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APPLICATION OF MODIFIED CELLULOSE FOR Pb^{2+} AND Cu^{2+} REMOVAL FROM AQUEOUS SOLUTIONS: KINETIC AND ISOTHERMS STUDIES

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ABSTRACT

In this work, acrylamide grafted Kolanut Pod Husk cellulose adsorbents were successfully prepared via chemical modification of Kola nut pod husk cellulose with acrylamide and N, N'-methylenebisacrylamide. The modified adsorbents were successfully applied for the adsorptive removal of Pb^{2+} and Cu^{2+} ions from aqueous solutions at different parameters, such as pH of the solution, adsorbent dosage, contact time, and initial metal ion concentrations were optimized. Qualitative analysis of the modified adsorbents was performed by Fourier Transformed Infra-Red Spectroscopy and Scanning Electron Microscopy. Characterization analyses portrayed the surface of adsorbents as being short elongated shaped with dispersed pores and composed of hydroxyl and carbonyl groups as the main binding sites. The optimum conditions for adsorption of Pb^{2+} and Cu^{2+} were found to be: pH; 5, adsorbent dosage; 3.5 and 4 g L^{-1}, concentration; 60 mg L^{-1} and contact time; 160 min. Adsorption data were fully fitted with the Freundlich, Langmuir isotherm model, and a pseudo-second order, Elovich kinetic model. The adsorption of metal ion was heterogenous in nature with q_{max} of 55.14 mg g^{-1} and 62.09 mg g^{-1} for Pb^{2+}, 54.82 mg g^{-1}, and 60.43 mg g^{-} for Cu^{2+} respectively. These results showed that the modified adsorbents were able to efficiently remove Pb^{2+} and Cu^{2+} from aqueous solutions.

Keywords*:* Adsorption, Kolanut pod husk, Toxic/trace metals, Isotherm, kinetic models

INTRODUCTION

Kolanut (*Cola nitida*) is one of the intensively cultivated cash crops in southwest Nigeria. It is an important crop in terms of revenue. Very large amounts of Kolanut Pod Husk (KPH) are generated as waste and subsequently abandoned after the seed harvest. The waste is neither useful economically nor suitable for the production of animal feeds. It is therefore of great interest to find a suitable application for this agrowaste.

Being a Softwood, KPH contains a high percentage of cellulose (74.5−87.2%), followed by hemicellulose (12.3−20.4%) and the least is lignin (3.46−8.7%) (Daochalermwong *et al.,* 2020). The cell wall of KPH is made up of cellulose fiber and this consists of a D-glucose monomer linked together with β (1- 4) glycosidic bonds to form a giant polymer, which can either be in crystalline and/or amorphous forms (Ogunneye *et al.,* 2020). As a result of the monomer linkage of D-glucose needed to form a giant molecule of polymer chains and the hydrogen bonding within the molecule of cellulose, cellulose fiber is naturally strong, tough, and insoluble in both inorganic and organic solvents

Cellulose as a polymer matrix for the synthesis of new adsorbents has been gaining more attention of recent as a new alternative to several agro-industrial wastes/ residues and activated carbon adsorbents due to the presence of –OH functional groups which have great affinity to different pollutants such as metal ion and dyes. Above all, cellulose is one of the most abundant natural substances in nature, and its surface –OH groups can be modified to improve its hydrophilicity as an adsorbent for the metal ion removal (Zhang *et al.,* 2014). In this regard, a great variety of modified cellulose materials have been reported in adsorption studies on removal of metal ion and dyes (Zhou *et al.,* 2013; Fakhre & Ibrahim, 2018; Daochalermwong *et al.,* 2020; Adegoke *et al.,* 2022).

Toxic metal pollution is a very serious environmental problem which demanded urgent attention due to the health risk it poses to humans, and the ecosystem (Aneja *et al*., 2010; Nowrouzi *et al*., 2014; Jamshaid *et al*., 2017). In contrast to the organic pollutants, heavy metals such as Cr, Cd, Cu, and Pb are the major freshwater pollutants (Babarinde *et al*., 2016) because of their carcinogenic and persistent nature (Bilal *et al*., 2013). The major origins of these heavy metals in the environment are the wastewaters discharged from the various industries such as paint and pigments, lead acid accumulator, mining, and the agriculture sector (Mousavi *et al*., 2011; Ibrahim & Mutawie, 2013). Severe health issues such as kidney damage, central nervous system disorders, and other system deterioration in humans could be linked to pollution by heavy metals due to their toxic nature (Lee *et al*., 2012; Lung *et al.,* 2015).

Therefore, it is necessary to efficiently remove the metals from the wastewater to solve the ecological, biological, and industrial problems before it is discharged to the environment. Adsorption using readily available agricultural waste is one of the most effective methods to remove several metal ions in water because the process is relatively simple, cheap, and highly efficient (Kaur *et al.,* 2022). However, the unfavourable interaction between the hydroxyl groups of the biomass and the metal ion results into low adsorption efficiency. To overcome this, there is a need to modify the biomass especially cellulose bisorbent. Several researchers have modified different biomass such as orange peel (Li *et al.,* 2007; Li *et al.,* 2008), sugarcane bagasse (Viera *et al.,* 2007; Gurgel *et al.,* 2008), corncob (Dai *et al.,* 2018), and wood sawdust (Zhou *et al.,* 2019) as metal ion adsorbents. The modification entails the introduction of metal-loving groups like; amidoxime (Saliba *et al.,* 2005; Hokkanen *et al.,* 2016), carboxyl (Wang *et al.,* 2017), ethylenediaminetetraacetic acid (EDTA) (d'Halluin *et al.,* 2017), and amide (Liu *et al.,* 2020) on the cellulose moiety. Daochalermwong *et al.* (2020) used isolated cellulose from pineapple leaf fiber modified with EDTA and carboxymethyl cellulose for the removal of Pb^{2+} and Cd^{2+}. They demonstrated an increase in the adsorption capacity of modified cellulose for both Pb^{2+} (83 mg g^{-1}) and Cd^{2+} (44 mg g^{-1}). This was attributed to an increase in the number of carboxylic acid groups. Similarly, mercerized sugarcane bagasse modified with ethylenediaminetetraacetic dianhydride (EDTAD), was found to have high removal capacities of 333 mg g^{-1} and 149 mg g^{-1} for Pb^{2+} and Cd^{2+}, respectively (Júnior *et al.* 2009). EDTAD was also used by d'Halluin *et al*. (2017) to modify cellulose fiber paper. Their modified cellulosic adsorbent was found to be very robust and had high hydrophilicity, disposability, and low toxicity with adsorption

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efficiencies of 227 mg g^{-1} for Pb^{2+} and 102 mg g^{-1} for Cd^{2+}, respectively.

