385	0.09412

Variation	SS	df	MS	F	P-value	$F_{critical}$
Between Groups	0.63021	2	0.31511			
Within Group	0.24486	3	0.08162	0.86061	**0.14802**	**9.55209**
Total	0.87508	3				

conditions of the experiment. The process was optimized considering the analysis cost, extraction time, and the equipment requirements.

The isolated lignin was analyzed through UV-Vis spectrophotometry. Low, mid, and high concentrations of lignin, prepared under basic medium (0.1M NaOH) were prepared for the analysis. Although the wavelength of maximum absorbance is near 220 nm (cellulosic peak), the peak involving the phenolic groups present in the lignin-matrix is near 280 nm. Using the method of Tian, et al. (2015), the considered wavelength of maximum absorbance for the isolated lignin is 282 nm.
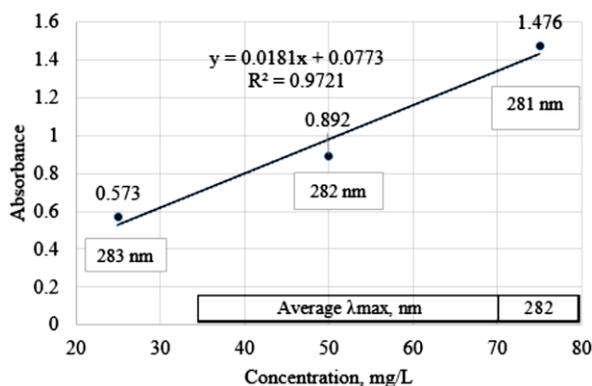
Figure 2. Lignin Concentration versus Absorbance (25, 50, and 75 mg/L)

It is theorized that some of the proteins present in lignin matrix may be responsible for the coagulation of the precipitated lignin, causing other peaks. Ethanol extraction removes these proteins from the lignin structure, thus increasing the purity of the extract.

Effect of Contact Time and the Mechanism of Adsorption. The isolated alkali-lignin was used for the adsorption of phenolphthalein dye and chromium (III) ion. In which, to study the adsorption kinetics of the dye and metal ion, the effect of contact time on the

adsorption was regressed through a linearized pseudo-first order (Equation 1) and pseudo-second order (Equation 2) kinetic equations (Do, 1998).

$$\log(q_{eq} - q_t) = (q_{eq}) - \frac{K_{pf}t}{2{,}303} \qquad (1)$$

Where q_{eq} (mg/g) is the adsorbate uptake per gram of lignin at equilibrium, q_t (mg/g) is the adsorbate uptake per gram of lignin at a certain time, K_{pf} (min^{-1}) is the rate constant of the pseudo-first order rate equation (Lagergren equation) and t (min) is the contact time for the adsorption.

$$\frac{1}{q_t} = \frac{q_{eq}^2}{K_{ps}} - \frac{t}{q_{eq}} \qquad (2)$$

Where K_{ps} (g/mol*min) is the rate constant of the second-order adsorption.

The plot of the effect of contact time on the adsorption process shows the time where equilibrium is achieved (maximum value) and how fast can the removal happen (Bulut & Aydin, 2006). The following plots illustrate the effect of the contact time on the adsorption process.
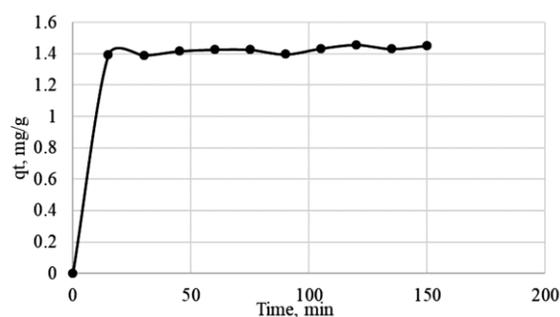
Figure 3. Effect of Contact Time on the Adsorption of Phenolphthalein on Lignin

It is observed in Figure 3 that phenolphthalein adsorbs readily into the lignin even at low contact time for the adsorption process. The equilibrium was

achieved at around 60 minutes, wherein the experimental q_e is 1.46 mg per gram lignin.
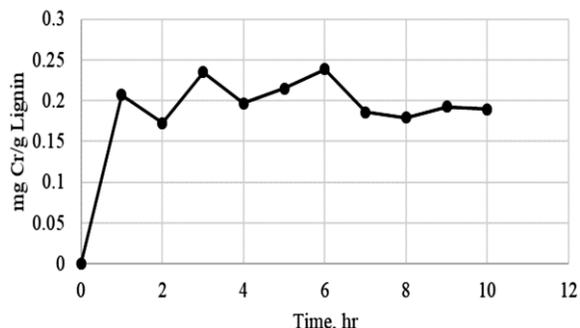
Figure 4. Effect of Contact Time on the Adsorption of Chromium (III) on Lignin

Contrary to that of the phenolphthalein, the adsorption of chromium (III) ion lignin needed 6.5 hours to attain its equilibrium. The experimental q_e is equal to 0.18 mg per gram lignin.

