Assessment of Chemical Modification, pH and Pore Size of Sorghum (*Sorghum bicolor*) hull In sorption of Ni²⁺ and Cu²⁺

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Abstract:

Aim of this study was to investigate the use of modified and unmodified Sorghum hull in the removal of Ni²⁺ and Cu²⁺ from aqueous solution. The effect of pH, particle size and chemical modification were investigated and reported. pH significantly affected the adsorption with maximum adsorption at pH of 10. Adsorption increased as chemical modification by thiolation increased. The smaller particle size of 106μm mesh showed greater adsorption than particle size of 250μm mesh. These results will serve as parameters to consider in the design of treatment plants for heavy metal detoxification using biosorbents.

KEYWORDS: Biosorbents, detoxification, heavy metals, pH, pore size, thiolation, biosorption.

INTRODUCTION

Recent environmental concerns as well as heightened defence against chemical terrorism call for both new protection technologies and for the improvement of existing ones including adsorption. Adsorption, an established industrial separation technique used in bulk separation technique used both in bulk/batch separation and purification suited for the solution of such problems. Current challenges call for more new efficient and selective adsorbents .To accomplish these needs, new direction point to the development of adsorbents of a combined and hybrid nature such as organic and inorganic material made, carbon and combined adsorbents, regulation of lingo-cellulosic materials sorption properties by modification for environmental application.

Biosorption consists of a group of applications which involve the detoxification of hazardous substances instead of transferring them from one medium to another by means of microbes and plants. This process is characterised as less disruptive and can be often carried out on site eliminating the costly need to transport the toxic materials to treatment sites (Igwe and Abia, 2006), biosorbents are prepared from naturally abundant and/or waste biomass. Due to high uptake capacity and very cost-effective source of the raw material, biosorption is a progression towards a perspective method. Various biomaterials have been examined for their biosorptive properties and different types of biomass have shown levels of high enough to warrant further research.

Biosorbent of plant origin are mainly agricultural by-products such as Sugar beet pulp (Zolgharnein*et al.,* 2011), Maize wrapper (Babarinde*et al*., 2008), Maize cob (Opeolu*et al*., 2009), modified Saw dust of Spruce (Urik*et al.,* 2009).

Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater.

Copper is an essential substance to human life, but in high doses can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. People with Wilson's disease are at greater risk for health effects from overexposure to copper. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth.

The most common reaction of nickel toxicity is a skin rash 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. Acute toxic effects occur in two stages, immediate and delayed. Headache, dizziness, shortness of breath, vomiting, and nausea are the initial symptoms of overexposure; the delayed effects (10 to 36 h) consist of chest pain, coughing, shortness of breath, bluish discoloration of the skin, and in severe cases, delirium, convulsions, and death. Several factors determine the adsorption of metals by adsorbents.

These include agitation rate in aqueous phase, sorbent structural properties(size, porosity, surface area and chemical groups), metal ion properties(ionic radius, hydration energy, hydrolysis constant, ionic charge, solubility, ionization energy, density, stability of complexes, initial concentration, pH, temperature and existence of the anions that may compete with the cations of interest for active adsorption sites. (Igwe and Abia, 2007).

In this study, a lingo-cellulosic material (Sorghum hull) was used as biosorbent in the removal of heavy metals Ni²⁺ and Cu²⁺ from aqueous solution in a batch sorption system. The effects of pH, Chemical modification and Particle size will be investigated.

2.0 MATERIALS AND METHODS

The Sorghum hulls (sorghum bicolour) were sourced from a brewery (Consolidated Breweries plc, Imo State). The material Sorghum hull was later abbreviated as 'SH'. All reagents used were analytical grades purchased and used without further purification.

2.1 METHODS

2.1.1 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 the mechanical sieve screen to obtain final sample sizes of 106μm and 250μm.

2.1.2 ACTIVATION OF SORGHUM HULLS

The screened fine 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 treatment of the biomass with 0.3M 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.

2.1.3 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 labelled A was left untreated and called unmodified sorghum hulls (USH).

500g of the second part labelled B was acid treated by dissolving it in excess of 0.5M Mercapto acetic acid($HSCH_2COOH$) solution, stirred for 30minutes and left to stand for 24 hours at 28°C and designated as 0.5M modified sorghum hulls (0.5MSH).

500g of the third part labelled C was also acid treated by dissolving it in excess 1.0M Mercapto acetic acid solution, stirred for 30 minutes and left to stand for 24 hours at 28°C and called 1.0M modified sorghum hulls (1.0MSH).

After 24 hours, the mixtures in the beakers designated as 0.5MSH and 1.0MSH 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 labelled USH, 0.5MSH, and 1.0MSH for the unmodified, 0.5M modified and 1.0M modified adsorbent respectively.