Considering the high adsorption efficiency, wide availability, high disposability, efficient and inexpensive methodology associated with modified cellulosic adsorbents, the current study, therefore aimed to isolate cellulose from KPH, modify it with acrylamide, for the removal of Pb^{2+} and Cu^{2+} in single metal ion system using batch method. Subsequently, adsorption isotherms and adsorption kinetic models were also used to investigate the behavior of the adsorbent to the adsorbate system.

MATERIALS AND METHOD

Materials and Reagents

Kola nut Pod Husks (KPH) was obtained from the Kola nut plantation in Mamu village, Ijebu North Local Government, Ogun State, Nigeria. All reagents were of analar grade. H_2SO_4, NaOH (Merck, Germany), $Cu(NO_3)_2$ (Sigma Aldrich), $Pb(NO_3)_2$, $NaClO_3$ (Merck, Germany) and HNO_3 (Merck, Germany).

Preparation of KPH Cellulose Powder

The adsorbent was prepared from KPH according to the modified method of Ogunneye *et al*. (2020) as shown in Figure 1. The dried KPH cellulose was milled into powdered form, and thereafter sieved to obtain fine particles.

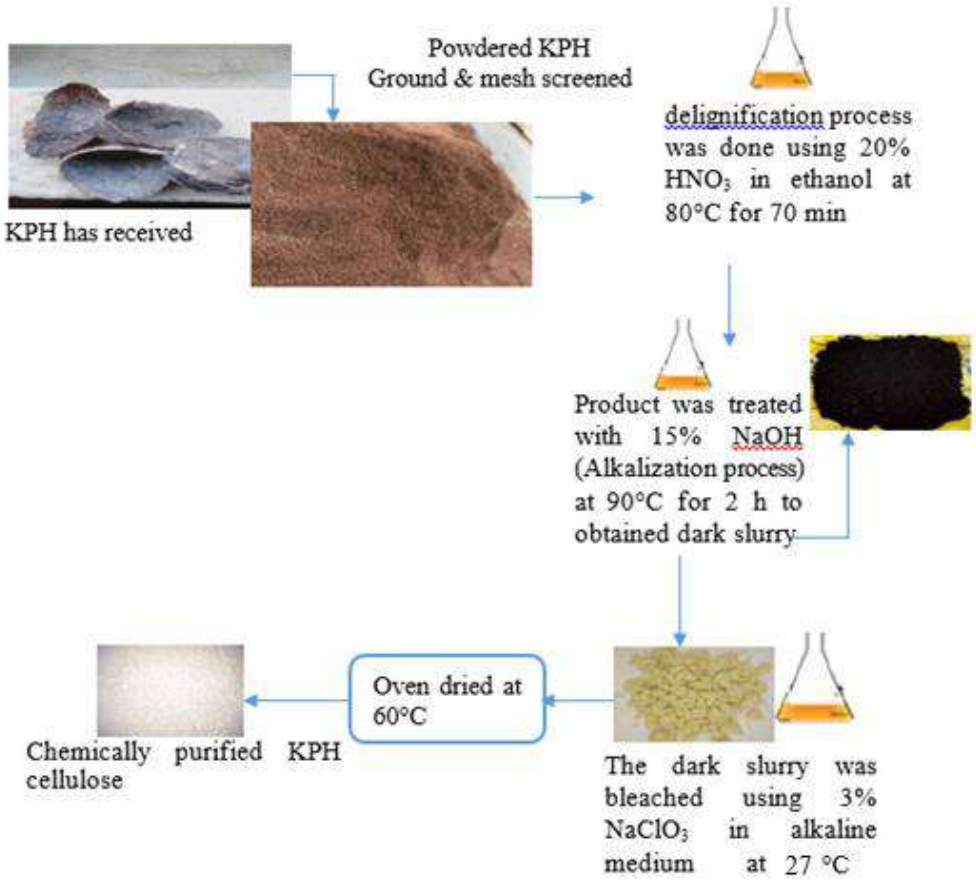

Figure 1. Schematic diagram for isolation of cellulose from KPH

The Yield of KPH Cellulose in Percentage

The KPH cellulose yield in percentage yield was determined using the equation (1)

$$\%Z = \frac{S}{E} \times 100 \qquad (1)$$

Where:

S= weight of KPH cellulose in grams

E= weight of KPH in grams

Modification of KPH Cellulose

Two grams of KPH cellulose was dispersed in 50 mL distilled deionized water to form a suspension. 2 mL of 0.1 g mL^{-1} ammonium persulphate solution was added into the suspension under continuous stirring for 15 min. Then 10 mL of aqueous solution containing 8 g acrylic acid, 2 g acrylamide and 0.06 g N, N'-methylenebisacrylamide added into above reaction mixture. The polymerization reaction was performed at 70 °C for 2 h. The product was neutralized with sodium hydroxide solution, dehydrated with ethanol, and finally oven dried at 60 °C

Characterizations

The chemical structures of KPH cellulose powders, KCB and metal loaded were characterized by Perkin Elmer Spectrum RXI Fourier Transform Infrared Spectrophotometer in the wavelength transmission range of 4000-400 cm^{-1} to determine the change in functional group before and after adsorption process. Similarly, SEM of KPH cellulose powders, KCB and metal loaded were obtained using Quanta 250 FEG (USA) to determine change in surface morphology. The difference in crystallinity of KPH cellulose powders and KCB were also investigated using X-ray Diffractometer, Philip – PW 1011 model.

