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Decontamination of Wastewater Effluent using Sugar Cane Bagasse and Soybean Hulls

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Abstract-

Wastewater effluents from industrial processes often pose environmental as well as health risks to humans when these waters are consumed without proper treatment. In this study, distilled water and citric acid were used as modifiers in order to establish the comparative abilities of modified soybean hull and sugarcane bagasse as means of reducing copper and zinc chlorides to their metals and subsequently adsorbing the metals in order to propose both materials as low cost adsorbents for heavy metals. Based on the results, the modified soybeans have good potential for adsorbing Cu metal while sugarcane bagasse showed preferential adsorption of Zn from waste water. Also, results from optimization gave a pH of 4 and 5 for the modified forms of the bagasse and soybean respectively. While a mass of 1g of each adsorbent gave the best removal rate for their preferred metals, the optimum volume for the highest metal adsorption was found to be for solvent of 35 ml/g adsorbent. Adsorption rate was found to increase with temperature and time for both adsorbents.

Keywords: Adsorption; agro-waste; modifiers; optimum pH; sugarcane bagasse; soybean hull

1. Introduction

There is apparently no doubt about the contributions of industrialization to the improvement of human life, however, the effluents released into the environment/water bodies have harmful consequences when they are consumed indirectly. The removal of heavy metals i.e. Zn, Cu, Pb [1] Ar, Cr, CN, Hg, Cd [2], Sn, Au and Ni, as well as other contaminants including acids (titanic and taric acids), alkalis, free chlorine, formaldehyde, mercaptans, greases, phenols, ammonia, NOx gases etc., has received attention as well as concerted effort in recent years [2-5]. Thus, it is important to remove heavy metals from wastewaters because of their abilities to inhibit enzyme activity or become destructive to the cell membrane. Heavy metals also have the tendencies of causing gastrointestinal effects such as muscle discomfort, malaise headache, anorexia, constipation, diarrhea [6], abdominal pain; neuromuscular effect such as muscle weakness and paralysis; effects on the central nervous system including insomnia, restlessness, irritability [1], vertigo, edema, focal necrosis, proliferative meningitis, low intelligence quotient (IQ), learning disabilities, behavioural abnormalities; haematological effects such as anaemia; renal effects such as proeinuria, aminociduria, glucosuria; carcinogenic effects which result in malignant growth or cancer. According to Hegazi [7], there is an urgent need to explore other viable alternative approaches as against popular techniques such as ultrafiltration [8-10] and



plant-waste adsorbents from potential agro-based materials [11] relative to conventional water treatment techniques since existing techniques are quite sophisticated and expensive; this will also reduce the death toll or adverse consequences resulting from heavy water consumption in rural areas. Bagasse is an inhomogeneous material consisting of pith fibre which is obtained from the core of sugar plant [12]. Both researchers investigated the adsorption of Cd and Zn using activated carbon made from sugarcane bagasse. Several species of sugarcane include *Saccharum barberi* which originated from India, the *Saccharum edule* and *Saccharum officinarum* whose origin can be traced to New Guinea; this was the specie adopted in this study. Soybean (*Glycine max*) is a legume. It varies from < 0.2 to 2.0 m (i.e. 0.66ft to 6.6 ft) in height. The leaves, stems, and pods are enclosed in grey or fine brown hairs. Soybean hull has been used for adsorbing heavy metals when modified with 0.6 M citric acid and NaOH [13]. A study was conducted which involves the use of maize cob for Cr removal [14]. Al-Qahtani [15] used the cotexes of fruit waste to purify waste water; some studies involving the use of groundnut shells have also been reported [16-17]. Based on the literature search conducted, no study has been tailored towards the use of KOH as well as 1 M citric acid and distilled water as major modifiers for soybean hull and bagasse respectively, hence, this work seeks to uncover the potential of their modified forms in heavy-metal removal from waste water.

