Complexation equilibrium studies of Cu^{2+}, Cd^{2+} and Pb^{2+} ions onto ethylenediamine quaternised *Artocarpus heterophyllus* L. seeds from aqueous solution

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Abstract

Heavy metals contamination in drinking water is of great concern because of their toxicity and non-biodegradability. Therefore, their removal is paramount. Recently, adsorption has gained a great attention from researchers due to availability of the materials and associated capacity compared to conventional methods of water treatment. Various chemical treatment methods have been employed to boost the capacity of the adsorbents, one of them being the use of ethylenediamine. In this study, a novel quaternised adsorbent was synthesized for complexation of Cu^{2+}, Cd^{2+} and Pb^{2+} ions from aqueous solution. Raw Artocarpus heterophyllus L. seeds were chemically modified with thionyl chloride followed by ethylenediamine. Both raw and quaternised adsorbents were characterized by FTIR and applied for equilibrium complexation batch experiments. Effect of pH, contact time, agitation speed, adsorbent dosage and initial concentration were investigated. FTIR results showed that amino groups were successfully anchored into the quaternised adsorbent and this increased its complexation capacity. Batch results indicated that complexation of the three metal ions was at optimal at pH values between 4.2 and 6.4. Contact time of 20 minutes and 15 minutes for raw and quaternised adsorbents respectively. Agitation speed of between 150 rpm and 175 rpm. Raw and quaternised dosage of 15 mg and 10 mg; 13 mg and 10 mg; 15 mg for Cu^{2+}, Cd^{2+} and Pb^{2+} ions respectively and optimal concentration of 30 ppm. Equilibrium experimental data fitted well in Langmuir isotherm with adsorption capacities of 21.3220 mg g^{-1}, 19.6850 mg g^{-1} and 21.8818 mg g^{-1} for raw and 33.7838 mg g^{-1}, 25.1256 mg g^{-1} and 34.0136 mg g^{-1} for quaternised adsorbent for Cu^{2+}, Cd^{2+} and Pb^{2+}ions respectively implying a chemisorption mechanism. The results confirmed potentiality of Artocarpus heterophyllus L. seeds for heavy metal ions removal from aqueous solutions.

Keywords: Artocarpus heterophyllus L. seeds, ethylenediamine, quaternised, equilibrium, complexation

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I. Introduction

Water is vital for survival and must be of good quality and free of contaminants (Yerima *et al.,* 2019). It's of paramount to safeguard it, by all means, to ensure life continuity due to its diverse uses such as drinking, cooking, washing and bathing amongst others (Ndambiri and Rotich, 2018). Surface and ground water sources such as rivers, streams, wells and boreholes are the main sources of water to majority (Chebet *et al.,* 2020). Therefore, pollution of these sources by heavy metal toxicants via natural and anthropogenic processes is lethal to the ecosystem (Vafakhah *et al.,* 2014).Industrialization and technological advancements have led to the release of a myriad of toxic loathsome heavy metal pollutants to the environment (Baby *et al.,* 2019; Sahare and Gharde, 2017). This has created problems of their proper disposal by many developing countries and are discharged carelessly to the environment posing a threat to human health (Mustapha *et al.,* 2019).

Heavy metal ions such as Cu^{2+}, Cd^{2+} and Pb^{2+} enter into the water bodies through discharge of domestic wastes (Rahman *et al.,* 2015) and industrial effluents from industries such as battery manufacturing, fertilizers, electroplating and other chemical industries therefore compromising water quality for consumption (Terdputtakun *et al.,* 2017). Exposure of these heavy metals to human beings beyond permissible levels has health effects such as mental deficiency, brain damage, anemia, vomiting, anorexia and lesions to the central nervous system for Pb^{2+} (Yousefi *et al.,* 2018). Cu^{2+} is associated with kidney damage, stomach intestinal distress, anemia and eventual death (Tofighy and Mohammadi, 2015). Cd^{2+} is known to cause destruction of

testicular tissues, high blood pressure, kidney damage, osteoporosis and destruction of red blood cells (Zare *et al.,* 2018). This has made quality of such drinking water questionable for use. Maximum limit for Cu^{2+}, Cd^{2+} and Pb^{2+} in drinking water are 2 mg L^{-1}, 0.003 mg L^{-1} and 0.010 mg L^{-1} respectively (WHO, 2011). However, even to their level of acceptance, when consumed for a very long time still accumulate in the body tissues compromising human health (Mwangi *et al.,* 2012). Therefore, an urgent need to mitigate this menace for a better tomorrow is paramount.

A number of physical and chemical conventional methods such as ion exchange, chemical precipitation, coagulation-flocculation and electrochemical treatments (Chaemiso and Nefo, 2019) among others have previously used to get the desired wastewater treatment results. They have however proved to be not only expensive (He *et al.,* 2019) but are also not effective when the concentration of the trace heavy metals levels ranges from 1- 20 µg.l^{-1} (Bii *et al.,* 2016). Thus, a need to source for economical and locally available alternatives to suit the local needs and environmental sustainability must be a matter of urgency. Adsorption technique has been a promising technique as it offers a great advantage of being easily available, cheap and easily regenerated (Terdputtakun *et al.,* 2017). Major interest at the heart of researchers recently has been to the use of adsorbents of natural origin from agricultural wastes such as sorghum husk (Tatah *et al.,* 2017), sugarcane bagasse (Salihi *et al.,* 2015) and avocado seeds (Nthiga *et al.,* 2016) among others in the remediation of heavy metals wastewater. This is because they are available in large quantities (Thakuria and Talukdar, 2012) and contain surface functional groups (El-Araby *et al.,* 2019) for complexation. Jackfruit seeds are about 15 % of the total fruit weight and are discarded as wastes (Madruga *et al.,* 2014).Very little has been explored on the use of the waste as an adsorbent. Therefore, this study explored the potential of the seed for heavy metal removal from wastewater.

