International Journal of Agriculture Innovations and Research
Volume 4, Issue 5, ISSN (Online) 2319-1473

Remediation of Lead, Cadmium and Copper Polluted Waters by Onion Skins (*Allium Cepa*)

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***Abstract* – The chemical structure of water makes it have special properties due to lopsided electrical charge that enable water to be a solvent for ionic compounds. That dissolving power is very important for life and has contributed to 97 % of the world's water being salty. As water interacts with the environmental matrix, it dissolves ionic material at different concentrations which may render this vital commodity polluted with dissolved matter of both organic and inorganic origin. Presence of heavy metals in water is a worldwide environmental concern due to pollution. Therefore, there is need to find a sustainable and affordable method to remove such pollutants from water to render it safe. This study investigated the sorption efficiency and mechanism of onionskin in both their raw and modified forms on the removal of lead, copper and cadmium in aqueous media. The modification of the study material was done by anchoring ethylene-1, 2-diamine (EDA) within the structure of the onionskins. This was anticipated to improve the quality of the adsorbent material for application on the removal process. Sorption parameters were optimized and the respective optimal values applied. Experimental results confirmed that best sorption pH range for the metals was ranging between 4.0 -6.0 which is within the physiological pH of water. It was also realized that the sorbent material could remove 90 % of the metals within the first 20 minutes of contact. The experimental data was analysed using Freundlich and Langmuir adsorption isotherms and found out that the three metal ions fitted best in Langmuir model. However, the unmodified onionskin leached soluble organic substances in the form of colour and smell thus causing a secondary pollution. This was overcome by modification of the material. The sorption capacities for lead, cadmium and copper were found to be 71.85, 68.03 and 79.36 mg g^{-1} in the modified sorbent material respectively and 87.49, 96.99 and 90.8 mg g^{-1} in the same order for the unmodified form. Despite the sorption capacity not improving, the effect of secondary pollution was minimized from 15.1 mg L^{-1} to 7.9 mg L^{-1} thus improving the quality of the sorbent material. The resulting material was then applied on environmental water samples whose concentration was determined and thereafter spiked with lead, cadmium and copper ions of varying concentration. The maximum percent recoveries were determined as 87.8±0.01%, 80.6±0.01% and 77.1±% for lead, cadmium and copper ions respectively. This indicated that the material which initially had no useful purpose with disposal problems has potential application for remediation of metal laden waters.**

***Keywords* – Adsorption, Sorbent, Heavy Metals Onion Skins, Modified.**

I. INTRODUCTION

The structure of water contributes to its pollution due to its dispersing ability of ionic species that result to dissolving them. When water interacts with the disposed wastes from anthropogenic and natural sources, it disperses them evenly and hence get polluted (Selivanovskaya and Latypova, 2003; Singh et al., 2004). Such wastes which are either organic or inorganic in nature can interfere with the equilibrium characteristics of the natural water body and further enhance metal solubility (Selivanovskaya and Latypova, 2003; Singh *et al*., 2004). This implies that when such wastes interact with water in the natural systems, they cause metal pollution in the water bodies. Metals are non-biodegradable and can accumulate in vital organs when ingested, and get concentrated through the food chain causing poisonous effects to living organisms (Cha *et al*., 1997). It is therefore essential to remove heavy metals from drinking water to diminish the effects of heavy metal poisoning.

Previously, the removal of metals from water had been achieved by methods which include; precipitation, coagulation, evaporation, and conventional membrane processes (Cha *et al*., 1997). These techniques have several shortcomings such as poor efficiency, sensitive operating conditions and production of a secondary sludge requiring further costly disposal (Abbas, 2010). Moreover they are not effective when the concentrations are in trace levels ranging from 1 mg/L to 20 mg/L (Lodeiro *et al*., 2006). Due to such limitations, this study explored the possibility of using onion waste skins which had no economic value, to develop an efficient removal method, and apply it for remediation of this vital commodity. To address the above challenge, the study investigated the efficiency of the removal of copper, lead and cadmium ion in water by ethylenediamine modified onionskins and it parent form with a view to offer a solution to heavy metal solution in drinking water as a green and low-cost method and as an alternative for water purification.

II. MATERIALS AND METHODS

2.1 *Chemicals and Reagents*

All the chemical reagents were of analytical grade. Stock solutions of lead, cadmium and copper (1000 ppm) were prepared by dissolving 1.000 g of their respective metal powder from Sigma Aldrich (United Kingdom) in 10 ml nitric acid and then diluted to one litre of 0.1 M sodium acetate solution in order to maintain a constant ionic strength.

2.2 *Preparation of Adsorbent*

Onionskins were collected from a local market (Githurai Kiambu County) in Kenya. They were put in to a clean plastic bag and transported to the laboratory. The onionskins were washed with water and rinsed with double distilled water to remove dirt. The material was then dried in a hot air oven at 45ºC until constant weight was attained. It was then ground and sieved through a fine-mesh (150-250 mm). The resulting material was kept in an airtight bottle prior to the experiment.

2.2 *Instrumentation*

An atomic absorption spectrometry (AAS; Buck Scientific 210 VGP) was used to determine the metal concentrations in the sample solutions. The functional groups on the sorbent material were characterized using Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer 100-Waltham, MA USA) while the dissolved organic matter was determined by UV-VIS spectroscopy (Specord 200- Germany).

2.3 *Experimental Procedures*

2.3.1 *Modification of Onion*

The dry powdered onionskins was activated at 80ºC for 12 hours, cooled in a desiccator, and then stored in a clean plastic bottle. A sample (10 g) was suspended in a 200 mL of N-N-dimethylformamide (DMF) followed by drop wise addition of 35 ml of thionychloride ($SOCl_2$) at 80ºC, under mechanical stirring. The stirring continued for 4 hours maintaining the temperature constant. The resulting mixture was washed with 0.1 M ammonium hydroxide solution to bring the pH to neutral. The solid composite was separated by filtration through a sintered glass crucible and dried under vacuum (Molony and Murthy, 2005).

