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Removal of Ni (II), Cu (II) and Zn (II) ions from synthetic wastewater using sorghum hulls as adsorbents

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ABSTRACT

Heavy metals are one of the major contaminants from industrial waste water which causes extensive damage to the environment. This study investigated the feasibility of using agro industrial waste sorghum hulls (SH) for adsorption of Ni, Cu, and Zn from simulated effluent. The sorption process was dependent on time, pH and initial metal ion concentration. Sorption process was rapid at initial time and attained equilibrium at about 10 min. Optimum pH for adsorption was found to be 8.0 for Zn (II) and 10.0 for Ni (II) and Cu (II) ions. The sorption process was found to be particle diffusion controlled and of chemisorption mechanism as the pseudo-second order gave a very good fit to the sorption kinetic data. Cu (II) had the highest removal efficiency of 61.23% on 106µm particle size. The sorption trend followed $Cu^{2+} > Ni^{2+} > Zn^{2+}$*. The adsorption equilibrium study showed that the adsorption of the ions was best represented by the Langmuir model for Cu (II) ion, Freundlich model for Ni (II) ion and Temkin model for Zn (II) ion. Therefore, SH and agro waste can be used as an effective adsorbent for the removal of metal ions from industrial effluent.*

Keywords: environment, wastewater, metal ions, sorghum hulls, adsorption.

INTRODUCTION

Industrialization has created several pollutants which have been released to the environment and are now, destroying the ecosystem. Among the most toxic and dangerous pollutants are heavy metals, dyes, green house gases , volatile organic compounds [1], which are constantly released to the environment through improperly controlled and unsupervised anthropogenic activities. Heavy metals are one of the major contaminants from industrial waste water which causes extensive damage to the environment. Heavy metals are loosely defined and include all toxic metals irrespective of their atomic mass [2, 3]. "Heavy metal poisoning" can possibly include excessive amounts of iron, manganese, aluminum, mercury, cadmium, or beryllium or such a semi-metal as arsenic. To many people, heavy metal pollution is a problem associated with areas of intensive industry. However, roadways and automobiles now are considered to be one of the largest sources of heavy metals. Zinc, copper, and lead are three of the most common heavy metals released from automobile exhaust, accounting for at least 90% of the total metals in road runoff [4]. Smaller amounts of many other metals, such as nickel and cadmium, are also found in road runoff and exhaust [5].

One of the largest problems associated with the persistence of heavy metals is the potential for bioaccumulation and biomagnifications causing higher exposure for some organisms than is present in the environment initially [6]. Bioaccumulation is the increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living organism any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply by industrial or consumer waste, or even from acid rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater [7].

Copper is an essential substance to human life, but in high doses can cause anemia, liver and kidney damage, and stomach and intestinal irritation [3]. The most common reaction of nickel is skin rashes at the site of contact. Less frequently, allergic people have asthma attacks following exposure to nickel. Lung effects, including chronic bronchitis and reduced lung function, have been observed in workers who breathed large amounts of nickel. Inhalation of fumes may result in sweet taste, throat dryness, cough, weakness, generalized aching, chills, fever, nausea and vomiting [8]. Zinc chloride fumes have caused injury to mucous membranes and pale gray cyanosis. Ingestion of soluble salts may cause nausea and vomiting [3].

Biosorption is a property of certain types of inactive, non-living microbial biomass and agricultural by-products, to bind, concentrate and sequester heavy metals from very dilute aqueous solution [9]. Biosorption was developed to remove pollutants from aqueous solutions to replace conventional methods such as reduction or oxidation, ion exchange, filtration, electrochemical treatment, membrane technology, evaporation recovery, chemical precipitation, chemical coagulation and solvent extraction [10]; which are quite complex to carry out and expensive to obtain [11]. These biosorbents can also be referred to as non-conventional adsorbents as they serve as means of treating effluents or wastewater. They can be highly selective, cheap and efficient compared to other conventional adsorbent like activated carbon, silica gel, zeolite, etc [12]. As the commercial adsorbents used to remove heavy metals in the wastewater are expensive, cheaper alternatives to serve as adsorbents have been developed.

Many biosorbents have been used as adsorbents for waste removal such as *Ficus religiosa* leaves [13], *citrus limett* peel [14], coconut fibre [15], Bitter leaf (*Vernonia amygdalina*) [16], sunflower waste biomass [17], fluted pumpkin pods [18] and so on. Sorghum hull waste is a viable adsorbent since it contains high fibre which would assist in the process of adsorption. Sorghum is genus of numerous species of grasses, one of which is raised for grain and many of which are used as fodder plants either cultivated or as part of pasture. The species are native to tropical and subtropical regions of all continents in addition to the southwest pacific and Australasia. Sorghum is in the family *panicoideae* and the *andropogoneae*. The sorghum specie (*Sorghum bicolor*) is an important world crop, used as food (as grain in sorghum syrup or sorghum molasses), fodder, the production of alcoholic beverages as well as biofuels [19]. It is an important food crop in Africa and South Asia and it is the fifth important cereal crop grown in the world [20]. In Nigeria, it is one of the major raw materials used in the production of alcoholic drinks. In this study, sorghum hull was investigated to ascertain its efficiency in adsorption of heavy metals (nickel (II), copper (II) and zinc (II)) from aqueous solutions. This is a contribution to recent alternative ways by which waste materials can be converted to wealth as they can be used industrially as adsorbents for effluent treatment and other related applications.