The use of biomasses in its raw form has been reported to not only to cause leaching of soluble organic matter in treated drinking water (Moyo *et al.,* 2013) but also have low complexation capacity and poor selectivity towards metal ions (Chen *et al.,* 2017). Therefore, stabilizing the material via chemical modification is necessary to overcome above challenge. Use of modifying agents for example organic compounds such as diethylenetriamine (Huang *et al.,* 2018), mineral acids such as sulphuric acid (Nthiga *et al.,* 2016) and basic compounds such as sodium hydroxide (Mopoung and Kengkhetkit, 2016) among others have been explored. Ethylenediamine, a low-toxicity and cheap strong chelating agent has recently been used for chemical modification and contains two amino groups that are introduced to the adsorbent surface (Huang *et al.,* 2018). Various researches have reported that using this modifying agent improved complexation capacity and reduced organic matter leaching to the treated water (Ding *et al.,* 2014; Mwangi *et al.,* 2012). Literature survey indicates no report on the use of Jackfruit seeds adsorbent on the removal of heavy metals in chemically modified form using chelating agents. Also, there is no detailed information on the complexation equilibrium studies on the use of Jackfruit seeds for the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} ions from aqueous media. The study therefore reports the use of ethylenediamine modified Jackfruit seeds adsorbent to study the equilibrium studies of Cu^{2+}, Cd^{2+} and Pb^{2+} ions from aqueous solution. The effect of pH, contact time, agitation speed, adsorbent dose and initial metal ion concentration were investigated. Equilibrium isotherm models were explored to determine the complexation capacity of the complexation of the three metal ions.

II. Materials And Methods

Chemicals and Reagents

All the solutions were prepared in double-distilled water and the chemicals were of analytic grade. Copper Nitrate, Cu (NO$_3$)$_2$, Cadmium Nitrate, Cd (NO$_3$)$_2$, Lead Nitrate, Pb (NO$_3$)$_2$, Hydrochloric acid (HCl), Sodium Acetate (NaOC$_A$), Potassium hydroxide (KOH), Thionyl chloride (SOCl$_2$), Ethylenediamine (EDA), N,N-dimethylformamide (DMF) and Ammonia (NH$_3$) were all supplied by Sigma Aldrich (Kobian, Nairobi Kenya). Jackfruits were obtained from City park market, Nairobi, Kenya.

Preparation of metal ion solutions

Stock solutions were prepared in 0.1 M NaOC$_A$ buffer solution to maintain a constant ionic strength from which working solutions were obtained. The pH of working solutions was adjusted with either 0.1M HCl or 0.1M KOH.

Adsorbent preparation

The fruits were cleaned with distilled water, cut open and all parts removed carefully. The seeds sample were then cut into small pieces and dried in an oven for 24 hours at 105 ^{o}C until constant weight was

obtained. The oven-dried materials were grounded and allowed to pass through a fine-mesh sieve (150 to 250 mm) and kept in an air tied bottle prior to subsequent experiments. Chemical modification was done as described by Da Silva Filho *et al.* (2006) with slight adjustments. The seeds powder were first pre-activated at 50 ^{o}C for 24 hours. 10.000 g of the activated Jackfruit seeds was suspended in 200 mL DMF in a three-necked flask, slow addition of 35 mL SOCl$_2$ using a dropping funnel followed and the mixture was mechanically stirred under a reflux for 4 hours at a temperature of 80 ^{o}C. The chlorinated material was then washed thrice with 25 mL of 2M Ammonia solution (NH$_4$OH) to adjust the pH to neutral confirmed by indicator paper. The chlorinated adsorbent was then washed with distilled water and filtered in sintered glass crucible and dried in *vacuo* at room temperature. 5.000 g of the chlorinated material was suspended in DMF which was followed by slow addition of 25 mL EDA in a three necked flask under reflux and mechanically stirred at 80 ^{o}C for 4 hours. The solution was then filtered through a sintered glass crucible and the adsorbent was then dried in *vacuo* at room temperature.

Instrumentation

Fourier Transform Infrared (FT-IR) spectrophotometer (IRTracer-100, SHIMADZU made in Japan) was used to determine the functional groups present in the adsorbent materials. Lab-line mechanical reciprocating shaker model SSL$_2$ (Harrogate, UK) was used for batch complexation experiments. pH meter (HANNA model) was used to monitor the pH of the metal solutions. The Atomic absorption Spectrophotometer, AAS (AA-6200, SHIMADZU) was used to determine the metal ion content in the solution.

FT-IR Characterization

Analysis of raw, chlorinated and quaternised adsorbents was done using FT-IR. KBr pellet disks were prepared by mixing 1.000 mg of each of the dried samples with 500.000 mg of KBr (Merck, spectroscopy grade) using a pestle in an agate mortar, grinded into a fine powder and pressed in a vacuum for 10 minutes into a pellet of 2 mm internal diameter in order to obtain the diffuse reflectance infrared spectrum for the samples. All spectra were plotted as the percentage transmittance (%T) against wave number (cm^{-1}) at a mid IR range of 4500-500 cm^{-1} at a room temperature. Signals for 10 scans were averaged for a single spectrum.

Batch complexation studies

All batch complexation experiments were carried out in 120 mL plastic screw cap bottles at a room temperature. 0.010 g of the adsorbent was added in a plastic screw cap bottles containing 20 mL of desired concentration of the respective metal solutions and then agitated thoroughly using a reciprocating mechanical shaker at 150rpm for one hour. Effect of pH (2.0-14.0), contact time (0-80 minutes), agitation speed (30 – 300 rpm), adsorbent dosage (0.001 – 0.100 g) and initial concentration (5 -50 ppm)were investigated. Each of the resulting mixture was then filtered through Whatman N$_o$. 42 filter paper and the amount of metal ions in the supernatant solution were determined by AAS. The amount of metal complexed was calculated by the equation 1:

$$q_e = \frac{C_i - C_e}{M} V \qquad (1)$$

Where q_e is the amount of metal ions adsorbed at equilibrium, C_i is initial adsorbate concentration and C_e is adsorbate final concentration at equilibrium (mg/L), V is the total volume of the solution and M is the adsorbent dosage mass.

Adsorption isotherms

In order to quantify the complexation of Cu^{2+}, Cd^{2+} and Pb^{2+} ions at equilibrium, Langmuir and Freundlich isotherm models were employed. Langmuir model assumes adsorption that occurs at fixed sites holding one metal ions at a time (monolayer) and a chemisorption adsorption process. The linear form of the Langmuir isotherm is given by equation 2:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} b} \qquad (2)$$

Where C_e is the equilibrium concentration of the metal ions in solution (mg L^{-1}), q_e is the amount of metal ions adsorbed per unit weight of the adsorbent (mg g^{-1}). Constants q_{max} and b are the characteristics of the Langmuir

equation. q_{max} is the maximum adsorption capacity (mg g^{-1}) and b is the energy of the adsorption (L mg^{-1}). A plot of $\frac{C_e}{q_e}$ against C_e gives as straight line and the plot is used to obtain the Langmuir constants.