2.1.4 DETERMINATION OF THIOL CONTENT

The extent to which the Mercapto acetic acid has incorporated the thiol (-SH-) group into the 0.5MSH and 1.0MSH of the sorghum hull was determined by the method described by Okiemen et al (1988).0.5g each of the adsorbents was weighed into different 250ml Erlenmeyer flasks and 20ml of 0.1M iodine solution was added at a pH of 7.1. The flasks were agitated on an electric shaker for 10minutes and then allowed to settle. The unreacted iodine was back titrated with 0.1M sodium thiosulphate until the colour of the solution turned yellow. Then 3ml of starch solution was added and the solution turned blue. The titration with sodium thiosulphate was continued until the solution finally became colourless indicating end- point. The titre values were recorded and the percentage degree of thiolation was evaluated as follows

$$\% \; degree \; of \; thiolation = \frac{m_T \times V_T \times M_T \times 100}{m_A} \; [1]$$

Where m_T = molarity of thiosulphate (mole)

V_T = volume of thiosulphate (L)

M_T = molar mass of thiosulphate (gmol^{-1})

m_A = mass of adsorbent (g)

2.1.5 DETERMINATION OF pH POINT OF ZERO CHARGE, pH_{pzc}

The pH point of zero charge of each of the adsorbents (USH, 0.5MSH and 1.0MSH) was carried out as described by Onyango et al ;(2004). 50cm^3 of 0.01M NaCl was placed in different closed conical flasks. The pH of each flask was adjusted to values from 2.0, 4.0, 6.0, 8.0, and 10.0 by adding 0.1MHCl or 0.1M NaOH solution. 0.5g of each of the adsorbents was added and agitated in a shaker for one hour and allowed to stay for 48 hours to reach equilibrium at 28°C. A graph of zeta potential versus initial pH was used to determine the pH point of zero charge of each adsorbent.

2.1.6 DETERMINATION OF SPECIFIC SURFACE AREA, SSA

The specific surface area of the adsorbents was determined using the European spot method used by Kandhal and Parker (1998) and Santamarina et al ;(2002).

In this method, methylene blue solution was prepared by mixing 1.0g of dry powder with 200ml of deionized water. 10g of air-dried adsorbent was suspended in 30ml of deionised water. The methylene blue solution was added to the suspension of adsorbent in 0.5ml increments. For each addition of methylene blue, the adsorbent suspension was mixed for one minute and a small drop of the suspension removed and placed on a filter paper.

When the unabsorbed methylene blue forms a permanent light blue halo around the adsorbent aggregate, the end point is reached meaning that there is an indication that methylene blue has replaced cations on the adsorbent surface.

The specific surface area (SSA) was calculated from the optimum amount of methylene blue adsorbed.

$$Specific\ SurfaceArea(SSA) = \frac{1 \times 0.5N \times A_V \times A_{MB} \times 1}{319.89 \times M_S}[2]$$

Where N = the number of methylene blue increments added to the adsorbent suspension

A_v = Avogadro's number: 6.02×10^{23}

A_{MB} = Area covered by one methylene blue molecule [Typically assumed to be 130 $Å^2$(1 $Å$ = 0.1 nm)]

M_S = Mass of adsorbent

319.89 = molar mass of methylene blue

2.1.7 PREPARATION OF ADSORBATE SOLUTIONS FOR SORPTION STUDIES

A stock solution of 1000ppm of the metals Nickel and Copper were prepared. Thereafter, serial dilutions was carried out on the stock solution to obtain working solutions of 10, 20,30,40,50 ppm of each metal ion. The concentrations of these standards were confirmed using an atomic adsorption spectrophotometer .The pH of the solutions was kept at 6.0.

2.1.8 SORPTION STUDY AT VARIOUS ADSORBATE pH

Sorption studies at different pH were carried according to the procedure described by *Horsfall and Spiff (2004)*. The pH of solution used for sorption for the metal ions Ni^{2+} and Cu^{2+} was determined for each biomass (USH, 0.5MSH and1.0MSH) for one hour at 28°C.100cm³ of 50mg/l standard solution of each metal was transferred and labelled.0.2g of each adsorbent (USH, 0.5MSH and1.0MSH) was added. The pH of each solution was adjusted to 2, 4, and 6,8,10 respectively using 0.1M HCl or 0.1M NaOH. Each solution was placed in a shaker and agitated for one hour after which the content of each flask was filtered using Whatman No.41 filter paper. 20cm³ of the filtrate was analyzed using Atomic Adsorption Spectrophotometer (GBC SCIENTIFIC AVANTA PM AAS A.C.N 005472686 manufactured by GBC Scientific equipment Pty Ltd. Dandenong Victoria Australia.) for the residual metal ion concentration. The concentration of the metal adsorbed at the different pH for each type of adsorbent used was calculated by difference.

3.0 RESULTS AND DISCUSSION

3.1 SURFACE CHARACTERIZATION OF ADSORBENTS

Results obtained from the surface characterization of the three adsorbents of two different pore sizes used for the sorption study are given below in table1.

