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Original Research Article

Microwave-Assisted Mercerization of *Hyphaene thebaica* Fiber for the Adsorption of Pb (II) And Cu (II) Ions from Aqueous Solutions

***Salisu, A. and Saleh, M.S.**
Department of Pure and Industrial Chemistry, Faculty of Natural and Applied Science, Umaru Musa Yar'adua University, Katsina State, Nigeria
*ahmed.salisu@umyu.edu.ng

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ABSTRACT

Cellulose can be obtained from various inexhaustible sources, therefore is considered as one of the most sustainable polymeric raw material in nature with attractive properties. In this study, Hyphaene thebaica fiber was subjected to pretreatment with sodium hydroxide solution (5% w/v) i.e. mercerization under the influence of microwave radiation (700 W). The mercerized fiber was evaluated for the adsorption of lead and copper ions (Pb^{2+} and Cu^{2+}) ions from aqueous solutions using batch adsorption method. The adsorption parameters such as the effects of contact time, initial metal ion concentrations, and solution pH were investigated. It was found that maximum adsorption *was observed at 80 minutes, 50 mg/L metal ion concentration and solution pH 6. The adsorption equilibrium data were tested using two isotherm models (Langmuir and Freundlich). The FTIR, SEM and XRD analyses showed significant evidence of the modification in the structure of the fiber after alkali pretreatment. The study also revealed that microwave-assisted pretreatment disrupts more lignin from Hyphaene thebaica fiber with shorter pretreatment period compared with the conventional alkali pretreatment. The maximum adsorption capacity (q_{max}) were 42.37 and 41.84 for Pb^{2+} and Cu^{2+} ions, respectively. Alkali pretreated Hyphaene thebaica fiber could be utilized as an inexpensive biosorbent for treatment of wastewater that contain Pb^{2+} and Cu^{2+} ions.*

1. INTRODUCTION

Continued interest in renewable resources and environmentally compatible materials has stimulated scientists and chemical engineers in harnessing the potentials of lignocellulose materials for numerous applications (Zhu et al., 2006). Cellulose (Figure 1) is a promising, sustainable, cheap and abundant biopolymer in nature (Walker and Wilson, 1991).

Agricultural byproduct such as sugar cane bagasse, rice husk, wheat straw, maize stalk, corn husk millet husk etc. contain huge amounts of lignocellulose that could be modified for various applications (Lasheen et al., 2012). For example, many chemical modifications such as esterification (Chand et al., 2014), etherification (Fox et al., 2011), oxidation (Batzma et al., 2014), alkali treatment (Memon et al., 2007), grafting polymers (Kumar et al., 2017) etc. have been explored to alter physical and chemical properties of cellulose. The most commonly used chemical methods in the pretreatment of lignocellulose are microwave-assisted alkali pretreatment and microwave-assisted acid pretreatment (Ethaib et al., 2015).

Doum palm (*Hyphaene thebaica*) is a desert palm plant with edible oval fruit, originally native to the Nile valley. It also grows very well in the northern part of Nigeria. The foliage is used to make some important items for domestic uses such as mats, ropes, and hats (Hsu et al., 2006).

Hyphaene thebaica fiber is one of the huge sources of lignocellulose biomass waste generated in most part northern Nigeria during early preparation of the farming season (Salisu and Sale, 2018). The practice of farmers in the region has been burning of the biomass after uprooting from the soils. This is an unhealthy practice leading to environmental pollution as a result of the introduction of particulate matter into the atmosphere and emission of greenhouse gas (Harrison, 1999).

The use of low-cost adsorbents for wastewater treatment is strongly recommended at present, due to their local availability, simple chemical modification, engineering applicability and cost effectiveness (Bailey et al., 1999). In view of this, *Hyphaene thebaica* cellulosic biomass waste could be utilized as an adsorbent by simple alkali pretreatment that reduce crystallinity and improve porosity.

