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### **Adsorption of Copper (Cu<sup>2+</sup>) & Zinc (Zn<sup>2+</sup>) Metal Ion from Waste Water by Using Soybean Hulls and Sugarcane Bagasse as Adsorbent**

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#### **ABSTRACT**

The aim of this research is to study the efficiency of removing copper ions and Zinc ions from Copper Chloride and Zinc Chloride, using naturally based adsorbents like soybean hulls and Sugarcane Bagasse respectively. Batch adsorption studies show that the modified Soybean hulls show a great ability for extracting metallic ions from wastewater samples as compared with the Sugarcane bagasse. For Soybean Hulls the experiment was divided into two parts. In the first part, the time to heat soybean hulls that were soaked in citric acid was determined. In the second part the factors affecting copper ion adsorption by soybean hulls were determined to be initial concentration and pH of the solution, ratio of soybean hulls to copper chloride solution and size of soybean hulls. The results showed that the Soybean hulls and sugarcane bagasse were found to be an attractive low cost alternative for the treatment of wastewater. A good efficiency to remove toxic metal ions was achieved by usage of such by-product.

**KEYWORDS:** Adsorption, Citric Acid, Copper Ion, Zinc Ion, Sugarcane bagasse, Soybean Hulls

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## **INTRODUCTION**

The tremendous increase in the use of heavy metals over the past few decades has resulted in an increased flux of metallic substances in the aqueous environment. The metals are of special concern because of their persistency. The study of pollution by toxic metal compounds assumes considerable importance in chemical process industries. In view of their high toxicity for human health, heavy metal concentrations in wastewater are restricted by strict standards.

A variety of low-cost biomass has been investigated for controlling pollution from diverse sources in different parts of the world. These include an aerobically digested sludge, bacteria, fungi and algae. Agricultural materials have also been used. These include rice bran, soybean and cottonseed hulls, crop milling waste, groundnut husk, maize cob meal, coir, jute and sawdust, canola meal, and coconut shell<sup>1</sup>. Copper is one such metal that requires considerable attention. Industrial wastewater from textile, leather tanning, electroplating, pigmentation and dyes contain copper in high concentration.

Large amounts of soybean hulls are produced each year and used in animal feed as a low priced raw material. Soybean hulls could be used as an adsorbent material for the removal of toxic metals from water and wastewater by adsorption. Published studies have demonstrated the utility of soybean hull modification is desirable enhancement of metal ion adsorbing properties. Many researchers have attempted to develop metal ion adsorbents from agricultural by-product, such as cottonseed and rice hulls, rice straw and rice bran, soybean hulls, sugarcane bagasse, almond hulls, cottonseed hulls and macadamia nut hulls. The results have demonstrated that soybean hulls shown the greatest potential as copper ion adsorbents<sup>2</sup>.

Zinc ( $Zn^{2+}$ ), one of the heavy metals on the US Environmental Protection Agency (USEPA) priority pollutant list has been indicated in serious poisoning cases. Symptoms of  $Zn^{2+}$  include dehydration, electrolyte imbalance, stomach ache, nausea, dizziness and muscular incoordination. It is widely used in coating iron and other metals, in wood preservatives, photographic paper, accelerators for rubber vulcanization, ceramics, textiles, pigments and batteries.

In some countries, sugar cane is considered as a type of fruit, in which the stem is chewed or used to extract the fresh juice. Sugar cane is a highly versatile plant, and can be grown successfully under a wide range of conditions. The by-products of sugar manufacture (molasses, bagasse and filter mud) are used in many ways, including food, as well as the basic raw material for the burgeoning sucro-chemical industry. In Nigeria, sugarcane fibre is usually discarded, and presently there is no known use for this residue in the country. The objective of this work was therefore to investigate the ability of

sugarcane biomass to remove  $Zn^{2+}$  from aqueous matrices, as well as its desorption and re-use potentials<sup>3</sup>.