Batch Adsorption Procedure

The adsorbates used in this study were Pb^{2+} and and Cu^{2+}, prepared from their metal salts – $Pb(NO_3)_2$ and $Cu(NO_3)_2$. To prepare metal ion solutions, accurately weighed amount of the respective metal salts were dissolved in deionized water in a 1 L standard volumetric flask and then made up to the mark (1000 mg L^{-1}). Appropriate working solutions were prepared from the stock solutions by serial dilution. To further confirm the concentration prepared, the metal solutions were standardized using Atomic Absorption Spectrophotometer (Bulk 2001 AAS).

The process of removal of the adsorbates (metal ions) from solutions containing them was carried out by batch adsorption study. Parameters whose effects on the removal process were studied include pH, dosage, contact time, and initial metal-ion concentration. The isothermal behaviour and kinetics of the removal process were also investigated. The chosen adsorbent mass for this study (excluding dose dependent study) was 1 g. With the exception of the effect of initial metal-ion solution, 1 g KCB was contacted with 100 mg L^{-1} metal-ion (Pb^{2+} and Cu^{2+}ions) solution in corked 250 mL conical flasks and allowed to equilibrate for 2 h (excluding effect of contact time) with orbital shaker. The studies were allowed to proceed at room temperature, which was at around 27°C. The pH dependent study was performed from pH 2 to 9. Solution pH was adjusted by dropwise addition of either HNO_3 or NaOH. Dose dependent study was performed by varying adsorbent mass from 1-5 g at the optimum pH. Time dependent study was performed by varying the agitation time from 20 – 240 min at optimum pH and dosage; initial metal-ion concentration was varied from 5-100 mg L^{-1} at optimum dosage, pH and

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contact time. The content of each flask were withdrawn using syringe and analyzed Samples were taken out from the shaker while the content of each flask were withdrawn using syringe (10 mL). Analysis of the filtrates for residual metal ions was performed using Atomic Absorption Spectrophotometer (Bulk 2001 AAS). Metal ion uptake (Adsorption capacity (q_e)) and percentage metal-ion uptake by KCB were subsequently determined according to Eqs. (2) and (3).

$$q_e = (C_o - C_e)\frac{V}{m} \quad (2)$$

$$\text{Metal removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (3)$$

Where, C_0 is the initial metal ions concentration (mg L^{-1}), C_e is the equilibrium concentration of metal ions (mg L^{-1}), V is the volume of solution (L) and m is the mass of adsorbent (g).

In order to determine the kinetics of the process and the best isotherms that describe the experimental data, models such as Lagergren pseudo-first order (Simonin, 2016), pseudo-second order (Ho & McKay, 1999), Elovich (Ayawei *et al.,* 2017), Weber-Morris Intraparticle Diffusion (Campos *et al.,* 2018), Langmuir (Langmuir, 1918), Freundlich (Ng *et al.,* 2002), and Temkin (Dada *et al.,* 2012) were applied to the experimental data. The linear equation for the above listed kinetics and isothermal models are represented by Eqs. (4) to (10).

Lagergren pseudo-first order: $log(q_e - q_t) = logq_e - \left(\frac{K_1}{2.303}\right)t$ (4)

Pseudo-second order:

$$\frac{t}{qt} = \frac{1}{K_2}q_e^2 + \left(\frac{1}{q_e}\right)t \quad (5)$$

Elovich: $q_t = A + B\ln t$ (6)

Weber-Morris Intraparticle Diffusion: $\log R = b\log t + \log K_d$ (7)

Langmuir: $\frac{1}{q_e} = \frac{1}{q_{max}}K_L\left(\frac{1}{C_e}\right) + \frac{1}{q_{max}}$ (8)

Freundlich: $\log q_e = \frac{1}{n}\log C_e + \log K_f$ (9)

Temkin: $q_e = B\ln A + B\ln C_e$ (10)

Where: q_e and C_e are as earlier defined; q_t (mg/g) denotes adsorbate uptake at time t; k1 (min^{-1}), k2 (g/mg min) and kα (mg/g min½) denote the rate constants for the pseudo-first-order, pseudo-second-order and intra-particle diffusion models, respectively; qmax (mg/g), KL (L/mg), Kf (mg/g) and n denote maximum adsorption capacity, Langmuir constant, Freundlich constant and intensity constant, respectively; R is the percent metal ions biosorbed, K_d (mg g^{-1} $min^{-1/2}$) is the intra particle diffusion rate constant, while b is the gradient of the linear plot; $RT/b_T = B$ where T is the temperature (K) and R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), and A and b_T are constants for Temkin. Required parameters (from the models applied) were obtained from the slopes and intercepts of the linear plots of the integral equations of the models. These parameters were interpreted to determine the models that suitably described the adsorption process.

RESULTS AND DISCUSSION

KPH Cellulose Preparation and Percentage Yield

The isolated cellulose obtained from KPH via alkalization process was white in colour, odourless and insoluble in water. The hypochlorite in the bleaching increases the brightness of the pulp with lower lignin content while maintaning the yield and strength of the pulp. The yield of the cellulose obtained based on the dry weight was 45.92%. This high amount of this cellulose isolated

from the KPH can be advantageous when using KPH as a natural source of adsorbent for pollutants removal (Daochalermwong *et al.*, 2020).