Contamination of water by toxic heavy metals as a result of the discharge of untreated effluents is a global problem, particularly more pronounced in less developed countries. Heavy metal pollution in water is threatening to human health and aquatic organisms even at trace levels (Baroni et al., 2008). Heavy metals such as lead, zinc, nickel, copper, arsenic and cadmium are released to the environment mainly as a result of human activities such as mining, production of paints, dyes and electroplating industries (Xuan et al., 2006).

It is important to treat wastewater laden with these trace metals ions before discharging it into the environment. Various methods have been reported and applied for removal of heavy metals from aqueous solution such as chemical precipitation, ion exchange, filtration and electrochemical treatment, but most of these methods are not practical for large scale treatments and are costly to be embraced by industries (Salisu et al., 2016a). Adsorption technique has recently become one of the alternative methods widely suggested due to its simplicity in operation and cost effectiveness (Sharma et al., 2013).

In the present study, *Hyphaene thebaica* fiber (mercerized fiber) was examined for its potential as adsorbent for removal of Cu^{2+} and Pb^{2+} from aqueous solutions using the batch adsorption method.

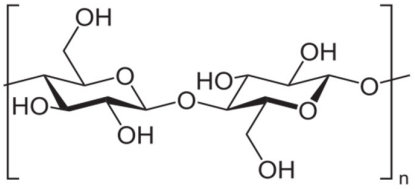


Figure 1: Structure of cellulose

2. MATERIALS AND METHODS

2.1. Material Collection and Preparation of Samples

$Pb(NO_3)_2$ and $Cu(NO_3)_2 \cdot 3H_2O$ salts, HNO_3 and NaOH were purchased from Loba Chemie (England). Stock solutions of Pb^{+2} and Cu^{+2} ions (1000 mg/L) were prepared by dissolving 3.880 g of $Cu(NO_3)_2 \cdot 3H_2O$ and 1.599 g of $Pb(NO_3)_2$ salts in separate beakers (250 mL) with deionized water respectively. The prepared stock solutions were transferred to a 1 liter volumetric flask each was followed by the addition of 100 mL of 0.1M HNO_3 in order to keep the metal ions in free state and finally they were made to mark. Desired concentrations of the metal solutions were prepared by serial dilution of the stock solutions using deionized water. Other chemical reagents were of analytical grade and used as received.

2.1.1. Samples collection and pretreatment

A fresh stalk of *Hyphaene thebaica* was collected from the local fields at Kayauki village, along Daura road, Katsina State, Nigeria. The stalk (300 g) was pulverized and soaked in distilled water at room temperature for 24 hrs. Thereafter, the fibers were removed and washed thoroughly with distilled water and dried in hot air oven at 50 °C until constant weight was obtained.

2.2. Microwave-Assisted Mercerization of *Hyphaene thebaica* Fiber

In this process, the method described by Zhu et al. (2006) was adopted with little modifications. *Hyphaene thebaica* fiber (200 g) was immersed into 500 mL of aqueous sodium hydroxide (5% (w/v) in 1000 mL beaker (Bomex). The beaker was placed at the center of a rotating ceramic plate in the domestic microwave oven (Model: WMO20L-MGSB, Skyrun, Nigeria) with an operating frequency of 2450 MHz. The reaction vessel was exposed to microwave radiation at 700W power for 20 minutes. Periodically, the microwave irradiation was paused and the reaction mixture cooled by placing the reaction vessel in cold water. This treatment removes lignin, wax and oil and also increases hydrophilicity (fiber wetting). The alkali treated fibers were washed thoroughly with distilled water up to pH 7 and dried in hot air oven at 50 °C for 1 hr and kept in a desiccator. The images of the sample material and pretreated fiber are shown in Figure 2.

Figure 2: Images of (a) *Hyphaene thebaica* plant (b) *Hyphaene thebaica* stalk (c) raw pulverized *Hyphaene thebaica* fiber (d) Mercerized *Hyphaene thebaica* fiber

2.3. Characterization Techniques

Fourier Transform Infrared analysis was conducted using FTIR VERTEX 70/70v spectrophotometer (Agilent Technologies, USA). The scanning electron microscope (SEM) micrographs of the fiber and its surface morphology were examined using PHENOM PRO X (Netherland). Powder X-ray diffraction patterns were recorded on ARL X'TRA X-ray Diffractometer (Thermoscientific, Switzerland) using graphite monochromatic CuKα1 (1.5406Å) and Kα2 operated at 40 kV and 30 mA.