The Freudlich isotherm model describes multilayer adsorption of metal ions on a heterogeneous surface in an adsorption process and assumes an exclusively physical adsorption process. The linearized equation for the model is given by equation 3:

$$\ln q_e = \ln K_F + \frac{1}{n} ln\ C_e \tag{3}$$

Where q_e is the amount of solute ions adsorbed (mg/L) at equilibrium, C_e is the concentration at equilibrium (mg/L). K_F (adsorption capacity) and n (adsorption intensity) are Freundlich constants. A plot of $\ln q_e$ against $\ln c_e$ gives a straight line and is used to determine K_F and n from the intercept and slope respectively.

III. Results And Discussions

FTIR characterization

The FTIR spectra of raw, chlorinated and quaternised adsorbents is presented in figure 1.
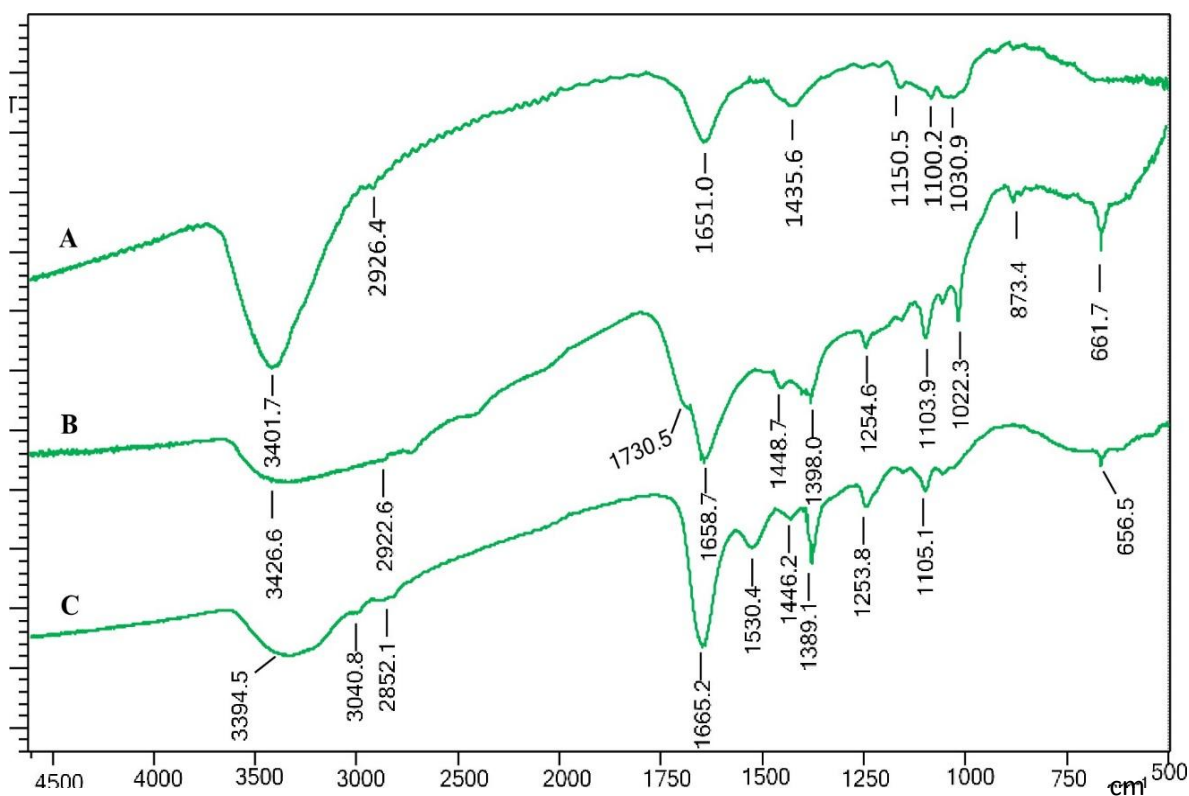

Figure 1: FTIR Spectra of (A) raw, (B) chlorinated and (C) quaternised *Artocarpus heterophyllus* L. seeds

The FTIR spectrum of raw material (A) exhibits a broad band at 3401.7 cm^{-1} ascribed to stretching vibrations of bonded hydroxyl (-OH) groups (Soldatkina and Zavrichko, 2019) as well as inter- and intra-molecular hydrogen bonding of polymeric compounds with alcoholic, phenolic or carboxylic moieties (Panadare *et al.,* 2014). A weak band at 2926.4 cm^{-1} is attributed to symmetric and asymmetric –C-H stretching vibration (Chethan and Vishalakshi, 2013). The band at 1651.0 cm^{-1} could be attributed to stretching vibration of C=O carbonyl groups of ionic and non-ionic carboxylic acid derivatives (Joseph *et al.,* 2017). The peak at 1435.6 cm^{-1} could be due to –CH bending vibrations of methylene, methyl and methoxy groups. The peak band at 1150.5 cm^{-1}and at 1030.9 cm^{-1} could be ascribed to symmetric C-O stretching vibrations of carboxylic acid derivatives and alcoholic groups (Feng and Guo, 2012).

The chlorinated material (B) shows appearance of two new peaks at 873.4 cm^{-1} (Chethan and Vishalakshi, 2013) and another pronounced one at 661.7 cm^{-1} (Mwangi *et al.,* 2012) which are ascribed to the

stretching vibration of C-Cl bond and a new weak band at 1730.5 cm^{-1} corresponding to its bending vibration (Ghali *et al.,* 2011). Also, the peak at 1030.9 cm^{-1} which is attributed to C-O stretching vibration of alcoholic groups (raw) is reduced to 1022.3 cm^{-1} (chlorinated) showing that –OH has been replaced by chlorine groups. The –OH peak in alcohol also shifted from 3401.7 cm^{-1} (raw) to 3426.6 cm^{-1} upon chlorination and its intensity decreased due to substitution.