Kinetic analysis of adsorption of phenolphthalein on lignin shows that it follows a second-order rate equation, where the calculated coefficient of determination of the second-order analysis is 0.9994, as compared to 0.5006 for the first-order analysis. The positive value of the reaction rate implies that the adsorption of the phenolphthalein in lignin is favorable. This explains the high removal rate of the substrate in aqueous solution, as well as the low required contact time.

The adsorption of chromium (III) ion follows the second-order rate equation as well (coefficient of determination of second-order 0.9701 is greater than the first-order coefficient of determination value of 0.0018). Table 3 shows the regression data for the kinetic analysis for chromium (III).

It is important to note that even though the mechanism is a pseudo-second order, the calculated reaction rate is negative. This implies that the formation/interaction of the substrate to the adsorbent is unfavorable, which explains the low percentage removal of chromium and its longer required contact time. This could also imply that too much contact time will result in the desorption of the chromium substrate from the lignin, causing it to re-dissolve into the aqueous medium.

Determination of the Adsorption Isotherm. Adsorption Isotherms are models that help predict the concentration of the free and adsorbed substrates at equilibrium. If

Table 2. Analysis of the Kinetics of Phenolphthalein Adsorption on Lignin.

Parameter	Pseudo-First Order Analysis	Pseudo-Second Order Analysis
Slope	-0.006288	0.6864
Intercept	-1.016	0.9835
q_{eq}	0.09643	1.457
Equilibrium Constant	0.01448 K_{pf} (min^{-1})	0.4790 K_{ps} (g mg^{-1} min^{-1})
Coefficient of Determination	0.5006	0.9994
Percentage Removal	74.98	
Optimum Contact time	60.0 min	

Table 3. Analysis of the Kinetics of Chromium (III) Adsorption on Lignin.

Parameter	Pseudo-First Order Analysis	Pseudo-Second Order Analysis
Slope	-0.005581	5.491
Intercept	-1.3626	-2.409
q_{eq}	0.04339	0.1821
Equilibrium Constant	(K_{pf}) 0.01285 hr^{-1}	(K_{ps}): -12.51 g mg^{-1} hr^{-1}
Coefficient of Determination	0.001829	0.9701
Percent Removal	31.70%	
Optimum Contact time	6.50 h	

Table 4. Summary of the Adsorption Isotherms Employed in the Study.

Isotherm	Equation (3 – 8)	Terms
		C_e = equilibrium substrate concentration
Langmuir (Equation 3)	$\dfrac{C_e}{q_{eq}} = \dfrac{1}{bQ_m} + \dfrac{C_e}{Q_m}$	b = Langmuir constant (binding affinity)
		Q_m = limiting adsorption capacity
Freundlich (Equation 4)	$\log(q_{eq}) = \log(K_f) + \dfrac{\log(C_e)}{n}$	K_f = Freundlich Constant (adsorbent capacity)
		1/n = adsorption intensity (0 < 1/n < 1)
Dubinin-Radushkevic (DR) (Equation 5)	$q_{eq} = \ln(X_f') - K'e^2$	X_m' = adsorption capacity
		e = Polanyi Potential, e = RT ln(1 + 1/C_e)
		K' = DR constant
		q_s = adsorption capacity
Breuner-Emett-Teller (BET) (Equation 6)	$\dfrac{C_e}{q_{eq}(C_s - C_e)} = \dfrac{1}{C_{BET}q_s} + \dfrac{C_{BET}-1}{C_{BET}q_s}\dfrac{C_e}{C_s}$	C_s = substrate saturation concentration
		C_{BET} = BET constant
		θ = degree of surface coverage
Flory-Huggins (FH) (Equation 7)	$\log\left(\dfrac{\theta}{C_o}\right) = \log(K_{FH}) + m\log(1-\theta)$	K_{FH} = FH constant
		m = slope
		A_T = Temkin binding constant
Temkin (Equation 8)	$q_{eq} = B\ln(A_t) + \dfrac{RT}{b}\ln C_e$	b = adsorption constant
		B = a constant related to heat of adsorption

applicable, one or more of these models could predict the stability and thermodynamic

favorability of the adsorption process itself. Table 4 shows the various isotherms used in this study.