2.4. Batch Equilibrium Studies

The adsorption experiments were performed by the batch equilibrium method. The experiments were carried out in 250 mL conical flasks by mixing 0.1 g of the mercerized fiber with 50 mL of each metal ion solution of concentrations, 50, 100, 150, 200, 250, and 300 mg/L at appropriate pH at room temperature using a shaker operating at 300 rpm. The sample solutions were taken out from the conical flask at certain time intervals and the solid in the solutions were separated by filtration and the filtrates were analyzed by using flame atomic absorption spectrophotometer (Shimdzu, 6800, Japan, 210) to determine the equilibrium metal ion concentrations. All the experiments were conducted in duplicate and averages of duplicate readings were reported. The amount of metal ions adsorbed on the fiber at equilibrium (q_e) and adsorption percentage were calculated using Equations (1) and (2) respectively.

$$q_e(mg/g) = \left(\frac{C_o - C_e}{M}\right)V \tag{1}$$

$$Adsorption\ \% = \left(\frac{C_o - C_e}{C_o}\right)\times 100 \tag{2}$$

Where C_o is the initial metal ions concentration (mg/L), and C_e is the equilibrium concentration of metal ions in solution (mg/L), V is the volume of metal ions solution used (L) and M is the mass of the fiber used (g). The equilibrium data obtained were tested using the linear forms of Langmuir and Freundlich isotherm models, as shown in Equations (3) and (4), respectively, (Langmuir, 1918; Freundlich, 1906).

$$\frac{C_e}{q_e} = \frac{1}{q_m Q_L} + \frac{C_e}{q_m} \tag{3}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{4}$$

3. RESULTS AND DISCUSSION

3.1. Characterization

3.1.1. Fourier transforms infrared spectroscopy

An FTIR spectrum of mercerized fiber is shown in Figure 3 which was scanned in the wave number ranged from 600 to 4000 cm^{-1}. The absorption peak at 3335 cm^{-1} is assigned to –OH group in the cellulose fiber (Faruk et al., 2012). The bands at 899 cm^{-1} and 1033 cm^{-1} may be due to β-glucosidic linkage and C–O stretching vibrations. The appearance of these bands successfully confirmed the isolation and delignification of *Hyphaene thebaica* cellulosic fiber by an alkali. pretreatment.