MATERIALS AND METHODS

Materials

All the reagents used were of analytical reagent grade. The metal ions solutions Ni (II), Cu (II) and Zn (II) were prepared from Nickel acetate $Ni(C_2H_3O_2)_2)$ 99% assay, Copper tetraoxosulphate (VI) ($CuSO_4$) 98% assay and Zinc tetraoxosulphate (VI) ($ZnSO_4$) 99% assay. The Sorghum hulls (*sorghum bicolor*) were sourced from Consolidated Brewery, Awomanma in Imo State, South East Nigeria. All glassware and plastic wares were washed with deionised water and rinsed with 0.1M HCl to eliminate errors.

Adsorbent Preparation

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 µm and 250 µm. The screened sorghum hulls powder was further soaked in excess of 0.3M 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 hours. The biomass was activated by treatment with 0.3M HNO_3 solution which also aids in the removal of any debris or soluble biomolecules that might interact with metal ions during sorption.

Preparation of Adsorbate Solutions for Sorption Studies

Stock solutions of 1000 ppm of each of the metal ions Cu (II), Ni (II) and Zn (II) were prepared. Thereafter, serial dilutions were carried out on the stock solutions to obtain working solutions of 10, 20,30,40,50 ppm 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.

Effect of Initial Concentration of Adsorbate on Equilibrium Sorption

Equilibrium sorption studies were carried out according to the procedure previously described [21]. Sorption of Ni (II), Cu (II) and Zn (II) were carried out for each adsorbent (106 µm and 250 µm) at pH of 6.0 and temperature of 28°C. 100 cm^3 of standard solutions of each metal ion with varying concentrations were transferred into 250 cm^3 Erlenmeyer flasks and labeled. Thereafter 0.2 g of each adsorbent (106 µm and 250 µm) was weighed into the different flasks and agitated in a shaker for 1 h. After that, the content of each flask was then filtered using Whatman No.41 filter paper.

Effect of Contact Time

Studies on kinetics of sorption were carried out according to the method described by Dermibas et al [22]. Kinetics of sorption for Cu (II), Ni (II) and Zn (II) ions was carried out for each adsorbent (106 µm and 250 µm) at pH of 6.0 and temperature of 28°C. 100 cm^3 of standard solutions of each metal ion, initial concentration of (50 mg/L) was transferred into various 250cm^3 Erlenmeyer flask and labeled. Then 0.2 g of each adsorbent (106 µm and 250 µm) was transferred into the different flasks and agitated in a shaker for different contact times (10, 30,50,70,90 min). After each agitation time, the contents of the flask were then filtered using Whatman No.41 filter paper.

Effect of pH

Sorption studies at different pH were carried out according to the procedure described by Horsfall *et al* [23]. The effect of pH of the solutions of each metal ion (Cu (II), Ni (II) and Zn (II)) was determined for each adsorbent for one hour at 28°C. 100 cm^3 of 50 mg/L standard solution of each metal ion was used. 0.2 g of each adsorbent (106 µm and 250 µm) was added. The pH of each solution was adjusted to 2, 4, 6, 8 and 10 respectively using 0.1M HCl or 0.1M NaOH. Each solution was placed in a rotary shaker and agitated for one hour after which the content of each flask was filtered using Whatman No.41 filter paper.

At the end of each experiment, the residual concentration of metal ions in the filtrate was determined using Atomic Absorption Spectrophotometer (AAS) model GBC SCIENTIFIC AVANTA PM AAS A.C.N 005472686 manufactured by GBC Scientific equipment Ltd, Australia. The concentration of each metal adsorbed at the different parameters for each type of adsorbent used was calculated by difference. The difference in the metal ion concentration of the solutions before and after sorption gave the amount adsorbed by each adsorbent. The removal efficiency of the metal ions were calculated by the equation

$$\% \text{ Removal} = (q_e/C_o) \times 100 \qquad (1)$$

Where q_e is the sorption capacity given by;

$$q_e = ((C_o - C_e)/m)\, V \qquad (2)$$

C_o and C_e are initial and final metal ion concentration (mg/L) respectively; V is the volume of the solution used (L) and m is the mass of the adsorbent used (g).

RESULTS AND DISCUSSION

Effect of Initial Concentration

The results for the effect of initial concentration on sorption of Ni (II), Cu (II) and Zn (II) ions onto SH are shown in **Fig. 1.** It could be observed that among the metal ions, Cu (II) was adsorbed more than Ni (II) and then followed by Zn (II) ion. Also, the amount adsorbed increased as the initial metal ion concentration was increased except for Zn (II) ion which decreased. The increase in amount adsorbed as initial metal ion concentration was increased has been reported [24-26]. Initial concentration has been reported to affect sorption of metal ions [27].

Effect of Contact Time

The effect of contact time is shown in **Fig. 2**. From Fig. 2, the rate of adsorption of each metal by the 250µm adsorbent increases as time increased from 0 to 10 min and then to 20 min where it had the highest sorption. This was followed by a relatively slower rate up to a maximum time of 90 min for Cu (II), Ni (II) and Zn (II). It was also observed that increase in amount of each metal ion varied with the adsorbent and the metal ion. For 106µm particle size, the adsorption increases from 0 to 10 min to a peak at 20 min and then decreased up to 90 min for the metal ions. This could be attributed to surface saturation. The time of the peak sorption might be the point where all the sorption sites were completely filled with metal ions. It decreased afterwards because of unavailable site as the metals there had to compete for the available vacant sites. The amount of each metal adsorbed by the adsorbents varied, with copper (II) being the highest adsorbed while zinc is the least adsorbed. The trend is $Cu^{2+}>Ni^{2+}>Zn^{2+}$. The effect of contact time on sorption of metal ions has also been reported [24-27].