For the adsorption of phenolphthalein and chromium on lignin using Langmuir analysis, the coefficient of determination is equal to 0.9919 and 0.9913. To check the favorability of the isotherm a dimensionless separation factor, RL can be used (Bulut & Aydin, 2006).

$$R_L = \frac{1}{1 + bC_0} \qquad (9)$$

The calculated separation factors for the adsorption of phenolphthalein and chromium (III) ion on lignin are -0.1249 and 1.0133, respectively. An R_L value between 0 and 1 is favorable; otherwise, the model cannot be used to predict the adsorption process, which is the case for both substrates.

Using the Freundlich model, the calculated coefficients of determination for the adsorption of phenolphthalein and chromium (III) are 0.9298 and 0.9950 respectively, while the calculated values of (1/n) are -2.04, and -0.56, respectively. Both (1/n) values are beyond the applicable range of the model,

thus, the Freundlich model cannot be used to predict the adsorption equilibrium.

Using the D-R model, the coefficients of determination for the analysis of both phenolphthalein and chromium (III) adsorptions are 0.9271 and 0.9971 respectively. In the model equation, the Polanyi potential e is related to mean adsorption energy, E (J/mol) by the equation:

$$E = \sqrt{2e} \qquad (10)$$

The mean adsorption energy provides pertinent information regarding the adsorption process (Argun, Dursun, Ozdemir, & Karatas, 2005). Values less than 8.00 kJ/mol suggest a *physiosorptive* mechanism, while values greater than 16.00 kJ/mol suggest a *particle diffusion* mechanism. However, adsorption energy values between 8.00 kJ/mol and 16.00 kJ/mol suggest a *chemisorptive* mechanism.

The calculated adsorption capacity for phenolphthalein and chromium (III) are 2.26 mg/g lignin and 1.18 mg/g lignin, respectively, suggesting a *physiosorptive* mechanism for both substrates. The calculated mean adsorption energy values are 3748.58 J/mol and 2047.21 J/mol. The larger

percentage removal of phenolphthalein in the system can also be explained by its larger

Table 5. Coefficients of Variation for both Phenolphthalein and Chromium (III) Adsorption on Lignin based on the Selected Equilibrium Isotherm Models.

Isotherm	Phenolphthalein	Chromium (III)
Langmuir	0.9919*	0.9913*
Freundlich	0.9298*	0.9949*
DR	0.9271	0.9971*
BET	0.9971	0.8327
FH	0.9997	0.9994
Temkin	0.9299	0.9997

*models deemed not valid based on the values of their other parameters

adsorption capacity according to the DR isotherm, which is about 1.92 times greater than that of chromium (III). Note that the removal of phenolphthalein is also greater by about 2.37 times that of chromium (III).

From the BET isotherm, the calculated coefficients of determination are 0.9971 and 0.8327 for phenolphthalein and chromium (III), respectively. The low coefficient for chromium (III) means the BET model is not a satisfactory model for its adsorption process on lignin.

From the FH isotherm, the calculated coefficients of determination are 0.9997 and 0.9994 for phenolphthalein and chromium (III), respectively. The K_{FH} values for phenolphthalein and chromium (III) are 1.072 and 1.030, respectively, which suggest that both substrates adsorb on lignin spontaneously at 298.15K.

Finally, from the Temkin isotherm, the calculated coefficients of determination for phenolphthalein and chromium (III) are 0.9299 and 0.9997, respectively. The value of B for a Temkin isotherm is related to its enthalpy of adsorption (Nechifor, Pascu, Traistaru, & Albu, 2015). If value of B is negative, then the process is exothermic, but endothermic if the value is positive. The calculated values of B for both phenolphthalein and chromium (III) are -0.70 J/mol and -0.37 J/mol. Thus, for both substrates, the process is exothermic.

In conclusion, only the BET, FH, and Temkin models can be used to predict the adsorption characteristics of chromium (III) and phenolphthalein. Among the 3 applicable models, the Flory-Huggins isotherm shows the strongest linear correlation, and thus best describes the adsorption characteristics of both substrates.