2. Methodology

2.1 Raw Materials and Reagents

Raw sugarcane and soya bean were purchased. Sugarcane bagasse was and the soya bean hulls were obtained from an open market in Abeokuta, Ogun State, Nigeria. Other materials/reagents used include distilled water, 0.2 M KOH 1 M Citric acid, $ZnCl_2$, $CuCl_2$, 0.5M HCl all made by Sigma Aldrich, Electric laboratory Oven by Visio Scientific co., Weighing Balance, sample Bottles (small transparent container for samples), 200 and 500 ml beakers, measuring cylinders, and conical flasks by J.L Borosilicate, plastic bowls, Emery filter paper, Atomic Absorption spectrophotometer, thermometer, spatula, stopwatch and magnetic stirrer.



(a)



(b)

Figure 1 a. Soybean hulls b. Sugarcane bagasse

Figure 1 shows samples of the pulverized soybean hull and sugarcane bagasse

2.2 Material Processing

2.2.1 Sample preparation

The adsorbent from the bagasse was prepared by washing samples of naturally dried sugarcane bagasse in distilled water. 2g sample of the bagasse measured and placed in an oven for 24 hours at 100°C. The dried adsorbent was ground and screened in order to obtain uniform bagasse-particles in the range of 1.5-1.8 mm; the separate samples were mixed with two separate 100 ml solutions of distilled water and KOH respectively. 20 ml each, of zinc chloride and copper II chloride were mixed with separate samples of the bagasse (i.e. 1g each) and kept in the magnetic stirrer. The resulting solution was filtered using filter paper. The filtrate was analysed by an atomic absorption spectrometer (AAS) in order to determine the concentration of zinc/copper in solution. The solution was treated at different pH, temperatures and times. Two separate portions (i.e. 1 g each) of soybean hulls, comprising of particles sizing 1.5-1.8 mm were also measured and added to 20 ml each of, 0.1 M KOH and distilled water. The resulting slurry was stirred at 300 rpm for 1hr. The mixture was added to 20 ml of distilled water and stirred at 300 rpm for 45 mins in order to remove any excess KOH. Thereafter, the hulls were mixed with 0.6 M of citric acid i.e. 1.0 gram of hulls to 7.0 ml acid. The resulting mixture was allowed to dry overnight at 50°C. The next day, the dried hulls were then heated at 120°C for 0, 15, 20, 60, 90 and 120 minutes. The acid-modified soybean hulls were then washed with distilled water and filtered; they were again dried for one more night at 50°C and sieved to assume the size of a pan. 20 ml each, of zinc chloride and copper II chloride were mixed with separate samples of the soybean (i.e. 1g each) and the acid + KOH (and kept in the magnetic stirrer. The resulting solution was filtered using filter paper. The filtrate was analysed by an atomic absorption spectrometer (AAS) in order to determine the concentration of zinc/copper in solution. The solution was then treated at different pH, temperatures and times.

2.2.2 Initial characterization of the wastewater

Waste water from an industrial plant in Lagos state, Nigeria, was obtained and characterized in order to ascertain the types of heavy metals therein. Standard solution concentrations of the metallic salts in solution were then prepared/simulated using laboratory grade chemicals in order to establish a calibration curve for zinc chloride and copper chloride. This was done by running several standard concentrated samples of known salt concentrations of the metal under the same conditions as proposed by Marshall et al. (2010); solution concentrations of the water were simulated for the salts of interest i.e. ZnCl₂ and CuCl₂. Also, the procedure for parameter estimation was mimicked to arrive at the quantities of metal adsorbed as well as the unknown residual concentration of the metal in the sample after adsorption using equations 1 and 2.

$$q_e = \frac{V(C_o - C_e)}{100M} \quad (1)$$

q_e = the amount of the adsorbate ion adsorbed mg/g, C_o = the initial Concentration of the metal ion before adsorption, C_e = the equilibrium concentration of the metal in the filtrate after adsorption process, M = the mass in grams of the adsorbent, V = the volume of solution in ml.