Results in FTIR spectrum of quaternised adsorbent (C) shows disappearance of 873.4 cm^{-1}, 661.7 cm^{-1}, 1730.5 cm^{-1} and 1022.3 cm^{-1} peaks. This is an indication of chloro substitution by EDA. The (-OH) absorption peak is shifted to 3394.5 cm^{-1} from 3401.7 cm^{-1} (raw) an indication of intermolecular interactions between –OH groups and –OH/NH$_2$ groups of the quaternised *Artocarpus heterophyllus* L. seeds (Xiao and Hu, 2017). The shifting of symmetric –CH$_2$ stretching vibration from 2922.6 cm^{-1} (chlorinated) to 3040.8 cm^{-1} (quaternised) is an indication of methylene groups of EDA moiety. Also, a new band at 2852.1 cm^{-1} arises due to the C-C stretching of the EDA moiety (Chethan and Vishalakshi, 2013). The shifting of the peak from 1651.0 cm^{-1} (raw) to 1665.2 (quaternised) and appearance of a new characteristic peak at 1530.4 cm^{-1} is attributed to N-H deformation vibrations (Adewuyi and Pereira, 2017) an indication that EDA was successfully anchored into the *Artocarpus heterophyllus* L. seeds cellulose. The band at 656.5 cm^{-1} could be assigned to –CN stretching (Ertugay and Malkoc, 2014).

Complexation capacity is expected to be higher in quaternised adsorbent as compared to raw adsorbent as supported by the above results.

Batch complexation results

Effect of pH
pH is crucial in determining the adsorbent surface charge and the chemistry of the metal ions in the solution. The results of effect of pH are presented in figure 2.
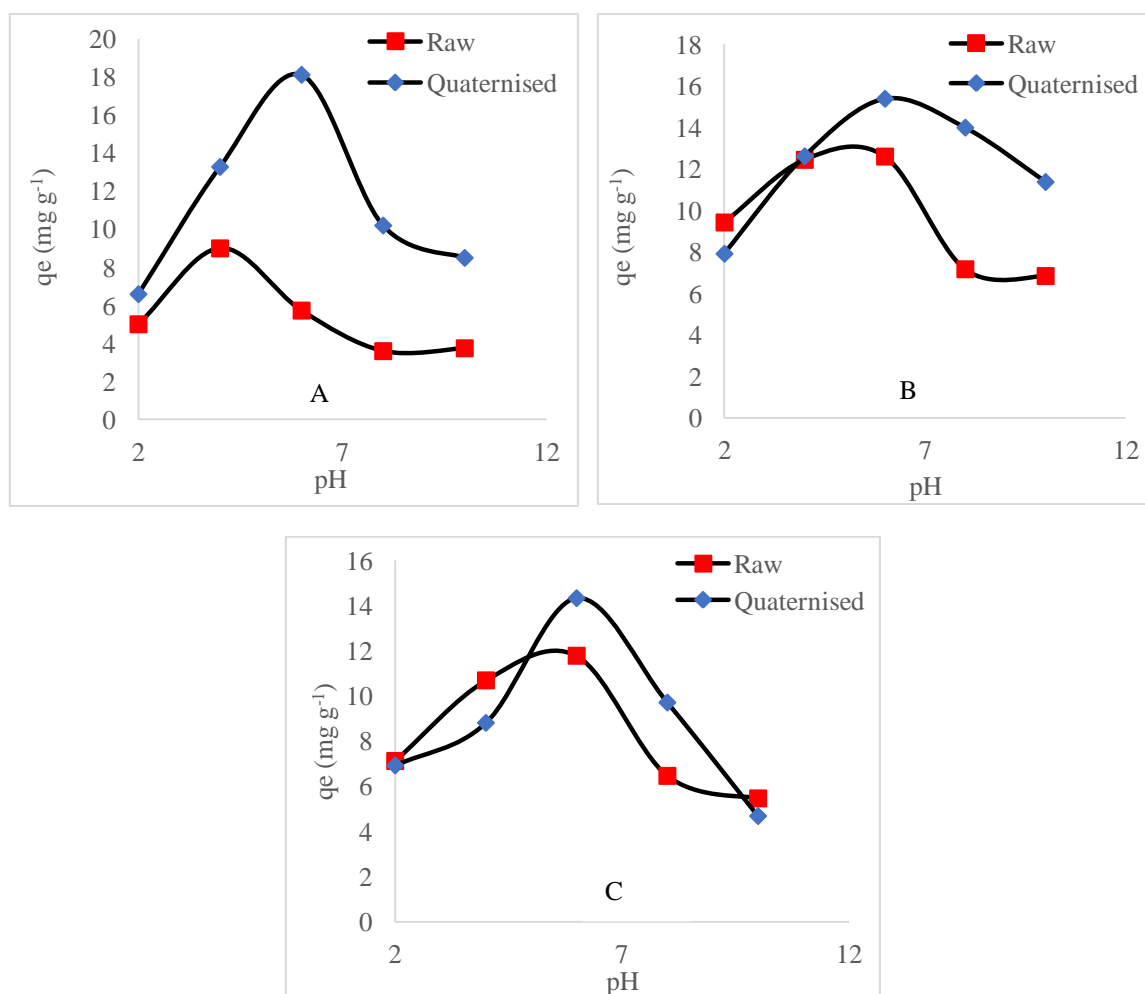

Figure 2: A plot of qe (mg g^{-1}) against pH for the complexation of Cu²⁺ (A), Cd²⁺ (B) and Pb²⁺ (C) ions

The results presented in figure 2 shows the effect of pH on the complexation of Cu^{2+}, Cd^{2+} and Pb^{2+} ions by the raw and quaternised *Artocarpus heterophyllus* L. seeds adsorbents. Complexation capacity increased as pH increased to a maximum of 4.2 (8.99 mg g^{-1}), 5.0 (12.60 mg g^{-1}) and 5.6 (11.77 mg g^{-1}) for raw adsorbent and 5.7 (18.11 mg g^{-1}), 6.4 (15.38 mg g^{-1}) and 6.0 (14.32 mg g^{-1}) for quaternised adsorbent for Cu^{2+}, Cd^{2+} and Pb^{2+} ions respectively after which further increase in pH led to a decrease. Therefore, complexation of the three metal ions worked best at pH values of between 4.2 and 6.4. This phenomenon is explained by the fact that at low pH values, the metal solution is highly acidic thus H$^+$ ions will compete with the metal ions in the solution. H$^+$ ions out-competes the metal ions therefore decreasing their complexation capacity (Salihi *et al.,* 2015).

At pH above values of 6.5, all the three metal ions precipitates to their respective metal hydroxides and this reduces the complexation capacity (Qiu *et al.,* 2016). At optimum, complexation capacity was higher in quaternised adsorbent than in raw adsorbent. This is due to the addition of the amine complexation centers which have a high affinity for Cu^{2+}, Cd^{2+} and Pb^{2+} metal ions (Dong *et al.,* 2019; Duan *et al.,* 2013). The results recorded are similar to those reported by (Nthiga *et al.,* 2016; Qiu *et al.,* 2016; Mwangi *et al.,* 2012).

