

## Adsorption Isotherm Studies of Ni (II), Cu (II) and Zn (II) Ions on Unmodified and Mercapto-Acetic Acid (MAA) Modified Sorghum Hulls

C. Imaga<sup>1\*</sup>, A. A. Abia<sup>1</sup> and J. C. Igwe<sup>2</sup>

<sup>1</sup>Department of Pure and Industrial Chemistry, University of Port Harcourt, Rivers State, Nigeria.

<sup>2</sup>Department of Pure and Industrial Chemistry, Abia State University P.M.B. 2000 Uturu Abia State, Nigeria.

### Authors' contributions

This work was carried out in collaboration between both authors. Authors CI and AAA designed the study and wrote the protocol. Authors JCI and CI performed the statistical analysis, managed the literature search and wrote the first draft of the manuscript with assistance from author AAA. Authors AAA, JCI and CI read and approved the final manuscript.

### Article Information

DOI: 10.9734/IRJPAC/2015/13510

#### Editor(s):

- (1) Luigi Campanella, Research Centre on Environment and Cultural Heritage Chemistry, University of Rome "La Sapienza", Italy.
- (2) Taicheng An, State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, P. R. China.
- (3) Sung Cheal Moon, Korea Institute of Materials Science (KIMS), Industrial Technology Support Division, Changwon, Republic of Korea.

#### Reviewers:

- (1) Anonymous, USA.
- (2) Anonymous, Iraq.

Complete Peer review History: <http://www.sciencedomain.org/review-history.php?iid=809&id=7&aid=7149>

Original Research Article

Received 20<sup>th</sup> August 2014  
Accepted 15<sup>th</sup> November 2014  
Published 9<sup>th</sup> December 2014

### ABSTRACT

**Aims:** To compare the efficiency of Sorghum Hull of two different particle sizes, different concentrations modified with mercaptoacetic acid and the effect of each on the heavy metal removal to obtain optimum conditions for sorption process.

**Study Design:** The concentrations of the metal ions were monitored using Atomic Absorption Spectrophotometer (AAS).

**Place and Duration of Study:** This study was carried out at the Industrial Chemistry laboratory, Department of Pure and Industrial Chemistry, University of Port Harcourt between February and August 2013.

\*Corresponding author: E-mail: [imagachinyere@yahoo.com](mailto:imagachinyere@yahoo.com);

**Methodology:** The Sorghum Hulls (SH) (*Sorghum bicolor*) obtained from a Brewery, were washed and air dried, crushed to smaller particles and sieved to obtain particle sizes of 106  $\mu\text{m}$  and 250  $\mu\text{m}$ . They were activated by soaking in excess of 0.3M  $\text{HNO}_3$  solution for 24 h, filtered through a Whatman No.41 filter paper, rinsed with deionised water and air dried for 24 h. The air-dried activated sorghum hulls were divided into three parts, one part was left unmodified and the other two parts were modified by 0.5M and 1.0M mercaptoacetic acid ( $\text{HSCH}_2\text{COOH}$ ). Equilibrium sorption of Ni (II), Cu (II) and Zn (II) were carried out for each adsorbent (106  $\mu\text{m}$  and 250  $\mu\text{m}$ ) at pH of 6.0 and temperature of 28°C to find the effects of initial concentration on the sorption process by preparing stock solutions of 1000 mg/L of Cu (II), Ni (II) and Zn (II) ions from  $\text{CuSO}_4$ ,  $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and  $\text{ZnSO}_4$  respectively. Working concentrations of 10, 20,30,40,50 mg/L were obtained by serial dilutions. The concentrations of these solutions were confirmed using Atomic Absorption Spectrophotometer (AAS). The difference in the metal ion concentration of the solutions before and after sorption gave the amount adsorbed by each adsorbent.

**Results:** Sorption efficiency followed the trend  $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$  and  $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$  for 106 $\mu\text{m}$  and 250 $\mu\text{m}$ , respectively. This was influenced by factors such as ionic radii, ionic charge, hydration energy, initial metal ion concentration, contact time, adsorbate pH and extent of acid modification. Sorption capacity followed the sequence: 1.0MSH>0.5MSH>USH. Equilibrium sorption of the three metals on the adsorbents using coefficient of determination ( $R^2$ ) showed that sorption of  $\text{Zn}^{2+}$  on 250 $\mu\text{m}$  size and sorption of  $\text{Ni}^{2+}$  on 106 $\mu\text{m}$  size followed Langmuir isotherm; sorption of  $\text{Zn}^{2+}$  on 106 $\mu\text{m}$  mesh and sorption of  $\text{Cu}^{2+}$  on 250 $\mu\text{m}$  size by Freundlich isotherm and sorption of  $\text{Cu}^{2+}$  on 106 $\mu\text{m}$  size and sorption of  $\text{Ni}^{2+}$  on 250 $\mu\text{m}$  mesh by Temkin isotherm. Sorption on 1.0MSH gave the highest value of constants: ( $q_{\text{max}} = 121.814 \text{ mg/l}$ ,  $K_F = 1.5281 \text{ mg/l}$  and  $b_T = 0.245 \text{ kJ/mol}$ ) and ( $q_{\text{max}} = 148.932 \text{ mg/l}$ ,  $K_F = 1.7246 \text{ mg/l}$  and  $b_T = 0.262 \text{ kJ/mol}$ ) for 106  $\mu\text{m}$  and 250  $\mu\text{m}$  size, respectively, for Langmuir, Freundlich and Temkin isotherms respectively.

**Conclusion:** Therefore, Sorghum Hulls were found to be good adsorbent for Ni, Cu and Zn ions with mercaptoacetic acid modification increasing the sorption capacity.

**Keywords:** Adsorption; environment; isotherm; metal ions; modification; sorghum hulls.

## 1. INTRODUCTION

Surface chemistry is the study of processes that occur at the interface of two bulk phases. The bulk phases can be of the solid-gas, solid-liquid or liquid-liquid. The bulk phase can be solution or pure compounds. Adsorption is a physical or chemical phenomenon by which the molecules present in a liquid or gas attach to the surface of an adsorbent. It involves separation of a substance from one phase accompanied by its accumulation at the surface of another. Adsorption occurs because of an affinity of the surface for the particular substance. The adsorption phenomenon provides an excellent method of separation of a variety of fluid mixtures particularly at low concentrations and as such it is recognized as an important mass transfer operation [1,2]. The solid that adsorbs a component is called an adsorbent.

Proponents for the use of adsorption for heavy metal treatment argue that the technique is economical, efficient and it produces high quality wastewater with minimal pollutant concentration [3-5]. Although these adsorbents are efficient to use, their production has been found to be relatively expensive. This therefore increases the research interest in using alternative low cost

adsorbents of agricultural origin for metal removal from effluents. Since effectiveness and cost of an adsorbent are important issues, a number of novel adsorbents have been investigated. These includes; bamboo root biomass [6]; cocoa pod husk [7]; sugar beat pulp [8]; egg shell [9]; groundnut shell [10]; bitter leaf [11]; *Citrus limetta* peel [12]; *Ficus religiosa* leaves [13]; *Citrullus lanatus* seed husk [14]; and Brewer's Spent Grain (BSG) [15]. These are natural biopolymers representing unused resources and have the ability to retain relatively high concentration of metal ions in waste water by passive sorption and or complexation based on metal-sequestration and they have high affinity for metals [16,17]. However, chemical modification process have been used to further increase the sorption capacity since research has shown that chemical modification of lingo-cellulosic materials increases their sorption capacity for heavy metals [18-22].