$$\% \text{ metal adsorbed} = \frac{(C_o - C_e)}{C_o} \quad (2)$$

2.2.3 Effect of varying contact time

1g each of the bagasse and soybean hull were weighed and added to 70 ml of $ZnCl_2$ and $CuCl_2$ solutions respectively. The mixture was kept at 30-33°C in a water bath at different times i.e. 1:30, 2:30, 4:30 and 6:30 h for bagasse and 10-360 mins for the soybean while stirring at 300 rpm. The mixture was then filtered and the filtrate was analysed using AAS.

2.2.4 Effect of varying pH

The pH of the modified samples in section 2.2.3 were adjusted using HCl and KOH to adjust the pH of the solution, the pH was varied from 1-9. 1g each of sugarcane bagasse and soybean hull were weighed and added to 70 ml of $ZnCl_2$ and $CuCl_2$ respectively; the mixtures were maintained at 30-33°C for 90mins while stirring at 300rpm. The mixture was filtered and analysed using AAS.

2.2.5 Effect of quantity of adsorbent

1g, 2g, 3g, 4g and 5g each of both samples i.e. bagasse and soybean hull were added in beakers containing 70 ml of $ZnCl_2$ and $CuCl_2$ solutions respectively. Each mixture temperature was maintained within 30-33°C. The contact time was 90 mins. The mixtures were whirled at 300rpm, after which it was filtered and analysed using AAS.

2.2.6 Effect of temperature

The temperature of the mixtures in section 2.2.5 were varied from 40-80°C at an interval of 10°C. 1g of each adsorbent was weighed and mixed with 70 ml of $ZnCl_2$ and $CuCl_2$ solutions and kept for 90mins. The mixtures were whirled at 300rpm, filtered and analysed using AAS.

3. Result and Discussions

In Table 1a, for $ZnCl_2$ solution of initial concentration of 49.58 ppm, the quantity of zinc after adsorption dropped while that adsorbed increased at increased solution pH; the optimum pH for Zn removal using bagasse is 5.

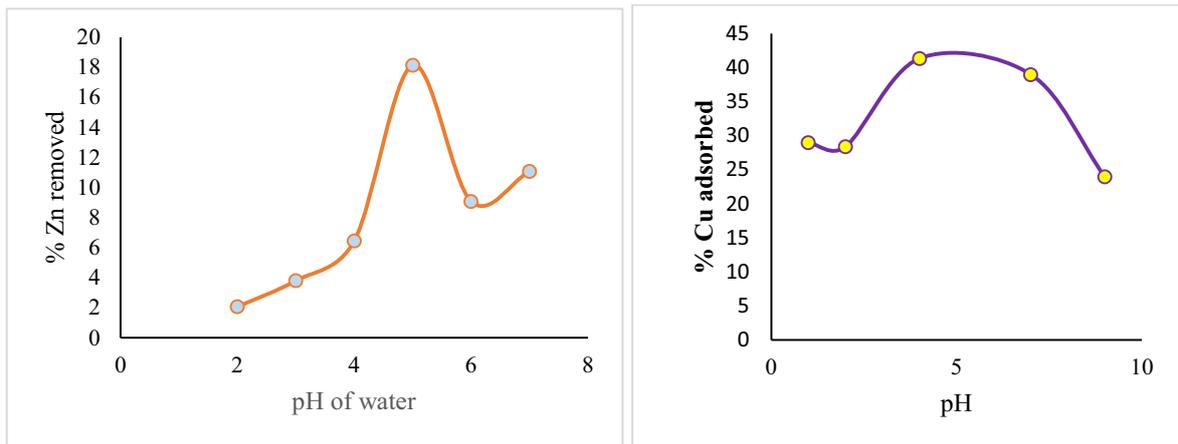
Table 1a: Adsorption of Zn for the bagasse sample

pH values	Zinc content after adsorption (C) (p/ppm)	Amount adsorbed $C_e - q_e$ (p/ppm)
2	48.5604	0.714
3	47.6890	1.320
4	46.3800	2.240
5	40.5890	6.290
6	45.0820	3.149
7	44.0890	3.840