Table 1: Surface Characterization of Three Adsorbents (USH, 0.5MSH, 1.0MMSH) of Pore Sizes 106μm and 250 μm

	PORE SIZES		
	106μm		
Parameter	**USH**	**0.5MSH**	**1.0MSH**
Specific Surface Area (m2g⁻¹)	221.70	263.20	316.19
Thiol content(%SH)	-	1.58	2.48
pH$_{PZC}$	7.4	7.0	6.6
	250μm		
Parameter	**USH**	**0.5MSH**	**1.0MSH**
Specific Surface Area (m2g⁻¹)	218.97	256.12	309.87
Thiol content(%SH)	-	1.69	2.33
pH$_{PZC}$	7.2	6.8	6.4

3.2 EXTENT OF THIOLATION OF ADSORBENTS

This gives the concentration of thiol groups on the adsorbent surface. This parameter, expressed in percentage, indicates the efficiency of the thiolation process. That is, it shows the degree to which the modified adsorbents incorporated the thiol group into the adsorbent matrix after it had been treated with Mercapto acetic acid. From table 1, the percentage thiol content in 0.5MSH was 1.58% and 1.69% for 106μm and 250μm,

respectively, and that of 1.0MSH was 2.48% and 2.33% for 106μm and 250μm, respectively. This means that an increase in the concentration of the modifying acid from 0.5M to 1.0M increased the percentage of thiol incorporated from 1.58 to 2.48 and 1.69 to 2.33 for 106μm and 250μm, respectively. The values obtained here are comparable with those obtained for acid treatment with maize cob meal (*Okiemen et al; 1988*) and that of cassava waste (*Horsfall et al; 2003*). Here, the Mercapto acetic acid incorporated thiol groups to maize cob in the percentages
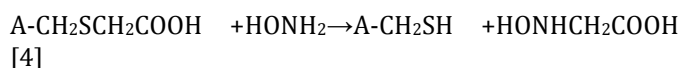
of 1.7 and 3.3 respectively; 3.7% of thiol was incorporated into cassava waste upon treatment with same acid.

It has been observed that incorporation of thiol groups into an adsorbent surface affects the sorption properties of the adsorbent positively. *Abia et al (2003)* reported that the incorporation of thiol groups on an adsorbent surface enhances the binding ability of the sorbent by increasing the number of binding sites., it also produces changes in the physical and chemical properties of the adsorbent; the process that results in the exchange of hydroxyl groups in the sorghum husk with sulphydryl groups from the acid.

The mechanism for the exchange as proposed by Horsfall et al ;(2004) is shown below:

$$A\text{-}CH_2OH + HSCH_2COOH \rightarrow A\text{-}CH_2SCH_2COOH + H_2O \quad [3]$$

The acetate group is then released upon treatment with hydroxylamine

$$A\text{-}CH_2SCH_2COOH + HONH_2 \rightarrow A\text{-}CH_2SH + HONHCH_2COOH \quad [4]$$

The equation for the adsorption of the metal ion through the sulphydryl group on the adsorbent is thus proposed as:

$$M^{n+} + A\text{-}CH_2SH \rightarrow (A\text{-}CH_2S)_n\text{-}M + H^+ \quad [5]$$
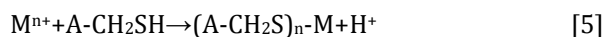
Where A= Adsorbent

M^{n+} = Metal ion

Hence, the chemical modification of the adsorbents incorporates sorghum hull that has fibrous cellulose material with competing adsorbent sites containing entities such as $-CH_2CH_2OH-$ and $-CH_2CH_2SH-$ and pores with areas of low potential energy.

3.3 SPECIFIC SURFACE AREA OF THE ADSORBENT

For a given mass of adsorbent, there is a considerable effect of particle size on specific surface area. The specific surface area of an adsorbent is the ratio of its surface area to its mass. A reduction in particle size corresponds to an increase in surface area. In this work, the results obtained show that the specific surface area calculated for 106μm (USH, 0.5MSH and 1.0MSH) and 250μm (USH, 0.5MSH and 1.0MSH) were (221.70, 263.20 and 316.19) m^2g^{-1} and (218.97, 256.12 and 309.87) m^2g^{-1}, respectively. This trend corresponds to increasing adsorbent modification with Mercapto acetic acid. It can be said that the specific surface area of the three adsorbents at the different pore sizes increased with chemical modification. Since specific surface area has an inverse relationship with particle size, then it can be concluded that chemical modification of the two adsorbents (0.5MSH and 1.0MSH) as the particle size is reduced, increased the number of binding sites,

increased adsorbent porosity and increased specific surface area. Also, increasing the concentration of Mercapto acetic acid used to modify the adsorbents had a significant effect by increasing the specific surface area. Researchers have shown that chemical modification of agricultural adsorbents increase the specific surface area of the adsorbents which help increase the number of binding sites; Rahman and Saad (2003) reported an increase in specific surface area of raw guava seed from $178 m^2g^{-1}$ to $314 m^2g^{-1}$ due to chemical activation with zinc chloride solution. Also, Dermibas *et al*; (2004) indicated that chemical modification of agricultural adsorbents using tetraoxosulphate (VI) acid produced high surface area adsorbent with high degree of micro porosity.