Sorghum hull, an agricultural waste product from the alcoholic brewing industry was used to investigate its potential in the sorption of Nickel, Copper and Zinc ions from aqueous solution. Therefore, this work was aimed at comparing the efficiency of the sorghum hull of two different

particle sizes, different concentrations of modification by mercaptoacetic acid and the effect of each on the heavy metal removal to obtain optimum conditions for sorption process.

## 2. METHODOLOGY

### 2.1 Adsorbent Preparation

The Sorghum hulls (SH) (*sorghum bicolor*) were sourced from consolidated Brewery, Awomanma in Imo State, south east Nigeria. The sorghum hulls were washed and air dried in preparation for the adsorption analysis. The air dried sorghum hulls were crushed with a manual blender to smaller particles and sieve analysis was performed using a mechanical sieve screen to obtain final sample sizes of 106  $\mu\text{m}$  and 250  $\mu\text{m}$ . The screened fine sorghum hulls powder was further soaked in excess of 0.3M  $\text{HNO}_3$  solution for 24 hours. It was then filtered through a Whatman No.41 filter paper and rinsed with deionised water. The rinsed sorghum hulls were later air dried for 24 h. The treatment of the biomass with 0.3M  $\text{HNO}_3$  solution aids the removal of any debris or soluble biomolecules that might interact with metal ions during sorption. This process is called chemical activation of the sorghum hulls.

### 2.2 Preparation of Adsorbate Solutions for Sorption Studies

All glassware and plastic wares were washed with deionized water and rinsed with 0.1M HCl to eliminate errors. All the reagents used were of analytical reagent grade. Stock solutions of 1000 mg/L of Cu (II), Ni (II) and Zn (II) ions were prepared from Copper tetraoxosulphate (VI) ( $\text{CuSO}_4$ ) 98% assay; Nickel acetate ( $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$ ) 99% assay and Zinc tetraoxosulphate (VI) ( $\text{ZnSO}_4$ ) 99% assay. Thereafter, serial dilutions were carried out on the stock solutions to obtain working solutions of 10, 20,30,40,50 mg/L of each of the metal ions. The concentrations of these solutions were confirmed using Atomic Absorption Spectrophotometer (AAS) model GBC SCIENTIFIC AVANTA PM AAS A.C.N 005472686 manufactured by GBC Scientific equipment Ltd Australia.

### 2.3 Chemical Modification of Sorghum Hulls with Mercapto-Acetic Acid (MAA)

The air-dried activated sorghum hulls were weighed and divided into three parts. 500g of the

first part labeled A was left untreated and called unmodified sorghum hulls (USH). 500 g of the second part labeled B was acid treated by dissolving it in excess of 0.5M mercaptoacetic acid ( $\text{HSCH}_2\text{COOH}$ ) solution, stirred for 30 min and left to stand for 24 h at 28°C and designated as 0.5M modified sorghum hulls (0.5 MSH). Another 500 g of the third part labeled C was also acid treated by dissolving it in excess of 1.0M mercaptoacetic acid solution, stirred for 30 min and left to stand for 24 h at 28°C and called 1.0M modified sorghum hulls (1.0 MSH). After 24 h, the mixtures in the beakers designated as 0.5 MSH and 1.0 MSH were filtered off using Whatman No. 41 filter paper and were air dried. The three working adsorbents were stored in air tight plastic containers and labeled USH, 0.5 MSH, and 1.0 MSH for the unmodified, 0.5 M modified and 1.0 M modified adsorbent respectively

### 2.4 Effect of Initial Concentration of Adsorbate on Equilibrium Sorption

Equilibrium sorption studies were carried out according to the procedure described by Ho et al. [23]. Sorption of Ni (II), Cu (II) and Zn (II) were carried out for each adsorbent (106 $\mu\text{m}$  and 250  $\mu\text{m}$ ) at pH of 6.0 and temperature of 28°C. 100 $\text{cm}^3$  of standard solutions of each metal with various concentrations (10, 20, 30, 40 and 50 mg/L) were transferred into 250  $\text{cm}^3$  Erlenmeyer flasks and labeled. Thereafter 0.2 g of each adsorbent (106 $\mu\text{m}$  and 250  $\mu\text{m}$ ) was weighed into the different flasks and agitated in a shaker for 1 h. After the agitation time, the content of each flask was then filtered using Whatman No.41 filter paper and the equilibrium concentration of each metal was determined using Atomic Absorption Spectrophotometer model GBC SCIENTIFIC AVANTA PM AAS A.C.N 005472686 manufactured by GBC Scientific equipment Ltd Australia. The difference in the metal ion concentration of the solutions before and after sorption gave the amount adsorbed by each adsorbent.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of Initial Metal Ion Concentration

The percentage of metal ion removed by the adsorbent was based on the initial concentration and equilibrium concentration. This value indicates the sorption efficiency of the adsorption

process. The percentage of the metals Cu (II), Ni<sup>2+</sup> (II) and Zn (II) removed by the adsorbents was calculated using the relationship:

$$R_E = 100 \times (C_i - C_e) / C_i \quad (1)$$

Where  $R_E$  is the removal efficiency and  $C_i$  and  $C_e$  are the initial and equilibrium metal ion concentrations respectively [24]. The results obtained for the percentage removal of the metal ions are shown in the Figs. below. The variation of percentage removal with initial concentration of the metal ions for the three adsorbents is shown in Fig. 1 for 106µm particle sizes and Fig. 2 for 250 µm particle sizes. From the results obtained, for 1.0MSH of 106µm particle size; Ni (II) decreased from 56.89% at 10 mg/L to 39.6% at 50 mg/L and for 250 µm particle size, decreased from 68.35% at 10 mg/L to 47.5% at 50 mg/L. Cu (II) on 106µm particle size decreased from 70.31% at 10 mg/L to 61.23% at 50 mg/L and on 250µm particle size, decreased from 79.15% at 10 mg/L to 65.39% at 50 mg/L while Zn (II) on 106 µm particle size decreased from 72.2% at 10 mg/L to 30.73% at 50 mg/L and on 250µm particle size decreased from 77.67% at 10 mg/L to 19.72% at 50 mg/L.

For 0.5MSH adsorbent of 106 µm, Ni (II) decreased from 64.08% at 10 mg/L to 43.08% at 50 mg/L and for 250µm particle size, increased from 17.83% at 10 mg/L to 89.56% at 50 mg/L; Copper on 106µm particle size decreased from 85.3% at 10 mg/L to 63.44% at 50 mg/L and on 250µm particle size decreased from 71.04% at 10 mg/L to 66.69% at 50 mg/L while zinc on 106µm particle size decreased from 89.57% at 10 mg/L to 10.72% at 50 mg/L and on 250µm particle size decreased from 54.52% at 10 mg/L to 16.13% at 50 mg/L. For USH of 106µm; Nickel increased from 5.94% at 10 mg/L to 31.49% at 50 mg/L and on 250µm particle size increased from 5.3% at 10 mg/L to 34.71% at 50 mg/L; Copper on 106µm particle size increased from 46.71% at 10 mg/L to 59.82% at 50 mg/L and on 250µm particle size increased from 54.44% at 10 mg/L to 60.14% at 50 mg/L while Zinc on 106 µm particle size decreased from 50.98% at 10 mg/L to 12.8% at 50 mg/L and on 250 µm particle size decreased from 45.04% at 10 mg/L to 14.5% at 50 mg/L.