In Table 1b, the amount of Cu adsorbed based on an initial concentration of $CuCl_2$ of 49.7 ppm, decreased for pH of 1-2, it increased for pH of 4 and dropped afterwards, while the residual Cu in the filtrate increased at increased solution pH. This then implies that for maximum Cu removal, the pH of the solution should be kept at 4.

Table 1b: Cu adsorption for the soybean sample

pH values	Cu content in filtrate after adsorption (C) (ppm)	Amount adsorbed (Ce) = qe (ppm)
1	49.7001	14.21
2	50.1008	13.92
4	41.0540	20.26
7	42.5911	19.18
9	53.2290	11.73



(a)

(b)

Figure 2: a. % Zn and b. %Cu removed using bagasse and soybean respectively

Figures 2a and b depict an optimum pH of 5 with the highest percentage of Zn and Cu removal rate of 17 and 40% respectively. This then implies that, in order to maximize the removal rate of Zn by bagasse, the solution pH must be maintained at 5.

Figure 2: a. %Zn and b. %Cu removed vs pH of residual solution

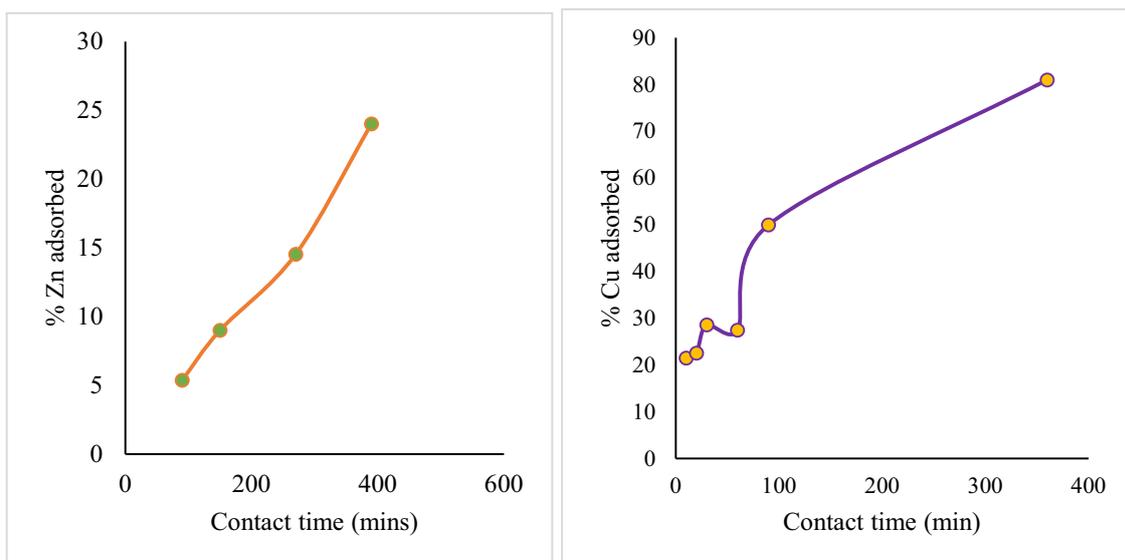


Figure 3: a. %Zn and b. Cu adsorbed vs contact time for the bagasse and soybean respectively

In Figure 3, the quantity of Zn and Cu adsorbed increased with time beyond 100 mins while, Figure 4 shows the effect of temperature on the rate of adsorption of Zn by the bagasse. The best temperature for removing Zn and Cu from solution is 30 °C. The best adsorption rate was obtained at $t = 390$ mins for Zn removal by bagasse, while it was 360 mins for Cu removal by soybean.