A number of technologies have been developed over the years to remove toxic metals from water. The most important technologies include chemical precipitations, electro flotation, ion exchange, reverse osmosis, and adsorption on activated charcoal. These methods are not cost effect. The high cost of activated charcoal has prompted a search for cheaper substitutes.

## **MATERIALS AND METHODS**

### ***Preparation of Stock Solution***<sup>2,3,4</sup>

#### ***0.6 M Citric Acid Solution:***

Stock solution is prepared by taking 11.52 gm of Citric Acid powder and dissolve it in 100ml of Distilled water. Finally stock solution was prepared.

#### ***0.1 N NaOH Solution***

Stock Solution is prepared by taking 1gm of NaOH pellets in 250 ml Distilled water.

#### ***Copper Chloride Solution (CuCl<sub>2</sub>)***

To prepare 50 ppm of stock Solution of CuCl<sub>2</sub>.0.775 gm of CuCl<sub>2</sub> is taken in 500 ml distilled water, so 1000 ppm CuCl<sub>2</sub> Solution is Prepared. Pipette out 25 ml solution from it and add to 475 ml distilled water to prepare 500 ml of 50 ppm CuCl<sub>2</sub> solution.

#### ***Zinc Chloride Solution (ZnCl<sub>2</sub>)***

0.1 M solution of ZnCl<sub>2</sub> is prepared by dissolving 13.62 gram of the ZnCl<sub>2</sub> in 1000 ml of the distilled water.

## **EXPERIMENTAL WORK**

To achieve the aim of this study, two experiments were conducted for Soybean hulls and Sugarcane Bagasse.

### ***Preparation of Organic Matter as Adsorbent***<sup>5</sup>

The adsorbent is prepared by taking natural dry Soybean Hulls and Sugarcane Bagasse. First wash the Adsorbents by Distilled water and then dry it. The Sugarcane Bagasse is kept into oven for 24 hrs at

100 °C. Dried Adsorbents are grinded in grinder at the fine size and meshed it with screen size between 1.5 to 1.8 mm mesh.

### ***Procedure of Modifying Soybean Hulls with Citric Acid***<sup>5</sup>

Ten grams of soybean hulls with a particle size of 1.5 to 1.8 mm will be taken in 200 ml of 0.1N NaOH. The slurry will be stirred at 300 rpm for 1 hr. and then will rinse with distilled water. The moist hulls will be then added to 200 ml of distilled water and stirred at 300 rpm for 45 min to remove the excess NaOH. This procedure will be repeated for three times to ensure removal of NaOH. The hulls will be then blended with 0.6M of citric acid in a proportion of 1.0 gram of hulls to 7.0 ml acid. The acid/soybean hulls slurry will then be allowed to dry overnight at 50°C. The dried hulls will be heated further up to 120°C for 0, 15, 20, 60, 90 and 120 minutes. The acid-modified soybean hulls were then cleaned by washing with distilled water and filtered. Finally, the modified hulls will be allowed to dry overnight at 50°C and sieved in the range of 1.5mm to 1.8 mm.



**Fig 1: Modification of Soybean Hulls with Citric Acid**

## **BATCH SORPTION PROCEDURE**

### ***Soybean Hulls***

The initial pH of the metal solution will be adjusted to values in the pH range of (1–9) by the addition of 0.1M HCl or 0.1M NaOH prior to experiment. Certain volume of CuCl<sub>2</sub> Solution (30 ml) was equilibrated with varying sorbent dosage(0.3 to 1.2 gr), pH values (1–9), and contact time (10 to 70 min). Experiments were carried out in 100 ml beakers to study the effect of parameters (sorbent dosage, pH values and contact time). The beaker shall be shaken for a prescribed length of time by magnetic stirrer. After thorough filtration the filter paper, Cu ions remaining in wastewater is determined by Atomic Absorption Spectrophotometer<sup>6</sup>.



