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P1B-09: VALOURISATION OF COTTON HULL FOR THE DECONTAMINATION OF KAGARA MINING WASTEWATER

Y. Ibrahim[1], M. D. Yahya[*,1], A.G. Olugbenga[1], U. Garba[2], J. M. Oyelude[3]
[1]Department of Chemical Engineering, Federal University of Technology, Minna, Nigeria
[2]Department of Chemical Engineering, School of Engineering and Environmental Design, UsmanuDanfodiyo University Sokoto, Sokoto State, Nigeria
[3]Department of Chemical Engineering, Ladoke Akintola University of Technology, Ogbomosho, Nigeria
[*]Corresponding author email: muibat.yahya@futminna.edu.ng,; Tel: +234 8032854148

Abstract
In this work, a fixed bed adsorption column was used in the decontamination of Pb (II) ions from illegal gold mining wastewater of Kagara mines, Niger State, North Central Nigeria. Flame Atomic Absorption Spectrometer analysis of the waste solution showed a high concentration of Pb (II) ion of 85 mg/L. Fourier Transform Infra-Red (FT-IR) spectroscopy revealed the presence of OH, C-O, C=O, C-O-H and CH_2 functional groups in cotton hull. Brauneur-Emmet Teller (BET) test results indicated surface area of 139.8 m^2/g and micropores size and radius of <2 nm and 9.237 Å respectively, while the Scanning Electron Microscope micrographs revealed the presence of pores on the raw adsorbent. Column adsorption scale-up data for the 120 L/hr of Kagara mining wastewater shows that 607.2 L of the effluent can be treated of Pb (II) in 5.06 hours using 4.75 kg of the cotton hull adsorbent. The maximum adsorption capacity of 27.65 mg/g, with correlation coefficients within 0.7674 and 0.9551 has an average experimental value of 23.09 mg/g and theoretical of 21.60 mg/g adsorption capacities of the cotton hull adsorbent (CHA) which signify that Thomas kinetics model fit the experimental data.

1.0 INTRODUCTION

The rapid industrialization and population growth rate of industries, agriculture, and mining activities have led to the increased disposal of toxic substances such as heavy metals into the environment (Mengistie *et al.* 2008). The presence of these heavy metals in the environment is a challenge for remediation because of the inability to degrade and bio-accumulation tendency. (Ruparelia *et al.* 2008). Metals which are specifically toxic to human beings and ecological environment include Copper (Cu), Nickel (Ni), Pb (II) (Pb), Cadmium (Cd), Chromium (Cr), Zinc (Zn), and Mercury (Hg) to mention a few. They are toxic, causes severe disorder, illness to plants, animal and human. Pb (II) (Pb) II, for example, is one of the heavy metals when exposed to children at low level causes blindness, low intellect quotient, learning disabilities, attention deficit disorder, stunted growth, impaired hearing, and kidney damage. At high levels of exposure, a child may become mentally retarded, fall into a coma, and even die from Pb (II) poisoning. In adults, Pb (II) can cause fertility problems, nerve disorders, muscle and joint pain, irritability, and memory or concentration problems (Farghali *et al.* 2012). Recent reports have shown that exposure to Pb (II) contaminated soil and dust resulting from battery recycling and mining has caused mass Pb (II) poisoning and multiple deaths in young children in Senegal and Nigeria (WHO, 2015). Saturnism/Pb (II) poisoning is one of the most common and best-recognized childhood diseases of toxic environmental origin. It accounts for about 0.6% of the global burden of disease (WHO, 2010).

In May 2015 the World Health Organisation, WHO (2015) reported that in Rafi Local Government Area of Niger State, North Central Nigeria where the Kagara Mines was located, a devastating effect of Pb (II) poisoning from illegal mining activities has caused the death of 28 young children and 65 others affected with many domestic animals lost to the tragedy.

The removal of heavy metals from contaminated soils can be achieved by various treatment methods such as chemical precipitation, ion exchange, and electrochemical removal. These processes which are generally known as conventional treatment methods have several disadvantages mainly due to high energy requirements and capital cost and low efficiency (Barakat, 2011). Biosorption has recently attracted a considerable amount of attention as an alternative method used for the removal and recovery of toxic metals due to numerous advantages such as low sludge production, low investment, and operational cost and above all higher efficiency (Eckenfelder, 2000). Thus, locally generated agricultural wastes such as cotton seed hull have been tested in the production of activated carbon in many developing countries, though very few research works have been published in this regard.

Cotton (*Gossypiumhirsutum*) is an important cash crop for several developing countries at both local and national levels. After oil and a few agriculture products, cotton is one of the largest industries in Nigeria with the country's alarmingly decreasing production put at 235,000 bales (183.43 kg/bale) for the year 2019 by the United States Department of Agriculture (2019). Cotton/textile activities are widespread in the country, largely in the Savannah geographical regions (https://www.cotton.org/oubs/cottoncounts/fieldfabric/uses.cfm). Production of cotton depends on various factors ranging from vagaries of weather, cotton price, problems of the textile industries.
In cotton production operations two products are of paramount importance. The cotton fibre used in textile industries and the kernel (meat) for refinery oil production. In cotton oil refineries, once the seed lint is removed, it is dehulled, by loosening the inner meat (kernel) from cotton hull which forms the tough outer part covering surrounding the seed (Heuzé *et al.*2015). The hull is turned out as waste to dump sites. In processing operations, the cotton seed products yield per ton of seed crushed are crude oil, 16%; hull, 27%; meat, 45%; lint, 8%; cotton residues 4% (American National Cotton seed Products Association, 2000).