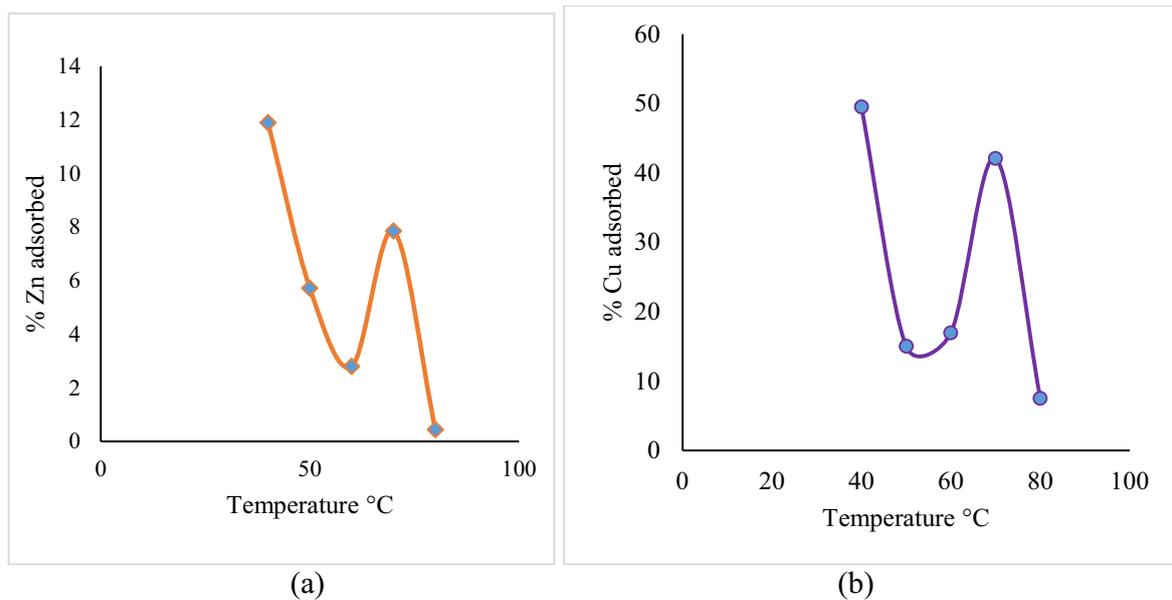


Figure 4: Temperature variation with amount of: a. Zn adsorbed; b. Cu adsorbed

Table 2: Mass of bagasse adsorbent and amount of Zn and Cu adsorbed

Mass of Bagasse (g)	Plain bagasse	Plain soybean hull	Zn content after adsorption (C) for modified bagasse (ppm)	Cu content in filtrate after adsorption (C) (ppm)	Volum of distilled water to bagasse ratio (ml/g)	Volum of citric acid to soybean hull ratio (ml/g)	Amount of Zn adsorbed (C_e) = q_e (ppm)	Amount of Cu adsorbed ($C_e = q_e$) (ppm)
1	24.22	30.15	42.38	42.71	70	70	19.1	7.142
2	21.36	26.41	39.21	30.22	35	35	13.92	9.367
3	17.57	22.56	35.23	28.78	46.7	23.3	9.8	12.15
4	14.66	20.72	33.42	27.85	35	17.5	7.376	13.27

5	12.90	19.89	32.93	25.78	48	14	6.19	13.76
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Also, the effect of treating the bagasse and soybean with distilled water and citric acid is evident from the results because, there was increased removal rates of both metals for the treated adsorbents. From the results in Table 2, the best volume for Zn adsorption is 35 ml because twice as much volume of distilled water is required to remove 42.4 ppm Zn whereas, 35 ml is ideal to remove Zn using 2g bagasse; also, 2g of bagasse is better treated with 35 ml/g distilled water than other higher bagasse quantities. However, the results suggest that, for high removal rate of Zn i.e. 42.4 ppm, the volume of distilled water must be kept at 70 ml/g. Furthermore, the equilibrium concentration increased all through for the different bagasse masses used. For the soybean hull, the quantity of copper adsorbed increased with increase in mass of the modified soybean hull although, the volume of water needed for the 5g soybean hull was lowest 14 ml/g but, the mass of Cu removed was highest also for 1g of soybean hull used while it dropped at higher masses. In Figure 5, it is evident that the mass of the bagasse is proportional to the percentage of Zn adsorbed.