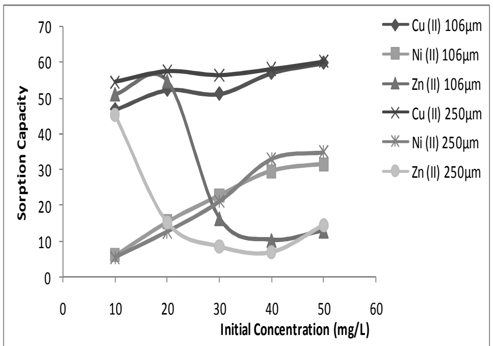

Fig. 1: Sorption capacity against initial concentration for adsorption of Ni(II), Cu(II) and Zn(II) ions onto sorghum hulls

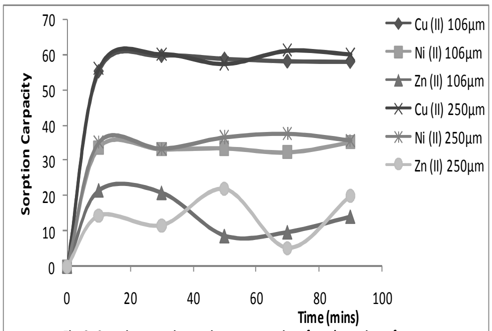

Fig. 2: Sorption capacity against contact time for adsorption of Ni(II), Cu(II) and Zn(II) ions onto sorghum hulls

pH Study of Cu (II), Ni (II) and Zn (II)

The pH of the adsorbate solution is one of the factors that influence adsorption. It affects the surface charge of the adsorbent, level of dissociation of functional groups on the adsorbent surface, degree of ionization and speciation of the adsorbate, solubility of metal ions and concentration of the counter ions in solution [28, 29]. Since sorption of metals at various pH values is affected by chemical characteristics of the metal, the degree of sorption may be influenced by the ionic radius of the metals. Ionic radius affects the sorption capacity of each metal as it affects the ease of hydration and transport mechanism of the metal on the adsorbent. Ni^{2+} with the least ionic radius was more highly adsorbed than the other two metals. Fig. 3 shows the graph of percentage of metal ions adsorbed against initial pH. From the results obtained, nickel has the highest amount adsorbed at pH of 10; this was followed by copper and then zinc. This result shows that adsorption was high mostly at pH of 10 for Ni (II) and Cu (II) and at pH of 8 for Zn (II) ion. It can be deduced that the degree of adsorption of the metal ions is in the order of $Ni^{2+}>Cu^{2+}>Zn^{2+}$. The low metal ion sorption at pH of 2-4 could be as a result of hydrogen ions competing with the metal ions for sorption sites [30, 31]. This is because the influence of protons in solution leads to charge reversal on the adsorbent surface which favours the columbic attraction of the metal ions thereby leading to a reduction in the binding ability of the adsorbent. When the pH is increased, the hydrogen ions are gradually dissociated and the positively charged metal ions are associated with free binding sites [32].

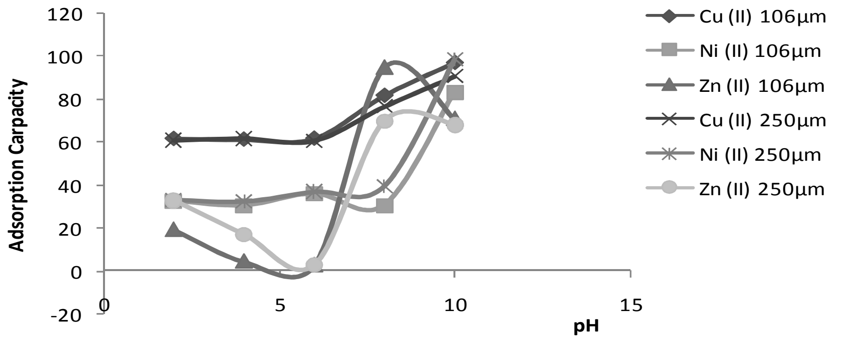

Fig. 3: Sorption capacity against pH for adsorption of Ni(II), Cu(II) and Zn(II) ions onto sorghum hulls

Adsorption Equilibrium and Sorption Isotherms

The Langmuir, Freundlich and Temkin isotherm models were used in the adsorption equilibrium study. The isotherms batch study was carried out by varying the initial adsorbate concentration in the range of 10 mg/L to 50 mg/L. The batches were run with adsorbent consistent at 0.2g and contact time of 60 min. The linear forms of the Langmuir, Freundlich and Temkin isotherms are given as [32]:

Langmuir: $1/q_e = 1/q_{max}K_L)(1/C_e) + 1/q_{max}$ (3)

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

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

Where q_{max} is the maximum sorption capacity on complete monolayer coverage; KL is the Langmuir constant; KF and n are Freundlich constant and exponent respectively; b_T indicates the adsorption potential of the adsorbent; K_T

is the Temkin isotherm constant (dm^3/g); q_e is the sorption capacity at equilibrium (mg/g); C_e is the equilibrium concentration of adsorbate (mg/L).