This study focusses on the use of plant-based adsorbent produced from cotton seed hull for the adsorption characteristics of Pb (II) ions found in gold mining liquid effluent. Since cotton seed hull can be regarded as a potentially promising cost-effective, sustainable source of adsorbent for the removal of harmful metallic waste from mining wastewater yet to be fully explored. Column flow experiment was conducted to investigate the effect of flow rate, bed height, and initial metal ion concentrations on breakthrough curves as well as adsorption kinetics of the Pb (II) ions in the mining waste solution onto the adsorbent.

2.0 MATERIALS AND METHODS

2.1 Collection of Mining Waste Water Sample

Waste water was gotten from three different mining waste water points and stored in three containers of about 25 liters. These were analyzed using atomic absorption spectrophotometer and a mean value deduced.

2.2 Preparation of Cotton Hull Adsorbent

Cotton seeds hull were gotten from a local market in Katsina State, it was sun dried for ten days in accordance with the method established by Biradarpatil (2009). The seeds lint was removed with H_2SO_4 at 100 ml/kg cotton seeds for 3 mins to have a complete removal of the fuzz. The seeds were instantly removed and rinsed several times with deionized water. The seeds were neutralized in 2% Na_2CO_3 solution for 15 minutes and it was thoroughly washed with deionized water. The seeds were separated and dried in an oven; it was then dehulled after being dried at constant weights of 12% moisture content. The cotton hull was separated from the inner kernel using sieve aperture of 2 mm and 1 mm mesh size (Biradarpatil (2009).

The cotton hull gotten was then rinsed thoroughly with deionized water and sun dried for 5 days. The dried cotton hull was grinded and sieved to 500 µm size and sun dried for another 2 days. The adsorbent powder was oven dried for

12 hours at 105°C, cooled in a desiccator for 30 minutes.

2.3 Characterization of cotton hull adsorbent

The prepared cotton hull was characterized to determine the important properties such as BET surface area test, FT-IR, SEM analysis and apparent density.

2.4 Scanning Electron Microscope (SEM) Analysis

Scanning electron microscope (model- DSM 9872 Gemni) was used to examine the surface morphology of cotton hull adsorbent. The SEM of the carbon was recorded at 5000 magnification through which a thin layer of the adsorbent was mounted on aluminum specimen holder coated with gold (Au) at a thickness of about 30 nm.

2.5 Fourier Transform Infra-Red (FT-IR) Spectroscopy

Diamond ATR Agilent Cary 630 infra –red spectrometer was used to carry out the FTIR of cotton hull adsorbent. The adsorbent sample was placed on cleaned crystal window and the overhead press tip was adjusted until the desired pressure put forth onto the introduced sample material. The system analyzed the sample being placed and a displayed graph result showed the intensity of the sample measurement within spectral range of 4000 cm^{-1} to 650 cm^{-1}.

2.6 BET (Brunauer Emmett and Teller) Surface Area Analysis

The prepared adsorbent was outgassed under vacuum for 3 hours at 300°C to get rid of moisture contents and contaminants from the solid surface. The degassed sample was cooled and transferred, firmly fixed in the analysis station of the equipment. Then nitrogen adsorption at 77K by the surface area analyzer was used to determine the pore volume and the surface area of the outgassed carbon samples.

2.7 Apparent Density of Cotton Hull Adsorbent

The sample earlier dried in an oven at 105°C was put into a 25 ml cylinder used to carry out the apparent density. It was then compacted by tapping on the bench top till the volume of the sample stopped decreasing of about 1 -2 minutes. The volume, mass and density were calculated and this procedure was repeated for three times to get the average value.

$$\text{Apparent density} = \frac{\text{dry weight of adsorbent(g)}}{\text{volume of packed sample}}$$

2.8 Sample Preparation for Pb (II) Adsorption

50 ml of the mining waste water was measured into nine sterile 250ml glass stoppered flasks, little portion of 0.1M HCl solution was added. The pH was adjusted within the range of 2 to10. 250 g of cotton hull adsorbent was measured into the nine sample flasks and the mixture agitated using a multi-purpose flask shaker at 200 rpm for 120 minutes at pre- determined time intervals. The resultant mixture was filtered and the filtrate analysed using AAS to evaluate the resultant Pb (II) concentrations.

2.9 Column Adsorption Procedure

A glass column of internal diameter 3 cm, 30 cm length was used to carry out the column study in which particle size of 500 μm was used. The prepared adsorbent was packed into the column with glass wool acting as support at the top and bottom ends of the bed. The bed heights were varied at 2, 4 and 7 cm and waste water was supplied by a peristaltic pump into the adsorption column at constant flow rate of 5, 7.5 and 10 ml/min while the initial adsorbate concentrations were varied 50, 65 and 85 mg/l. The targeted heavy metal is Pb (II) ions as it was extremely high and the major cause of the death and ill health of the community. Atomic Absorption Spectrophotometer, model Accusys 211 from Buck Scientific, USA was used to determine the resulting concentration and the effluent samples were collected at various time intervals. The experiment was discontinued when the exhaustion of column was reached.