A portion (5.0 g) of the chlorinated biomaterial was refluxed with 25 ml of ethylene-1, 2-diamine for 2 hours. The resulting mixture was then filtered through a sintered glass crucible and the residue dried in a vacuum at room temperature for 24 hours. The level of modification was determined with FTIR and later the product was used for sorption experiments (Tashiro and Shimura, 1982).

2.3.2 *Batch Sorption Experiments*

Sorption studies were carried out in batch equilibrium experiments to determine the adsorption capacities, effect of sorbent dose and pH for the maximum adsorption. The experiments were done by agitating approximately 0.3 g of the dried adsorbent with 30 ml of the model solution, in a mechanical reciprocating shaker (model SKZ-1 NO. 1007827-India) using plastic screw cap bottles. Optimum adsorption parameters were investigated by varying one while maintaining the others constant. The pH of the model solutions containing a known concentration were adjusted to a value between pH 3 and pH 8. The respective mixtures were allowed to equilibrate and removed from the mechanical shaker at different time intervals. The resulting mixtures were filtered through Whatman No.42 filter paper and the metal ions in the filtrate were determined by AAS. The concentrations of dissolved organic matter (DOC) were determined by UV-Vis method.

2.3.3 *Optimization of pH on the Modified and Unmodified Onion*

Sorbent material weighing approximately 0.3 g was placed in 100 mL polythene screw cap bottles. There after 30 ml of the metal model solutions of 10 mg/L concentration, adjusted to the desired pH values of between pH 3 and pH 8 were added to each sample. The mixtures were equilibrated for 1 hour and then filtered. The metal ions in the filtrate were determined and the optimum pH for the sorption was established.

2.3.4 *Effect of Time*

The effect of time on adsorption of metals was determined by mixing 0.3 g sorbent material with 30 mL of the metal solution of 10 mg/ L concentration. The initial pH of the model solutions was adjusted to the optimum values for each respective metal under study. Adsorption of cadmium was adjusted at 6.0 while the value for lead was set at 5.4. The best pH for the sorption of copper was found to be 5.9, 4.2 for modified and unmodified sorbents respectively. The sorption kinetics was done by equilibrating the mixture at predetermined time intervals between 2-120 minutes. After the set time interaction, the sorbent was filtered off and the metal ion concentration for each equilibration time in the filtrate determined by AAS.

2.3.5 *Effect of Metal Ion Concentration on Sorption*

The adsorption capacity was determined by mixing 0.3 g with 30 ml model metal solution (concentration 10-200 mg/L) at their optimum pH values. The mixtures were agitated for 1 hour, and the resulting filtrate obtained and the concentration of the metal ions determined.

2.3.6 *Effect of Sorbent Dose on Percent Recovery of Metals Ions*

Masses varying from (0.1-0.3 g) of modified and unmodified onionskin were packed in separate columns. Model solutions 100 ml, with a concentration of 0.1 mg/L and their pH adjusted to each metal's optimum value were loaded onto the column at a flow rate of 3 ml/ min. Content of the metal in the solution was then analyzed.

2.3.7 *Determination of Dissolved Organic Carbon (DOC)*

Dissolved organic carbon originating from leaching of soluble organic matter in the solution during the adsorption process was determined by dichromate reduction method as used by Baumann (1974) and Gonzalez (1986) as they used potassium dichromate for the determination of DOC in waste and saline waters. The concentration of the reduced dichromate ions was determined using a UV-Vis spectrophotometer. The method was adopted according to Baumann (1974) and

Gonzalez (1986) who used potassium dichromate for determination of DOC in waste and saline water (Baumann, 1974).

A standard stock solution was prepared by accurately weighing 200 mg of tannic acid dissolving it in 1 L of water (Vazquez *et al.*, 2009). To this solution, 50 mL were taken and treated with 3 g potassium dichromate which was previously dried for 2 hours at 103ºC followed by addition of 167 mL of concentrated sulphuric acid, and 3.33 g of mercurous sulphate. The mixture was refluxed for 2 hours, cooled and then diluted to 100 mL with double distilled water. The absorbance reading for the standard solutions and samples were then recorded at 606 nm using a UV-Vis spectrophotometer. A calibration curve was prepared and concentrations of unknown were evaluated.

A known weight of 0.3 g of bio-sorbents was placed in to a 250 mL plastic bottle containing 100 mL of double distilled water. The mixture was placed on to a magnetic stirrer plate and stirred for a period of 1 hour to extract soluble organic compounds. The solid was filtered off, and the absorbance readings of the resulting solution were recorded. From the experimental data, the concentration of the leached organic material was evaluated.

2.3.8 *Analysis of Metal Content in the Environmental Water Samples*

Water samples were collected from Chania River (Kiambu County, Kenya). Known concentration of copper, cadmium and lead ions were spiked separately in to each sample (10 mL). The concentration of the respective metals was determined by the standard addition method. The samples were then loaded on to the solid-phase extraction (SPE) column containing 0.3 g of each adsorbent and the retained metal ions were then stripped with 5 mL of 0.5 M nitric acid. Their concentration determined by AAS.

2.3.9 *Calculation of Metal Ion Adsorption Capacity of Modified and Unmodified Onionskin*

The amounts of metal ions adsorbed per unit mass by the modified and unmodified onionskin, during the batch investigation were calculated as;

Amount adsorbed

$$q_e = \frac{(C_o - C_e)v}{w} \qquad (1)$$

Where C_0 and C_e are the initial and equilibrium concentration (mg/L) of metal ions in solution, respectively. V is the volume of the solution in (mL) while W is the mass of the adsorbent in (g).