3.4 pH POINT OF ZERO CHARGE (pHpzc) OF ADSORBENTS

The pH point of zero charge (pHpzc) as defined by Nomanbhay and Palanisamy (2005) is the pH of a suspension at which the surface acidic (or basic) functional groups of an adsorbent no longer contribute to the pH value of the solution. The pHpzc of the adsorbents was determined using 0.01M NaCl as the background electrolyte. A plot of initial pH against zeta potential was employed to determine the pHpzc for each adsorbent. Zeta (ζ) potential is a parameter characterizing electric properties of interfacial layers in dispersions, emulsion, porous bodies. Its unit is in millivolts (mV). It depends mostly on the ionic strength of the liquid phase. It varies from nanometres in aqueous solutions to microns in non-polar liquids.

The plots are shown in figures 1a to 1c, the result is presented in table 1. From the graph, it is seen that each adsorbent was positively charged over the pH of 2 to 6; from a pH of 8, there was a charge reversal. The pHpzc was found to be (7.4, 7.0 and 6.6) and (7.2, 6.8 and 6.4), for 106μm (USH, 0.5MSH and 1.0MSH) and 250μm (USH, 0.5MSH and 1.0MSH), respectively.

It has been reported by earlier researchers that the pHpzc of an adsorbent decreases with increase in acidic groups on the surface of the adsorbent. From the result obtained, it is apparent that acid modification of the adsorbents gave positive surface charge for the adsorbents over a pH range of 2-6. At pH above the value of pHpzc value for each adsorbent, the surface has a positive charge. The surface acidity of 0.5MSH and 1.0MSH which leads to a reduction in pHpzc is due to the introduction of thiol (SH) functional groups on the adsorbent surface. The unmodified adsorbents had high pHpzc because they were not chemically modified with Mercapto acetic acid. There exists a relationship between pHpzc and adsorption capacity of an adsorbent that cations adsorption on any adsorbent will be favourable at pH value higher than the pHpzc while anions adsorption will be favoured at pH values lower than the pHpzc (Nomanbhay and Palanisamy,2005).
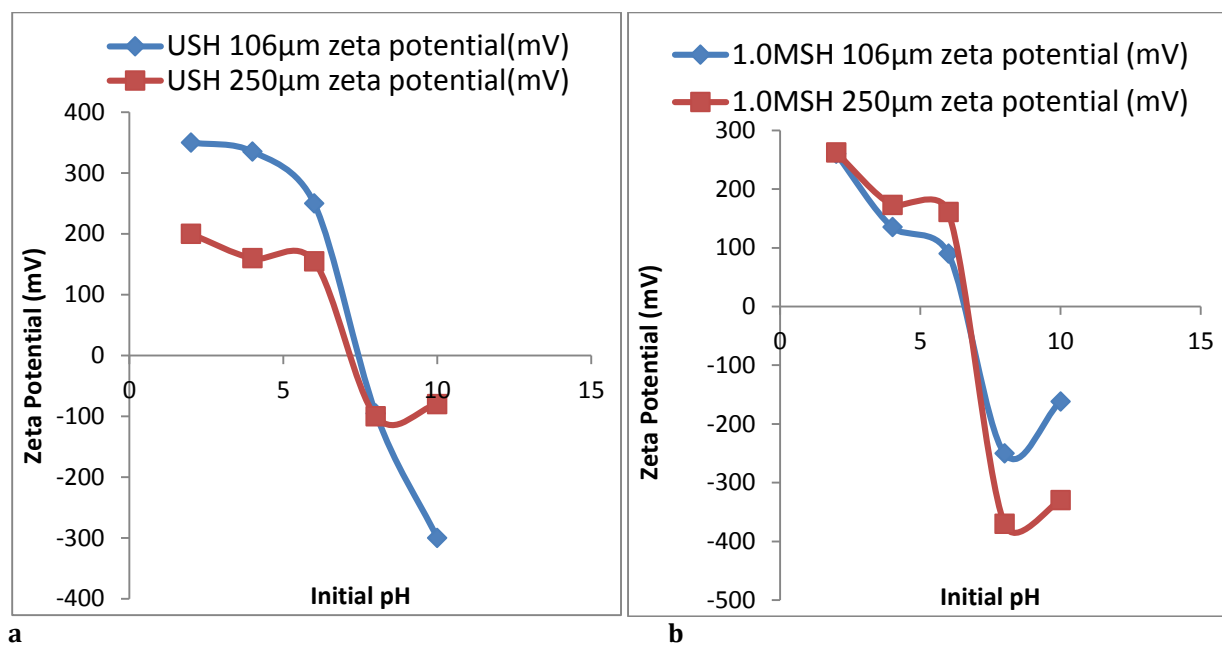
Fig. 1a, b Plot of Zeta Potential against Initial pH of USH and 1.0MSH (106μm and 250μm)
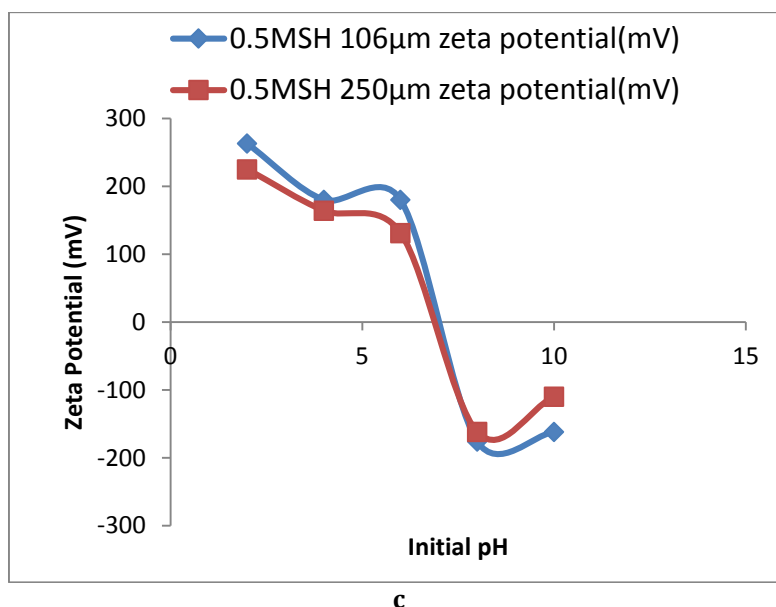