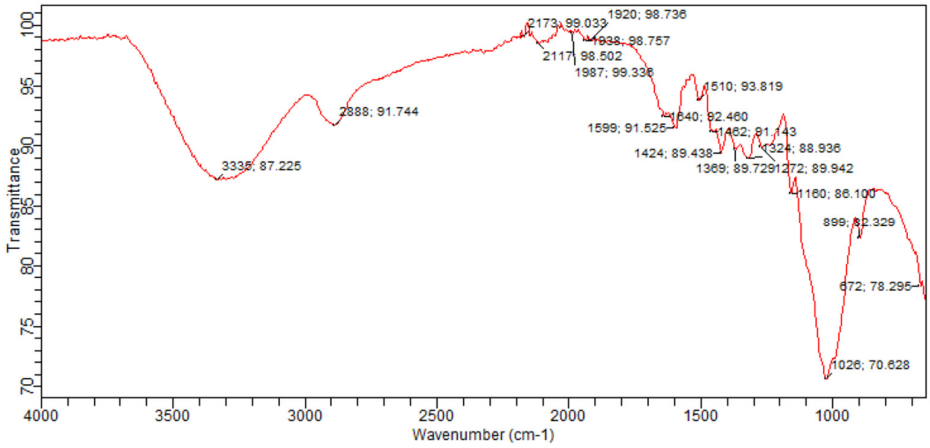


Figure 3: FTIR Spectrum of mercerized fiber

3.1.2. X-ray diffraction (XRD)

The solid state of cellulose is represented by areas of both high order (crystalline) and low order (amorphous). Furthermore, cellulose may occur in other crystals structure (i.e. Cellulose II, III and IV), of which cellulose II is the most stable structure that can be obtained from cellulose I by treatment of cellulose with aqueous NaOH (mercerization) (Klemm et al., 2005). The XRD pattern of raw and mercerized fiber is shown in Figure 4. The characteristic peaks of unmercerized fiber were observed at 20.7° and 17.1° (2θ angle) with relative intensities of 1012 and 806 respectively. The peaks of microwave-assisted mercerized fiber were observed at 21.2° and 18.1° (2θ angle) with relative intensities of 864.8 and 676.1 respectively. This showed that mercerization has altered the crystalline order towards low order structure resulted in the decrease in the peak intensity of mercerized fiber. Furthermore, the fiber showed broadening of the peak after mercerization due to disruption of the crystallinity of the fiber toward low order amorphous phase.

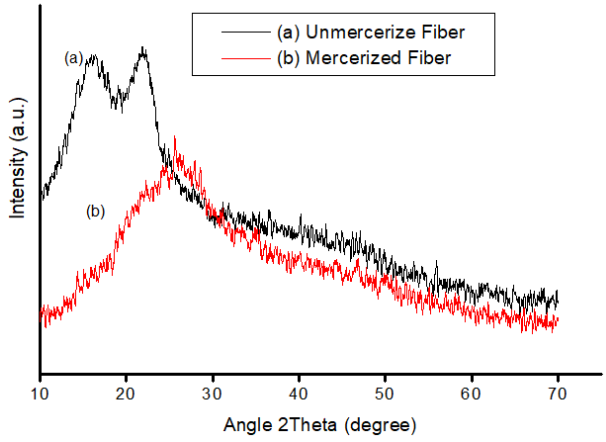
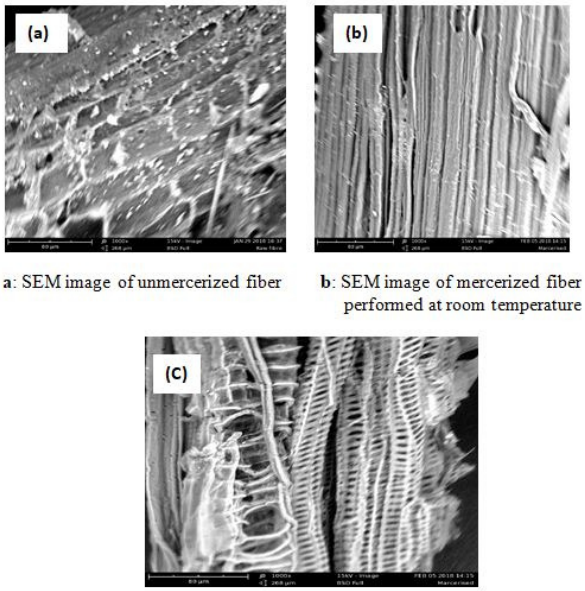


Figure 4: X-ray diffractogram of (a) unmercerized fiber and (b) mercerized fiber

3.1.3. Scanning Electron Microscopy (SEM)

The morphological changes that were caused by mercerization were compared with unmercerized *Hyphaene thebaica* fiber at the same magnification (1000 ×) for suitable comparisons. The SEM image in Figure 5**a** showed the surface structure of unmercerized fiber. It is clear that some rough structure was observed, which could be attributed to non-cellulosic components such as lignin, pectin, lipids, and waxes. Figure 5**b** showed the surface morphology of the fiber pretreated with 20% aqueous NaOH at room temperature for 24 hours. It can be seen that the surface was smooth and intact without any disruption of micro fibrils of the cell walls. Figure 5**c** showed the image of the microwave-assisted mercerized fiber. It is evident from the image that some porous structure occurred as a result of removal of lignin and other noncellulosic components in the fiber during pretreatment. Similar results were reported by Diaz et al. (2015) and Agu et al. (2015). From these observations, it can be concluded that microwave-assisted mercerization is more sophisticated as it can cause the disruption of the physical structure of cellulosic fiber by breaking the lignin barriers, disrupting the crystallinity and also removed non-cellulosic component in order to increase the cellulose accessibility (El-Seoud et al., 2008).