The plot of the Langmuir isotherm of $1/q_e$ against $1/C_e$ is shown in **Fig. 4**. Fig 4a for 106 µm particle size and Fig 4b for 250 µm particle size. From the slope and intercepts, the values of maximum sorption capacity (q_{max}) and Langmuir isotherm constant (K_L) were obtained.

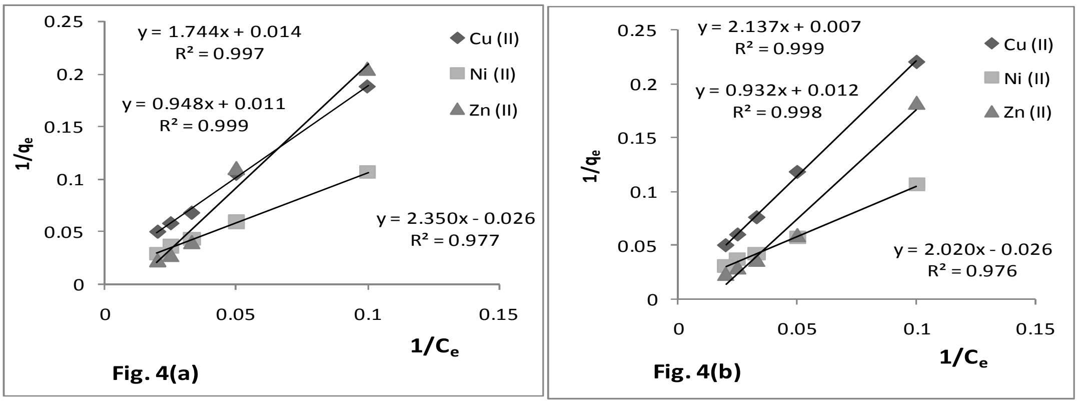

Fig. 4(a) **Fig. 4(b)**

Fig 4: Langmuir isotherm plot; 4a for 106 µm particle size and 4b for 250 µm particle size

The plot of the Freundlich isotherm of ln q_e against ln C_e is shown in **Fig. 5**, (a) for 106 µm particle size and (b) for 250 µm particle size. The Freundlich isotherm constant (K_F) and exponent (n) were obtained from the intercept and slope of the plots respectively.

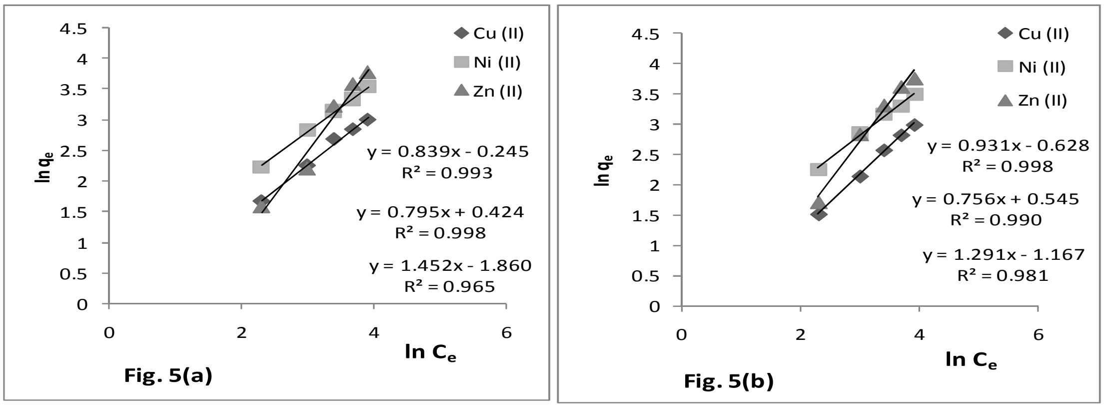

Fig. 5(a) **Fig. 5(b)**

Fig 5: Freundlich isotherm plot; 5a for 106 µm particle size and 5b for 250 µm particle size

The Temkin isotherm was evaluated by plotting q_e against ln C_e and this is shown in **Fig. 6**, (a) for 106 µm particle size and (b) for 250 µm particle size.

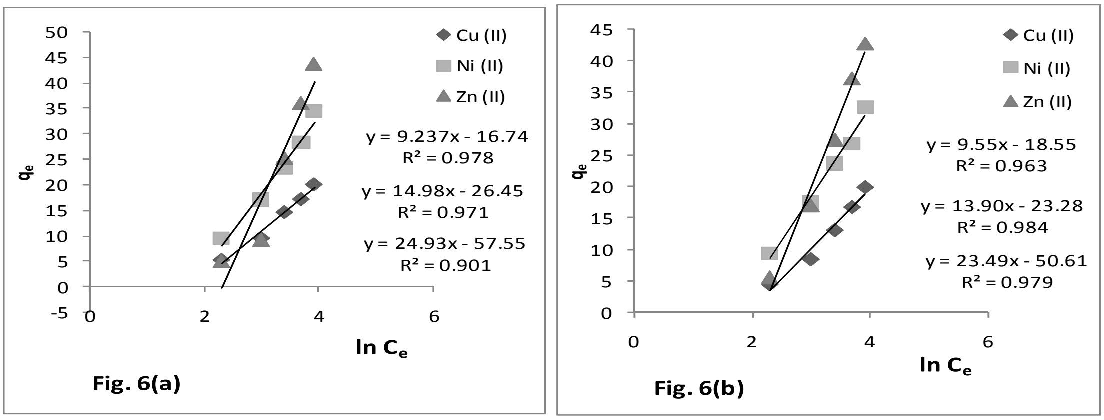

Fig. 6(a) **Fig. 6(b)**

Fig 6: Temkin isotherm plot; 6a for 106 µm particle size and 6b for 250 µm particle size

The constants A and B were obtained from the intercepts and slopes of linear plots respectively. All the isotherm constants and the coefficient of determination (R^2) are shown in **Table 1**.