III. RESULTS AND DISCUSSIONS

3.1 *FTIR Characterization*

Both modified and unmodified forms of the adsorbents were characterized using FTIR and the resulting spectra presented in Figures 1, 2 and 3. The results from FTIR-characterization of the onionskin indicated the presence of several functional groups such as –NH, C=O,-COOH, S=O, -OH and C-H stretching which are responsible in binding of metal cations (Moran *et al., 2008*). The unmodified onionskin was characterised and the results presented in Figure 1 below.

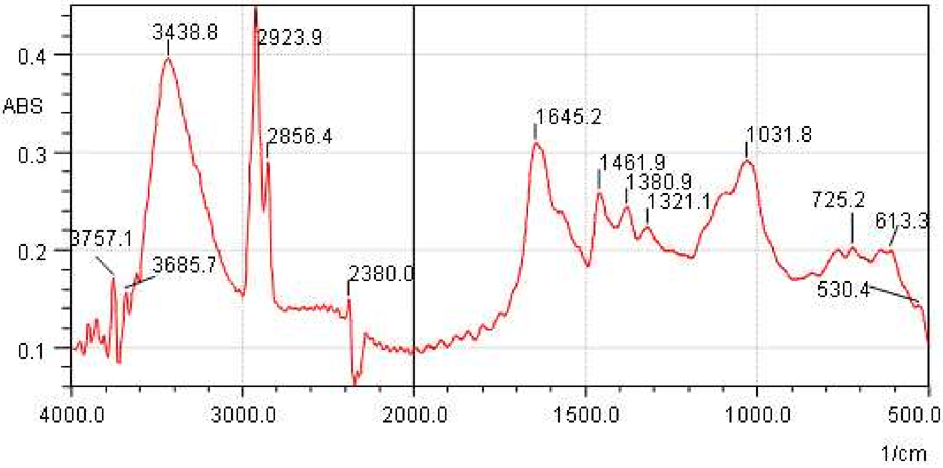

Fig. 1. FTIR Spectra of the unmodified onionskins

The spectra in Figure 1 show strong bands between 3438 cm^{-1} which may be as result of either –OH or –NH groups (Avisha *et al.*, 2012), however the peak appears as one sharp peak, thus an indicator that it is most likely due to –OH groups (Stuart, 1996). The 2923.9 cm^{-1} may be attributed by -CH stretches of the aromatic ring and 2856.4 cm was attributed to –COOH groups (Avisha *et al.*, 2012). The band at 1645.2 cm^{-1} which appears to be broad, may be due to the presence of the carbonyl group (Torres *et al.*, 2003) while the band at 1031.8 was assigned sulfoxide group which resulted after oxidation of thiosulfonate group which is unstable and quite reactive (Koch *et al.*, 1970).

The raw onionskin was chlorinated and presented in in Figure 2.

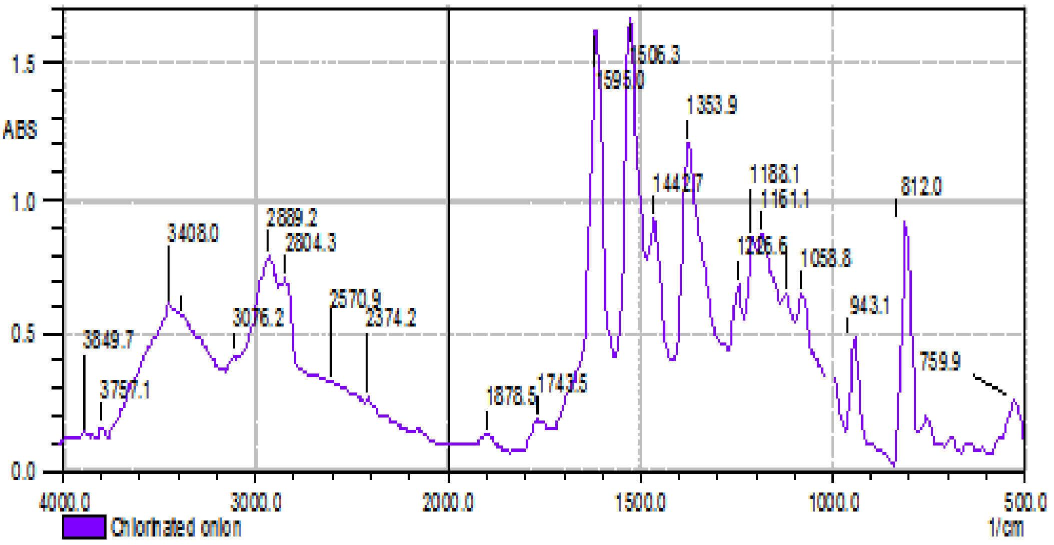

Fig. 2. FTIR Spectra of the chlorinated onionskins

The spectra in Figure 2 Shows strong band at 1596 and 1506 cm^{-1}, which could be as a result of carboxylic group or N-H bending (Khazael *et al.*, 2007). At 1353.9 cm^{-1}, this was because of sulfonylchloride while the band at 2889 cm^{-1} could be as result of –COOH group. The peak at 812 cm^{-1} which was absent in spectra A was as result of C-Cl due to chlorination. The band at 1645.2 cm^{-1} earlier suggested to be as a result of carbonyl functional group is absent in the chlorinated form. This is because the oxygen was replaced during chlorination process giving way for the anchoring of ethylene-1, 2-diamine.

Part of the chlorinated sorbent was treated with ethlene-1,2-diamine and then characterization was done. The spectra of the modified form were presented in Figure 3.

