

Profiling of Zn²⁺ Ion Sorption in Modeled Aqueous Solutions by different Parts of Maize Biomass

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Abstract: The efficiency of the husk, stalk, cob and seed chaff from maize biomass in the removal of Zn²⁺ ions from solution under different conditions was studied and compared. Fourier Transform Infrared spectra of the different biomass parts before and after adsorption of metal ions showed that the husk and cob had more available functional groups and as such active sites for the adsorption of Zn²⁺ ions than the seed chaff and stalk. Percentage removal of Zn²⁺ ions from solution increased with increase in the studied pH range for all the parts. This value also increased with increase in biomass load for the husk and cob but showed an alternating increase and decrease in Zn²⁺ ions removal as biomass load increased when the seed chaff and stalk were studied.

At optimum pH and biomass load for the studied parts the maize husk gave the best removal efficiency of 72.8 %, making it a promising green packing material for industrial scale water treatment application.

Keywords: Functional group, Active sites, Adsorption, Biomass, Maize husk, Removal efficiency, Water treatment

I. Introduction

Freshwater constitutes about 3 % of the total water on the earth surface and only 0.01 % of this water is available to man [1]. This small amount of freshwater has always been under pressure due to rapid growth in population and industrial activities [2]. More often than none it has faced the challenge of pollution by heavy metals [3]. Due to this problem, the contamination of water and soil by heavy metals has attracted a lot of research attention [4-6].

Some techniques used in removing heavy metals from commercial portable water usually include chemical precipitation, ion exchange, membrane process, crystallization, and electrochemical treatment. These processes however may be ineffective or expensive, especially when the heavy metal ions are in concentrations greater than 100 mg/L [7]. The use of agro-wastes as sorbents for removal of heavy metals from aqueous systems has attracted lots of research interest because of their abundant availability and also low cost owing to their relatively high fixed carbon content and the presence of porous structure [8]. Plant biomass or lignocellulose is composed of cellulose, hemicellulose and lignin. Different functional groups have been found on this material by researchers [9-14]. High concentrations of zinc ions in tap water occur as a result of corrosion and leaching of zinc from water supply piping and fittings [15]. Fever, nausea, vomiting, stomach cramps, diarrhea and copper deficiency have been reported as effects of high zinc intake by humans [16]. Recent studies have revealed the ability of plant biomass to remove zinc ions from solutions [17-18]

Maize husk is a major waste generated during maize harvest within cities in the south-eastern part of Nigeria and some other countries. Improper disposal of this waste biomass has resulted in environmental pollution arising from blocking of drainages and other water channels. Recycling of this waste and its use in the treatment of polluted water would not only be economical but also help to stabilize the environment. Though there have been studies on the use of maize parts in the removal of zinc ions from aqueous solutions [19], reports on the most efficient part of this biomass for sorption of different metal ions from solution are unavailable or scarce.

As the search for efficient biosorbents for removal of heavy metals in polluted water continues, the present study profiles the different parts of maize biomass in a bid to determine their different efficiencies in the sorption of zinc ions from aqueous solutions.

II. Methodology

Reagents and solution preparation

All chemicals used were of analytical reagent grade and purchased from Finlab Nigeria Ltd Owerri, Nigeria. A stock solution of zinc nitrate (1000 mg/L) was used as adsorbate and a solution of 50 mg/L were obtained by diluting the stock solution with distilled water.

Collection and preparation of biosorbent

Matured maize crops were collected from a farm in Eziobodo Ihiagwa, Owerri West, Imo State, Nigeria. They were washed repeatedly with distilled water to remove dust and soluble impurities. The different parts of the plant which comprised of husk, stalk, cob and seeds were separated and cut into small pieces. The seeds were crushed, washed and sieved to remove the starch they contain. These parts were then dried for 5 hours in a convection oven at a temperature of 100 °C. The dried parts were crushed with a mechanical grinder to a fine powder which was passed through a sieve of 30 mesh size and stored in plastic bottles for further use.

Instrumentation

Characterization of biosorbent was done with Fourier Transform infrared spectrophotometer (Agilent Cary 630 FTIR). Pressed pellets were prepared by grinding the powder specimens with spectroscopic grade KBr. Characterization was done before and after the biosorption process. The concentrations of Zn²⁺ ions in the different solutions were determined using HI 83200 Multiparameter Bench Photometer by HANNA Instruments.