3.0 RESULTS AND DISCUSSION

3.1 Chemical Composition of Kagara Mining Effluent

Atomic absorption spectrophotometer was used to determine the composition of Kagara mining effluent. The effluent indicates that the Pb (II) ions content is extremely high (85 mg/l) and its release poses significant harm to the environment. The threshold value for Pb (II) is 0.5 mg/L (NIS, 2007). Other potentially harmful elements found in significant quantities in the effluent include copper (2.5861 mg/l) and zinc (0.4281 mg/l).

3.2 Scanning Electron Microscopy

The scanning electron micrographs before adsorption Figure 1A revealed that the surface texture and morphology of biosorbent at high (× 5000) magnifications. The morphology was that of smooth surface with no presence of metals seen, when untreated cotton hull carbon with metal ions were seen under SEM. In Figure1B after the adsorption of Pb (II), it was observed that the fresh adsorbent discloses spots of microscopic pores and crevices indicated with white arrow headlines on the raw cotton hull adsorbent micrographs. Pb (II) metal adsorption by the fresh adsorbent were attained from the SEM results which displayed that the mapping of Pb (II) ions onto biomass surface are spotted with some red arrows on the surface of cotton hull on the micrograph. The micrograph of the ion loaded carbon adsorbent also displayed that the formation of white layers on the surface was because of the adsorption of Pb (II) ions. From this SEM analysis of cotton adsorbent after the adsorption of Pb (II), more uneven and rough surface morphology existed in the adsorbents. The irregular surface outlook could be due to ions and foreign molecules deposition emanating from the contaminated fluid containing the adsorbate onto the carbon surface. Hence, the micrograph structures of the cotton hull attained from SEM represented a large surface area for heavy metal ion adsorption which indicates the difference between before and after loading of ions on the biomass surface.

Figure1A: Micrographs of cotton hull

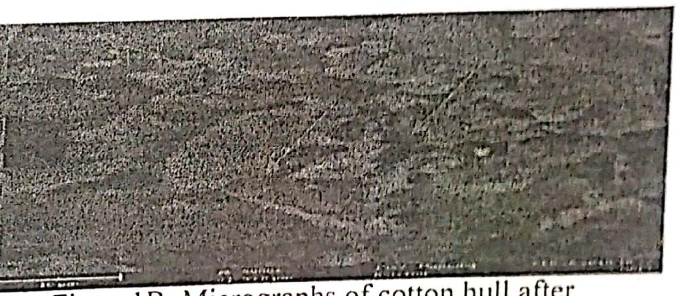

Figure1B: Micrographs of cotton hull after Pb (II) equilibration

3.3 FT-IR Spectrum Analysis of Cotton Hull Adsorbent

Figures 2 and 3 respectively shows FTIR carried out before and after Pb (II) ions. At adsorption ranges of 4000 to 650 cm^{-1}which shows shift in the wave number of emerging peaks associated with the plots after adsorption process. The raw adsorbent showed five energy bands within the range of 3947.3 and 3503.7 wave number which are broad but short peaks. The absorbance is associated with stretching variations of O-H groups found in polysaccharides, absorbed water, hemicellulose and lignin. This corresponded to free hydroxyl and carboxylic acids on the surface of the adsorbent (Blanes *et al.* 2016), the presence of the OH^- group enhanced the removal of Pb (II) through the surface reaction between the hydroxyl terminal and the Pb (II) (Icoranu *et al.*, 2018) C-H stretching vibration was indicated from 2639-2516 cm^{-1}, C≡C symmetric variation for 2366.9 - 2050 cm^{-1}, also 2016.5 – 1986.7 cm^{-1} for C=C asymmetric stretch while 1848.8 cm^{-1} is attributed to C = O stretch in the xylan tissue of the organic adsorbent. The peak at 1420.1 cm^{-1} represented H-C-H and O-C-H in plane bending vibrations. The almost flattened spectra from Figure 3 at 3333.2 cm^{-1} is broadened and

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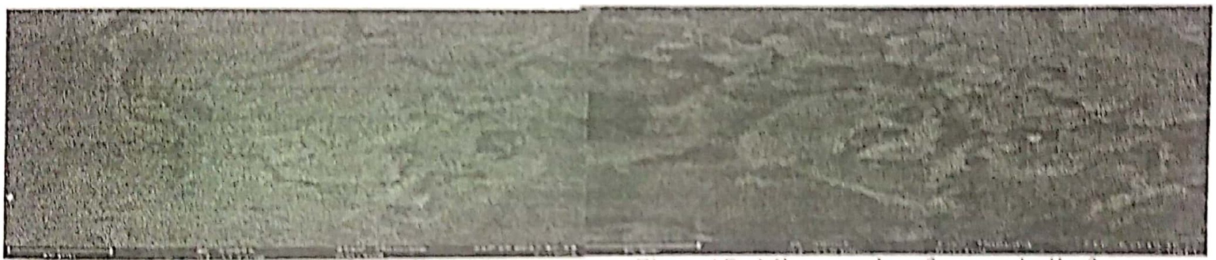