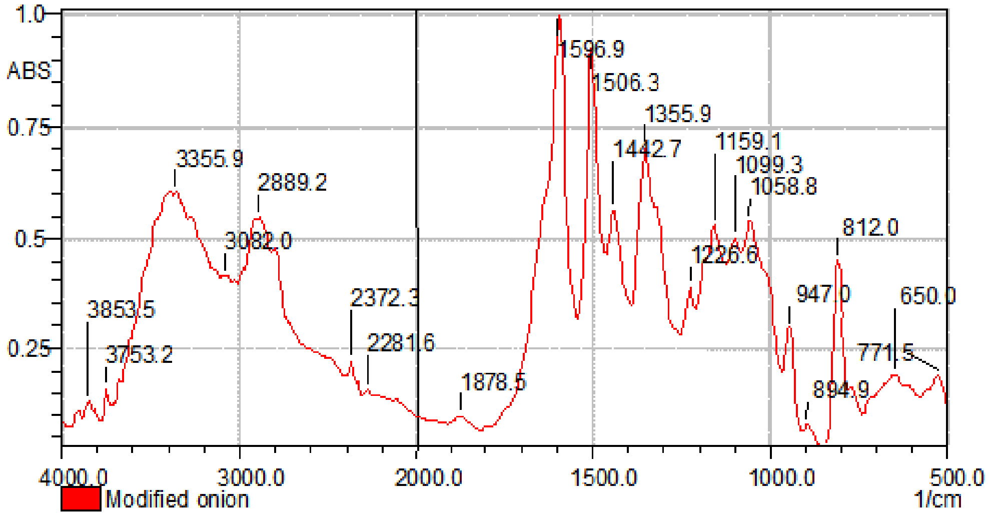

Fig. 3. FTIR Spectra of modified onionskin

Spectra in Figure 3 Show strong band at 3355 cm^{-1} which may have been because of an amine group which appears as two bands (Avisha *et al.*, 2012). The displacement of the band at 3438.8 to 3355.9 cm^{-1} after modification and the appearance of the band at 1596.9 and 1506.3 cm^{-1} shown in figure 3 is due to the angular deformation of the N-H (amine group) which is an indicator of EDA immobilization of the adsorbent (Silvertein *et al.*, 1991; Pavia *et al.*, 1996). The band at1355.9 cm^{-1} was assigned sulphonylchloride (Matheickal and Yu, 1996; Kappoor and Viraraghavan, 1997), while the band at 1226.6 cm^{-1} was assigned N-H group (Khazael *et al.*, 2007).

The absence of 1031.8 cm^{-1} peak in both chlorinated and modified form was an evidence that the sulfoxide group which resulted from oxidation of thiosulfinate group which is responsible for the pungent smell in an onion was replaced making modification viable (Krest *et al.*, 2000). The presence of 3355 cm^{-1} in modified onion shows there was successful anchoring of an N-H group from ethylenediamine which was absent in unmodified onion. Absence of 2923 cm^{-1}, 3355 cm^{-1} and 1645 cm^{-1} peaks in the modified onion shows lack of C=H stretch , N-H and C=O respectively which could be the reason why sorption capacity was not improved after modification.

3.2 *Determination of Dissolved Organic Matter in Water*

The organic matter content inform of DOC was determine by UV-VIS spectrophotometer (model.specord®200. made in Germany) based on carbon. Tannic acid standard solution was used as a source of carbon. The analysis was carried out at a wavelength of 606 nm. A linear plot of $y = 0.0091x$ over the concentration range of 20-100 mg/L with a slope of 0.0091 and a correlation coefficient of (R^2) > 0.998 was obtained.

The sample had a content ranging between 15.1 and 7.9 mg/L for the unmodified and modified onion respectively. The result shows that modification has a significant effect on the reduction of leaching out of organic matter from the bio sorbents into the treated water (Chen and Yang, 2005).The finding of this study agree with the observation made by the other researchers who reported DOC content of 9.85-19.55 mg/L (Mwangi *et al.*, 2012) when they modified green sea weed.

3.3 *Effect of pH on Adsorption of Metal Ions*

Adsorption of metal ions by sorbents is pH dependent as it influences the charge of the binding sites of the sorbent and the chemistry of the metal ion (Unlu and Ersoz, 2006). In this study, the optimum pH for metal ions uptake was determined through batch adsorption experiments. The optimum values were then applied for subsequent experiments. The effect is due to the fact that, sorbents have sorption sites due to the presence of functional groups, whose charges are influenced by the pH (Fourest and Serre, 1996).

Results for the adsorption experiments at different pH values are presented in Figure 4.