Characterizations

The FTIR spectra of KPH cellulose and KCB are shown in Figure 2. In the spectrum of KPH cellulose, the observed broad peak around 3600−3200 cm^{-1} was due to the −OH stretching vibration while the absorption peak at 2890 cm^{-1}, belonged to the stretching vibrational mode of C−H. The bands at 1428, 1364, 1320, 1025, and 896 cm^{-1} were ascribed to the stretching and bending vibrations of the $-CH_2$, −CH, −OH, and -CO bonds in the KPH cellulose backbone (Hokkanen *et al.*, 2014). Moreover, the spectrum of KCB showed new peaks at 1667, 1564, 1411, and 1330 cm^{-1} respectively. The peaks at 1667 and 1564 cm^{-1} were attributed to the stretching vibration of CO-NH, and asymmetric -COOH stretching vibration functional group (Naidu *et al.*, 1994). The absorption peaks at 1411 cm^{-1} and 1330 cm^{-1} were assigned to the symmetrical stretching vibration of COOH, and C-OH in-plane bending, respectively (Jawed *et al.*, 2020). Moreover, the peak at 3434 cm^{-1} became sharper and stronger, assigning to N-H stretching vibration. These results confirmed that the acrylic acid and acrylamide monomers were successfully grafted onto the cellulose molecules, providing more adsorption sites for metal ion adsorption (Naidu *et al.*, 1994; Jawed *et al.*, 2020). Similarly, to further characterize the KCB after adsorption with Pb^{2+} or Cu^{2+}, they were analyzed by FT-IR, and the spectra were compared with those before adsorption, as presented in Figures 3a and b. For the KCB loaded with Pb^{2+} (Figure 3a), there was band shift at OH broad band and –CH stretch with complete disappearance of C-O stretching of the carboxyl group (1727 cm^{-1}) while KCB loaded with Cu^{2+} also showed very small peak at C-O stretching (Figure 3b).

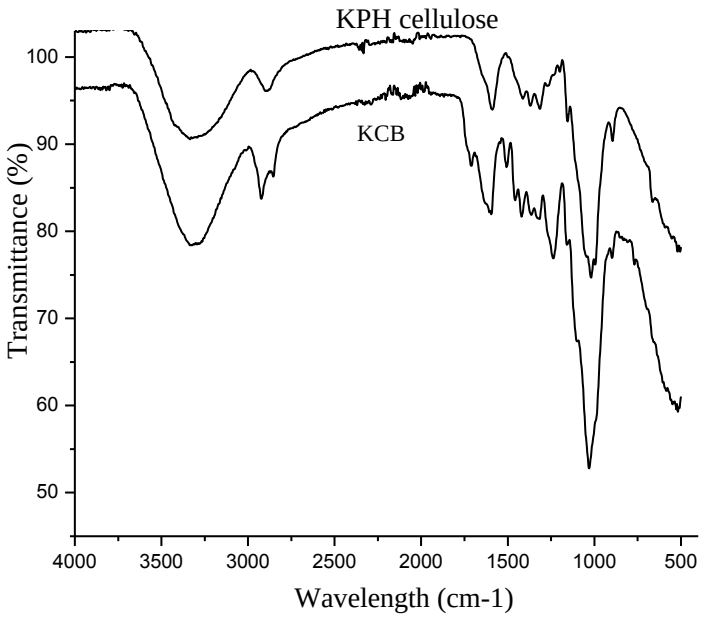

Figure 2: FT-IR spectra of prepared KPH cellulose and KCB

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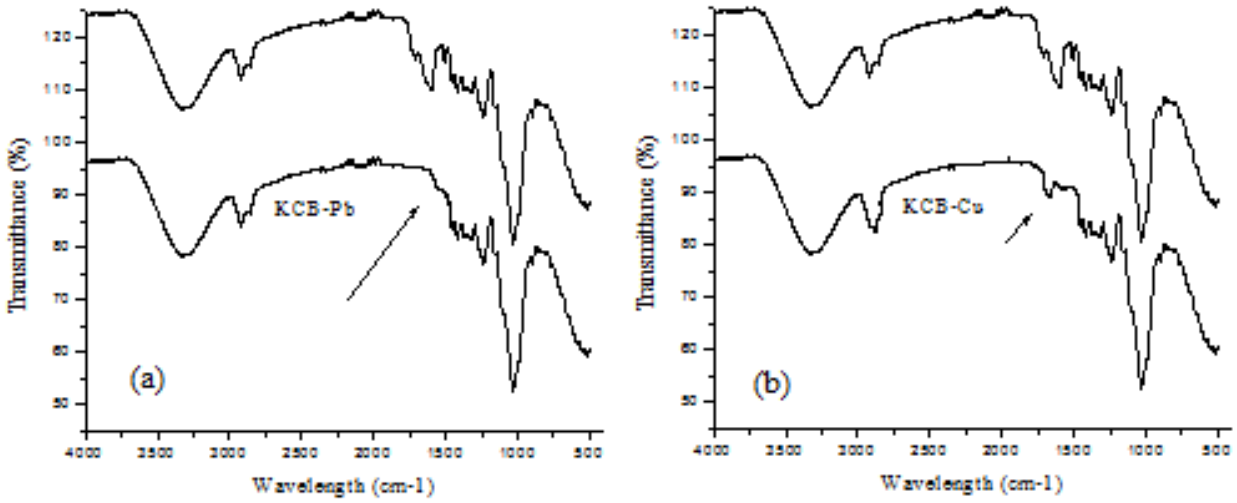

Figure 3. FT-IR spectra of before and after adsorption of KCB with (a) KCB-Pb^{2+}, (b) KCB-Cu^{2+}

Figure 4a shows that the surface of the KPH cellulose had a long thick elongated fibrils structure, while the surface of unloaded KCB (figure 4b) was characterised with short elongated shape, revealing dispersed pores (Oh & Park, 2002), which could serve as potential sites adsorption from polluted water (Oninla *et al.,* 2018). The micrographs of metal-loaded KCB are shown in Figs 4(c and d). Although the long shaped fibrils could still be noticed after the adsorption of $Pb^{2+}$and Cu^{2+} ions, nonetheless, the adsorption of the metal ions resulted in surface folding, indicating marked changes in the surface morphology of the adsorbent after metal loading. Figure 5a shows the EDS spectra of KPH cellulose. Two elements present were carbon and oxygen (cellulose backbone), this indicated that cellulose isolated from the raw sample is pure as there are no other elements aside carbon and oxygen. Figure 5b shows that Lead and copper were not detected in the KPH sample but 52.46% carbon, 44.02% oxygen and 3.52% nitrogen were observed after modification to KCB. The presence of nitrogen in KCB is due to modifying agent. However, after adsorption, small peaks for Lead (Figure c) and copper (Figure c inset) were respectively detected in the sample loaded with the corresponding metal, thus confirming the interaction of KCB with the metal ions.