a: SEM image of unmercerized fiber

b: SEM image of mercerized fiber performed at room temperature

c: SEM image of mercerized fiber using microwave-assisted method

Figure 5: SEM Images of *Hyphaene thebaica* Fiber

3.2. Adsorption Studies

3.2.1. Effect of pH of solution

The pH of solution greatly affects the adsorption of metal ions in aqueous solutions. It affects the functional groups on the surface of the adsorbent as well as the solubility of the metal ions in solution. The plot of adsorption percentage as a function of solution pH of Pb^{2+} and Cu^{2+} is shown in Figure 6. The maximum percentage adsorption was observed at pH of 6 with values of 88% for Pb^{2+} and 81% for Cu^{2+} respectively. However, at low pH, the percentage adsorption was not significant. This could be due to increase in positive charges on the adsorbent surface which will lead to repulsion between adsorbent surface and metal ions, resulting in increase in competition between H^{+} and metal ions for the available adsorption sites (Liu et al. 2009).

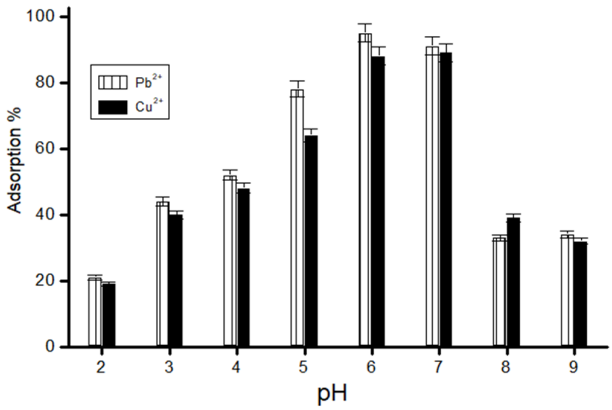


Figure 6: Effect of pH on the adsorption of Pb^{2+} and Cu^{2+} by mercerized fiber

3.2.2. Effect of initial metal ion concentration and contact time

The influence of initial metal ion concentration affecting the overall adsorption process was determined. Various batch adsorption experiments were carried out for different concentration in the range of 50 to 300 mg/L, keeping other parameters constant. The results are presented in Figure 7. The amount of metal ions adsorbed per unit mass of the adsorbent relatively decreased with increase in metal ion concentration. At lower concentration of metal ions, there was highest adsorption, and this could be due to more availability of the adsorptive sites and less competition of the metal ions (Chen et al. 2008). The effect of time was studied using 0.1 g of the adsorbent at a fixed concentration of the metal ions (200 mg/L) in different conical flasks. Figure 8 showed the effect of contact time on the adsorption of Pb^{2+} and Cu^{2+} by the adsorbent. It was observed that slower adsorption rate occurred at the beginning, but gradually increased until equilibrium points were attained in 80 minutes for both the metal ions. The percentage adsorption was 98% for Pb^{2+} and 96% for Cu^{2+} ions.

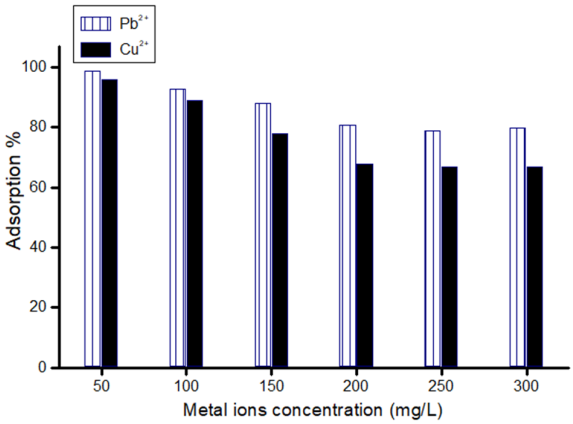


Figure 7: Effect of initial metal ion concentration on adsorption of Pb^{2+} and Cu^{2+} by mercerized fiber