Table 1: Sorption isotherm constants for adsorption of Ni (II), Cu (II) and Zn (II) ions onto Sorghum hulls adsorbent of 106 µm and 250 µm particle sizes

Metal ions	Langmuir				Freundlich			Temkin		
	q_{max} (mg/L)	K_L (dm^3/mg)	S_F	R^2	K_F (mg/L)	n	R^2	K_T	b_T (kJ/mol)	R^2
					106µm					
Ni^{2+}	50.487	0.012	0.667	0.999	0.234	0.803	0.998	0.171	0.173	0.971
Cu^{2+}	71.429	0.020	0.500	0.957	0.053	0.644	0.993	0.163	0.271	0.978
Zn^{2+}	5.376	0.018	0.535	0.965	0.054	0.584	0.965	0.122	0.148	0.901
					250µm					
Ni^{2+}	68.712	0.015	0.572	0.998	0.055	0.584	0.990	0.187	0.180	0.984
Cu^{2+}	131.085	0.013	0.602	0.999	0.109	0.760	0.998	0.143	0.287	0.963
Zn^{2+}	8.569	0.020	0.502	0.981	0.006	0.426	0.981	0.116	0.116	0.840

From Table 1, the Langmuir adsorption coefficient K_L which is related to apparent energy of adsorption for all the metals is high. This indicates steep beginning of the isotherm reflecting high affinity of the adsorbent. The highest value of maximum sorption capacity q_{max} corresponding to monolayer coverage for the metal ions adsorption was obtained for copper as 131.08 mg/L and 71.42 mg/L for 250µm and 106µm sizes respectively. The order of q_{max} for both pore sizes is Cu>Ni>Zn. The result shows that copper is best described by the Langmuir model.

The suitability of the Langmuir model is tested by the separation factor (S_F) which is an essential characteristic of the Langmuir isotherm. The separation factor is given by [33]:

$$S_F = 1/(1 + K_L C_o) \qquad (6)$$

Where K_L and C_o are the Langmuir constant and initial concentration of metal ions respectively. The separation factor is shown in **Fig. 7**. The isotherm is favourable when $0< S_F< 1$ and unfavorable when $S_F > 1$ [33]. From Fig. 1, it could be seen that all the values are between 0 and 1, that is $0< S_F < 1$ and this means that all the separation factor for the adsorbent is less than unity, showing that the sorption of the metal ions on the adsorbent is favourable under the conditions of this study.

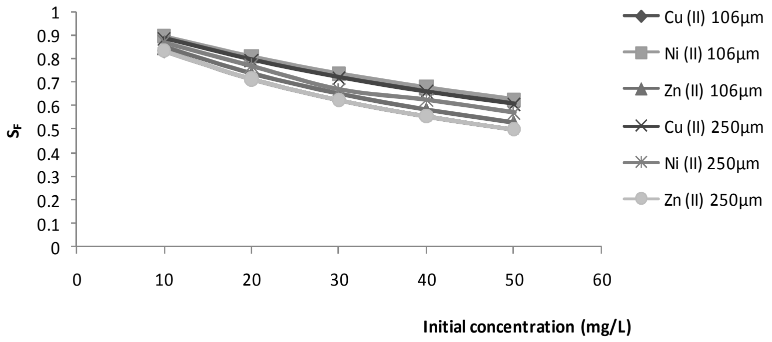

Fig. 7: Separation factor for adsorption of Ni(II), Cu(II) and Zn(II) ions onto sorghum hulls

The R^2 values show that Freundlich isotherm is a good model for the metal sorption. The rate of adsorption increases in the order Ni > Cu > Zn for both pore sizes. This trend may be attributed to the small ionic radius of Nickel leading to its high adsorptivity. It is also observed that the n value which is a heterogeneity factor of the metal ion adsorption are all less than unity, thus indicating a stronger bond between the metal ions and the adsorbents. Research has shown that the more the n values approximate to unity, the closer the sorption process is represented by Freundlich isotherm [23, 34].

It is also observed that the Temkin isotherm model generally fits the adsorption process on the adsorbents of 106µm and 250µm particle sizes for Ni^{2+}, Cu^{2+} and Zn^{2+} because their R^2 values are relatively high. The constant b_T describes the energy required for a transition from the physisorbed surface to a possible primary chemisorbed surface [32]. It apparently depicts transition from physisorption to chemisorption. The K_T is the rate constant required to transit through the two phases. The subsurface adsorption energy (b_T) for 106 µm size were (0.1732 kJmol^{-1} for Ni^{2+}, 0.2709 kJmol^{-1} for Cu^{2+} and 0.1483 kJmol^{-1} for Zn^{2+}) and for 250µm size were (0.1800 kJmol^{-1} for Ni^{2+}, 0.2867 kJmol^{-1} for Cu^{2+}, 0.1163 kJmol^{-1} for Zn^{2+}). Zn^{2+} has the least energy indicating that it is the metal ion that is easily adsorbed by the adsorbent. The trend in the rate of metal removal is $Zn^{2+} > Ni^{2+} > Cu^{2+}$ for both pore sizes.