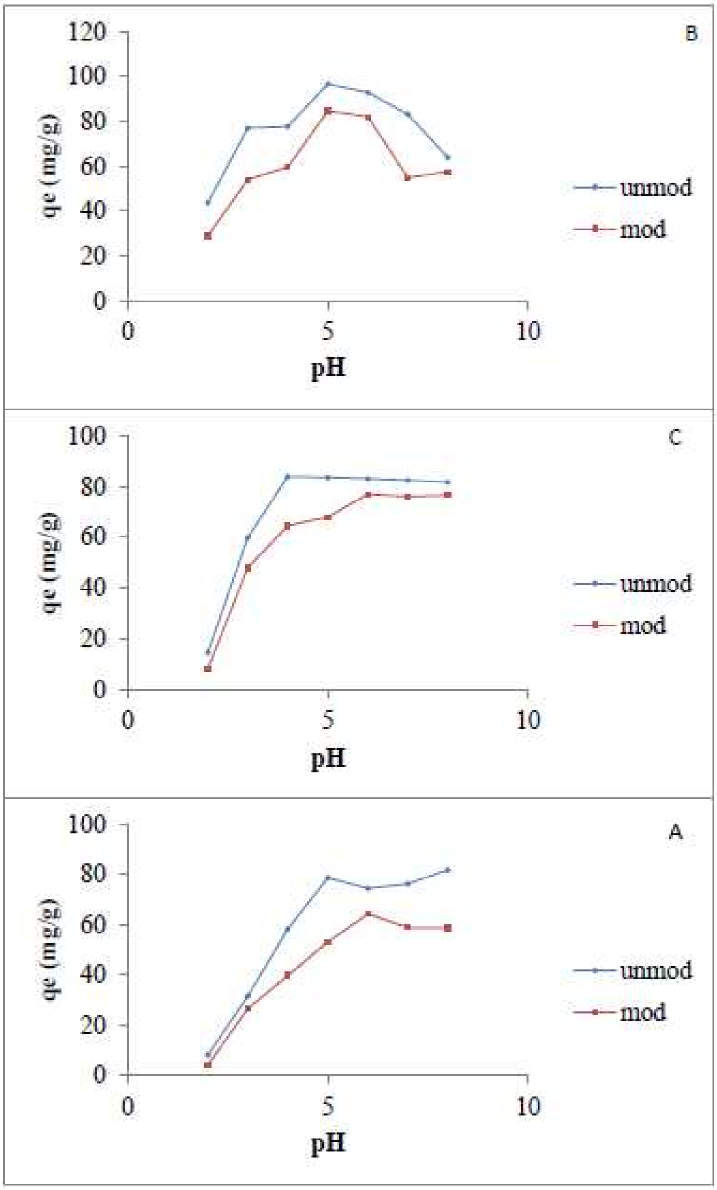

Fig. 4. Effect of pH on metal ions sorption; (A) Pb^{2+}, (B) $Cu^{2+}$and (C) $Cd^{2+}$by modified and unmodified onion.

The pH value for maximum sorption of lead ions by unmodified and modified onion skin was observed at a value of 5.0 for both unmodified and modified onion. Such a pH value was reported by Mwangi and co-workers (2012) as they investigated sorption of metal ions by maize tassels. The optimum pH value for onion was adopted as 5.0 for sorption of lead ions in this study. The sorption of cadmium ions was carried at pH 6.0 and pH 5.0 for modified and unmodified onion respectively while sorption of copper ions was carried at 4.2 and 5.9 for the unmodified and modified respectively. Abu Al- Rub and co-workers (2006) reported a similar observation as they studied sorption of those metals using sorbents of biological origin.

The reason why copper had two pH values could be due to the presence of two oxidation states of copper (I) and (II) in solution. Malik and Salahuddin (1963) reported a similar observation. They attributed the observation to the reductions of copper (II) ions in solution due to distortion by the nitrogen containing ligands in the presence of other functional groups.

The metal ions adsorption capacity was seen to increase with an increase in pH from 3-6. At low pH, the adsorption in all the three metal ions was observed to be lower. This may be as a result of the overall positive charge on the adsorbent surface which is caused by H_3O^+ ions in the acidic media that would hinder metal access to the ligands of the adsorbent due to repulsive forces (Hamead and Ahmad, 2009). It is also possible that, there was competition between protons and metal ions resulting to low adsorption capacity of these metals (Hamead and Ahmad, 2009)

At high pH, the adsorbent is relatively more negatively charged as compared to solution. This contributes to a high adsorption of metal species in solution (Singh *et al*., 2006). This arises from the fact that, when the metal is in solution it is positively charged and will be attracted to the negatively charged surface at that high pH, favoring adsorption. At pH > pH 6, there is metal hydrolysis, leading to precipitation due to formation of hydroxyl metal ions hence the removal may not only be due to adsorption (Wang and Qin, 2005).

3.4 *Effect of Contact Time*

The rates of metal ions uptake is related to the efficiency of the adsorbent binding sites to hold the metal ions and the activity of the metal, therefore determine the residence time of sorbate at the solid-liquid interface (Demirbasa *et al*, 2004). The results obtained are as presented in Figure 5.

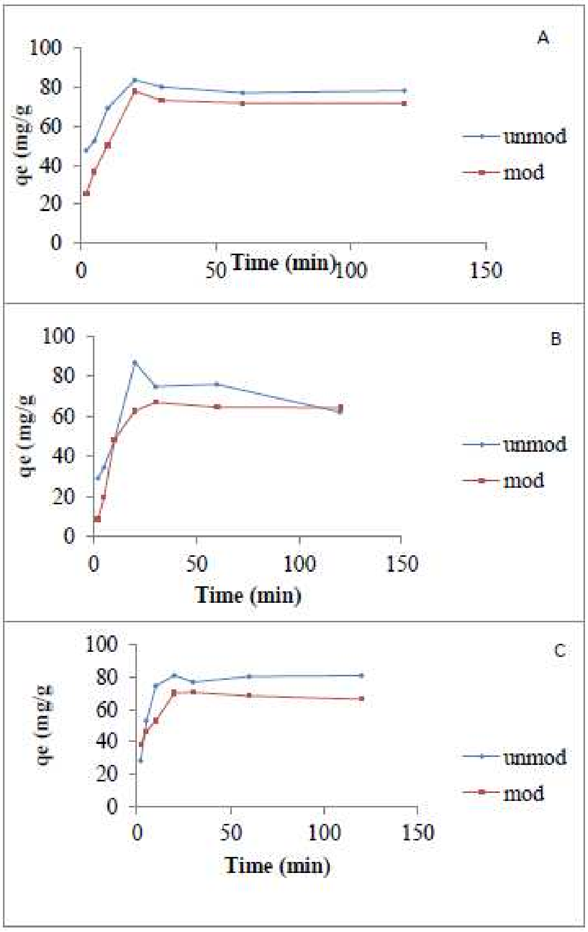

Fig. 5. Effect of contact time between sorbents and the metal ions; and (A) Pb^{2+} (B) Cd^{2+} and (C) Cu^{2+}

From Figure 5, the plot reveals that, the rate of all metal ions uptake was fast at the beginning, such that > 90 percentage of the total uptake occurred within 30 min, after which a slower uptake rate which was followed by a steady state where no significant adsorption occurred. This is probably due to large surface area of the adsorbent available at the beginning resulting to physical sorption or ion exchange at the cell surface. On the hand, the slower phase may have been attributed by other mechanisms such as micro-precipitation, complexation or saturation of the binding site (Khani, 2006). All these mechanisms will make the driving force of mass transfer between liquid and solid phase in an aqueous adsorption system to decrease with time elapse (Khani, 2006). Furthermore, the metal ions have to pass through the deeper surface of the pores for binding and encounter a much large resistance slowing down the adsorption during the later phase of adsorption (Srivastava *et al.*, 2008).