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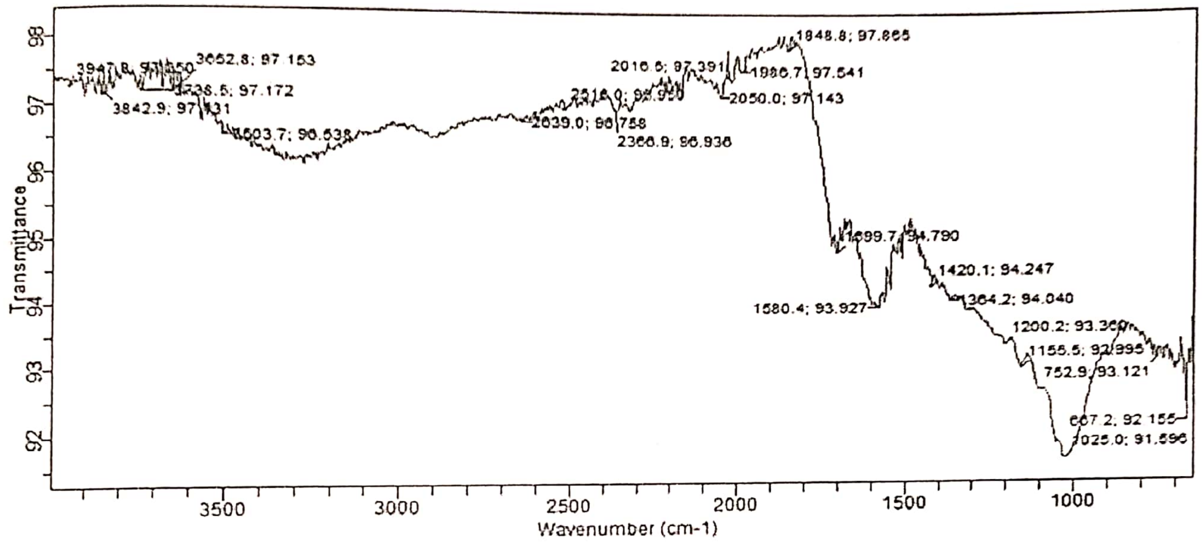

Figure 2: FTIR spectrum of cotton hull before Pb (II) ions adsorption

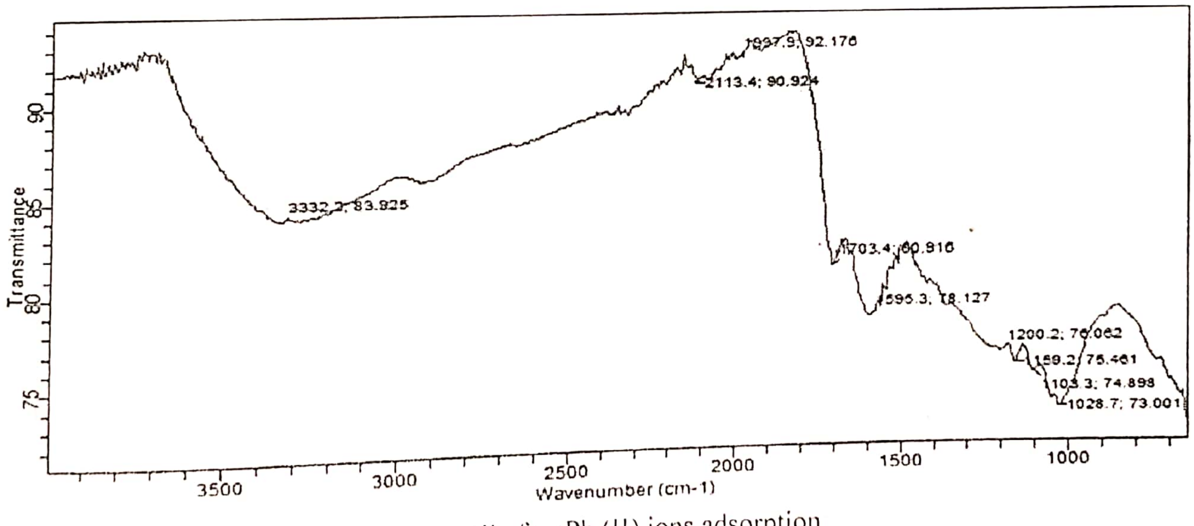

Figure 3: FTIR spectrum of cotton hull after Pb (II) ions adsorption

3.4 Evaluation of BET Analysis

The BET result for the cotton hull material showed relatively high surface area of 139.8 m^2/g as compared to some untrea ted agricultural adsorbents such as soy meal hull with 0.7623 m^2/g (Arami *et al*, 2006); cotton seed shells with specific surface area 124.35 m^2/g (Thinakaran *et al.* (2008); banana peel with 20.6–23.5 m^2/g (Annadurai *et al.* (2002) and orange peel with 20.6–23.5 m^2/g (Annadurai *et al.* (2002). The specific surface contributed greatly to the Pb (II) ions adsorption onto the cotton hull. The micro-pore volume and pore radius values were provided. The adsorbent characterized by important micro porosity of 9.237Ǎ (< 2nm) in this adsorbent are responsible for adsorption of metallic ions from solutions. Micro porosity is needed in adsorbing lower molecular weight material like Pb (II) atom (3 Ǎ diameter) and trace organics in water to a non – detectable level. The adsorbent has a low volume of micro pores radius of 0.0217 cm^3/g. The values got i.e. 9.237 Ǎ for micro pore radius and 139.8 m^2/g for cotton hull surface area material makes it a suitable adsorbent.