From the average R^2 values of the isotherms for the two particle sizes, which gave; for Langmuir 0.9737 and 0.9927; for Freundlich 0.9853 and 0.9897 and for Temkin, 0.9500 and 0.9290; for 106 µm and 250 µm sizes respectively. It can be generalized that the Langmuir isotherm best describes the sorption on 250 µm size while the Freundlich isotherm best describes the sorption on 106 µm particle size.

Comparative Study

The maximum sorption capacity for monolayer coverage (q_{max}) from this study was compared with that reported in literature for Cu (II), Ni (II) and Zn (II) ions on other adsorbents. **Table 2** shows the comparison of adsorption capacities of Nickel (II), Copper (II) and Zinc (II) ions using different biosorbents with that obtained from the results of this study. From Table 2, it could be seen that the biosorption capacities of sorghum hulls compares favourably with other adsorbents mentioned. In some cases, the q_{max} for sorghum hulls is higher and in other cases it was lower. Therefore, it could be noteworthy that sorghum hulls have high potential for removal of Cu (II), Ni (II) and Zn (II) ions from aqueous solution. Also, the table clearly shows that sorghum hull has the potential to be an effective biosorbent as the efficiency is relatively high and comparable to other biosorbents.

Table 2: Comparism of biosorption capacities of sorghum hulls and some adsorbents reported in literature

Metal ion	Adsorbent	q_{max}	Reference	Metal ion	Adsorbent	q_{max}	Reference
Cu(II)	Tea waste	48.0	[35]	**Ni(II)**	Chitosan coated PVC	120.5	[43]
	Orange peel	50.0	[36]		Beal tree leave powder	1.527	[44]
	Potato peels	0.38	[37]		Activated carbon from almond husk	37.175	[45]
	Newspaper pulp	10.94	[38]		Palm shell activated carbon	0.130	[46]
	Spent tea leaves	90.00	[39]		Sorghum hulls (106um)	12.62	This study
	Pomegranate peel	13.87	[40]		Sorghum hulls (250 um)	17.178	This study
	Dried sunflower leaves	89.37	[41]	**Zn(II)**	Maize wrapper	111.111	[47]
	Cassava tuber bark waste	33.3	[42]		Lady fern leaf waste	0.051	[24]
	Sorghum hulls (106 um)	17.86	This study		Cassava tuber bark waste	22.2	[42]
	Sorghum hulls (250 um)	32.77	This study		Natural bentonite	57.14	[48]
Zn(II)	Kaolin	37.03	[48]	**Zn(II)**	Sorghum hulls (250 um)	2.142	This study
	Sorghum hulls (106um)	1.344	This study				

Sorption Kinetics

Sorption kinetics is another important factor in adsorption systems design and monitoring. It shows the rate of sorption reactions and is used to determine the effective hydraulic retention time in reactors. This enhances effective design of reactor columns. The sorption kinetic experimental data was modeled by pseudo-first and pseudo-second order kinetic equations. These equations are respectively given as [13]:

Pseudo-first order: $\ln (q_e - q_t) = \ln q_e - K_1 t$ (7)

Pseudo-second order: $t/q_e = 1/h_o + t/q_e$ (8)

where q_e is the equilibrium biosorption capacity, q_t is sorption capacity at any time t; K_1 is the rate constant for pseudo-first order rate constant and initial sorption rate $h_o = K_2 q_e^2$ where K_2 is the pseudo-second order rate constant.

The plot of the pseudo-first order is not shown as the data could not be generated because pseudo-first order did not give any measure of fit to the kinetic data. The plot of the pseudo-second order is shown in **Fig 8**. It could be seen that good straight lines were obtained with R^2 values of 0.897-0.999. Cu (II) gave the best fit followed by Ni (II) and then Zn (II). The constants for pseudo-second order plot is shown in **Table 3**.

From Table 3, it could be seen that for 106 µm particle size, q_e, K^2 and h_o varies as: Cu(II) > Ni(II) > Zn(II); Ni(II) > Zn(II) > Cu(II); Ni(II) > Zn(II) > Cu(II) respectively and for 250 µm as: Cu(II) > Ni(II) > Zn(II); Ni(II) > Cu(II) > Zn(II); Ni(II) > Cu(II) > Zn(II) respectively. The higher values of R^2 and the closeness of the calculated q_e values to the actual values indicate that the pseudo-second order model gave a very good fit to the kinetic experimental data. Similar results have been reported [25, 49, 50]. Chemisorptive bonds have been reported as the rate limiting step in pseudo-second order model [51], which has been reported as a more superior model for binding of divalent cations [52].