The sorption remained constant after equilibrium was attained. This could be because the binding sites were limited and the remaining vacant surface sites were difficulty to be occupied by metal ions due to the formation of repulsive forces between metal ions on solid phase and the liquid phase (Srivastava *et al.*, 2008). The experimental data obtained for the adsorption of the metal ions showed that, a contact time of 30 min was enough to achieve maximum adsorption as there was no further change observed in concentration with time. Equilibrium was set at 120 minute for the sorption capacities of lead, copper and cadmium in order to allow ample time contact.

3.5 *Effect of Initial Metal Ion Concentration (Determination of Sorption Capacity)*

Metal adsorption is significantly influenced by the initial concentration of metal ions in aqueous solutions. In this study, the initial metal ion concentration was varied from 20-200 mg/L maintaining the adsorbent dosage at 0.3 g/mL.

In order to obtain the sorption capacity of both bio sorbents, the data collected for each metal was plotted as the concentration of the metal adsorbed in mg/g of the sorbent (q_e) against the initial metal concentration in solution (C_o). The results obtained are as presented in Figure 6.

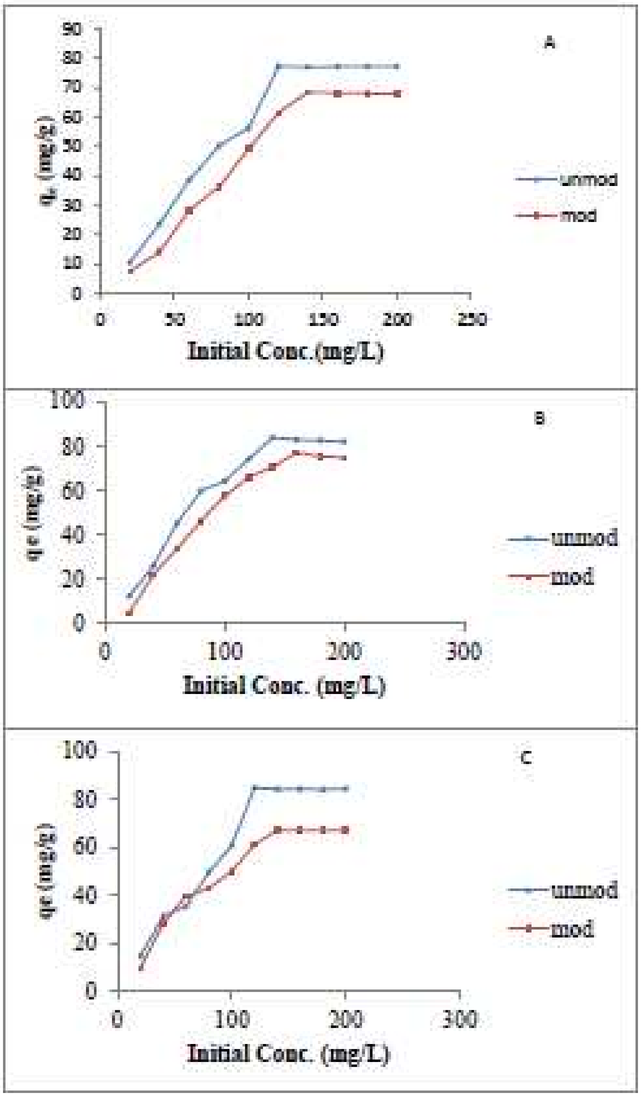

Fig. 6. Effect of initial metal-ion concentration on adsorption - (A) Pb^{2+} (B) Cu^{2+} and (C). Cd^{2+}

The modified onion showed little bit lower adsorption capacity compared to it unmodified onion form. This may be due to complete removal of S=O and C=O compounds during modification, resulting to decrease in binding sites of the modified sorbent. The profile of sorption of metal ions was observed to increase with an increase in the initial metal concentration up to 150 mg/L in copper after which a plateau was observed.

An overall observation for all the metals shows a continuous metal uptake followed by plateau as the concentration of the metal ion in the solution was increased. This may be due to an increase in metal ions for the fixed amount of the adsorbent material and due to saturation of available sites on the sorbent resulting in a saturation effect showing a steady state on the regression plot (Benhima *et al*., 2008). At this stage, the sorbent is said to have attained its operational maximum adsorption capacity. The maximum adsorption capacity for Cu^{2+}, Pb^{2+} and Cd^{2+} ions were 77.2 mg/g, 68.3 mg/g and 67.1 mg/g respectively for the modified onion, while that of the unmodified sorbent were 83.7 mg/g,77.3 mg/g and 84.8 mg/g in the same order.

3.6 *Application Studies*

3.6.1 *Effect of Sorbent dose on Percentage* (%) *Removal of Copper, Lead and Cadmium Ions*

Masses varying from (0.10-0.30 g) of modified and unmodified onionskins were packed in separate columns. Model solutions 100 mL, with a concentration of 0.1 mg/L and their pH adjusted to each metal's optimum value were loaded onto the column at a flow rate of 3 mL/ min. The content of the metal ions in the solution was then analyzed. The results are presented in Figure 7.