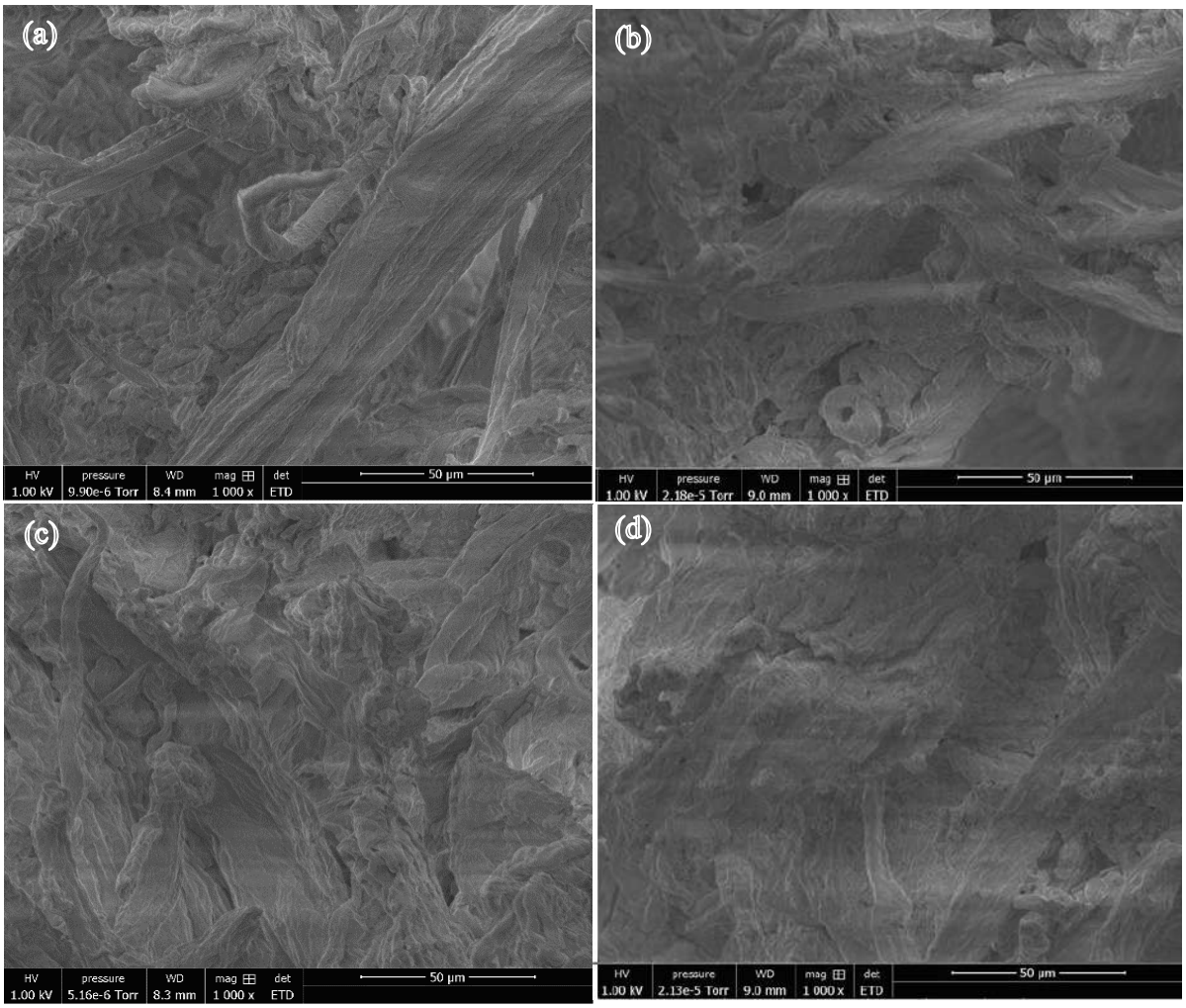

Figure 4: SEM micrograms for adsorption of (a) KPH cellulose and (b) unloaded KCB (c) Pb-loaded and (d) Cu-loaded KCB

The crystallinity of KCB was determined by X-ray diffractometry (XRD) The XRD diffractograms of KCB (unloaded and metal-ion loaded) are depicted in Fig. 5d. The XRD pattern of unloaded reveals one intense and prominent peak at around 2θ=23.8º and other secondary peaks at around 2θ =17º, 32º and 35.2º respectively 17°, 30° and 41°. The prominent and intense peak at around 2

2θ=23.8º is characteristic of highly ordered crystalline cellulose (Adigun *et al.,* 2019). Other non-prominent peaks indicate the presence of a substantial amount of less ordered amorphous moieties such as lignin and polysaccharides in KCB [36]. After the uptake of Pb^{2+} and Cu^{2+} ions, the intensity of the prominent peak at around 2θ=23.8º was observed to have decreased with the presence of additional two peaks at 21º and 29º respectively, while all other three secondary peaks appeared more pronounced, signifying the effects of metal ions uptake.