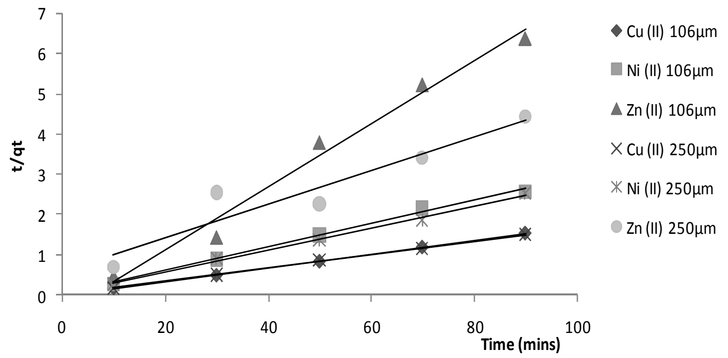

Fig. 8: Pseudo second order plot for adsorption of Ni(II), Cu(II) and Zn(II) ions onto sorghum hulls

Table 2: Pseudo-second order constants for sorption of Ni(II), Cu(II) and Zn(II) ions onto Sorghum hulls adsorbent of 106 µm and 250 µm particle sizes

Metal ions	**Constants (units)** **q_e (mg/g)**	**K_2(g.mg^{-1}.min^{-1})**	**h_o (mg g^{-1} min^{-1})**	**R^2**
		106 µm		
Ni(II)	35.71	0.0212	27.03	0.994
Cu(II)	58.82	-0.145	-500.00	0.999
Zn(II)	12.82	-0.014	-2.24	0.982
		250 µm		
Ni(II)	37.04	0.026	35.71	0.996
Cu(II)	62.50	0.015	58.82	0.998
Zn(II)	24.39	0.003	1.72	0.897

CONCLUSION

This study shows that sorghum hull, an agro industrial waste can serve as a low cost biosorbent for the removal of Ni (II), Cu (II) and Zn (II) ions from aqueous solution. The maximum sorption capacity q_{max} was highest for Cu(II) and lowest for Zn(II) ion. The two particle sizes showed good sorption efficiency for the metal ions. Three isotherms namely the Langmuir, Freundlich and Temkin were favourably applied to model the sorption equilibrium data. Pseudo-second order gave very good fit to the sorption kinetic data. Thus in this research, sorghum hulls as an adsorbent have been proven to be a good sorbent for metal ions removal. Further study can be carried out to improve the efficiency and performance of Sorghum hull in the areas of activation and modification of the powder using different organic solvents.

REFERENCES

[1] M.G. Mulgund, S.P. Dabeer, S. Dhar, V.Makani, B. Jadhav, *Aust. J. Basic & Appl. Sci.*, **2011**, 5(4), 135-142.
[2] C.M. Zvinowanda, J.O. Okonkwo, P.N. Shabalala, N.M. Agyei, *Int. J. Environ. Sci. Tech.*, **2009**, 6(3), 425-434.
[3] K. Ahmed, I.A. Bhatti, M. Muneer, M. Iqbal, Z. Iqbal, *Int. J. Chem. & Biochem. Sci*. **2012**, 28, 48-53.
[4] M.S. Dauda, R. Odoh, *Der Chemica Sinica*, **2012**, 3(5), 1329-1336.
[5] D.L. Jacob, M.L. Otte, *Water, Air and Soil Pollution*, **2003**, B, 91-104.
[6] A. Pandey, A. Shukla, L. Ray, *Am. J. Biochem. & Biotech*., **2009**, 5(1), 14-20.
[7] C.M.A. Ademorati, *Environmental Chemistry and Toxicology. Pollution by heavy metals*, 171-172pp
[8] M.A. Hanif, H.N. Bhatti, *Int. J. Chem. & Biochem. Sci*., **2012**, 2, 54-59.
[9] N.A.A. Babarinde, J.O. Babalola, S.O. Sanni, *Int. J. Phys. Sci*. **2007**, 2(8), 207-211.
[10] S.H. Hasan, K.K. Singh, O. Prakash, M. Talat, Y.S. Ho, *J. Hazard. Mater*., **2008**, 152, 356 – 365.
[11] J.C. Igwe, A.A. Abia, *Afr. J. Biotechnol*, **2006**, 5(12), 1167-1179.
[12] S. Idris, Y.A. Iyaka, B.E.N. Duada, M.M. Ndamitso, M.T. Umar, *Am. Chem. Soc. J*. **2012**, 2(1), 13-24.
[13] R. Gayathri, M. Thirumarimurugan, T. Kannadasan, *Der Chemica Sinica*, **2013**, 4(3), 79-87.
[14] J. Sirajudeen, J. Naveen, S. Arul Manikandan, M.M. Mohamed Mubashir, *Der Chemica Sinica*, **2013**, 4(2), 133-143.
[15] J.C. Igwe, A.A. Abia, F.H. Okereke, *Terrestrial and Aquatic Environmental Toxicology*, **2011**, 5(1), 19-24.
[16] A. Babarinde, J.O. Babalola, J. Ashidi, J. Adegoke, A. Osundeko, K. Ogundipe, A. Omojola, A. Obisanya, *Int. J. Chem. & Biochem. Sci*, **2013**, 3, 101-109.
[17] A. Majeed, M.I. Jilani, R. Nadeem, M.A. Hanif, T.M. Ansari, *Int. J. Chem. & Biochem. Sci*., **2012**, 2, 78-82.
[18] S.O. Eze. J.C. Igwe, D. Dipo, *Int. J. Biol. Chem. Sci*., **2013**, 7(2), 852-860