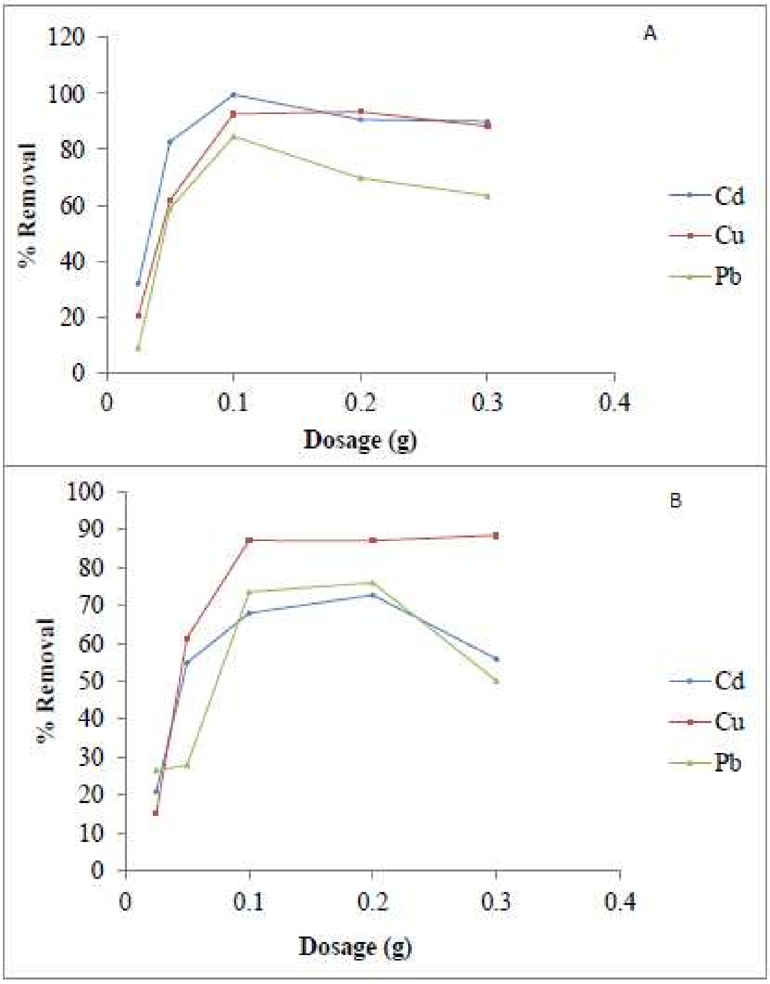

Fig. 7. Effect of adsorbent dose on removal of metals ions (A) unmodified and (B) modified

The general observation made for all metals was that, adsorption increased with increase in sorbent concentration. This is because the more the sorbent, the more the adsorption site hence more metal ions will occupy the available adsorption sites (Ilhan *et al*., 2004). However, the increase of adsorbent against constant metal ions concentration leads to depletion of metal ions in solution hence a plateau.

The order of percentage removal with unmodified onionskin was Cd > Cu > Pb. This could have been attributed to the fact that the binding sites available in the unmodified onionskins had high affinity for cadmium ions (Koch *et al*., 1970). On the other hand, the percentage removal with modified onionskin was Cu > Pb > Cd. This may be due to the fact that, the affinity for the binding sites are related to the ionic sizes of the respective metals hence the polarizing power being responsible for the observation (Horsfall *et al*., 2006).

The maximum adsorption of copper for modified onion (Figure 7) was 84.6 % when the sorbent dose was 0.1 g, above 75.9 % for lead at 0.2 g and 72.6 % for cadmium when the sorbent was 0.2 g. It was observed that the modified onion removed less metal ions from the solution than the unmodified onionskin. This could be because of the derivatization of functional groups such as the thio, carbonyl and amino groups, which have a relatively higher affinity for these metal ions in unmodified adsorbent (Koch *et al*., 1970). However, unmodified onionskin leached red color and smells to the solution during the adsorption process lendering the method unapplicable, unlike modified sorbent. Hence, need to modify the raw onionskin before their use in the water treatment process, in order to prevent secondary pollution (Chen *et al*., 2002)

3.6.2 *Analysis of Environmental Water Samples*

The results of river samples analysis for the content of copper, lead and cadmium ions are given in Table 1.

Table 1. Percentage removal of metal ions from water samples (metal ion concentration in mg/L)

Metal	**Added/mg L^{-1}**	**Found/mg L^{-1}**	**% Removal**
Lead	**0.00**	**0.086**	-
	2.00	0.245±0.002	87.8±0.01
	4.00	1.031±0.001	74.2±0.02
	6.00	1.816±0.001	69.7±0.01
	8.00	2.928±0.001	63.4±0.01
Copper	**0.00**	**0.105**	-
	2.00	0.386±0.011	80.6±0.01
	4.00	1.071±0.001	73.2±0.01
	6.00	2.067±0.001	65.6±0.01
	8.00	3.237±0.001	59.5±0.02
Cadmium	**0.00**	**0.067**	-
	2.00	0.458±0.001	77.1±0.01
	4.00	1.167±0.001	70.8±0.01
	6.00	2.000±0.001	66.6±0.02
	8.00	3.500±0.002	56.3±0.01

The results show that there was high removal of metal ions at low concentration but decreased with an increase in the spiked metal ions concentration. This may be due to an increase of the metal ions against constant adsorbent material.

The sorption of lead by modified onionskin was found to be the highest followed by copper and then cadmium. This adsorption trend may be explained by the fact that copper ions compared to lead ions, have relatively higher affinity for ligands containing a quaternary N- atom in DOC (Topperwien *et al*., 2007). This would result in the removal of copper by the DOC and hence posing less competition for the lead ions to adsorb on the modified onionskins (Topperwien *et al*., 2007). Such ligands, which are smaller than the adsorbent, have a higher affinity for the metal due to their high basicity (Comuzzi *et al*., 2001). The result shows that the method was effective and reliable.

3.7 *Adsorption Isotherms*

Adsorption isotherms describe how the adsobate interacts with the adsorbents (Shokoohi *et al.*, 2009) The model isotherms applied in this study were Freundlich and Langmuir adsorption isotherms' (Langmuir, 1918; Freundlich, 1906).