Fig.1c, A plot of Zeta Potential against Initial pH of 0.5MSH 106μm and 0.5MSH 250μm

3.5 EFFECT OF ADSORBATE pH ON THE PERCENTAGE OF METAL ION REMOVED

The pH of the adsorbate affects the percentage metal ion Ni^{2+} and Cu^{2+} uptake. The percentages of metal ion removed as a function of pH are shown in table 2. Figures 2(a-d) shows the percentages of each Ni^{2+} and Cu^{2+} removed as a function of initial pH of the metal ion solution and the percentage metal uptake by the adsorbents.

From the results obtained, the highest extent of removal was at pH of 10 for Ni^{2+} and Cu^{2+}. At 1.0MSH Ni^{2+} had 98.685% and 99.376% while Cu^{2+} had 94.646% and 97.016% removal for 106μm and 250μm, respectively. The trend of metal ion removal was **Ni^{2+}> Cu^{2+}**for the metal ions and **1.0MSH>0.5MSH>USH** for the adsorbents at the different pore sizes.

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 **(Ni^{2+} and Cu^{2+})** and concentration of the counter ions in solution. Since sorption of metals at various pH is affected by chemical characteristics of the metal, the degree of sorption may be influenced by the ionic radius of Ni^{2+} and Cu^{2+}. Ionic radius affects the sorption capacity of each Ni^{2+} and Cu^{2+} as the smaller the radius, the higher the ease of hydration and transport mechanism of the metal on the adsorbent. This can be observed from the high adsorptivity of $Ni^{2+}$and Cu^{2+} with ionic radius of 0.69A° and 0.77A° respectively, hence the high adsorptivity. Ni^{2+} is the most adsorbed because it has lower ionic radius and ionization radius than Cu^{2+}. It is possible that Ni^{2+} ions diffuse through the sorbent pores

faster than the bulkier metal ion. This will make it available to the other ligands on the adsorbent surface which are not accessible to the bulkier ions, thus making it to be more adsorbed on the surface.

It was observed that the final pH of the adsorbate decreased after sorption as indicated in table 2. This could be as a result of more hydrogen ions being released from the adsorbent surface into solution as the Ni^{2+} and Cu^{2+} are sorbed onto the adsorbent surface thus, decreasing the final pH of the adsorbate solution. The low metal ion sorption at pH of 2-6 could be as a result of hydrogen ions competing with the metal ions for sorption sites (Igwe et al, 2005). 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 (Igwe and Abia, 2007). The pH dependence of Ni^{2+} and Cu^{2+} sorption by Sorghum hull suggests that about pH10, a large proportion of the adsorbed Ni^{2+} and Cu^{2+} may be recovered. Thus, this can be used as a basis for the study of desorption and recovery of Ni^{2+} and Cu^{2+} from solution. Chemical modification also enhanced the degree of adsorption as the trend of adsorption is **1.0MSH>0.5MSH>USH**. Chemical modification led to increased surface area with the introduction of thiol group. This made 0.5MSH and 1.0MSH to have higher binding sites than the USH, hence their increased adsorption capacity.

3.6 PORE SIZE ANALYSIS

One of the most important adsorbent parameters is the pore size and pore size distribution. Adsorbent surface area is the factor directly affecting the analyte retention. Pore size is defined as the ability of the analyte molecules to penetrate inside the particle and interact with its inner surface. This is especially important because the ratio of the outer particle surface to its inner one is about 1:1000. The surface molecular interaction mainly occurs on the inner particle surface. Micro-pores are easily accessible to the analytes since there is little or no steric hindrance effect. Meso-pores are partially accessible but molecular diffusion into the pore spaces are restricted by steric hindrance effect which significantly slows mass transfer and decreases the adsorption efficiency.