Sorption efficiency can be said to be dependent on the type of metal ion and the nature of adsorbents. This can be used to explain why some of the adsorbents had an increase in percentage removed as the concentration of metal ion increased while some had a decrease

in sorption efficiency as the initial metal ion concentration increased. From the results, the chemically modified adsorbents exhibited an increase in their removal efficiency when compared with the unmodified adsorbent. It is evident that chemically modified adsorbent exhibits better removal capability than unmodified adsorbent suggesting that surface modification of the adsorbent generates more adsorption sites on its solid surface matrix for metal adsorption [25]. The trend in sorption efficiency is USH < 1.0MSH < 0.5MSH and for the metal ions; Ni<sup>2+</sup> < Zn<sup>2+</sup> < Cu<sup>2+</sup>. Decreases in percentage adsorbed as initial metal ion concentration is increased have also been observed by other authors [10,11,13,26]. This was generally attributed to the increase in the effective collision between the metal ions and the active sites as a result of decrease in the number of available sites at higher concentration.

### 3.2 Adsorption Equilibrium Study of Cu (II), Ni (II) and Zn (II)

Adsorption isotherm is a functional expression that correlates the equilibrium distribution of adsorbate between the sorbent and the solution to determine the maximum sorption capacity. It is important to establish the most appropriate correlations for the batch equilibrium data using empirical or theoretical equations as it plays a functional role in predictive modeling procedures for analysis and design of adsorption systems [27-30]. The adsorption equilibrium data was modeled using three sorption isotherms namely the Langmuir, Freundlich and Temkin isotherm models. These isotherms were employed to model the sorption experimental data and to find out that which best fits the equilibrium sorption experimental data.

#### 3.2.1 Langmuir isotherm model

The Langmuir equation is given as [31]:

$$q_e = q_{max} K_L C_e / (1 + K_L C_e) \quad (2)$$

This linearizes as:

$$1/q_e = (1/q_{max} K_L)(1/C_e) + 1/q_{max} \quad (3)$$

Where  $q_{max}$  is maximum adsorption capacity corresponding to monolayer coverage;  $K_L$  is the Langmuir isotherm constant. A plot of  $1/q_e$  against  $1/C_e$  for the Langmuir isotherm is shown in Fig. 3 for Ni(II), Fig. 4 for Cu(II) and Fig. 5 for Zn(II) ions. The linear correlation equations obtained were used to determine the adsorption

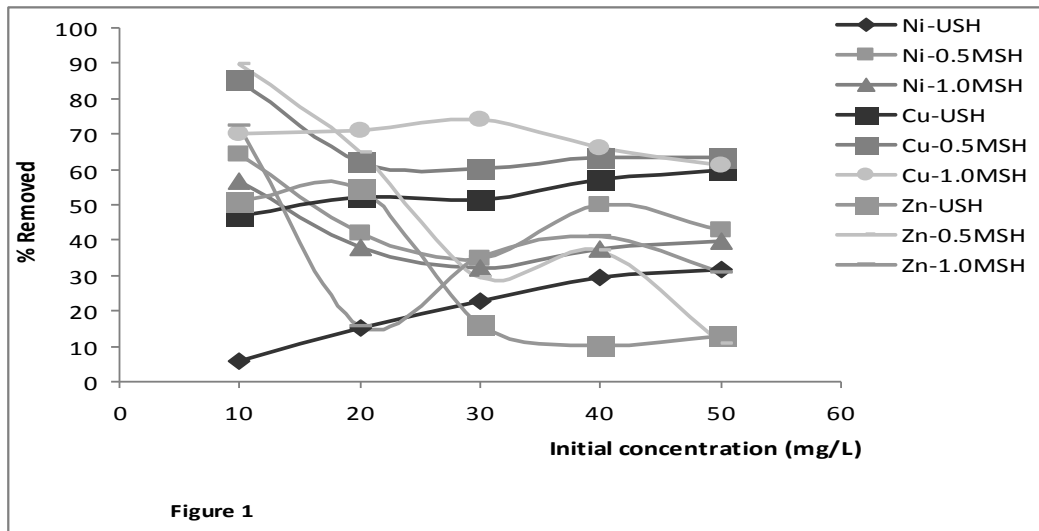


Fig. 1. Percentage removed against Initial concentration of metal ion solution for 106 µm

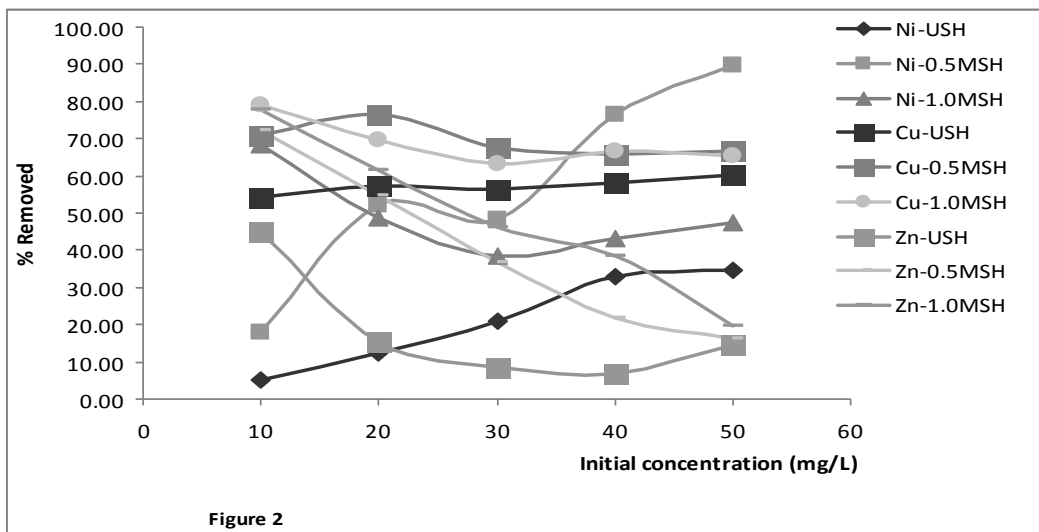


Fig. 2. Percentage removed against Initial concentration of metal ion solution for 250 µm

capacity ( $q_{max}$ ), the Langmuir isotherm constant ( $K_L$ ) from the slopes and intercepts and the correlation coefficient ( $R^2$ ) for the metal ions.