3.5 Evaluation of Apparent Density.

The apparent density had a value of 0.42 g/ml which showed that the material is good for water treatment process. The value is relatively high compared to other agricultural adsorbents such as empty palm oil fruit bunches of 0.21 g/ml (Wahi *et al.*, 2009) and is not likely to pose challenge of being trapped and suspended in water during application Wahi *et al.* (2009).

3.6 Effect of pH on Pb (II) adsorption

It is clear from the results represented graphically in Figure 4 that with the increase in pH, the Pb (II) removal increased gradually from its initial value of 2. At low pH of 2, the acidity of the medium shows high competition between hydrogen ions and Pb (II) ions in solution This is because at lower pH values, biosorption of metal ions was inhibited since the cell wall of the cotton hull contains various functional groups. The positively charged functional groups increase competition between protons and metal cations for binding active sites of cotton hull, resulting in decreasing the metal cations adsorption on its surface as explained by Yalcin (2014). At higher pH values of 5, several hydroxides low – soluble species such as Pb $(OH)_2$ was formed. Hence, considering the pH value of 5 requires little acid solution, it has minimal effect on both the processing equipment and the environment. Also, it gives optimum removal of Pb (II) from aqueous solution. This result is in agreements with the findings of Rahman & Sathasivam (2015) for heavy metal adsorption onto *Kappaphycus sp.* From aqueous solutions.

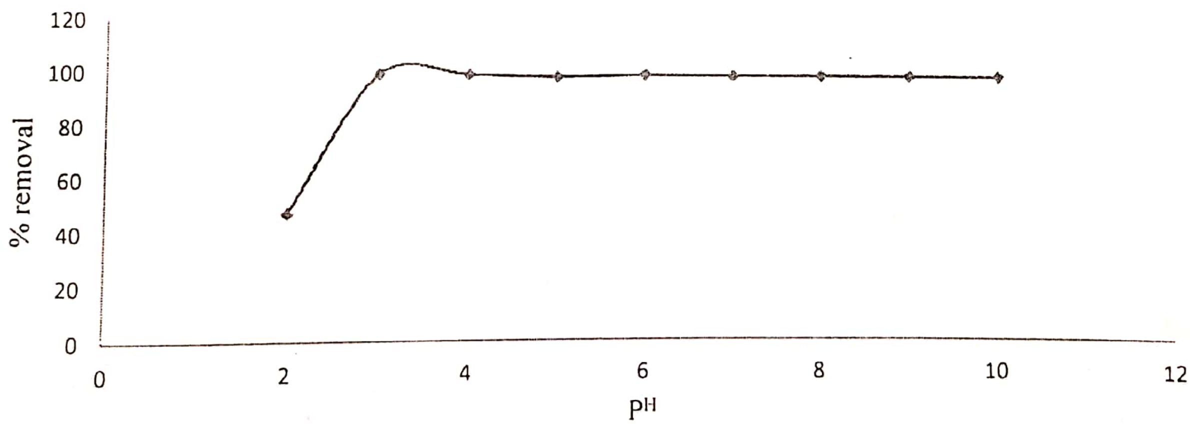

Figure 4: Effect of *pH* on Removal of Pb (II) (II) ions from solution

3.7 Column Adsorption Parameters

3.7.1 Effect of Feed Flow Rate

This was investigated by varying the feed flow rate at a constant bed height of 4 cm and an initial concentration of 50 mg/l. The breakthrough time obtained are 721, 480 and 240 minutes for flow rate values of 5, 7.5 and 10 ml/min respectively which indicated that the breakthrough time decreased with increasing flow rates. Also, there was a decrease in total percentage removal of Pb (II) ions in the fluid bed operations from 50.68% to 29.14% with increasing flow rate from 5 -10 ml/min. Similarly, increase in initial metal concentration with decreasing time from 3120 to 1920 minutes was observed. Hence, the contact time between the ions and cotton hull adsorbent decreases with increasing feed flow which results in decrease in adsorption capacity from 27.65 mg/g to 19.56 mg/g. This can be explained by the lack of sufficient residence time of the solute to diffuse into the pores of the cotton and thus reduces the volume of the water treated and the solute left the column before equilibration. This finding is in line with that of Nwabanne & Igbokwe (2012) for the removal of Pb (II) ions using oil palm fibre and that of Nouri & Ouederni (2013) for the adsorption of phenol from an aqueous solution on an activated carbon.

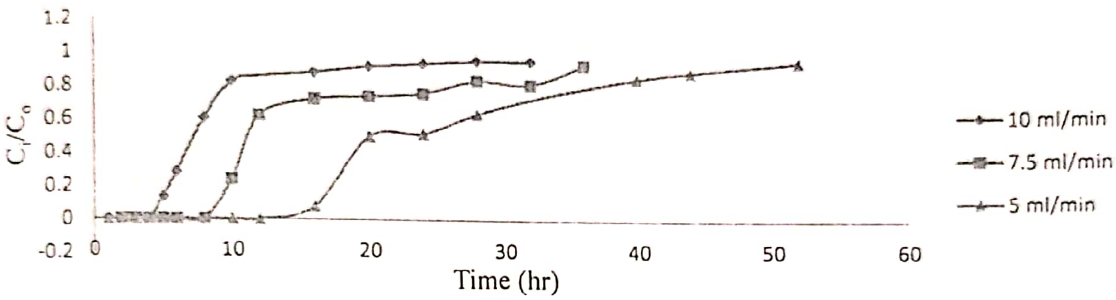

Figure 5: Effect of flow rate on breakthrough curve for Pb (II) adsorption on CHA