Fig 2. Batch For Copper Adsorption

### ***Sugarcane Bagasse***

20 ml of zinc chloride solution and different amount of the dosage of the adsorbent added to the solution and kept into the magnetic stirrer. Then solution is filtered with filter paper. Filtered solution is analysed by an atomic absorption spectrometer (AAS) to know concentration of zinc in solution. solution is treated at different pH, different temperature, different time of contacts<sup>6</sup>.



Fig 3. Batch for Zinc Adsorption

## **RESULTS AND DISCUSSIONS (*Soybean Hulls*)**

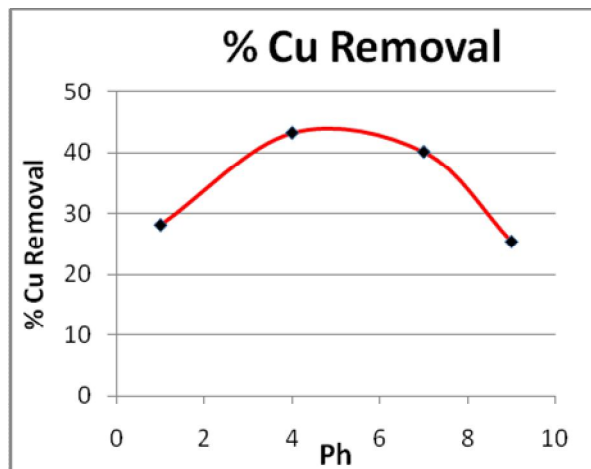
### ***The Optimum pH Value Analysis***

The pH value of synthetic cuprous solution was controlled at 1, 4, 7 & 9. The effect of pH on absorption of copper is presented in graph -1. From graph we can see that maximum removal of copper will occurs at pH-4 and follow by pH7. After pH-7 there is slightly a decrease in adsorption and at low pH i.e. below pH-7 very less copper is removed.

Initial Concentration of copper solution: - 70 ppm.

Dosage: - 0.3 gm of Acid Modified Soybean hulls.

Temperature: -30°C - 33°C



Graph 1. % Adsorption of Cu Vs. pH

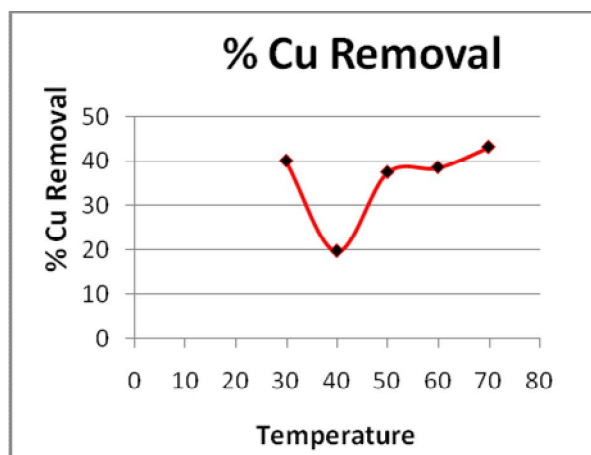
### Effect Of Temperature

The temperature of synthetic Cu solution was maintained at 30°, 40°, 50°, 60°, 70° Celsius. The effect of temperature on adsorption of copper is presented in graph-2. From graph we can see that peak % adsorption is attended at 70° Celsius and very low adsorption is at 40° Celsius<sup>7</sup>.

Initial concentration of Cu working solution: - 70 ppm

Dosage: - 0.3 gm of Acid Modified Soybean hulls.

Temperature: - 30°c - 70°c



Graph 2. % Adsorption of Cu Vs. Temp.

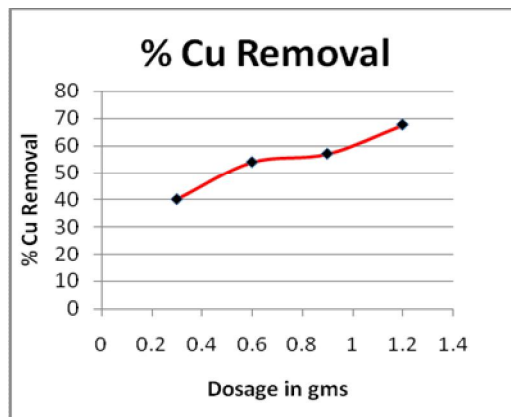
### ***Effect of Dosage***

The doses of Acid activated Soybean Hulls were taken as 0.3, 0.6, 0.9, 1.2 gm. From Graph-3 we can see that the peak values are attended at 1.2gm dose and min adsorption is at 0.3 gm. This is due to more surface area available for adsorption<sup>9</sup>.