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[19] T. R. Choudhury, K.M. Pathan, Md. N. Amin, N. Ali, S.B. Duraishi, A.I. Mustafa, *J. Environ. Sci. Water Resourc*., **2012**, 1(6), 144-150.
[20] E. Mutegi, F. Sagnard, M. Muraya, B. Kanyenji, B. Rono, C. Mwongera, C. Marangu, J. Kamau, H. Parzies, S. de Villiers, K. Semagna, P. Traore, M. Labuschagne. *Genetic Resources and Crop Evolution*, **2010**, 57(2), 243-253.
[21] Y.S. Ho, C.T. Huang, H.W. Huang. *Process Biochem*., **2002**, 37(5), 1421-1430.
[22] E. Demirbas, M. Kobya, E. Senturk, T. Ozkon. *Water SA*, **2004**, 30(4), 533-539.
[23] M. Horsfall Jnr, A.A. Abia, A.I. Spiff, *Bull Korean Chem. Soc*., **2004**, 25(7), 969 - 976
[24] A.K. Asiagwu, I.H. Owamah, J.O. Otutu, *Chem. & Process Eng. Res*., **2012**, 3, 1-13.
[25] C. Sirilamduan, C. Umpuch, P. Parthasarathy, *Songklanakarin J. Sci. Technol*, **2011**, 33 (6), 725-732.
[26] B.R. Venkatraman, U. Gayathri, S. Parthasarathy, S. Arivoli, *Der Chemica Sinica*, **2012**, 3(4), 914-928.
[27] T. Nalini, P. Nagarajan, *Der Chemica Sinica*, **2013**, 4(2), 152-158.
[28] M. Teker, M.Imamogul, O. Saltabas, *Turk J. Chem*., **1999**, 23, 185-191.
[29] M. Mamatha, H.B. Aravinda, E.T. Puttaiah, S. Manjappa, *Int. J. Innovative Res. in Sci. Eng. & Technol*., **2013**, 2(4), 1091-1098.
[30] K.S. Low, C.K. Lee and K.P. Lee, *Bioresource Technol*., **1993**, 44(2), 109-112.
[31] J.M. Dhahab, *J. Sci. Environ. Impact*, **2012**, 1(1), 007 – 013.
[32] T.Y. Kim, S.K. Park, S.Y. Cho, H.B. Kim, Y. Kang, S.D. Kim, S.J. Kim, *Korean J. Chem. Eng*., **2005**, 22(1) 91-98.
[33] M. Ozacar, I.A. Sengil, H. Turkmenler, *Chem. Eng. J*., **2008,** 143 (1-3), 32-42.
[34] M. Kashefi, P. Salaryan, N. Hazeri, J. Valizadeh, A. Abdi, M.S. Mohammadnia, *Int. J. Chem. & Biochem. Sci*., **2012**, 1, 48 – 53.
[35] A.A. Abia, M. Horsfall Jnr., O. Didi, *J. Appl. Sci. & Environ. Manag*, **2002**, 6(2), 89-96.
[36] B.M.W.P.K. Amarasingbe, R.A. Williams, *Chem. Eng. J*., **2007**, 132, 299-309.
[37] F. Ningchuan, G. Xueyi, L. Sha, T. Qinghua, *Global Symposium on Recycling Waste Treatment and Clean Technology* REWAS, **2008**, 1389pp.
[38] T. Aman, A.A. Kazi, M.U. Sarri, Q. Bano, *Colloids, Surface & Interface*, **2008**, 63(1), 116-121.
[39] S. Chakravarty, S. Pimple, H.T. Chaturvedi, S. Singh, K.K. Gupta, *J. Hazard. Mater*., **2008**, 159 (2-3), 396-403.
[40] S.K. Bajpai, A. Jain, *Water SA*, **2010**, 36(3), 221-228.
[41] E.S.Z. El-Ashtoukhy, N.K. Amin, O. Abdelwahab, *Desalination*, **2008**, 223, 162-173.
[42] H. Benaissa, M.A. Elouchdi, *Chem. Eng. Process*, **2007**, 46(7), 614-622.
[43] M. Horsfall Jnr., A.A. Abia, A.I. Spiff. *Bioresource Technology*, **2006**. 283-291
[44] S.R. Popuri, Y. Vijaya, V.M. Boddu, K. Abburi, *Bioresour. Technol*., **2009**, 100, 194-199.
[45] P. Senthil Kumar, K. Kirthika. *J. Eng. Sci. Tech*, **2009**, 4(4) 351-363.
[46] H. Hasar, *J. Hazard. Mater*., **2003**, B 97, 49-57.
[47] Y.B. Onundi, A.A. Mamun, A.L. Khatib, Y.M. Ahmed, *Int. J. Environ. Sci. Tech*., **2010**, 7(4) 751-758.
[48] N.A.A. Babarinde, J.O. Babalola, O.B. Adebisi, *Int. J. Phys. Sci*., **2008**, 3(2), 050-056.
[49] K. Chee, K.S. Tushar, *Chemeca Conference, Hilton Sydney, Australia*, **2011**, 18th – 21st.
[50] X. Fan, B. Tu, H. Ma, X. Wang, *Bulletin of Korean Chemical Society*, **2011**, 32(8), 2560-2564.
[51] S. Schiewer, B. Santos, *Bioresource Technol*., **2007**, 40, 1896-1903.
[52] Y.S. Ho, *J. Hazard. Mater*, **2006**, B136, 681-689.
[53] I.C. Olivares, C. Perez-Alonso, C. Barrera-Diaz, R. Natividad, M.C. Chaparro-Mercado, *Chem. Eng. J.*, **2011**, 166, 814-821.