3.7.2 Effect of concentration

The effluent flow rate of 5 ml/min with a fixed bed of depth 4 and concentration of (50, 65 and 85 mg/l) were used to evaluate the effect of concentration on adsorption. It was observed from Figure 6 that as the effluent concentration increased, the breakthrough curves became sharper and the column with the highest inlet concentration saturated faster. That is from 3120 to 1920 minutes saturation. Also, a lower concentration gradient results in a slower transport because of decrease in the diffusion coefficient or the mass transfer coefficient as explained by Sivakumar and Palanisamy (2009) as well as Baek *et al*, (2007).

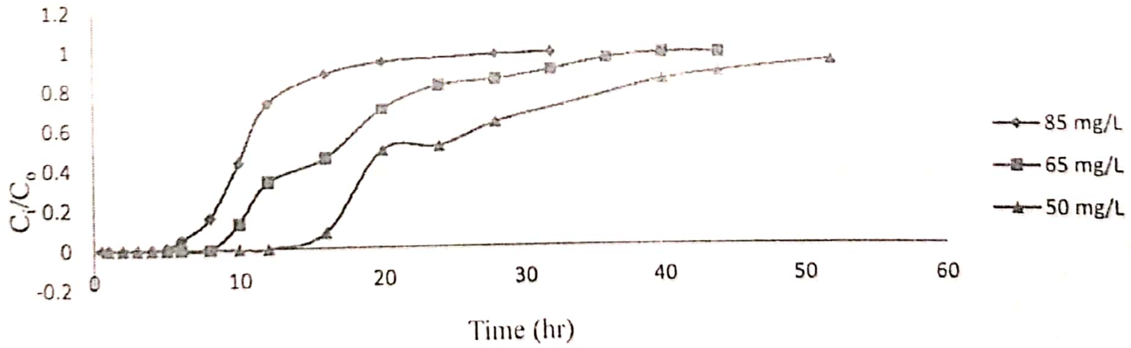

Figure 6: Effect of change in feed concentration on adsorption of cotton hull adsorbent with raw effluent

3.7.3 Effect of Adsorbent Bed Height

The effect of cotton hull bed length varied from 2.7 – 7 cm plots shown in Figure 7. The plots showed that the slope gradient of the breakthrough curves was slightly different with variation in bed depths with an earlier exhaustion for lower bed lengths. The results shown on Table 2 indicates that the breakthrough time of the adsorption increased sharply from 62 to 1212 mins with slight increase in the adsorbent bed height from 2.7 to 7 cm. This reveals that the cotton hull adsorbent had more contact time with the Pb (II) ion as the bed height was increased from 2.7 to 7 cm. Also, this may be due to the increase in the number of sorption sites (Radhika *et al.*, 2018). The increase in the adsorption capacity with increase in the bed height further suggested that at smaller bed height, the effluent adsorbate concentration ratio decreased more rapidly than for a higher bed height. Furthermore, low amount of the adsorbent in the column corresponds to smaller bed height and hence, less saturation time (Nwabanne *et al.*, 2012). The decrease in the slope of the breakthrough curves with increase in bed height observed may be due to the broadened movement of the influent at the mass transfer zone (Sekhula *et. al.* 2012).

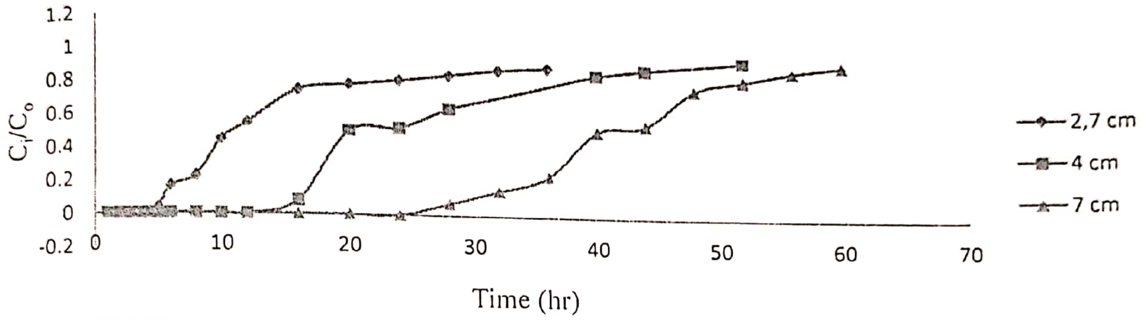

Figure 7: Effect of bed heights on column adsorption at constant concentration

Table 2 Evaluation of Column efficiency using experimental data

Q (ml/min)	conc.(mg/)	Bed (cm)	q_e, exp(mg/g)	t_{total}(min)	V_b(ml)	t_{break}(min)	q_{total}(mg)	% removal	R_a (mg/ml)
5	50	4	27.65	3120	3605	721	780	50.68	3.967
7.5	50	4	25.58	2160	3600	480	810	45.16	3.972
10	50	4	19.56	1920	2400	240	960	29.14	5.958
5	65	4	24.01	2400	2400	480	780	44.02	5.958
5	85	4	20.05	1920	905	181	816	35.14	15.8
5	50	2.7	20.95	2160	310	62	540	41.12	34.19
5	50	7	23.81	3600	6060	1212	900	69.83	4.356

q_e experimental average =23.09 mg/g and q_e theoretical average =21.60 mg/g

3.7.4 Column flow Adsorption Models

Three models (Thomas, Yoon-Nelson, and Adams- Bohart models) were used to analyse the column performance.