Adsorption studies

Batch adsorption tests were conducted in triplicates to study the effect of different parameters i.e.; pH, adsorbent dosage and time for maximum removal of Zn²⁺ ions from solution by the different parts of maize biomass.

Effect of pH on adsorption

Cob, husk, stalk and seed chaff each of weight 0.2 g were added to 50 mL of 50 mg/L Zn²⁺ solutions in separate glass reactors. Four sets of solutions with pH values 1.0 – 4.0 for each set were prepared. This pH range was used for the study because the precipitation of metal ions occurred simultaneously at pH higher than 6 [20-21]. They were covered with aluminum foils and shaken for 120 minutes with an orbital shaker. After this time the suspensions were filtered and the concentration of Zn²⁺ ions in the filtrates were measured.

Effect of adsorbent dose on adsorption

This study was carried out at the optimum pH obtained for each biomass part in the first study. Four different sets of 50 mL of 50 mg/L Zn²⁺ solutions at this pH were prepared and to each set adsorbent masses of 0.1 g, 0.2 g, 0.4 g and 0.8 g were added. They were covered with aluminum foils and shaken for 120 minutes with an orbital shaker. After this time the suspensions were filtered and the concentration of Zn²⁺ ions in the filtrates were measured.

Effect of contact time

The dependence of metal uptake by biomass adsorbents as a function of time was determined at the optimum pH and adsorbent dose obtained for each biomass part. Five sets of 50 mL of 50 mg/L Zn²⁺ solutions in glass reactors at the optimum pH and biomass load for each part were prepared. They were covered with aluminum foils and shaken with an orbital shaker. A set was removed every 15 minutes and the suspensions were filtered and concentrations of Zn²⁺ ions in the filtrate were measured. This process was carried out for a period of 75 minutes.

Evaluation of biosorption capacity

Concentrations of Zn²⁺ ions in the filtrates were determined by diluting each sample to a ratio of 1:50, enabling reading and analysis of the concentration of metal ions. The value of the percentage of metal adsorbed from solution (γ) was calculated from the equation [22]:

$$\gamma = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Where C_0 and C_e are the initial and equilibrium concentrations of Zn²⁺ ions in the solutions (mg/L).

III. Results and Discussion

FTIR scans of the maize biomass parts before and after metal ion uptake are shown in figure 1a-1d and the shifts in absorption bands of the functional groups compared table 1.