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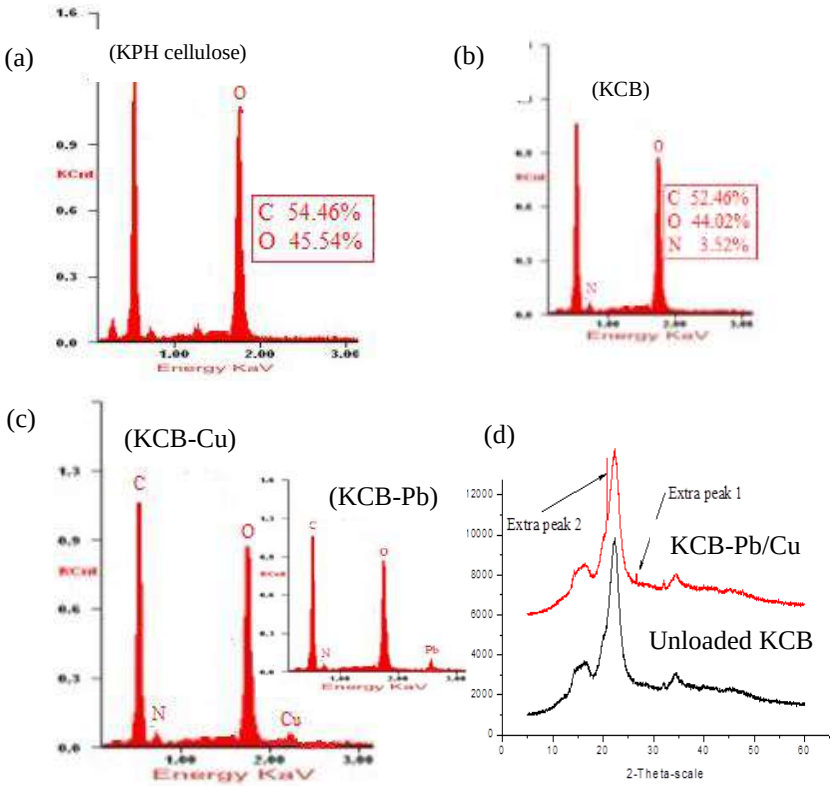

Figure 5. EDS of (a)KPH cellulose (b) KCB (c) Cu-loaded & Pb-loaded KCB (inset) and inset and XRD diffractograms of KPH cellulose

Batch Adsorption

Effect pH

Solution pH plays important role in the interaction of the adsorbates at the adsorbent surface as it regulates adsorbate speciation, complexation, hydrolysis, solubility, precipitation, as well as density of charged species on the surface of an adsorbent during sorbate–sorbent interaction (Kushwaha *et al.*, 2017). As shown in Figure 6a, solution pH greatly influenced the bisorption of Pb^{2+} and Cu^{2+} onto KCB. At 27°C, optimum removal occurred at pH 5 for both metal ions that is sorption increased with pH rise from 1 – 5. An explanation for these observations is the presence of high degree of protons at low pH. When an adsorptive solution is at very low pH, the binding sites on the adsorbent surface become protonated, thus rendering them unavailable for the cationic metal binding. With increase in pH, gradual deprotonation occurs at the surface, hence, more negatively charged metal ion become available at the surface. The presence of negative charge density at the surface then promotes electrostatic attraction between the cationic metal ion and the negatively charged species, leading to increasing cationic metal binding (Babarinde *et al.*, 2013). This is possibly responsible for the gradual rise in % metal uptake observed. The present investigation was limited to pH $\leq$ 7 because of the difficulties in distinguishing real adsorption from precipitation of metal ions from solution at higher pH. Precipitation of $Cu^{2+}$and Pb^{2+} have been reported at pH > 8 (Bernabé *et al.*, 2019). Therefore, in order to eliminate any possible interference as a result of precipitation, solutions were maintained at pH 5 for all subsequent studies.

The Effect of KCB Dosage

The right choice of solid (adsorbent) to liquid (adsorbate) ratio in any batch adsorption process goes a long way in determining the efficiency of the pollutant removal process. Hence the need to investigate the quantity of KCB needed to effectively remove Pb^{2+} and Cu^{2+} ions from aqueous medium at a fixed adsorbate (metal ions) concentration 100 mg L^{-1} under the chosen experimental condition. Increase in metal ions uptake was observed with increase in adsorbent mass (Figure 6b). For example, with 0.5 g KCB in contact with the metal ions solution, 57 and 62 % Pb^{2+} and Cu^{2+} were removed respectively. However, the percent removal was increased to around 90 and 100 for Cu^{2+} and Pb^{2+} ions, with KCB mass of 3.5 and 4 g respectively. This can be ascribed to the fact that at low adsorbent mass, fewer active sites were available for the binding of the metal ions. As the KCB mass increased, more active sites became exposed to the adsorbate, hence the steady increase in the percent metal removal observed but at the higher mass above 4 g, agglomeration and a consequent reduction in intercellular distance occurs, protecting the metal ions from binding sites (El-Sikaily *et al*., 2011).

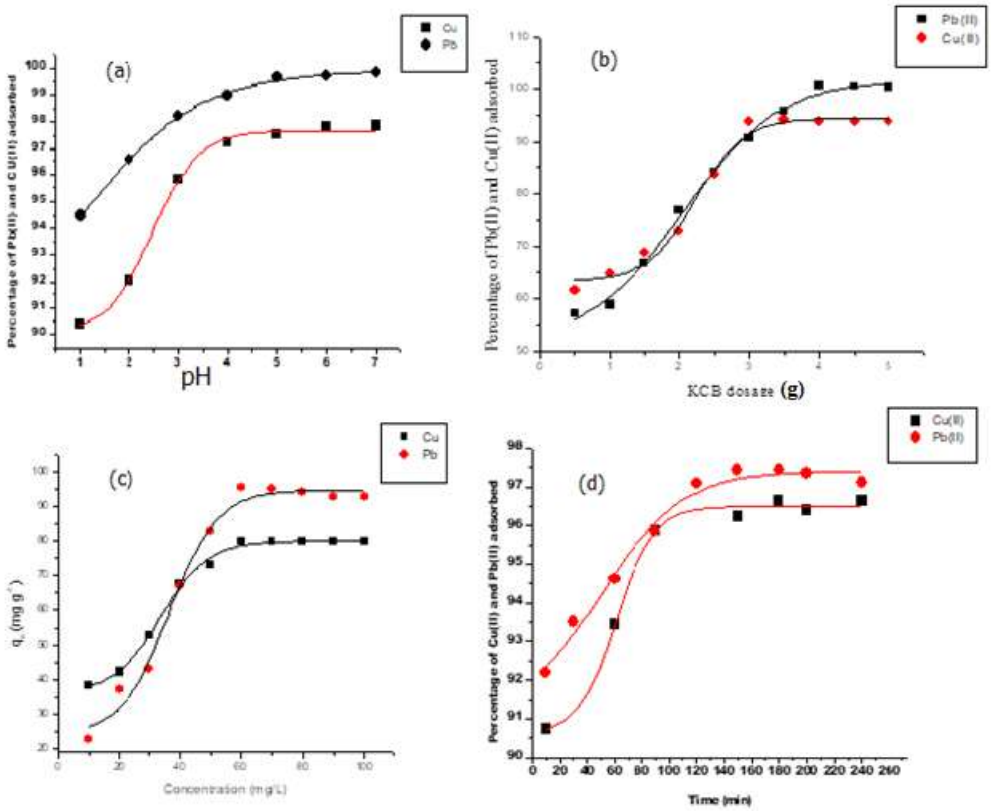

Figure 6: Plots of effect of (a) pH and (b)KCB dosage on the adsorption of metal ion onto KCB