Initial concentration of Zn working solution: - 70 ppm

Dosage: - 0.3 to 1.2 gm of Acid Modified Soybean hulls.

Temperature: - 30°C - 33°C



***Graph 3. % Adsorption of Cu Vs. Dosage***

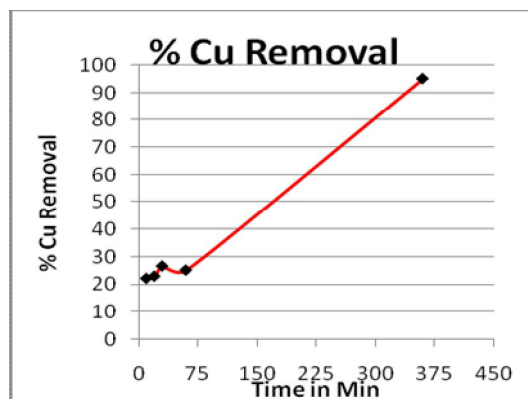
### ***Effect of Contact Time***

The Acid Modified Soybean Hulls and Cu solution were kept in contact for various time periods i.e. 10, 20, 30, 60, 360 min. From the graph-4, we can see that peak value was attained at 360 min<sup>10</sup>.

Initial Concentration of Cu working solution: - 52 ppm

Dosage: - 0.3 gm of Acid Modified Soybean hulls.

Temperature: 30°C - 33°C



***Graph 4. % Adsorption of Cu Vs. Time***

## RESULTS AND DISCUSSIONS (*Sugarcane Bagasse*)

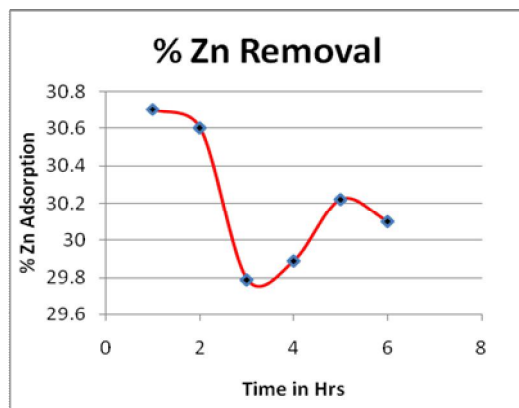
### *Effect Of Contact Time*

The adsorbent and ZnCl<sub>2</sub> solution were kept in contact for various time periods i.e. 1, 2, 3.5, 5, 6.5 Hrs. From the graph-1, we can see that peak value was attained at 6.5 hrs<sup>11</sup>.

Initial Concentration of Zn working solution: - 33 gm/lit

Dose: - 0.2 gm/20 ml. sugarcane bagasse

Temperature: 35°C - 40°C



**Graph 1. % Adsorption of Zn Vs. Time**

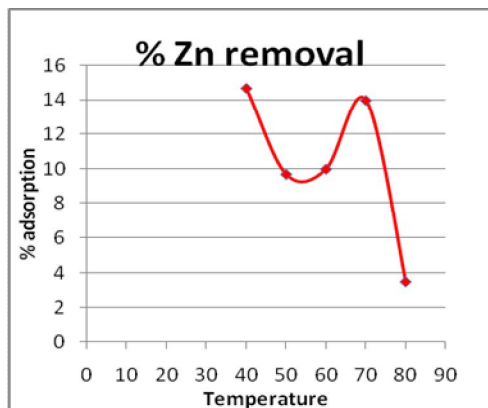
### *Effect of Temperature*

The temperature of ZnCl<sub>2</sub> solution was maintained at 40°, 50°, 60°, 70°, 80° Celsius. The effect of temperature on adsorption of Zn is presented in graph-2. From graph we can see that peak % adsorption is Zn attended at 40° Celsius and very low adsorption is at 80° Celsius.