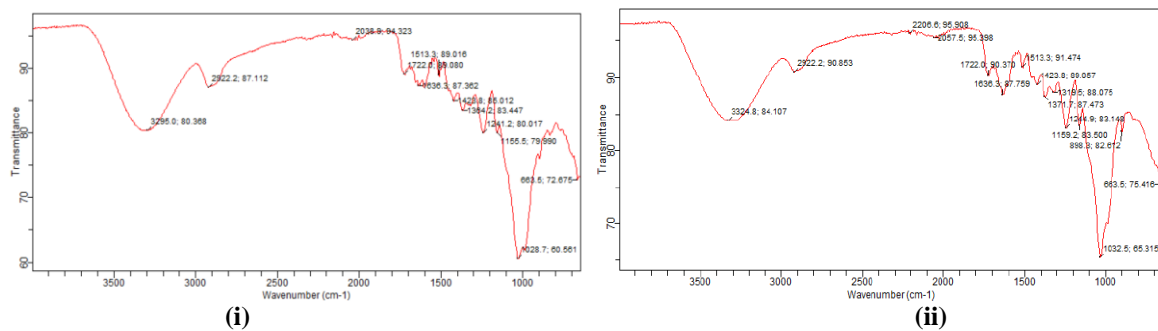


Figure 1a: FTIR spectra of maize cob before (i) and after (ii) adsorption

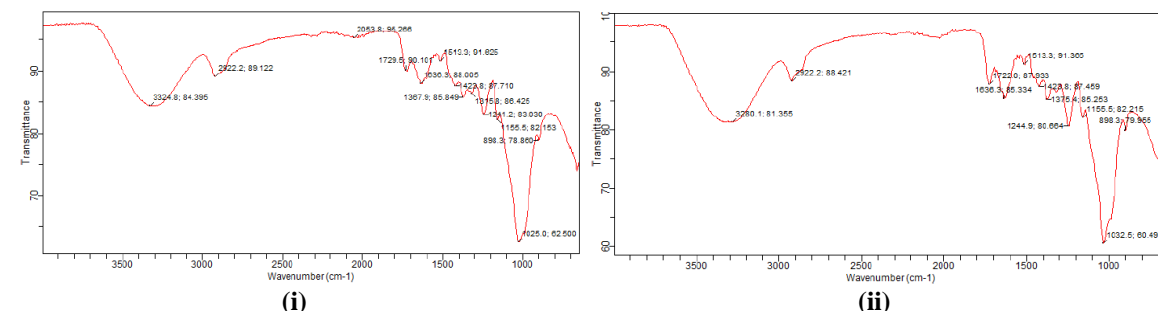


Figure 1b: FTIR spectra of corn husk before (i) and after (ii) adsorption

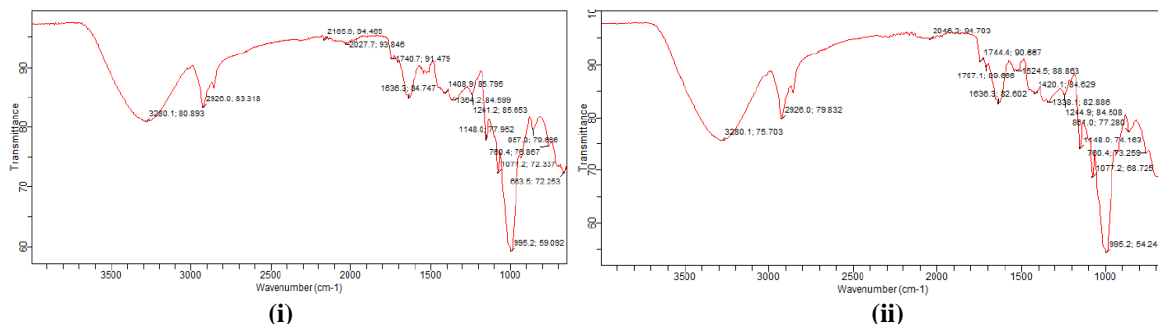


Figure 1c: FTIR spectra of corn seed chaff before before (i) and after (ii) adsorption

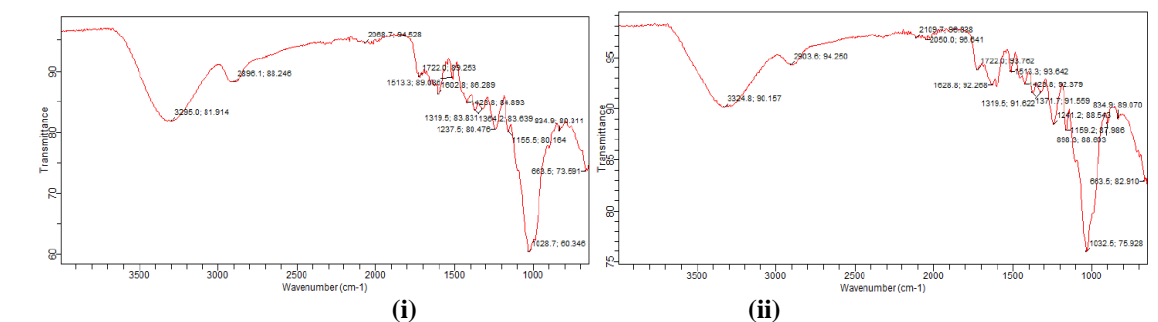


Figure 1d: FTIR spectra of corn stalk before and after adsorption

Table 1: Comparison of shifts in absorbance of functional groups in maize biomass parts before and after adsorption

Adsorption	Part	O-H	OCH ₃	HO-C=O	C=O	O-H-Ar
Before adsorption	Cob	3295	2922	1722	1636	1364
	Husk	3324	2922	1729	1636	1367
	Seed	3280	2920	1740	1636	1364
	Stalk	3295	2896	1722	1602	1319
After adsorption	Cob	3224	2922	1722	1636	1319
	Husk	3280	2922	1722	1636	1375
	Seed	3280	2926	1707	1636	1338
	Stalk	3324	2903	1722	1513	1371

The shift in FTIR absorption bands to lower frequencies indicates the involvement of the functional groups in the biomass in chemical coordination with metal ions [23]. The functional groups used by the different biomass parts for coordination with Zn^{2+} ions were cob- O-H, O-H-Ar husk- O-H, HO-C=O, seed- O-H-Ar and stalk- C=O. The maize husk and cob had greater number of available functional groups and as such more coordination sites for the removal of Zn^{2+} ions from solution. The percentage removal of Zn^{2+} ions from solution by the different biomass parts as a function of pH is shown in figure 2.