The Langmuir adsorption coefficient ( $K_L$ ) is related to apparent energy of adsorption and for all the metal ions was high. High values of  $K_L$  indicate a steep beginning of the isotherm reflecting high affinity of the sorbent [32,33]. The maximum sorption capacity ( $q_{max}$ ) corresponding to monolayer coverage for the metal ions adsorption by 1.0MSH on 106 µm and 250µm was also represented. The values of  $K_L$  ( $dm^3g^{-1}$ )

and  $q_{max}$  ( $mgg^{-1}$ ) are summarized in Table 2. The order of  $q_{max}$  for adsorption on 1.0MSH of both particle sizes was  $Cu^{2+} > Ni^{2+} > Zn^{2+}$  indicating that  $Cu^{2+}$  was most efficiently adsorbed with the highest maximum sorption capacity for both particle sizes. On the whole, the result of the Langmuir isotherm constants show that the adsorbents of 106µm particle size (USH, 0.5 MSH and 1.0 MSH) and 250µm particle size (USH, 0.5 MSH and 1.0 MSH) were both good for the sorption of the metal ions.

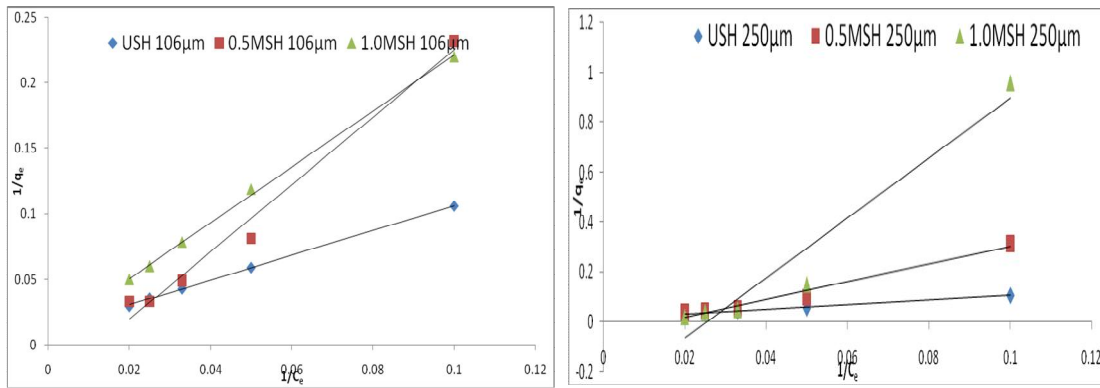


Fig. 3. Langmuir isotherm for Ni<sup>2+</sup> 106 μm (a) Langmuir isotherm for Ni<sup>2+</sup> 250 μm (b)

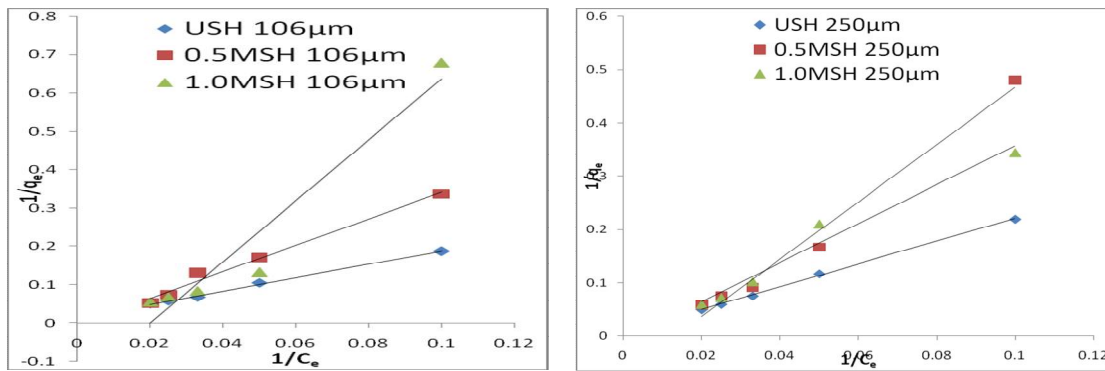


Fig. 4. Langmuir isotherm for Cu<sup>2+</sup> 106 μm (a) Langmuir isotherm for Cu<sup>2+</sup> 250 μm (b)

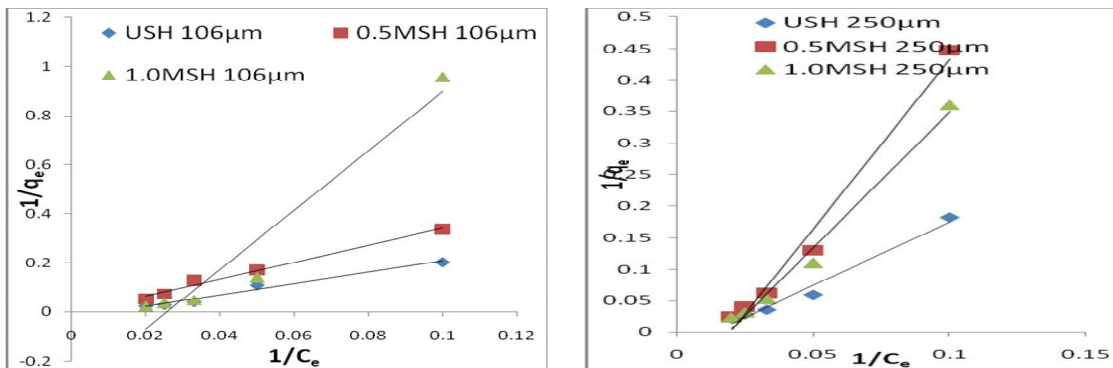


Fig. 5. Langmuir isotherm for Zn<sup>2+</sup> 106 μm (a) Langmuir isotherm for Zn<sup>2+</sup> 250 μm (b)

Maximum sorption capacity ( $q_{max}$ ) of the same range as the one obtained from this work have been reported and summarized in Table 2. Values of  $q_{max}$  greater than that found in this work have also been reported [28].

**3.2.2 Freundlich isotherm model**

The Freundlich isotherm equation is given as [30]:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (4)$$

where  $K_F$  is the Freundlich isotherm constant and  $1/n$  is the Freundlich exponent. The Freundlich isotherm plots are shown in Fig 6 for Ni (II), Fig. 7 for Cu (II) and Fig. 8 for Zn (II) ions. By employing the Freundlich model and plotting  $\ln q_e$  against  $\ln C_e$ , linear equations were obtained and used to determine the value of  $n$ , which determines the suitability of the adsorbent and

the adsorption process, the Freundlich constant ( $K_F$ ) and the correlation coefficient  $R^2$  for the metal ions on the three adsorbents. The Freundlich constant for adsorption of the metals ( $K_F$ ),  $n$  and the  $R^2$  values of the various metal ions for 106 $\mu$ m and 250  $\mu$ m are listed in Tables 1 and 2, respectively. The highest values of these constants were obtained for the adsorption of  $Ni^{2+}$ . This trend may be attributed to the small ionic radius of  $Ni^{2+}$  leading to its high adsorptivity.