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Effect of Initial Metal Concentration

The result in Figure 6c shows that adsorption of different metal ion increased at the initial stage and reached the maximum adsorption percentage of 79.79 and 95.38 at 60 mg L^{-1} for Cu^{2+} or Pb^{2+} respectively. After that, with increased metal ions concentration, the adsorption capacity remained unchanged. This behavior is attributed to the fact that all active sites on the surface of KCB were vacant, resulting in high metal adsorption at the beginning (Jan *et al*., 2013).

Effects of Contact Time

The effect of contact time is an important parameter to determine optimum for the adsorption. Fast adsorption kinetics is an indication that a high efficiency of industrial wastewater remediation can be performed within a relatively short time. The removal of Pb^{2+} and Cu^{2+} ions were relatively fast within the first 10 and 60 min, respectively (Figure 6da). After this first stage, metal uptake slowed and eventually approached equilibrium after 140 min. This observation is in agreement with a report by Azouaou *et al.* (2010). At the initial stage of the process, there was copious number of active sites available on the surface of KCB which were rapidly occupied by the metal ions, hence the sharp increase observed in metal uptake during the first stage. The slow stage observed later was due to depletion in sorption sites which eventually appeared to be completely filled after 140 min (Bhagat *et al*., 2020; Jawed *et al*., 2020). Therefore, a contact time of 140 min was chosen for subsequent studies.

Kinetic Study for Metal ION Adsorption on KCB

Kinetic modelling of the experimental data obtained at optimum conditions were performed to ascertain the best model that suitably describe the kinetics of the adsorption process; predict the rate limiting step and propose the mechanism of the adsorption processes. Models evaluated were the pseudo-first-order, pseudo-second order, Elovich and Intraparticle. The suitability of a particular model was determined by the coefficient of determination, R^2 which measures the conformation of the regression line to the experimental data. A perfect fit is indicated by unity, although a value close to unity can be an indication of good fit. Values < 0.8 expresses the inadequacy of such a model in explaining the experimental data (Adigun *et al.*, 2020). As detailed in Table 1, all the kinetic models evaluated were suitable to describe the kinetic data because the R^2 values ≥ 0.9. Although the pseudo-first order (figure 7a) model also demonstrated good fit of the experimental data, but pseudo-second order (figure 7b) demonstrated more good fit than pseudo-first order due to its R^2. Moreover, the q_e for pseudo-second order were slightly greater than q_e of pseudo-first order and also very close to qe experimental, suggested that the pseudo-second-order kinetic model best explain the kinetic of the adsorption processes. Therefore, the rate-limiting step of the adsorption process is chemisorption (Adigun *et al.*, 2020).

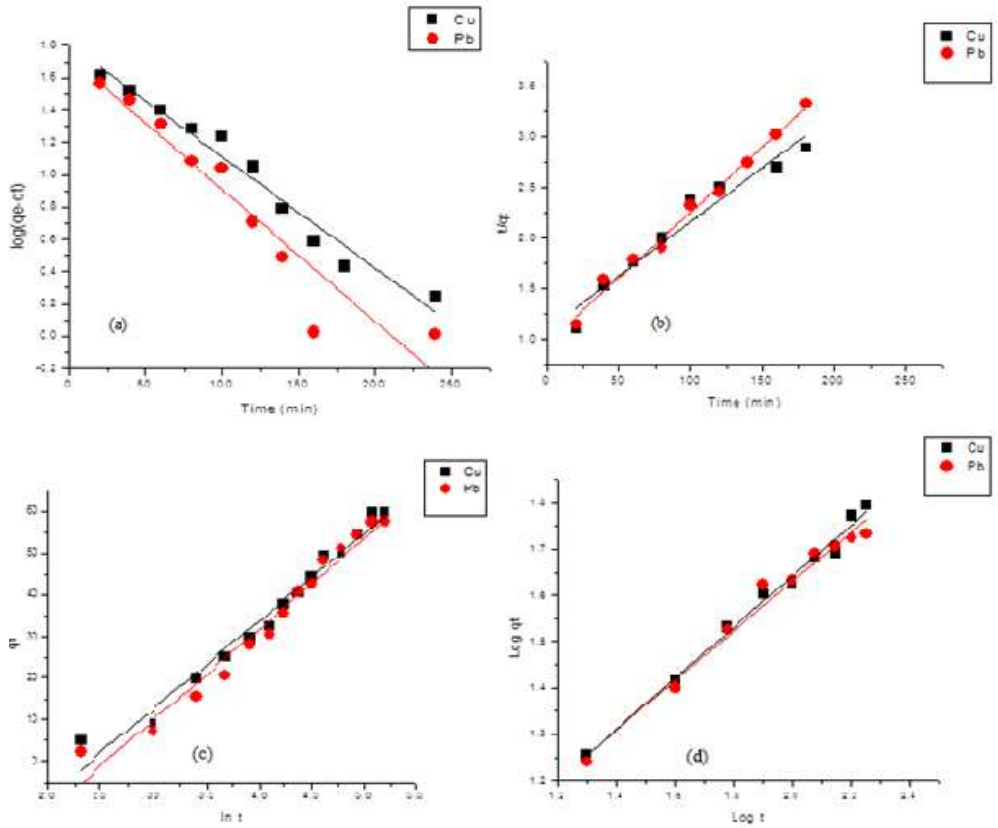

Figure 7: Pseudo-first order (a), pseudo-second order (b), Elovich (c) and intraparticle plots for the adsorption (d), of $Pb^{2+}$and Cu^{2+} onto KCB.