From the results in the table 2 overleaf, the two pore sizes can be used to adsorb the Ni^{2+} and Cu^{2+} efficiently. Although, 106μm had higher values of percentage adsorption than 250μm, the values obtained from 250μm, still indicate that the pore size is effective to use and can equally serve as a good low cost adsorbent for the sorption of Ni^{2+} and Cu^{2+} from aqueous solution.

CONCLUSION:

The conclusions based on experimental study were:

(i)   Adsorbent preparation by chemical modification of biosorbent using Mercapto acetic acid showed high affinity for Ni^{2+} and Cu^{2+}.

(ii)   The maximum adsorption capacities of the modified biosorbent were high at pH 10.

(iii)   These results can be used as a basis for the study of desorption and recovery of **Ni^{2+} and Cu^{2+}** from solution

(iv)   Pore size analysis showed that 106μm mesh had higher adsorption than 250μm mesh, although both recorded high adsorption values.
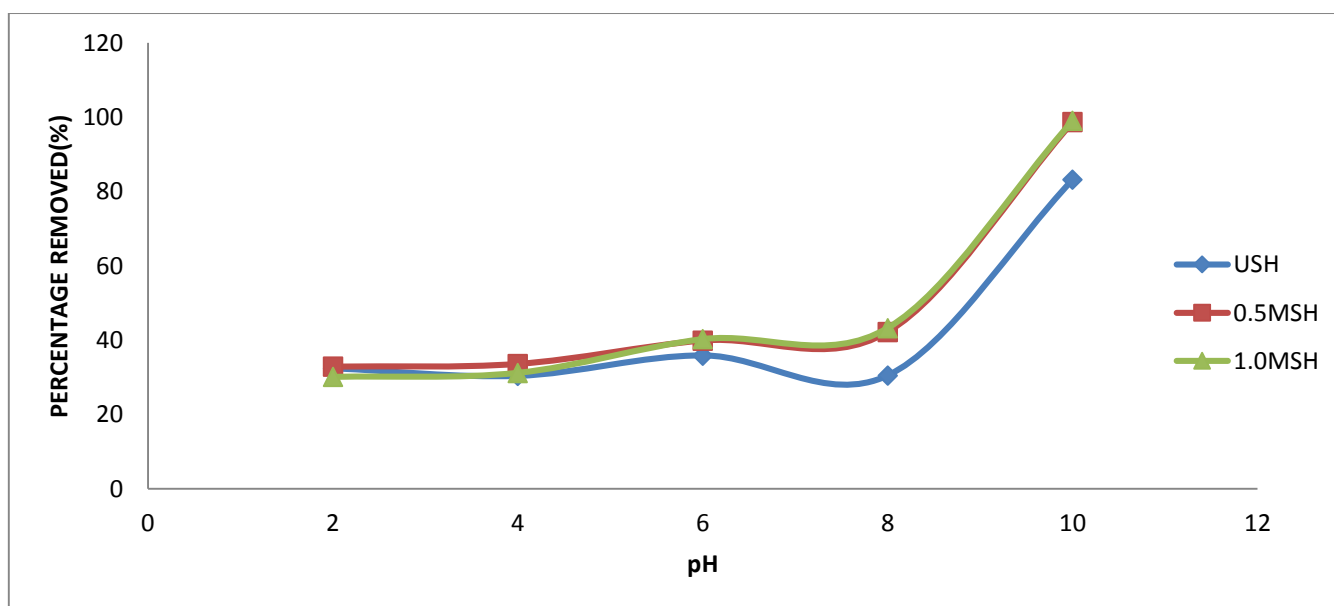
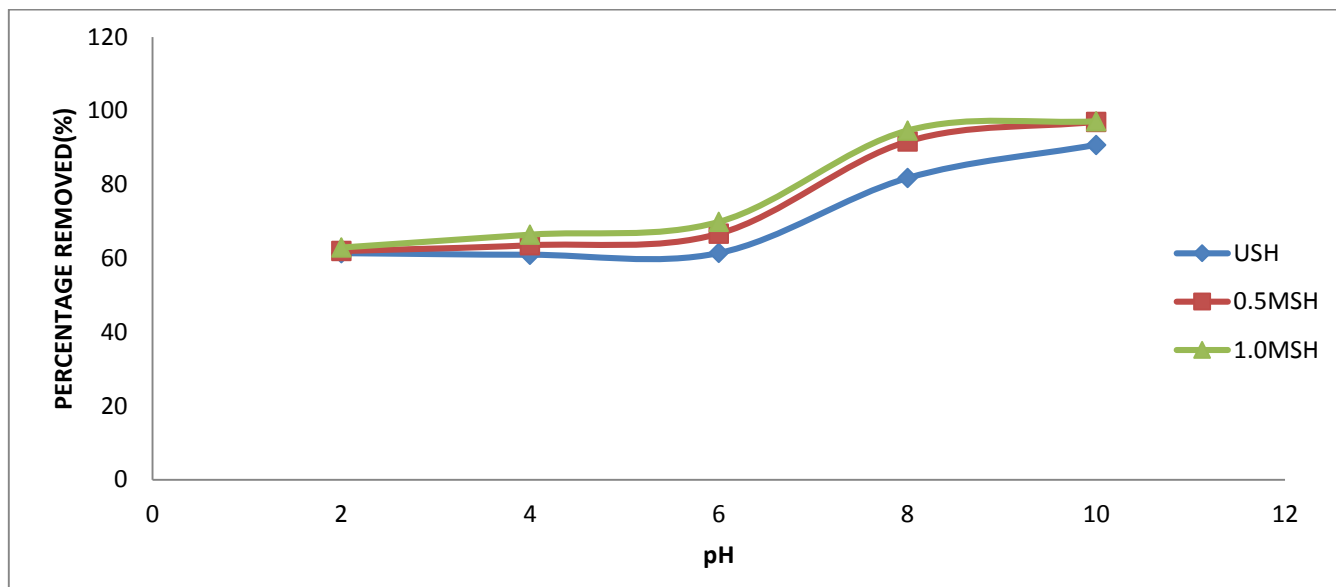**Fig 2a** Plot of percentage metal ion removal against pH for Ni^{2+} 106μm