3.8 Application of Thomas Model

The behavior of the column was modelled using the Thomas model. Effect of bed heights and flow rate of the raw water on the removal of the Pb (II) by the cotton hull adsorbent were studied. This model is highly suitable for processes where external and internal diffusion will not be limiting step (Yahaya *et al.*, 2012) the results obtained are shown on table 2, the initial concentration increases with the value of k_{th} increasing from 0.042 to 0.068 ml/mg.min. The initial sorption capacity decreases with increasing initial concentration. This as a result of the slow mass transfer at lower concentration (Tor *et al.*, 2009), this was also reported in the modelling of the biosorption of Pb (II) by residue allspice (Cruz *et al.*, 2013). The q_{th} values decreases as the coefficient k_{th} increases when the fluid flow was increased. When the fluid flow rate increases from 5 to 7 ml/min, there was high system turbulence which reduces the effects of film diffusion and lower solute ions uptake q_{th}. Also, it was observed that the Thomas bed capacity, q_{th} gradually rises and the coefficient k_{th} decreases with an increase in bed length. The qth metal uptake is 21.60 mg/g compared with the experimental uptake of 23.09 mg/g. The correlation values are high (0.7674 ≤ R^2 ≤ 0.9551). Therefore, R^2 values and the closeness of predicted adsorption capacity to experimental data indicated the fitness of Thomas model to the experimental data. The relationship between the model and the initial concentration is to provide information on the adsorbent capacity, volume of contaminant treated and the total time needed to attain equilibrium. It is a suitable kinetic model to describe Pb (II) ions adsorption in a fixed bed column of cotton hull adsorption, Baek *et al.* (2007) and Nwabanne & Igbokwe (2012) but in contrast with the report of Sivakumar and Palamisamy (2009).

Table 2: Thomas model Parameters at different flow rates, initial concentrations and bed heights

Q_f (ml/min)	Conc.(mg/l)	Bed ht(cm)	t_{total}(min)	V_{eff} (ml)	K_{TH} (ml/mg.min)	q_{TH} (mg/g)	q_e, exp(mg/g)	R^2
5	50	4	3120	15600	0.042	27.25	27.65	0.9021
7.5	50	4	2160	16200	0.036	18.93	25.58	0.7883
10	50	4	1920	19200	0.054	14.90	19.56	0.7741
5	65	4	2400	12000	0.046	23.02	24.01	0.9551
5	85	4	1920	9600	0.068	22.92	20.05	0.9028
5	50	2.7	2160	10800	0.070	19.70	20.95	0.7674
5	50	7	3600	18000	0.068	24.46	23.81	0.9261

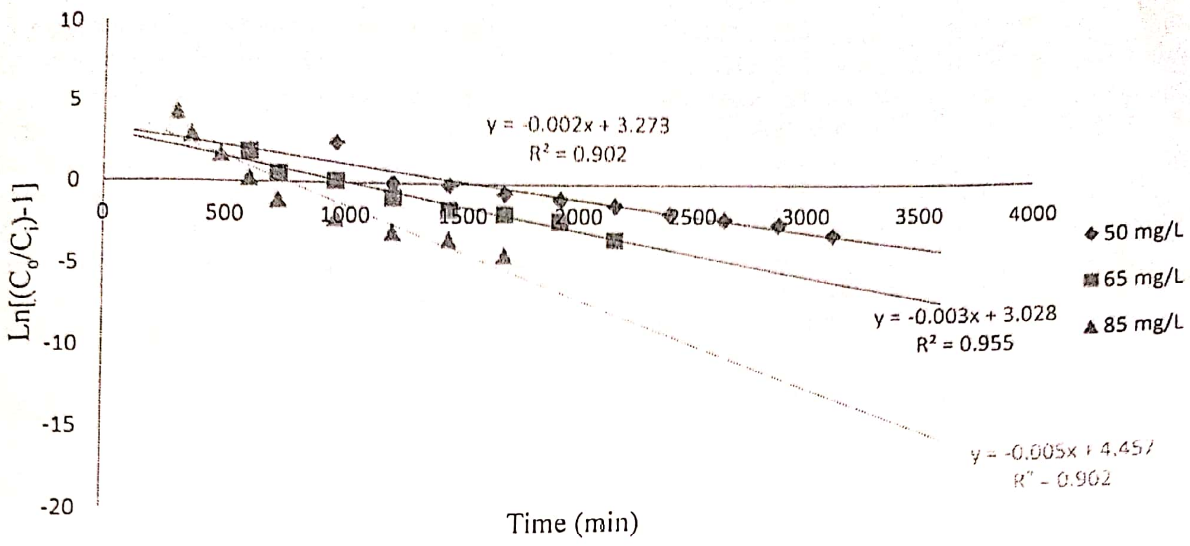

Figure 8: Linear plot of Thomas model with experimental data at different concentrations and fixed bed heights and initial metal ions concentrations