Effect of contact time

The effect of contact time investigated by varying shaking times at intervals of 10 minutes and the results are presented by figure 3.
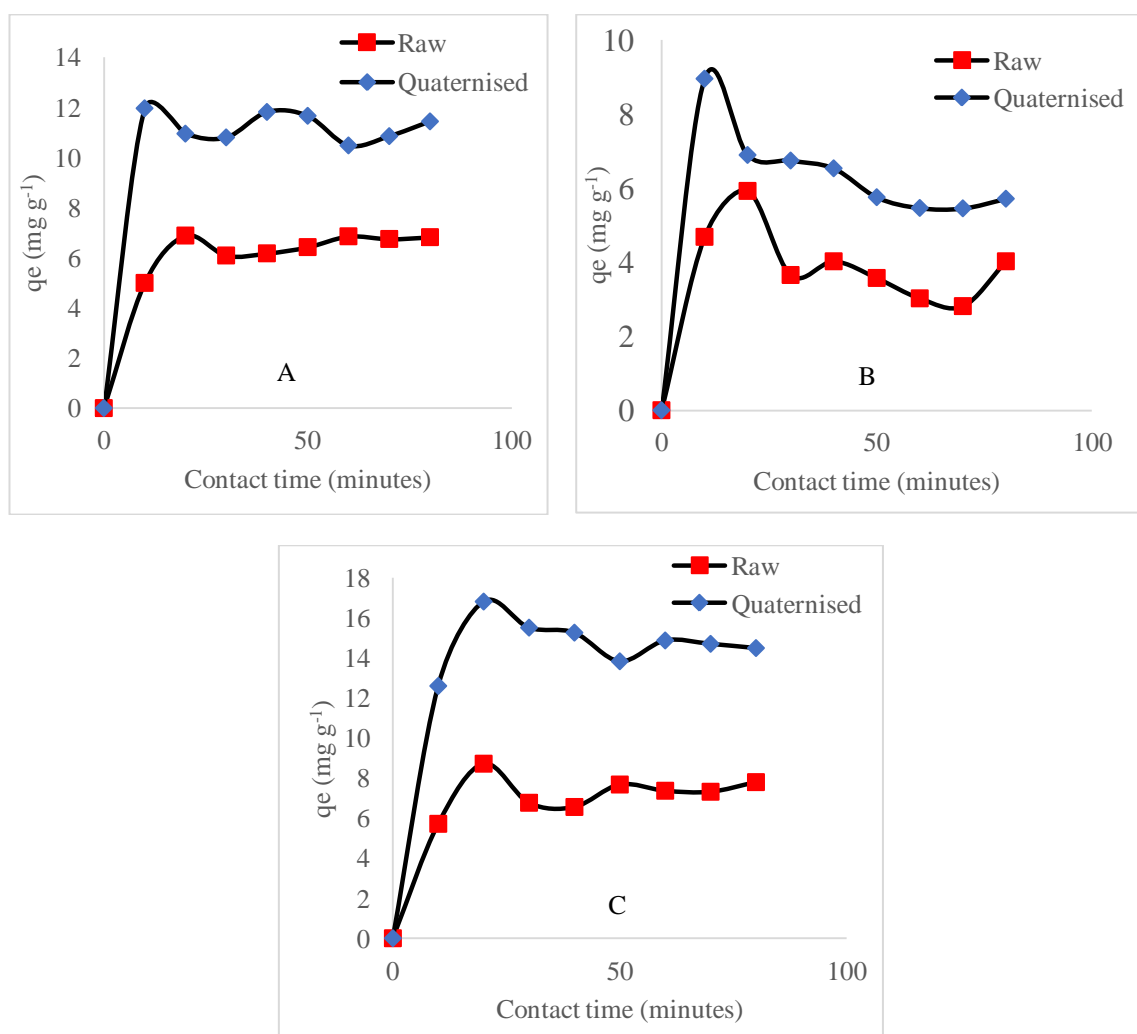

Figure 3: A plot of qe (mg g^{-1}) against contact time for the complexation of Cu^{2+} (A), Cd^{2+} (B) and Pb^{2+} (C) ions

The results shows that metal ions complexation was rapid with maximum complexation capacity at maximum of 6.61 mg g^{-1}, 5.89 mg g^{-1} and 8.63 mg g^{-1} within the first 20 minutes for raw adsorbent and 11.91 mg g^{-1}, 8.64 mg g^{-1} and 16.55 mg g^{-1} within 15 minutes for quaternised adsorbent for Cu^{2+}, Cd^{2+} and Pb^{2+} ions respectively. Beyond this time, a plateau state was observed. Rapid metal uptake at lower contact time may be attributed to the availability of the surface binding sites on both raw and quaternised adsorbents (El-Araby *et al.,* 2019). A steady state at equilibrium is attributed to the saturation of the binding sites (Wang *et al.,* 2018) and the repulsive forces between the metal ions on the adsorbent phase and the solution phase making the remaining vacant binding sites difficult to be occupied by the metal ions (El-Araby *et al.,* 2019).

Quaternised adsorbent attained equilibrium within a shorter contact time and a higher complexation capacity compared to the raw Jackfruit seeds for the three metal ions. This may have been attributed to adequate surface area saturated with grafted amine centers on the quaternised adsorbent for metal ions chelation (Tshwenya and Arotiba, 2017).The results indicate that chemical modification not only increased the rate of complexation but also the complexation capacity (Su *et al.,* 2017; Duan *et al.,* 2013). The contact time was made to 30 minutes for the subsequent studies to allow enough time for the complexation process. The results agree with those reported by (El-Araby *et al.,* 2019; Li *et al.,* 2019; Vafakhah *et al.,* 2014; Liang *et al.,* 2013).