Fig 2b Plot of percentage metal ion removal against pH for Cu^{2+} 106μm

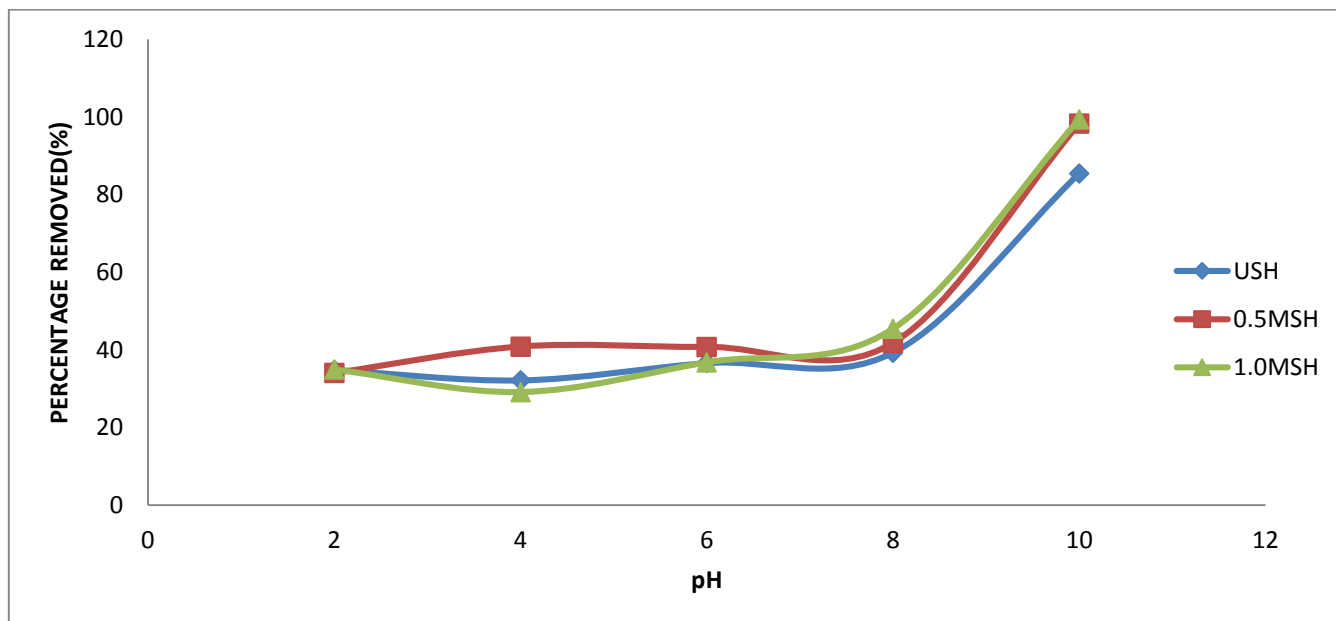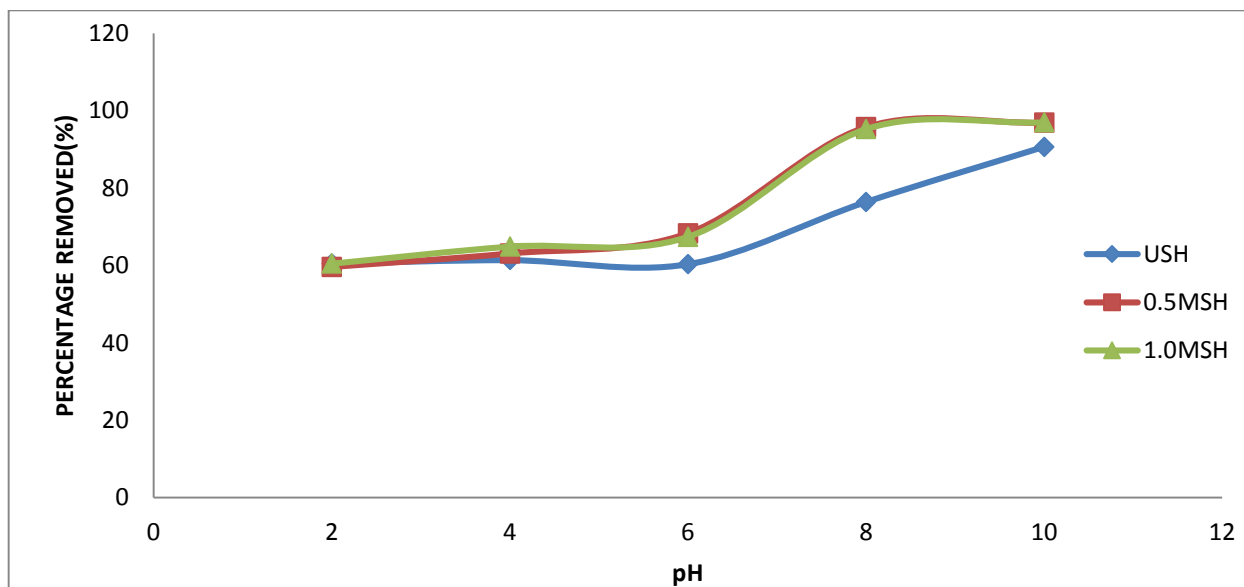**Fig 2c** Plot of percentage metal ion removal against pH for Ni^{2+} 250μm