3.9 Application of Yoon – Nelson Model

Yoon–Nelson was used to examine the breakthrough behavior of Pb (II) ions on cotton hull adsorption. The values of k_{YN} and τ were determined from the plot of $L_n[C_i / C_o - C_i]$ against time at different operating conditions, to predict the rate constant and time required for 50% adsorbate breakthrough. The results obtained are shown on table 3. As initial concentration was increased at constant bed height and flow rate, the k_{YN} and τ decreased and increased respectively with increase in the initial concentration of the adsorbate. As the bed height increase, the values of τ increases from 1098.03, 1559.29, 2572.29 minutes for 2.7, 4 and 7 cm beds respectively. This is similarly reported on the study of adsorption of Cu (II) onto maize tassel-PVA beads (Sekhula *et al.*, 2012), removal of perchlorate using modified activated carbon (Redhika *et al.*, 2018). This further suggests that increase in the bed height increased the contact time of the adsorbent on the adsorbate. The predicted τ obtained from the Yoon-Nelson model are closed to the experimental values. The regression coefficient R^2 values ($0.7661 \leq R^2 \leq 0.9551$) provide a good fit for the model, this agrees with the report provided by Radhika *et al.*, 2018. Therefore, Yoon-Nelson model could give depiction of an adsorption process for a single component Pb (II) adsorption of cotton hull adsorbent.

Table 3: Yoon-Nelson model Parameters at different flow rates, initial concentration, and bed heights.

Qf (ml/min)	Conc. (mg/L)	Bed height (cm)	K_{YN} (1/min)	$\tau_{Predicted}$ (min)	R^2	τ_{exp} (min)
5	50	4	0.0021	1559.2857	0.9031	1442
7.5	50	4	0.0017	751.8823	0.7881	960
10	50	4	0.0027	417.6296	0.7661	480
5	65	4	0.003	1009.4667	0.9551	960
5	85	4	0.0058	768.5345	0.9028	362
5	50	2.7	0.0034	1098.0294	0.7865	124
5	50	7	0.0034	2572.2941	0.9244	2424

Key: $\tau_{exp} = \tau_{experiment}$

3.10 Application of Adams –Bohart Model

From table 4, adsorption capacity of adsorbent, No increased from 21358 to 42025 mg/l. The increase of adsorption capacity of the adsorbent with increase in bed height was similarly reported by Asif and Chen (2015), Yahuza *et al*.,(2017) while the kinetic constant of the model, *Kab* decrease with incresing adsorbent height (2.7 – 7 cm). It was observed that adsorption capacity of the adsorbent N_o decreased from 23140 to 13623 mg/l with increasing flow rate (5-10 ml/min). The R^2 value decreased with increase in flow rate at constant concentration and bed height. For instance, at 10, 7.5 and 5 ml/min, the R^2 were 0.4692, 0.5424 and 0.5698 respectively. At higher concentrations, the bed capacity has no defined pattern. This probably indicates that the model is not fit for a process at a very high flow rate (Yagub *et al*. 2014).

Table 4: Application of Adams-Bohart model to the experimental Data

Q_f(ml/min)	Conc. (mg/L)	Bed h_t(cm)	K_{AB} (ml/mg.min)	N_o (mg/L)	R^2
5	50	4	0.016	23140	0.5698
7.5	50	4	0.012	16932	0.5424
10	50	4	0.016	13623	0.4692
5	65	4	0.011	26290	0.679
5	85	4	0.023	22753	0.578
5	50	2.7	0.046	21358	0.606
5	50	7	0.04	42025	0.7282

4.0 CONCLUSION

Cotton seed hull is an economically viable adsorbent for the removal of Pb (II) ions from mining waste waters. Three models were used to evaluate the behavior of the experimental adsorption. Thomas model showed the comparison between the average experimental adsorption capacity of 23.09 mg/g and a theoretical value of 21.60 mg/g as well as a reasonably high correlation ($0.7674 \leq R^2 \leq 0.9551$). The Yoon–Nelson model showed the data regression analysis results also high linear correlation ($0.7661 \leq R^2 \leq 0.9551$). Hence, the Yoon – Nelson model is suitable model to foretell the behavior of the experimental adsorption. Adams –Bohart model predicts poor efficiency of fixed – bed column.

Characterizations of the untreated adsorbent carried out which included FTIR, SEM and BET. FTIR showed that the adsorbent has functional groups such as OH, C-O, C=O, C-O-H and CH_2. The SEM result showed that the micrograph structures of raw cotton hull carbon represent a large surface area for heavy metal ions adsorption. The BET provided a summary of specific surface area (139.8 m^2/g), micro-pore volume (0.0217 cm^3/g), micro pores (< 2 nm) and pore radius (9.237 Å). Column adsorption scale-up data for the 120 L/hr of Kagara mining wastewater shows that 607.2 L of the effluent can be treated of Pb (II) in 5.06 hours using 4.75 kg of the cotton hull adsorbent. Also, the column adsorption parameters investigated which included initial metal ions concentration, pH, feed flow rate, apparent density (0.42 g/ml) indicated that cotton hull as an adsorbent has high potential for removing heavy metal ions especially Pb (II), from aqueous solutions.

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