Effect of Agitation speed

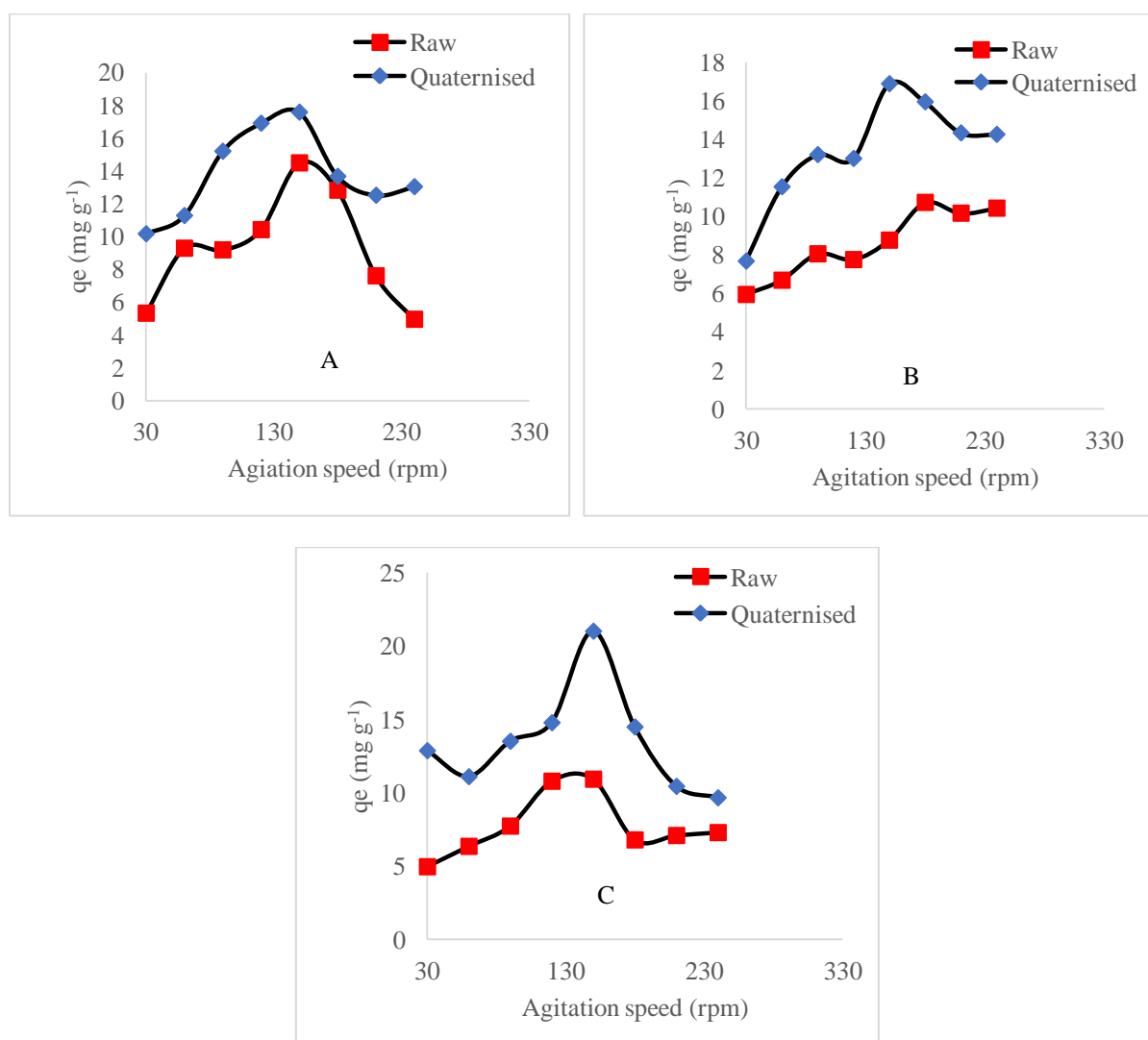The effect of agitation speed results are presented by figure 4.

Figure 4: A plot of qe (mg g^{-1}) against Agitation speed for the complexation of Cu^{2+} (A), Cd^{2+} (B) and Pb^{2+} (C) ions

Optimal shaking speed for Cu^{2+} ions was 150 rpm both raw and quaternised Jackfruit seeds, 175 rpm (raw) and 150 rpm (quaternised) for Cd^{2+} ions and 150 rpm both raw and quaternised for Pb^{2+} ions. Chemical modification improved metal ions uptake from 14.48 mg g^{-1} to 17.57 mg g^{-1}, 10.72 mg g^{-1} to 16.88 mg g^{-1} and 10.91 mg g^{-1} to 21.39 mg g^{-1} for Cu^{2+}, Cd^{2+} and Pb^{2+} ions respectively. This can be attributed by additional amine groups on the adsorbent surface which has higher affinity for the metal ions (Dong *et al.,* 2019). The complexation capacity of Cu^{2+}, Cd^{2+} and Pb^{2+} ions increased with increase agitation speed to optimal for both raw and quaternised forms beyond which a decrease was reported.

Low complexation capacity at low agitation speed can be attributed to the fact that the adsorbent particles are not well distributed therefore reducing the number of binding sites available for complexation (El-Araby *et al.,* 2019) and low diffusion of the metal ions towards the surface active sites (Berhe *et al.,* 2015). At optimal speed, there is maximum exposure of all active sites for metal ions maximum adsorption of both adsorbents. At elevated agitation speeds, the adsorbent particles are strenuously spread and therefore not giving enough time for interaction between the metals and the adsorbent for complexation and too vigorous agitation speed may make more metal ions desorbed from the adsorption sites (Saraeian *et al.,* 2018). These results are compared with those reported by (Saqaf Jagirani *et al.,* 2020; Alwared and Sadiq, 2019; Olabemiwo *et al.,* 2017).