Fig 2d Plot of percentage metal ion removal against pH for Cu^{2+} 250μm

TABLE 2: Effect of pH of adsorbate on Ni^{2+} and Cu^{2+} sorption for both pore sizes 106μm and 250μm

Ni^{2+} 106μm									
Initial pH	**USH**			**0.5MSH**			**1.0MSH**		
	Final pH	a_e mg/l	%Re	Final pH	a_e mg/l	%Re	Final pH	a_e mg/l	%Re
2	1.860	16.207	32.414	1.790	16.449	32.898	1.680	15.065	30.130
4	3.750	15.192	30.384	3.620	16.817	33.634	3.490	15.611	31.222
6	5.890	17.946	35.892	5.710	19.967	39.934	5.520	20.149	40.298
8	7.820	15.243	30.486	7.450	21.133	42.266	7.220	21.643	43.286
10	9.790	41.594	83.188	9.610	49.344	98.688	9.550	49.522	99.044
Cu^{2+} 106μm									
Initial pH	**USH**			**0.5MSH**			**1.0MSH**		
	Final pH	a_e mg/l	%Re	Final pH	a_e mg/l	%Re	Final pH	a_e mg/l	%Re
2	1.760	30.717	61.434	1.690	31.000	62.000	1.630	31.477	62.954
4	3.750	30.501	61.002	3.680	31.786	63.572	3.590	33.225	66.450
6	5.320	30.731	61.462	5.120	33.350	66.700	5.030	34.953	69.906
8	7.760	40.879	81.758	7.340	45.842	91.684	7.160	47.323	94.646
10	9.780	45.376	90.752	9.630	48.508	97.016	9.570	48.581	97.162
Ni^{2+} 250μm									
Initial pH	**USH**			**0.5MSH**			**1.0MSH**		
	Final pH	a_e mg/l	%Re	Final pH	a_e mg/l	%Re	Final pH	a_e mg/l	%Re
2	1.890	17.431	34.862	1.760	17.032	34.064	1.520	17.483	34.966
4	3.870	16.085	32.170	3.750	20.439	40.878	3.540	14.585	29.170
6	5.870	18.311	36.622	5.560	20.395	40.790	5.210	18.412	36.824
8	7.870	19.657	39.314	7.460	23.907	41.814	7.240	22.743	45.486
10	9.600	42.570	85.440	9.350	49.155	98.310	9.050	49.688	99.376
Cu^{2+} 250μm									
Initial pH	**USH**			**0.5MSH**			**1.0MSH**		
	Final pH	a_e mg/l	%Re	Final pH	a_e mg/l	%Re	Final pH	a_e mg/l	%Re

2	1.980	30.268	60.536	1.850	29.803	59.606	1.790	30.246	60.492
4	3.780	30.695	61.390	3.670	31.542	63.084	3.590	32.451	64.902
6	5.840	30.167	60.334	5.730	34.149	68.298	5.630	33.702	67.404
8	7.520	38.200	76.400	7.460	47.883	95.766	7.470	47.617	95.234
10	9.650	45.330	90.660	9.580	48.463	96.926	9.250	48.485	96.970

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