From the results obtained, the  $R^2$  values show that Freundlich isotherm is a good model for the metal sorption on the sorghum hull. The rate of adsorption increased in the order  $Ni^{2+}>Cu^{2+}>Zn^{2+}$  for all the adsorbents. The values of  $K_F$  increased from USH to 1.0 MSH. This suggests that the Freundlich isotherm model could be used to describe the adsorption of these metals by the adsorbents. Also, it is observed that the  $n$  values are less than unity. This indicates a stronger bond between the metals and the adsorbents [34]. However, research has shown that the more the  $n$  values approximates to unity,

the closer the sorption process is represented by the Freundlich isotherm model [35,36]. The chemical modification of the adsorbents equally enhanced adsorptivity which follows the trend 1.0MSH>0.5MSH>USH for both pore sizes.

### 3.2.3 Temkin isotherm model

The Temkin equation is given as [37]:

$$q_e = (RT/b_T) \ln K_T + (RT/b_T) \ln C_e \quad (5)$$

Where  $b_T$  indicates the adsorption potential of the adsorbent;  $K_T$  is the Temkin isotherm constant ( $dm^3g^{-1}$ );  $q_e$  is the sorption capacity at equilibrium ( $mg g^{-1}$ );  $C_e$  is the equilibrium concentration of adsorbate ( $mgL^{-1}$ );  $R$  is gas constant and  $T$  is absolute temperature. The plots of the Temkin isotherm are shown in Fig. 9 for Ni(II), Fig. 10 for Cu(II) and Fig. 11 for Zn(II) ions. By employing the Temkin model and plotting  $q_e$  against  $\ln C_e$ , the Temkin isotherm constants  $K_T$ ,  $b_T$  and correlation coefficient ( $R^2$ ) values were obtained.

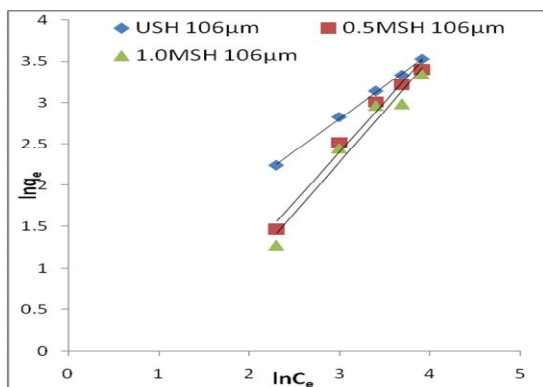
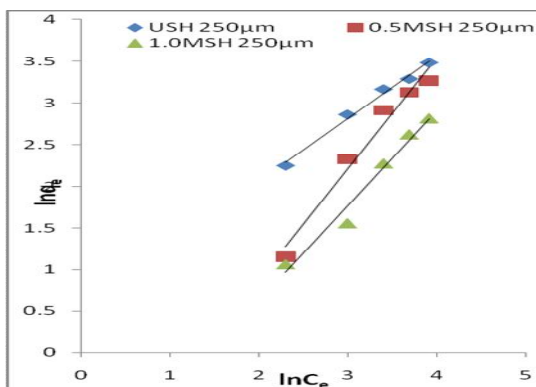


Fig. 6. Freundlich Isotherm for  $Ni^{2+}$  106  $\mu$ m (a)



Freundlich Isotherm for  $Ni^{2+}$  250  $\mu$ m (b)

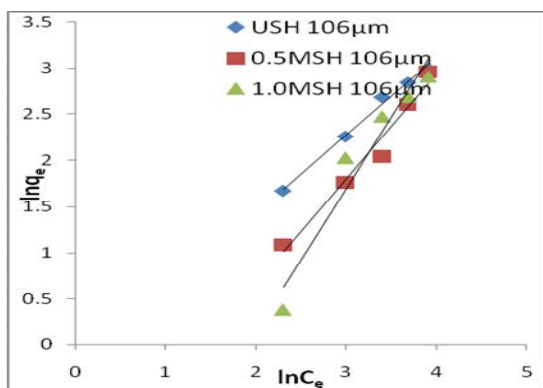
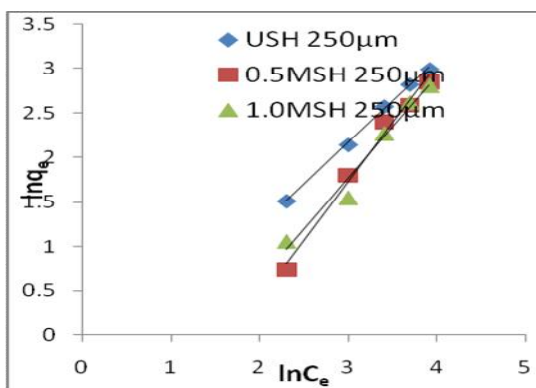


Fig. 7. Freundlich isotherm for  $Cu^{2+}$  106  $\mu$ m (a)



Freundlich isotherm for  $Cu^{2+}$  250  $\mu$ m (b)

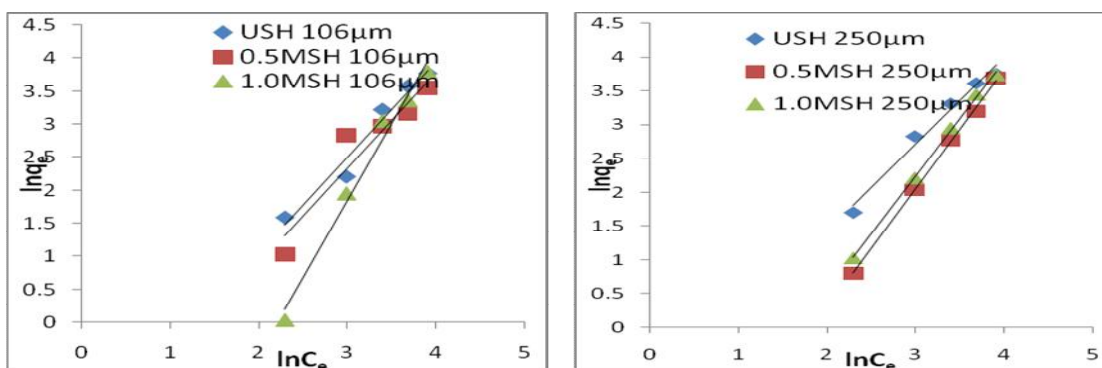


Fig. 8. Freundlich isotherm for Zn<sup>2+</sup> 106 μm (a) Freundlich isotherm for Zn<sup>2+</sup> 250 μm (b)

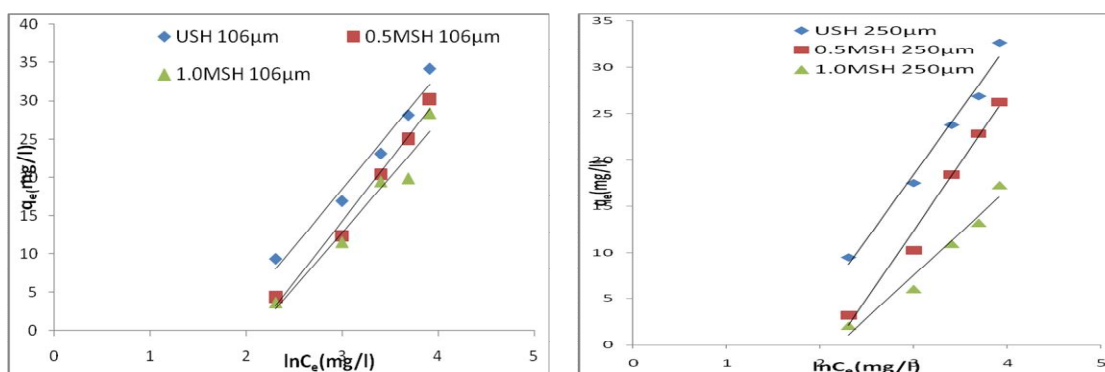


Fig. 9. Temkin isotherm for Ni<sup>2+</sup> 106 μm (a) Temkin isotherm for Ni<sup>2+</sup> 250 μm (b)