Effect of adsorbent dosage

The effect of adsorbent dosage on Cu^{2+}, Cd^{2+} and Pb^{2+} ions complexation was investigated (figure 5).
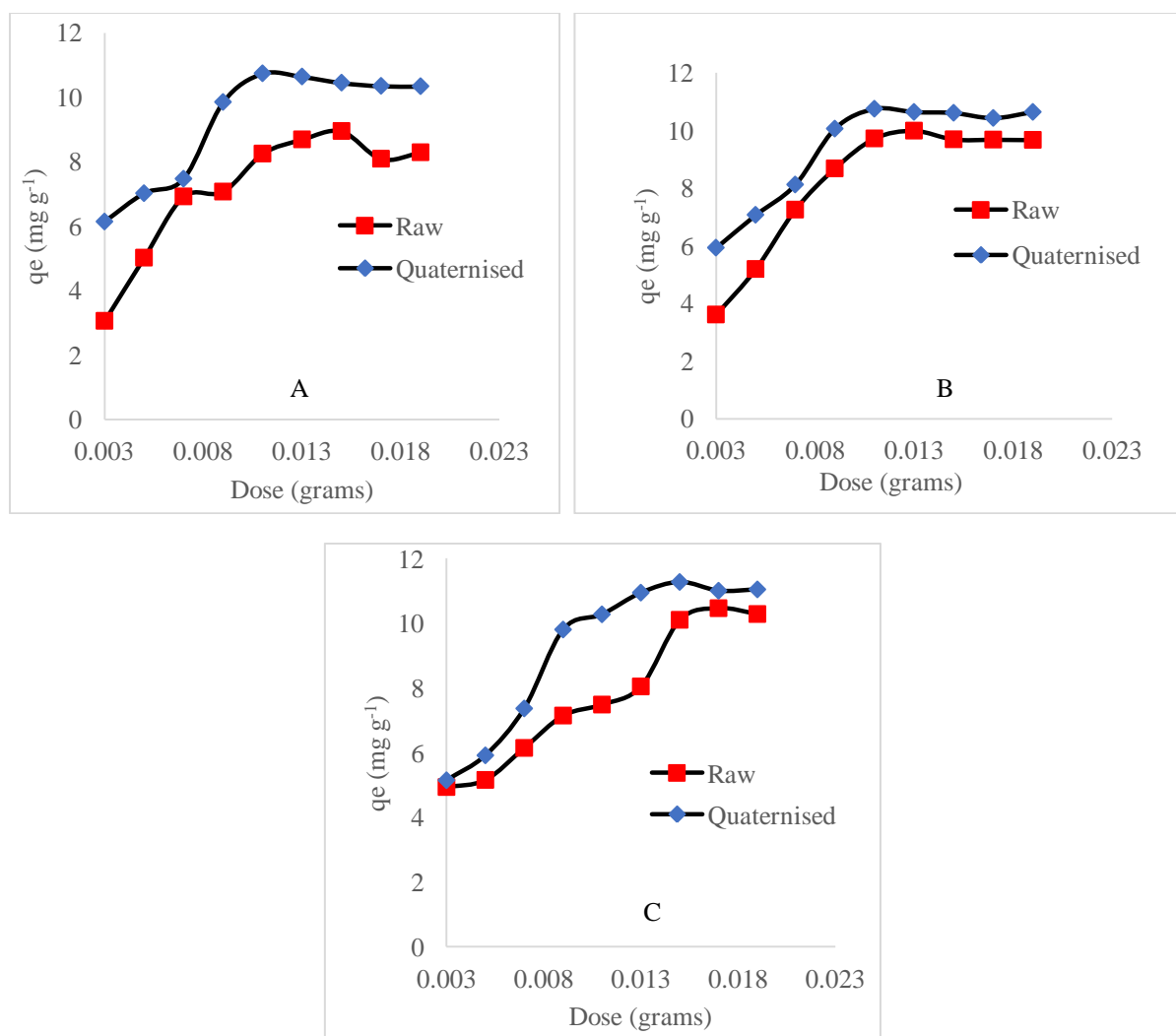

Figure 5: A plot of qe (mg g^{-1}) against dosage for the complexation of Cu^{2+} (A), Cd^{2+} (B) and Pb^{2+} (C) ions

From the results in figure 5, experimental data revealed that complexation capacity of Cu^{2+}, Cd^{2+} and Pb^{2+} ions increased with dosage increase to optimum then a steady state. Maximum complexation capacity was observed at 15 mg (raw) and 10 mg (quaternised), 13 mg (raw) and 10 mg (quaternised) for cadmium and 15 mg (both raw and quaternised) with maximum complexation capacity increasing from 8.95 mg g⁻¹ to 10.74 mg g⁻¹, 9.99 mg g⁻¹ to 10.69 mg g⁻¹ and 10.11 mg g⁻¹ to 11.28 mg g⁻¹ for Cu^{2+}, Cd^{2+} and Pb^{2+} ions respectively.

This phenomena is attributed to low number of active sites at lower dosages and availability of active sites as the amount of dosage is increased to equilibrium (Hassan *et al.,* 2020). A plateau beyond optimal is attributed to the overlapping of the active sites as a result of overcrowding of adsorbent particles and screening effect leading to shielding of the binding sites of adsorbent from metal ions uptake (Yousefi *et al.,* 2018). The results are similar to those reported (Hosseini *et al.,* 2019; Mehdinia *et al.,* 2019; Younes and El-Maghrabi, 2019; Feng and Wen, 2017).

Effect of initial metal ion concentration

Figure 6 shows initial metal ions concentration effect (5-50 ppm) on their complexation on both raw and quaternised adsorbents.
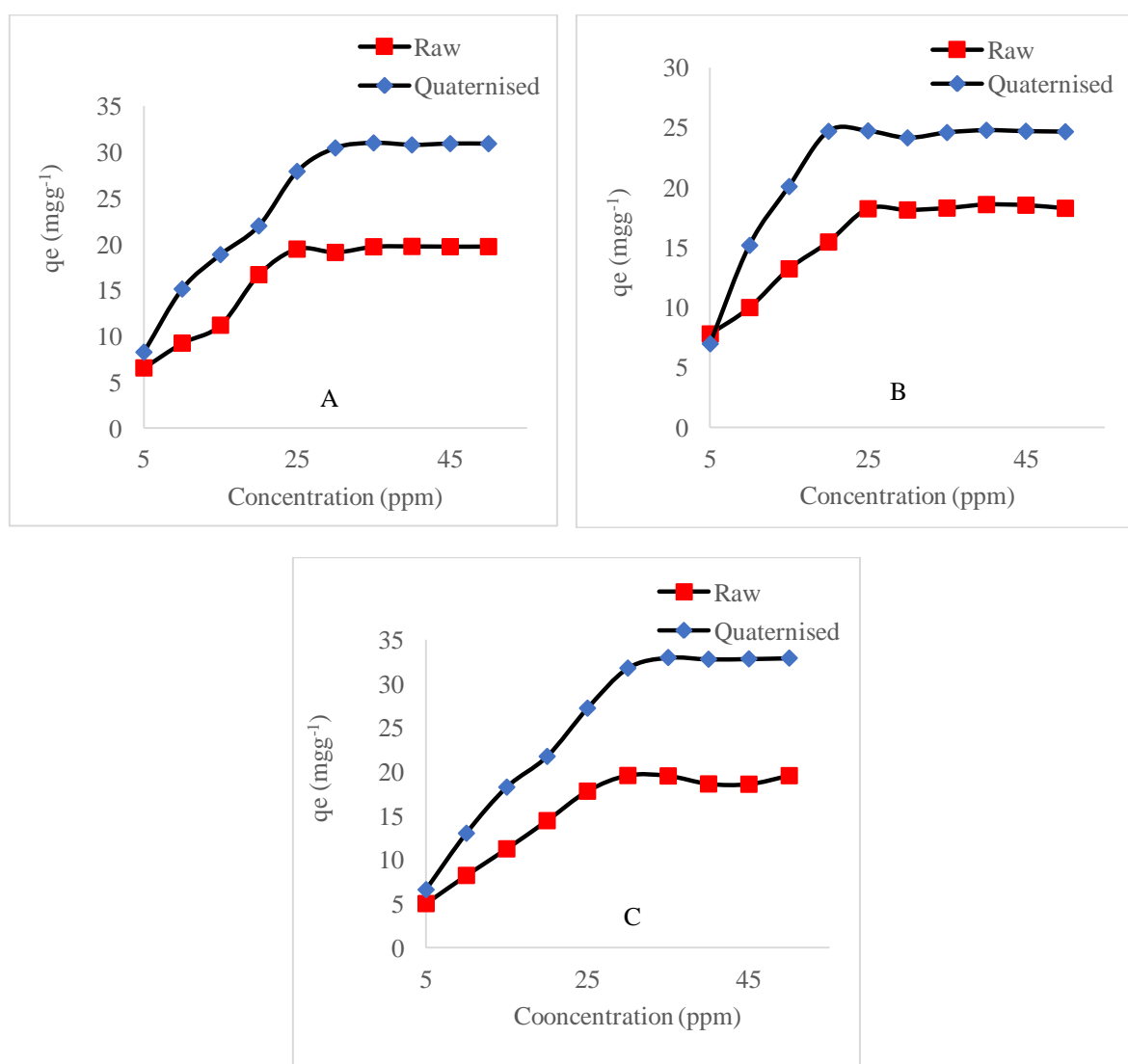