3.7.1 *Langmuir Isotherms*

Langmuir isotherm has been used extensively for the sorption of many heavy metal ions. Langmuir assumes adsorption of an ideal gas on an ideal surface. It assumes that sorption occurs on a homogeneous surface and that adsorption can only occur at fixed sites and can only hold one adsorbate molecule at a time (monolayer). A further assumption is that all sites available are equivalent and there is no transmigration of sorbate in the plane of the surface even on adjacent sites (Boukhiar *et al*., 2008). The Langmuir equation may take the form shown below (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}} \tag{2}$$

Where; q_e is the amount of solute adsorbed (mg/g), C_e the equilibrium concentration of the solute in the bulk solution (mg/L), $Q_{\max}$ is the monolayer adsorption capacity mg g^{-1} and b is the constant related to the energy of adsorption (L/g)

The experimental data were applied to the equation above and a plot of $\frac{C_e}{q_e}$ against C_e was plotted. A plot with a good linear correlation indicates that the Langmuir model describes the adsorption process, (Langmuir, 1918; Ng *et al*., 2003).

3.7.2 *Freundlich Isotherms*

It is a multi-site sorption isotherm for heterogeneous surfaces. It says that the ratio of the amount of solute adsorbed on to a given mass of sorbent to the concentration of the solute in solution is not constant at different concentration. It is widely used in highly interactive species. The general equation is as shown below (Oubagaranadin *et al.*, 2007)

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (3)$$

The equation is made linear by taking logarithms and then applying it on heterogeneous systems with highly interactive species. The three metals were tested on this isotherm and the experimental data were subjected to equation 4.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

Where q_e and C_e has the same meaning as that of Langmuir, K_F constant, is an indicative of the relative adsorption capacity of the adsorbent (mg/g), while $\frac{1}{n}$ is the function of the strength of adsorption in the adsorption process, (Freitas *et al.*, 2008). A plot of $\log q_e$ versus $\log C_e$ with a good linear correlation implies that the sorption fits the Freundlich model. The results obtained after testing the three metal ions with the two models are presented in Tables 2, 3 and 4.

Table 2. Adsorption isotherm of lead ions

	Langmuir			Freundlich		
Sample	q_{max}mg/g	b dm^3/g	R^2	1/n	K$_f$mg/g	R^2
Modified	71.85	0.1529	0.9566	0.9211	1.239	0.6437
Unmodified	87.49	0.1048	0.9573	0.2856	24.045	0.5829

Table 3. Adsorption isotherm of copper ions

	Langmuir			Freundlich		
Sample	q_{max} mg/g	b dm^3/g	R^2	1/n	K$_f$ mg/g	R^2
Modified	79.36	0.2552	0.8987	0.1413	42.01	0.7679
Unmodified	90.8	0.1115	0.9435	0.8502	3.205	0.9086

Table 4. Adsorption isotherm of cadmium ions

	Langmuir			Freundlich		
Sample	q_{max} mg/g	b dm^3/g	R^2	1/n	K$_f$ mg/g	R^2
Modified	68.03	0.0316	0.9174	0.5740	5.0686	0.8727
Unmodified	96.99	0.1383	0.9509	0.5417	7.994	0.9217

The result revealed that all the metal ions prescribed to the Langmuir model in both raw and modified onion. Cu^{2+} ion had an R^2 =0.8987, Cd^{2+} had R^2=0.9174 while that of Pb^{2+} was R^2=0.9566 for the modified sorbent (appendices 10, 14 and 6 respectively). The R^2 for Cd^{2+}, Cu^{2+} and Pb^{2+} ions were R^2= 0.9509, R^2= 0.9435 and R^2=0.9573 respectively for the unmodified sorbent (appendices 15, 11 and 7 respectively). Cd^{2+} ion had the highest adsorption capacity of 96.99 mg/g in an unmodified onion. On the other hand, Cu^{2+} had the highest adsorption capacity of 79.36 mg/g for the modified onion.

The unmodified bio sorbent had the highest affinity for Cd^{2+} ion with a b value of b=0.1383 dm^3/g, while the modified bio sorbent had the highest affinity for Cu^{2+} with a b value of b=0.2552 dm^3/g. A similar observation was made by Wang and co-workers (2009) as they studied the sorption of copper using rice bran. This implies that, the mechanism was a chemisorption (Ng *et al.*, 2003), which is in agreement with (Mwangi *et al.*, 2012) who studied sorption of the same metal ions using maize tassels. It is also an indication that, lead, copper and cadmium ions are possibly chemically attached on to the adsorbent (Bayrak, 2003).

The function of the strength of adsorption (1/n) in both modified and unmodified onion was less than one, an indication that the process was favorable in Langmuir isotherm model. The adsorption capacity of copper ions was higher than that of lead ions in the modified onion. This may be explained by the high interaction between copper and adsorbent arising from lanthanide contraction due to high polarizing ability of copper ions (Huang and Vansant, 1973). A similar observation was made by Mwangi and co-workers (2012) as they studied the sorption of copper using both raw and modified algae.

IV. CONCLUSIONS

The study successfully functionalised the onionskin with ethylenediamine as confirmed by the FTIR analysis. The anchored functional group then acted as the binding sites for adsorption of metals under study. It was observed that both modified and its unmodified form removed lead, copper and cadmium ions but the unmodified form had a higher capacity. The adsorption capacity of unmodified adsorbent was found to be higher than the adsorption capacity of the modified sorbent. The sorption capacity for lead, cadmium and copper were found to be 71.85, 68.03 and 79.36 mg g^{-1} in the modified sorbent respectively and 87.49, 96.99 and 90.8 mg g^{-1} in the same order for the unmodified sorbent. The observation made could be due to the absence of the functional groups which were previously in the unmodified biosorbent being derivertised with ethylenediamine in the modified sorbent. The ethylenediamine form then happens to have a lower stability constant with the metals under study. However, modification provided a significant reduction in leaching of organic matter from 15.1 mg L^{-1} to 7.9 mg L^{-1} hence alleviating the risk of secondary pollution during water treatment. The rate of sorption was very fast as more than 90% of the total metal ions were removed from the solution within the first 30 min. The metal removal was effective in the pH range of 4-6. Use of onionskin is expected to improve the quality of metal polluted waters and make it safe for consumption

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