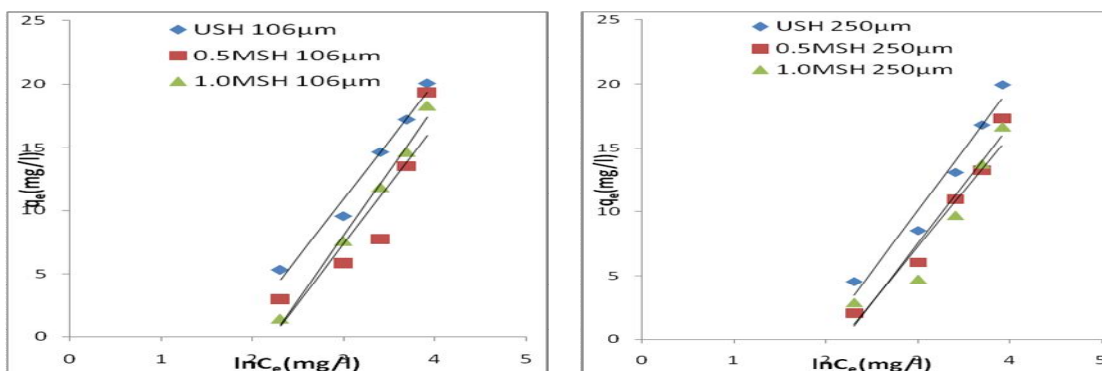


Fig. 10. Temkin isotherm for Cu<sup>2+</sup> 106 μm (a) Temkin isotherm for Cu<sup>2+</sup> 250 μm (b)

From the results obtained, it is observed that the Temkin isotherm model is generally obeyed by the adsorption process on the adsorbents on 106 μm size (USH, 0.5 MSH, 1.0 MSH) and on 250 μm size (USH, 0.5 MSH, 1.0 MSH) for Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> because their R<sup>2</sup> values are relatively high. The constant b<sub>T</sub> describes the energy required for a transition from the physisorbed surface to a possible primary chemisorbed surface. It apparently depicts transition from physisorption into chemisorption. The K<sub>T</sub> is the

rate constant required to transit through the two phases. The b<sub>T</sub> and K<sub>T</sub> values decreased from USH to 1.0 MSH for both pore sizes (106 μm and 250 μm) of the adsorbents. These high values compared with those of the unmodified and the modified is due to the improved adsorption resulting from improved adsorbent surface, that is, increased thiolation. This trend is possibly due to increased charge density with increasing thiolation, which reduces the energy required in crossing the primary interfacial energy barrier



[38]. This is due to increasing degrees of freedom of the metal ion in an adsorbent environment with increasing surface area. The subsurface adsorption energy ( $b_T$ ) for 1.0MSH of 106  $\mu\text{m}$  and 250 $\mu\text{m}$  are summarized in Table 2 below.  $\text{Zn}^{2+}$  had the least energy indicating that it was the metal ion that was easily adsorbed by the adsorbate. The trend in the rate of metal removal was  $\text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$  for both pore sizes.

### 3.3 Analysis of Coefficient of Determination of Isotherms

Coefficient of determination ( $R^2$ ) is a regression method that can be used to show the isotherm equation that best fits the data for adsorption of metals on various adsorbents. The coefficient of

determination from three sorption models namely Langmuir, Freundlich and Temkin for Ni(II), Cu(II) and Zn(II) sorption on the adsorbents of 106  $\mu\text{m}$  particle size (USH, 0.5MSH and 1.0MSH) and 250  $\mu\text{m}$  particle size (USH, 0.5MSH and 1.0MSH) were comparable and are shown in Table 1. The  $R^2$  values that are closest to unity indicate a close conformity of the experimental data to the model of the adsorption process (the isotherm equation). From Table 1, it can be concluded that no single isotherm best fits the data from the sorption of the metals on the adsorbent. Different isotherms appear to describe the equilibrium established between adsorbed metal ions on adsorbents and metal ions in solution at a constant temperature.

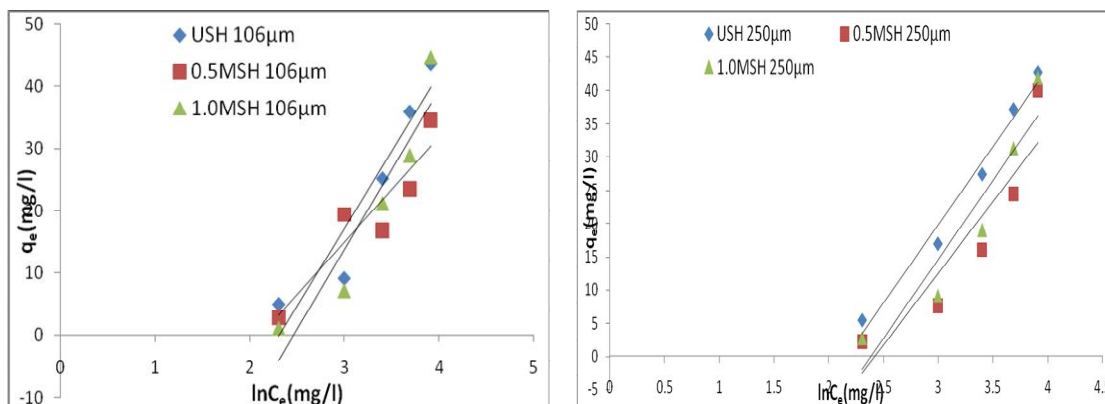


Fig. 11. Temkin isotherm for  $\text{Zn}^{2+}$  106  $\mu\text{m}$  (a) Temkin isotherm for  $\text{Zn}^{2+}$  250  $\mu\text{m}$  (b)

Table 1. Coefficients of determination ( $R^2$ ) values for the langmuir, freundlich and temkin isotherms for metal sorption on the different adsorbents

Adsorbent	Coefficients of determination( $R^2$ )					
	106 $\mu\text{m}$ particle size			250 $\mu\text{m}$ particle size		
	Langmuir	Freundlich	Temkin	Langmuir	Freundlich	Temkin
<b>Ni(II) ion</b>						
USH	0.999	0.998	0.971	0.998	0.990	0.984
0.5MSH	0.982	0.979	0.984	0.972	0.971	0.983
1.0MSH	0.966	0.957	0.951	0.940	0.973	0.962
<b>Cu(II) ions</b>						
USH	0.997	0.993	0.978	0.999	0.998	0.963
0.5MSH	0.987	0.967	0.823	0.983	0.973	0.962
1.0MSH	0.939	0.941	0.990	0.970	0.986	0.907
<b>Zn(II) ions</b>						
USH	0.965	0.965	0.901	0.981	0.981	0.979
0.5MSH	0.987	0.899	0.865	0.982	0.998	0.840
1.0MSH	0.940	0.998	0.883	0.985	0.982	0.892