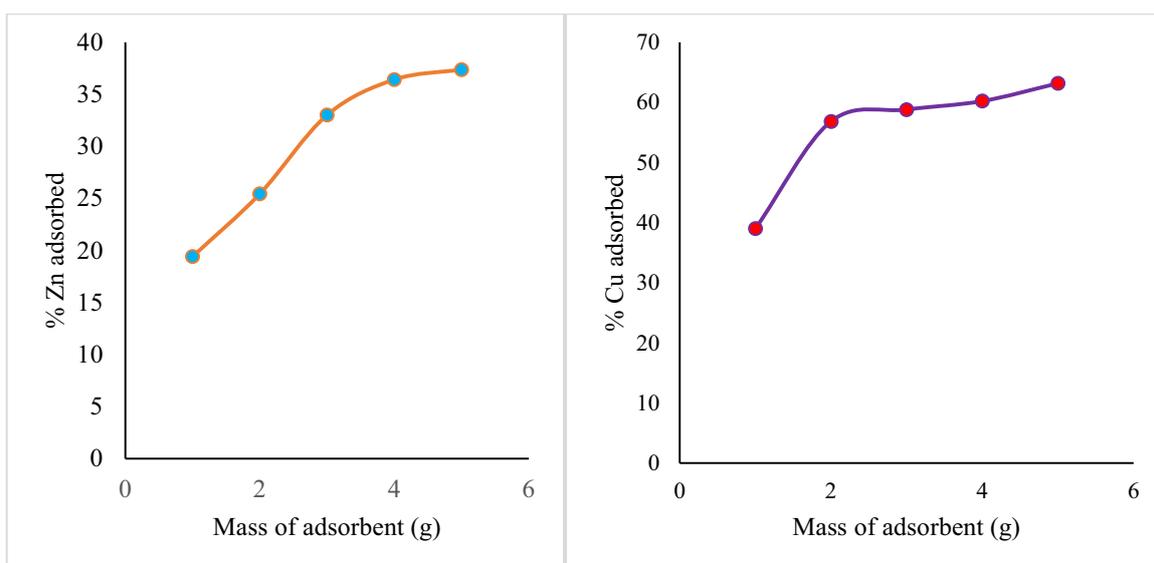


Figure 5: Mass of a. bagasse vs %Zn adsorbed b. mass of soybean hull vs %Cu adsorbed

4. Conclusion

For both adsorbents, the adsorption rate was found to be dependent on pH, contact time, concentration, adsorption dose and temperature. Modified sugarcane bagasse has great potential for the adsorption of Zn. But it needs to be modified or activated to give the maximum adsorption. The use of modified soybean hull for adsorption of Cu was found to be very effective in the adsorption of Cu hence, the consideration of both agro-waste materials as suitable adsorbents is economical relative to the use of expensive chemicals and equipment. Also, treating the bagasse and soybean samples helps improve the removal rates of both metals owing to the dirt removed from both samples and subsequent activation.

5. Recommendation

Considering the results obtained from this research, it is necessary to test the ability of the substrates (soybean hulls and sugar cane bagasse) used in carrying out this research, for their capacities to absorb other heavy metals/toxic substances in wastewater effluents from soils and the textile industries. Furthermore, the influence of pore size distribution for the different particle sizes of the adsorbents can be investigated via SEM/EDS characterization.

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