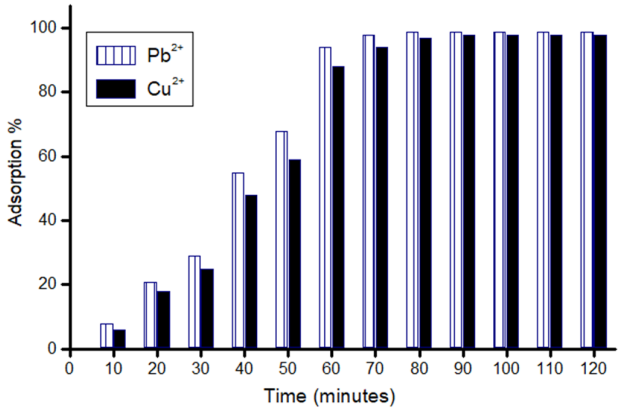


Figure 8: Effect of contact time on the adsorption of Pb^{2+} and Cu^{2+} by mercerized fiber

3.2.3. Adsorption isotherm

The batch experimental adsorption data were simulated with Langmuir and Freundlich isotherm equations to determine the possible adsorption mechanism. In this study, the correlation coefficients were used to determine good linearity of the adsorption processes as illustrated in Figures 9 and 10 for Pb^{2+} and Cu^{2+} respectively. The calculated parameters for the two popular isotherm models are summarized in Table 1. The Langmuir isotherm equation showed the highest correlation coefficients for both metal ions, thus, described a better fitting of the model than Freundlich isotherm. In addition, the values of adsorption intensity (n) for Freundlich isotherm (>10) for both ions indicated unfavorable adsorption (Liu et al., 2009). The Langmuir isotherm model has been reported most suitable or fitted biopolymer-based adsorbents (Crini, 2005). This implicates that the adsorption is monolayer and all sites are equivalent and the interaction between adsorbed ions adsorbent is merely physisorption (strong intermolecular attraction). As shown in Table 1, the maximum monolayer adsorption capacity (q_{max}) was found as 42.37 mg/g and 41.84 mg/g for Pb^{2+} and Cu^{2+} respectively. Furthermore, separation factors (R_L), a dimensionless constant, were found to be less than unity for both ions indicating adsorption was favorable. The value was described as follows: unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Salisu et al., 2016b).

Table 1: Isotherms constants and Correlation coefficients for adsorption of Pb^{2+} and Cu^{2+}

Metal ion	Langmuir model				Freundlich model		
	q_{max} (mg/g)	R_L	Q_L (L/mg)	R^2	K_F (mg/g)	*n*	R^2
Pb^{2+}	42.37	0.005	0.421	0.998	22.45	17.10	0.835
Cu^{2+}	41.84	0.002	0.621	0.996	19.13	22.30	0.844

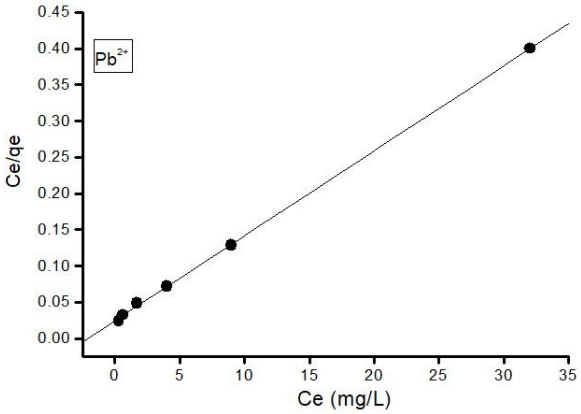


Figure 9: Langmuir isotherm for adsorption of Pb^{+2} onto mercerized Hyphaene thebaica fiber