**Table 2. Comparison of biosorption capacities of sorghum Hulls and some adsorbents reported in literature**

Metal ion	Adsorbent	q <sub>max</sub> mg/g	Ref.	Metal ion	Adsorbent	q <sub>max</sub>	K <sub>L</sub>	Ref.	
Pb <sup>2+</sup>	Barley Straw	23.20	33	Cu <sup>2+</sup>	Sorghum Hull (106µm)	121.814	2.0x10 <sup>-3</sup>	This Study	
	Modified Luffa Cylindrical fiber	13.68	29		Sorghum Hull (250µm)	148.000	1.9x10 <sup>-3</sup>	This Study	
Ni <sup>2+</sup>	Salvinia Plant Biomass	46.00	34	Ni <sup>2+</sup>	Sorghum Hull (106µm)	90.909	1.21x10 <sup>-2</sup>	This Study	
		44.05	34		Sorghum Hull (250µm)	83.333	1.29x10 <sup>-2</sup>	This Study	
Cr <sup>3+</sup>		61.72	34		Sorghum Hull (106µm)	15.781	1.43x10 <sup>-2</sup>	This Study	
Cr <sup>6+</sup>	Neem and Mango Dust	58.82	34	Zn <sup>2+</sup>	Sorghum Hull (250µm)	12.500	1.86x10 <sup>-2</sup>	This Study	
		37.73	34						
<b>FREUNDLICH CONSTANTS</b>									
Metal ion	Adsorbent	n	K <sub>F</sub> mg/g	Ref.	Metal ion	Adsorbent	n	K <sub>F</sub> mg/g	Ref.
Cu <sup>2+</sup>	Sorghum Hull (106µm)	0.919	0.7827	This study	Cu <sup>2+</sup>	Sorghum Hull (250µm)	1.014	0.5337	This study
Ni <sup>2+</sup>		1.0025	1.5281	This study	Ni <sup>2+</sup>		1.018	1.7246	This study
Zn <sup>2+</sup>		0.6887	0.1557	This study	Zn <sup>2+</sup>		0.7746	0.3113	This study
<b>TEMKIN CONSTANTS</b>									
Metal ion	Adsorbent	b <sub>T</sub> kJ/mol	K <sub>T</sub>	Ref.	Metal ion	Adsorbent	b <sub>T</sub> kJ/mol	K <sub>T</sub>	Ref.
Cu <sup>2+</sup>	Sorghum Hull (106µm)	0.2455	0.1102	This study	Cu <sup>2+</sup>	Sorghum Hull (250µm)	0.2620	0.1125	This study
Ni <sup>2+</sup>		0.1562	0.1212	This study	Ni <sup>2+</sup>		0.1689	0.1024	This study
Zn <sup>2+</sup>		0.9718	0.0853	This study	Zn <sup>2+</sup>		0.1053	0.0891	This study

For sorption with 106  $\mu\text{m}$  at 1.0 MSH, the Langmuir isotherm seems to give the best fit and hence the best representation of the sorption process of Ni (II) ion; the Freundlich isotherm best describes the sorption of Zn (II) ion while the sorption of Cu (II) ion is best described by the Temkin isotherm. For sorption on 250  $\mu\text{m}$  at 1.0 MSH, the Langmuir isotherm best describes the sorption of Zn (II) ion; Freundlich best describes the sorption of Cu (II) ion while the Temkin isotherm best describes the sorption of Ni (II) ion. From the data obtained, all the adsorbents had high  $R^2$  value indicating that they can be used as low cost adsorbents for the removal of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) from their aqueous solutions. Also, results with the isotherms indicate that the isotherm models can be used to assess the potential of sorghum hull as low cost adsorbent.

#### 4. CONCLUSION

This result obtained from this work showed that the sorption of the heavy metals onto the sorghum hull adsorbent was feasible. The sorption process was dependent on initial concentration and adsorbent modification. Percent adsorbed decreased with increase in initial concentration and modified adsorbent gave better sorption capacity. These results will help in the selection of appropriate conditions for the efficient use of the adsorbent in the treatment of industrial effluents for the removal of heavy metals. The conditions that yield maximum sorption efficiency for the heavy metals can be adopted and modified for the design of batch/semi-continuous adsorbents for use in various small scale industries in tertiary waste water treatment.

#### ACKNOWLEDGEMENTS

My thanks go to my Supervisor Prof. A.A. Abia and Dr. J.C Igwe whom by their able supervision and guidance made this work to be a finished work starting from manuscript preparation. . All sources of funding was personal as there was no role of funding agency in the study design, collection, analysis, interpretation of data and in the writing of the manuscript.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

#### REFERENCES

1. Idris S, Iyaka YA, Dauda BEN, Ndamitso MM, Umar MT. Kinetic Study of Utilizing Groundnut Shell as an Adsorbent in Removing Chromium and Nickel from Dye Effluent. *Am. Chem. Sci. J.* 2012; 2(1):12-24.
2. Krishna RH. Comparative Studies of Isotherm and Kinetics on the Adsorption of Cr (VI) and Ni (II) from Aqueous Solutions by Powder of Mosambi Fruit Peelings. *Intern. Res. J. of Pure & Appl. Chem.* 2014;4(1):26-45.
3. Adeyemo AO, Adebowale KO, Olu-Owolabi BI. Adsorption of Copper by Biochar. *Intern. Res. J. of Pure and Appl. Chem.* 2014; 4(6): 727-736.
4. Uzoije AP, Uche CC, Ashiegbu D. Analysis of Thermodynamics, Kinetics and Equilibrium Isotherm on  $\text{Fe}^{3+}/\text{Fe}^{2+}$  Adsorption onto Palm Kernel Shell Activated Carbon (PKSAC): A Low-cost Adsorbent. *Am. Chem. Sci. J.* 2014 4(3):298-325.
5. Onyango MS, Kojima Y, Aoyi O, Bernardo EC, Matsuda H. Adsorption Equilibrium Modeling and Solution Chemistry Dependence of Fluoride Removal from Water by Trivalent Cation-exchange Zeolite F-9. *J. Colloid and Interface Sci.* 2004;279:341-350.
6. Babatunde AI, Abiola OK, Osideko OA, Oyelola OT. Kinetic and equilibrium studies on the adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions from aqueous solutions by bamboo root biomass. *Afr. J. Biotechnol.* 2009;8(14):3364-3368.
7. Igwe JC, Abia AA, Nwankwo SO. Bioremediation of Al (III), Cr (III) and Ni (II) ions from aqueous solution using cocoa pod husk: kinetics and intraparticle diffusivities. *Bioremediation, Biodiversity and Bioavailability.* 2011;5(1):28-35.
8. Zolgharnien J, Asanjarani N, Shariatmanesh T. Removal of thallium (I) from aqueous solution using modified sugar beet pulp. *Toxicol. and Environ. Chem.* 2011;93(2):207-214.
9. Rajendran A and Mansiya C. Extraction of Chromium from Tannery effluents using waste egg shell material as an adsorbent. *British J. of Environ. & Climate Change.* 2011;1(2):44-52.
10. Choudhury TR, Pathan KM, Amin MN, Ali M, Quraishi SB, Mustapha AI. Adsorption