The suitability of the FH isotherm is due to its ability to account for the presence of solvent particles in the system. In the FH model, the substrate substitutes the solvent molecules surrounding the lignin adsorbent, as shown by the equilibrium reaction below:

lignin(solvent) + substrate
$\rightleftharpoons$
lignin (substrate) + solvent
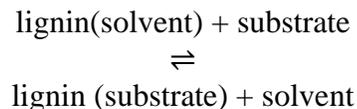
Based on the K_{FH} values, the displacement of the solvent particles by the substrates is slightly more favored than the displacement of the substrates by the solvent particles in the system.

The adsorption process is more effective for phenolphthalein since their structures are more similar compared to that of chromium (III). The aromatic structures in the lignin adsorbent is similar to that of phenolphthalein, which could cause a more stable interaction due to the ring current which is known for aromatic compounds. Chromium (III), on the other hand, contains a

strong positive charge, which would repel other incoming substrates once it adsorbs in the lignin surface, which explains the lower percentage removal.

CONCLUSIONS

Lignin was extracted from *Saccharum spontaneum* L. using the alkaline method. It was found that the yield of the extraction is consistent at an average of 15.19% by mass, which is within the range of the conditions of the experiment.

Quantitative assessment of the adsorption capabilities of lignin towards chromium (III) and phenolphthalein was achieved through (1) determination of the optimum percentage removal of chromium (III) and phenolphthalein in the prepared aqueous

solutions, and (2) determination of the kinetics of the adsorption process through model-fitting with selected adsorption isotherms based on the time-dependent adsorption data.

The adsorption mechanism of lignin towards phenolphthalein and chromium (III) was assessed through the pseudo-first order and the pseudo-second order analyses. The latter showed more satisfactory results based on the comparisons on the values of the coefficients of determination. However, the results for chromium (III) indicate that the adsorption is unfavorable, which explains the lower percentage removal and higher contact time (31.70% and 6.5 hours, respectively) compared to that of phenolphthalein (74.98% and 60 minutes, respectively).

In the determination of the appropriate adsorption isotherm, it was found that the Flory-Huggins isotherm model best describes the equilibrium adsorption of both substrates, based on the comparison of the coefficients of determination (Table 5). Results from the FH analysis also show that the K_{FH} values for phenolphthalein and chromium (III) are 1.072 and 1.030, respectively, which suggests a spontaneous mechanism of adsorption for both substrates.

It is recommended that alternative methods of extraction be done to determine the effect of the differences in the lignin structure to its capability as an adsorbent. Also, it is recommended to study the adsorption characteristics of substrates other than phenolphthalein and chromium (III).

REFERENCES

Busman L, Lamb J, Randall G, Rehm G, Schmitt M. Nutrient Management: The nature of phosphorus in soils. Regents of the University of Minnesota, 2002. http://www.extension.umn.edu/distribution/cropsystems/dc695.html

Chien SH, Clayton WR. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. Soil Sci Soc Am J. 1980 Mar; 44(2):265-268. https://doi.org/10.2136/sssaj1980.03615995004400020013x

Kitson RE, Mellon MG. Colorimetric determination of phosphorus as molybdivanadophosphoric acid. Ind Eng Chem Anal Ed. 1944 Jun; 16(6):379-383. https://doi.org/10.1021/i560130a017

Mukhopadhyay SS. Nanotechnology in agriculture: prospects and constraints. Invited Review. Nanotechnol Sci Appl. 2014 Aug; 4(7):63-71. doi: 10.2147/NSA.S39409\

Mckenzie R. Crop nutrition and fertilizer requirements. Lethbridge:Alberta Agriculture Food and Rural Development; 1998.

Rosbero TMS, Camacho DH. Green preparation and characterization of tentacle-like silver/copper nanoparticles for catalytic degradation of toxic chlorpyrifos in water. J Environ Chem Eng. 2017 Jun; 5(3):2524-2532. https://doi.org/10.1016/j.jece.2017.05.009

Shariatmadari H, Shirvani M, Jafari A. Phosphorus release kinetics and availability in calcareous soils of selected arid and semiarid topo sequences. Geoderma. 2006 Jun; 132(3–4):261–272. https://doi.org/10.1016/j.geoderma.2005.05.011

Solanki P. Bhargava A. Chhipa H, Jain N, Panwar J. Nano-fertilizers and their smart delivery system. In: Rai M, Ribeiro C, Mattoso L, Duran N. editors. Nanotechnologies in Food and Agriculture. Switzerland: Springer International Publishing; 2015. p. 81-102.

Subbaiya R, Priyanka M, Masilamani Selvam M. Formulation of green nano-fertilizer to enhance the plant growth through slow and sustained release of nitrogen. J Pharm Res. 2012 Nov; 5(11):5178–518