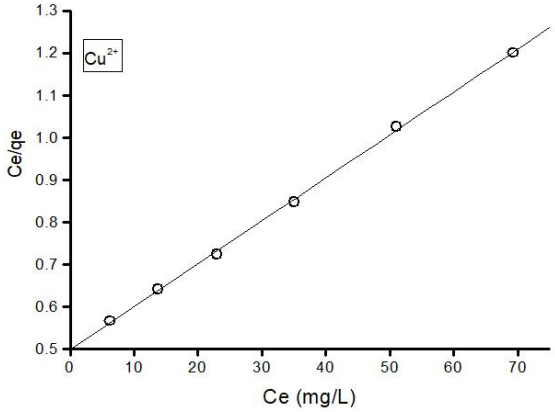


Figure 10: Langmuir isotherm for adsorption of Cu^{+2} onto mercerized Hyphaene thebaica fiber

4. CONCLUSIONS

The following conclusions can be drawn from this study:

1. Microwave-assisted alkali pretreatment of *Hyphaene thebaica* fiber was capable to breakdown the lignocellulosic matrix, thus releasing lignin (binding agent) resulting in easy accessibility of the active sites.
2. The amount of metal ions adsorbed was optimum at solution pH of 6 for both metal ions.
3. The Langmuir isotherm model showed the best fitting of experimental adsorption data, thus the signifying monolayer surface coverage.
4. The maximum adsorption capacity of Pb^{2+} and Cu^{2+} ions were 42.37 and 41.84 mg/g, respectively.
5. This study has also revealed the possibility of using *Hyphaene thebaica* as an inexpensive material for sequestration of Pb^{2+} and Cu^{2+} from aqueous solution.

5. ACKNOWLEDGEMENT

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

REFERENCES

Agu, O.S., Tabil, L.G. and Dumonceaux, T. (2015). Microwave-assisted alkali pretreatment, desification and enzymatic saccharification of Canola straw and Oat hull. *Bioengineering*, 4, pp. 25-32.

Baroni, P., Viera, R.S., Meneghetti, E., da Silva M.A.C. and Beppu, M.M. (2008). Evaluation of batch adsorption of chromium ions on natural and cross-linked chitosan membranes. *Journal Hazardous Materials,* 152, pp. 1155-1163.

Bailey, S.E., Lin, T.J. Bricka, R.M. and Andrial, D.D. (1999). A revew of potentially low-cost sorbents for heavy metals, *Water Research,* 11, pp. 2469-2479

Batzma, R., Mohammed, N., Zaman, M., Minhas, G., Berry, R., Tan, K., (2014). Cellulose nanocrystal as promising adsorbents for the removal of cationic dyes. *Cellulose*, 21, pp. 1655-1665.

Chand, P., Shil, A.K., Sharma, M. and Pakade, Y.B. (2014). Improved adsorption of cadmium ions from aqueous solution using chemically modified apple pomace: mechanism, kinetic and thermodynamics. *International Biodeterioration. Biodegradetion*, 90, pp. 8-16.

Chen, A.H., Liu, S.C. and Chen, C.Y. (2008). Comparative adsorption of Cu(II), Zn (II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin. *Journal Hazardous Materials,* 154, pp. 184-191.

Crini, G. (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science*, 30, pp. 38–70.

Diaz, A.B., Moretti, M.M., Benzerra-Bussoli, C., Nunes, C.D., Blandino, A., da-Silva, R. and Gomes, E. (2015). Evaluation of microwave-assisted pretreatment of lignocellulosic biomass immersed in alkaline glycerol for fermentabe sugars. *Bioresource Technology,* 185, pp. 316-323.

El-Seoud, O.A., Fidale, L.C., Ruiz, N., D'Almeida, M.L.O. and Frollini, E. (2008). Cellulose swelling by protic solvents: which properties of the biopolymer and the solvent matter? *Cellulose*, 15, pp. 371-392

Ethaib, S., Omar, R., Kamal, S.M.M. and Biak, D.R.A., (2015). Microwave-assisted preatment of lignocellulosic biomass: A review. *Journal Engineering Science and Technology*, 2(1), pp. 97-109.