- of Cr (III) from aqueous solution by groundnut shell. J. Environ. Sci. and Water Resources. 2012;1(6):144-150.
11. Babarinde A, Babalola JO, Ashidi J, Adegoke J, Adebola O, Ogundipe K, Omojola A, Obisanya. Batch equilibrium biosorption of Ni(II), Cr(III) and Co(II) from solutions using Bitter leaf (*Vernonia amygdalina*): kinetics, isotherm and thermodynamics. Int. J. Chem. Biochem. Sci. 2013; 3: 101-109.
  12. Sirajudin J, Naveen J, Arul Manikandan S, Mohamed Mubashir MM. Removal of chromium (VI) from aqueous solution using *Citrus limetta* Peel as an adsorbent. Der Chemica Sinica. 2013;4(2):133-143.
  13. Gayathri R, Thirumarimuru M, Kannadasan T. A study on adsorption of chromium (VI) ions from aqueous solution by *Ficus religiosa* leaves as adsorbent. Der Chemica Sinica. 2013;4(3):79-87.
  14. Adelagun ROA, Berezi EP, Itodo AU, Oko OJ, Kamba EA, Andrew C and Bello HA. Adsorption of Pb<sup>2+</sup> from aqueous solution by modified melon (*Citrullus lanatus*) seed husk. Chemistry and Materials Research. 2014;6(2):113-121.
  15. Adelagun ROA, Itodo AU, Berezi EP, Oko OJ, Kamba EA, Andrew C and Bello HA. Adsorptive removal of Cd<sup>2+</sup> and Zn<sup>2+</sup> from aqueous system by BSG. Chemistry and Materials Research. 2014; 6(2):104-112.
  16. Sun G, Shi W. Sunflower stalk as adsorbents for the removal of metal ions from wastewater. Ind. and Eng. Chem. Res. 1998;37(4):1324-1328.
  17. Cordero B, Lodeiro P, Herrero R, Vincent, MES. Biosorption of cadmium by *Fucus spiralis*. Environ. Chem. 2004;1(3):180-187.
  18. Abia AA, Horsfall M Jnr, Didi O. The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution. Bioresource Technology. 2003;90(3):345-348.
  19. Igwe JC, Eche EN, Abia AA. Binding of Hg (II), Ni (II) and Pb (II) from aqueous solutions onto thiolated and carboxymethylated sawdust. Intern. J. Chem. 2006;16(3):121-128.
  20. Mamisahebei S, Jahed Khamiki GR, Torabian A, Nasser S, Naddaki K. Removal of arsenic from aqueous solution by pretreated waste tea fungal biomass. Iran J. Environ Health Sci. Eng. 2007;4(2): 85-92.
  21. Boddu VM, Abburi K, Talbott JL, Smith ED, R. Haaseh R. Removal of arsenic (III) and arsenic (V) from aqueous medium using Chitosan-coated biosorbent. Water Res. 2008;42(3):633-642.
  22. Urik M, Littera P, Ševc J, Kolenčik M, Čerňanský S. Removal of arsenic (V) from aqueous solutions using chemically modified sawdust of spruce (*Picea abies*): Kinetics and isotherm studies. Int. Environ. Sci. Tech. 2009;6(3):451-456.
  23. Ho YS, Huang CT, Huang HW. Agricultural by-Products as a Metal Sorbent: Sorption of Copper Ions from aqueous Solution onto Tree Fern. Process Biochem. 2002;37(5):1421-1430.
  24. Demirbas E, Kobya M, Senturk E, Ozkon T. Adsorption kinetics of the removal of Chromium (VI) from aqueous solutions on the Activated Carbons prepared from Agricultural wastes. Water SA. 2004;30(4):533-539.
  25. Igwe JC. Equilibrium and kinetic studies of Al, As, Cr and Ni ions adsorption from aqueous solutions using cocoa (*Theobroma cocoa*) pod husk, PhD thesis University of Port Harcourt, River State Nigeria. 2010;1-354.
  26. Nameni M, Alavi Moghadam MR, Arami M. Adsorption of hexavalent chromium from aqueous solution by wheat bran. Int. J. Environ. Sci. Technol. 2008;5:161-168.
  27. Igwe JC, Abia AA. Sorption isotherm studies of Cd<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> detoxification from wastewater using EDTA modified and unmodified maize cob. Eclética Quimica. 2007;32(1):33-42.
  28. Okoronkwo NE, Igwe JC, Aniekwu CC. Effects of adsorbent activation on Bioremediation of Hg (II) and Cd (II) ions from aqueous solutions using Boiler fly ash. Bioremediation, Biodiversity and Bioavailability. 2011;5(1):36-45.
  29. Igwe JC. A Review of Potentially Low Cost Sorbents for Heavy Metal Removal and Recovery. Terrestrial and Aquatic Environmental Toxicology. 2007;1(2):60-69.
  30. Vinodhini V, Das N. Relevant approach to assess the performance of sawdust as adsorbent of chromium (VI) ions from aqueous solutions. Intern. J. of Environ. Sci. and Technol. 2010;7(1):85-92.
  31. Saueprasearsit P, Nuanjaraen M, Chinlapa M. Biosorption of lead (Pb<sup>2+</sup>) by *Luffa cylindrical fibre*. Environ. Res. J. 2010;4(1): 157-166.

32. Ho YS, McKay G. A multi-stage batch sorption design with experimental data. *Adsorpt. Sci. Technol.* 1999;17:233-243.
33. Pehlivan E, Altun T, Parlayici S. Utilization of barley straws as biosorbents for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions. *J. Hazard. Mater.* 2008;164:982-986.
34. Ahalya N, Kanamadi RD, Ramachandra TV. Biosorption of chromium (VI) from aqueous solutions by the husk of Bengal gram (*Cicer arietinum*), *Electr J. Biotechnol.* 2005;8(3):258-264.
35. Abia AA, Horsfall M Jnr, Didi O. Studies on the use of agricultural by-product for the removal of trace metals from aqueous solutions. *J. Appl. Sci. Environ. Manag.* 2002;6(2):89-96.
36. Horsfall M. Jnr, Abia AA, Spiff AI. Studies on the Influence of Mercaptoacetic Acid (MAA) modification of Cassava (*Manihot esculenta Cranz*) Waste biomass on the Adsorption of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  from Aqueous Solution. *Bull Korean chem. Soc.* 2004;25(7):969-976.
37. Özacar M, Sengil IA and Turkmenler H. Equilibrium and kinetic data and adsorption mechanism for adsorption of lead onto *Valonia tannin* resin *Chem. Eng. J.* 2008;143(1-3):32-42.
38. Dhir B, Kumar R. Adsorption of heavy metals by *Salvinia* Biomass and agricultural residues. *Int. J. Environ. Res.* 2010;4(3):472-432.

© 2015 Imaga et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited.

*Peer-review history:*

*The peer review history for this paper can be accessed here:*  
<http://www.sciedomain.org/review-history.php?iid=809&id=7&aid=7149>