Figure 6: A plot of qe (mg g⁻¹) against Initial metal ion concentration for the complexation of Cu^{2+} (A), Cd^{2+} (B) and Pb^{2+} (C) ions

Initial concentration is important parameter in determining the amount of metal ions that can be complexed by an adsorbent at equilibrium. Results in figure 6 indicate that complexation of the three metal ions increased with increase in metal ion concentration to 30 ppm above which no significant change was observed.

The trend may be due to increased concentration of metal ions with unchanging number of available active sites on the adsorbent surface (Nthiga *et al.,* 2016). At low concentrations, metal ions are easily complexed by the active sites but as concentration is increased, the available active sites becomes saturated with metal ions to optimum beyond which they become unavailable for complexing metal ions that remained in the solution (Berhe *et al.,* 2015; El-Araby *et al.,* 2019). Anchored amine groups on the quaternised Jackfruit seeds adsorbent improved the uptake of Cu^{2+}, Cd^{2+} and Pb^{2+} ions compared to raw Jackfruit seeds adsorbent.

Chemical modification improved the complexation capacity of Cu^{2+}, Cd^{2+} and Pb^{2+} ions to 30.99 mg g^{-1}, 24.75 mg g^{-1} and 32.97 mg g^{-1} from 19.55 mg g^{-}, 18.56 mg g^{-1} and 19.57 mg g^{-1} respectively. The results are similar to those reported by (Fooladgar *et al.,* 2019; Li *et al.,* 2019; Panhekar *et al.,* 2019).

Complexation capacity

The complexation capacity for the three metal ions as a function of initial metal ion concentration was analyzed by Langmuir and Freundlich models and results are presented by table 1.

Table 1: Isotherm models for Cu^{2+}, Cd^{2+} and Pb^{2+} ions on raw and quaternised adsorbent

Metal ion		Langmuir				Freundlich			Comment
	Sorbent	Q$_{max}$, exp (mg g^{-1})	Q$_{max}$, cal (mg g^{-1})	b (L g^{-1})	R^2	$1/n$	K$_F$ (mg g^{-1})	R^2	
Cu^{2+}	Raw	19.55	21.3220	0.4433	0.9846	0.1951	10.230	0.8442	Langmuir
	Quaternised	30.99	33.7838	0.3978	0.9931	0.3226	11.517	0.9549	Langmuir
Cd^{2+}	Raw	18.56	19.6850	0.4673	0.9926	0.1950	9.6775	0.8758	Langmuir
	Quaternised	24.75	25.1256	0.9779	0.9993	0.2090	13.658	0.6521	Langmuir
Pb^{2+}	Raw	19.57	21.8818	0.2515	0.9844	0.4097	5.4352	0.9042	Langmuir
	Quaternised	32.97	34.0136	0.9639	0.9959	0.2448	17.598	0.9360	Langmuir

Results in table 1 gave R^2> 0.98 which showed that complexation of Cu^{2+}, Cd^{2+} and Pb^{2+} ions on raw and quaternised adsorbents fitted Langmuir isotherm model describing a monolayer complexation and a chemisorption process (Huang *et al.,* 2018) and this was confirmed by the closeness of [Q$_{max}$] (experimental) and [Q$_{max}$] (calculated). The values of Q$_{max}$ for the quaternised adsorbent were higher than those of the raw adsorbent a clear indication that the chemical modification improved complexation capacity of the adsorbent. The values of b< 1 from all the complexation processes indicates the high affinity of both raw and quaternised adsorbents for Cu^{2+}, Cd^{2+} and Pb^{2+} ions (Hossain *et al.,* 2012).

The sequence of complexation capacity [Q$_{max}$] of the three metal ions was in the decreasing order of Pb^{2+}> Cu^{2+}> Cd^{2+}. The results agreed well with the predicted order of affinity of the metal ions for active sites on both adsorbents is based on the Pauling order of electronegativity of Pb^{2+} (2.33) > Cu^{2+} (1.90) > Cd^{2+} (1.69). (Salam *et al.,* 2012). These results agree with those reported by (Li *et al.,* 2019).

IV. Conclusion

In the study, *Artocarpus heterophyllus* L. seeds adsorbent was successfully quaternised with EDA confirmed by FTIR. Complexation capacity of raw and quaternised forms for the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} ions was evaluated. Experimental parameters of pH, contact time, agitation speed, dosage and initial concentration greatly influenced the complexation of the three metal ions. Equilibrium was described by Langmuir isotherm model which explained a chemisorption process with quaternised adsorbent showing higher complexation capacities of 32.97 mg g^{-1} (Pb^{2+}), 30.99 mg g^{-1} (Cu^{2+}) and 24.75 mg g^{-1} (Cd^{2+}). The adsorbent showed promise in the field of adsorption as cheap, re-usable and environmentally friendly novel adsorbent in the removal of vast organic and inorganic pollutants in wastewater.

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