Faruk, O., Bledzki, A.K., Fink, H.P. and Sain, M., (2012). Biocomposite reinforced with natural fibers, *Progress in Polymer Science,* 37(11), pp. 1552-1596.

Fox, S.C., Li, B., Xu, D., Edgar, K.J. (2011); Regioselective esterification and etherification of cellulose: A review *Biomacromolecules* 12(6), pp. 1956-1972.

Freundlich, H.M.F. (1906). Uber die adsorption in *losungen Zeitschrift fur physikalische chemie* (Leipzig). 57A, pp. 385-470.

Harrison, R.M. (1999). Understanding our Environment: An introduction to Environmental Chemistry and Pollution. Royal Society of Chemistry, Thomas Graham House, Cambridge, UK, pp. 413-420.

Hsu, B., Ken, N. and Coupar, I.M. (2006). Antioxidant activity of hot water extract from the fruit of the Doum palm, *Hyphaene thebaica. Food Chemistry,* 98, pp. 317-328.

Kumar, R., Sharma, R.K. and Singh, A.P. (2017). Cellulose based grafted biosorbent-journey from lignocellulos biomass to toxic metal ions sorption applications- A review. *Journal Molecular Liquids,* 232, pp. 62-93.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of Chemical Society,* 40, pp. 1361-1403.

Lasheen, M.R., Ammar, N.S. and Ibrahim, H.S. (2012). Adsorption/desorption of Cd(II), Cu(II), and Pb(II) using chemically modified orange peel: Equilibrium and kinetics studies, *Solid State Science*, 14, pp. 202-210.

Liu, F., Luo, X., Liang, L. and Chen, Y. (2009). Removal of copper and lead from aqeous solution by carboxylic acid functionalized deacetylated konjac glucomannan. *Journal Hazardous Materials*, 171, pp. 802-808.

Memon, S.Q., Memon, N., Shah, S.W., Khuhawar, M.Y. and Bhanger, M.I. (2007). Sawdust- A green and economical sorbent for the removal of cadmium ions. *Journal Hazardous Materials*, 139(1), pp. 116-121.

Salisu, A., Mohd, M.S., Ahmedy, A.N., Ibrahim, WAW, and Khairil J. A. (2016a). Removal of lead ions from aqueous solutions using sodium alginate-graft-poly(methyl methacrylate) beads. *Desalination and Water treatment*, 57(33), pp. 15353-15361.

Salisu, A., Mohd M.S., Ahmedy A.N., Ibrahim W.A.W. and Khairil J.A. (2016b). Alginate graft polyacrylonitrile beads for the Removal of lead ions from aqueous solutions, *Polymer Bulletin,* 73, pp. 519-537.

Salisu, A., and Sale, M.S. (2018). Graft copolymerization of acrylamide onto Hyphaene thebaica fiber and its performance for removal of heavy metal ions from aqeouse solutions. *Bayero Journal of Pure and Applied Science,* 11, pp. 288-294

Sharma, S., Pathania, D. and Singh, P. (2013). Preparation, characterization and Cr(VI) adsorption behavior study of poly(acrylic acid) grafted Fiscus carica bast fiber, *Materials Letters,* 4, pp. 271-276.

Walker, L.P. and Wilson, D.B. (1991). Enzymatic hydrolysis of cellulose: an overview, *Bioresource Technology*, 36, pp. 3-14.

Xuan, Z., Tang, Y., Li, X., Liu, Y. and Luo, F. (2006). Study on the equilibrium, kinetics and isotherm of biosorption of lead ions onto pretreated chemically modified orange peel, *Biochemical Engineering Journal,* 31, pp. 160-164

Zhu, S., Wu, Y., Yu, Z., Chen, Q., Yu, F., Wang, C. and Jin, S. (2006). Microwave-assisted alkali pretreatment of wheat straw and its enzymatic hydrolysis, *Biosystem Engineering*. 94, pp. 437-442.