Initial concentration of Zn<sup>2+</sup> solution: - 43.1305

Dose: - 0.2 gm/20 ml. sugarcane bagasse

Temperature: 40°C - 80°C



**Graph 2. % Adsorption of Zn Vs. Temp.**



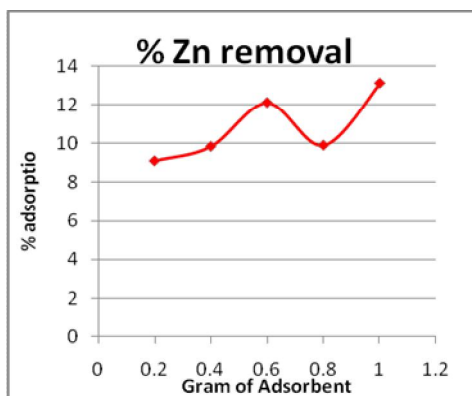
### ***Effect of Doses***

The doses of adsorbent were taken as 0.2,0.4,0.6,0.8,1.0 gm. From Graph-3 we can see that the peak values is attended at 1gm dose and min adsorption is at 0.2gm. This is due to more surface area available for adsorption.

Initial concentration: - 41.3527

Dose: - 0.2 gm – 1.0 gm / 20ml solution.

Temperature: - 35°C - 40°C.



***Graph 3. % Adsorption of Zn Vs. Dosage***

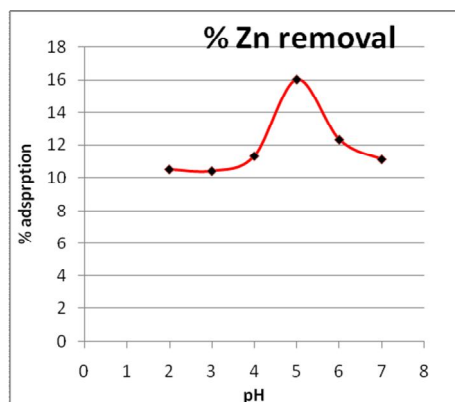
### ***The Optimum pH Value Analysis***

The pH value of ZnCl<sub>2</sub> solution was controlled at 2,3,4,5,6,7. The effect of pH on absorption of copper is presented in graph-4. From graph we can see that maximum removal of zinc will occurs at pH-5. After pH-7 there is slightly a decrease in adsorption and at low pH i.e. below pH-7 very less copper is removed.

Initial Concentration of Zinc solution: - 29.0245.

Dose: - 0.2 gm/20 ml.

Temperature: - 35°C - 40°C.



***Graph 4. % Adsorption of Zn Vs.pH***

## **CONCLUSIONS**

Pollution control board has very strict rules for the effluents which are leaving in the industries, because some of the constituents of these effluents are the harmful. They cause effect on human beings and leaving organisms. Also effluent causes poisoning of agro lands and natural water sources like river, ponds etc.

This project serves better for Cu removal, because Soybean Hulls are easily available & they can reduce the expensive uses chemical, machineries for removal of heavy metal from industrial waste.

From the above results from the graph no 1,2,3,4 we can say that the removal of zinc ( $Zn^{2+}$ ) by activating sugarcane bagasse is not satisfactory. But as activation procedure is simple & cheap for sugarcane bagasse, it may be used where % zinc removal required is less.

The study indicated that adsorbent prepared from Soybean Hulls could be used as an effective adsorbent material for the treatment of aqueous waste streams containing copper. The adsorption of Copper onto Soybean Hulls is found to be time, concentration and pH dependent. So it can be varied as per the industrial requirement to achieve more removal of heavy metals.

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