Table 1: Kinetic parameters for the adsorption of Pb^{2+} and Cu^{2+} onto KCB

Kinetic Model	Parameter	Cu^{2+}	Pb^{2+}
Pseudo-first order	$q_e(mgg^{-1})$	54.82	55.14
	$K_1(min^{-1})$	2.17×10^{-2}	1.97×10^{-2}
	R^2	0.9201	0.9645
Pseudo-second order	q_e (mg g^{-1})	60.43	62.09
	K_2(g mg^{-1} min^{-1})	3.46×10^{-4}	3.14×10^{-4}
	R^2	0.9882	0.9430
Elovich	A	-20.27	-27.37
	B	1397	19.08
	R^2	0.9665	0.9723
Intraparticle diffusion	K_d (mgg^{-1} $min^{-1}/_2$)	2.8940	2.2543
	B	0.42	0.65
	R^2	0.9778	0.9899

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Biosoption Isotherms of Metal ION

To determine the isotherm that best describes the adsorption of the metal ions, experimental data were fitted to the Langmuir (figure 8a), Freundlich (figure 8b), and Temkin (figure 8c) equilibrium models and Table 2 lists the various parameters obtained from the models. The Temkin model is considered inappropriate in explaining the isothermal behaviour of Cu^{2+} (R^2 = 0.8934) but suitable in explaining the isothermal behaviour of Pb^{2+} (R^2 = 0.9185). However, the Freundlich isotherm exhibited the best fit of all (R^2 of 0.9738 and 0.9838 for Cu^{2+} and Pb^{2+} respectively), thus suggesting adsorption of metal ions occur via multiple layers (heterogeneous nature of a particular surface during adsorption process) instead of single layer (Adigun *et al.*, 2020).

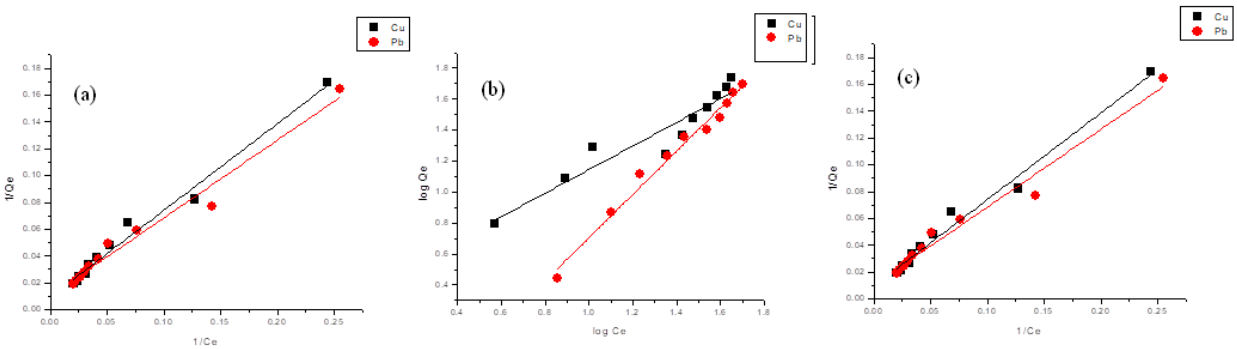

Figure 8. Langmuir (a), Freundlich (b), and Temkin (c) isothermal plots for the adsorption of $Pb^{2+}$and Cu^{2+} onto KCB.

Table 2: Isotherm parameters for adsorption of Cu^{2+} and Pb^{2+}

Isothermal Model	Parameter	Cu^{2+}	Pb^{2+}
Freundlich	n	1.12	1.11
	K_f (mgg^{-1}) Lmg	1.57	1.57
	R^2	0.9738	0.9838
Langmiur	q_{max} (mgg^{-1})	53.54	96.53
	K_L (Lmg^{-1})	1.90 x 10^{-2}	1.70 x 10^{-2}
	R^2	0.9655	0.9068
Temkin	A	-68.24	-24.37
	B (mgg^{-1})	30.22	14.57
	R^2	0.8934	0.9185

The higher efficiency of KCB to remove Cu^{2+} and Pb^{2+} were indicated in the table 3. The q_e values obtained were compared with previous work reported in the literature. This comparison demonstrates

that KCB is a potential adsorbent for different Pb^{2+} and Cu^{2+} because of its high maximum adsorption capacity.

Table 3: Comparison of the adsorption capacity of KCB with other previously used adsorbents

Adsorbent	Adsorption capacity (mg g^{-1})				References
	Cd^{2+}	Pb^{2+}	Cr^{3+}	Cu^{2+}	
Pinus sylvesteris	19.1	22.2	-	-	Taty-Costodes *et al*., 2003
Chestnut shell	7.19	-		-	Vázquez *et al*, 2009
Oak wood	-	-	3.03	-	Mohan *et al.*, 2011
Phaseolus hulls activated carbon	15.7	21.8	19.5	-	Rao *et al*., 2009
Modified Celluloses Prepared from Pineapple Leaf Fiber	41.2	33.2	-	-	Daochalermwong *et al*., 2020
Kolanut pod husk cellulose adsorbent (KCB)	-	55.14	-	62.09	This study

CONCLUSIONS

KCB adsorbent prepared from cellulose isolated from KPH using alkaline hydrolysis was used for the adsorption of Pb^{2+} and Cu^{2+} ions in single-adsorption systems. SEM indicated the presence of long fibers prior to adsorption, while enlarged and swollen fibrils were observed after adsorption due to the surface adsorption of metals. The presence of chemical functional groups and band shifts before and after adsorption was evidence in the FTIR. The optimum adsorption condition was found to be pH around 5.0, contact time 160 min, initial concentration of 60 mg L^{-1} adsorbent dosage of 4 g L^{-1} (Pb^{2+}) and 3.5 g L^{-1} (Cu^{2+}) respectively. KCB was found to be efficient in removing heavy metal and could be adopted in the design of an effective technology for the removal of metal ions from contaminated water in our environment.

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Declaration of conflict of interest

The authors declared no conflict of interest

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