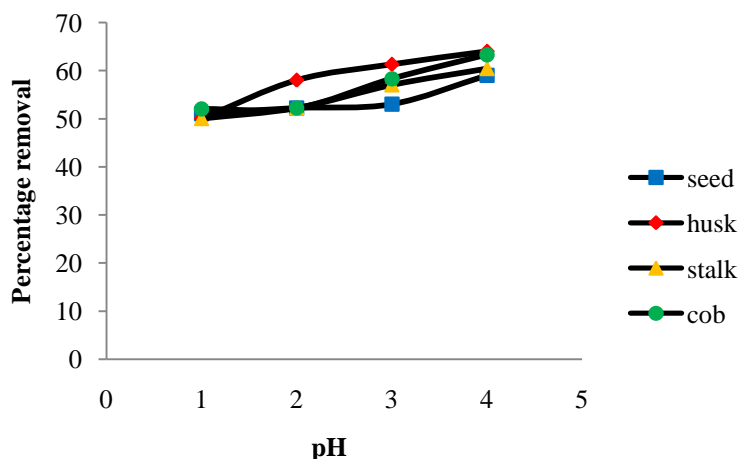


Figure 2: Plot of pH vs percentage removal of Zn^{2+} by 0.2 g of different biomass parts

All the biomass parts showed an increase in Zn^{2+} ion uptake as solution pH increased. The highest metal uptake was observed using the husk as adsorbent and was least with the seed chaff. At pH 4, the ion removing capacity of the husk and cob were very close, giving percentage removals of 64 % and 63.3 % respectively. At low pH values (1.0–3.0) more H_3O^+ ions would be available to compete with the Zn^{2+} ions in solution for the adsorption sites of the biosorbents. Also at low pH most of the functional groups on the biomass are protonated [24]. This will reduce the number of binding sites available for the adsorption of Zn^{2+} ions. The pH can also affect the solution chemistry. In acidic pH, Zn^{2+} ions remain with the positive charge, but in alkaline pH, the hydroxide ions (OH^-) cause precipitation of Zn^{2+} ions in the form of $Zn(OH)_2$ [25] leading to decrease in ion concentration in solution not dependent on adsorption.

The effect of biomass load on the percentage removal of Zn^{2+} ions from solution by the different biomass parts is shown in figure 3.

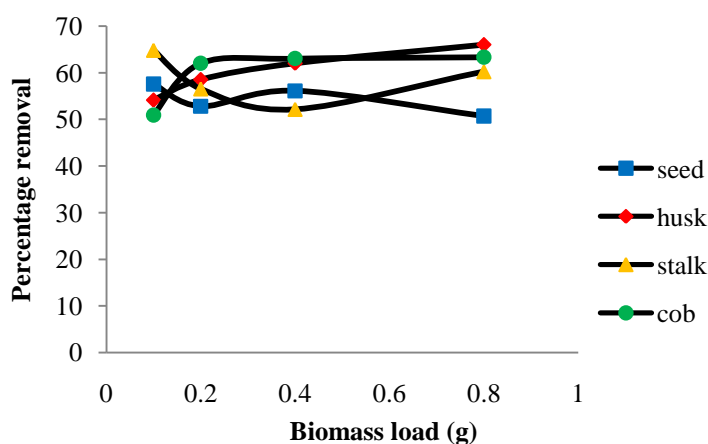


Figure 3: Plot of percentage removal of Zn^{2+} ions vs biomass load at pH 4

It is logical that at higher adsorbent doses, there would be more exchangeable sites for the metal ions [26]. This was observed in the husk and cob which showed a steady increase in metal uptake with removal efficiencies of 66 % and 63.3 % respectively at 0.8 g load each. However, the adsorptive capacity of the seed chaff and stalk did not conform to this linearity and showed an alternating increase and decrease in metal removal efficiency as biomass load increased. The seed chaff gave a maximum removal efficiency of 57.6 % at 0.4 g load while the stalk gave 64.8 % at 0.1 g. This tendency was observed by Garg *et al* [27] while studying

the removal of dyes from solution using sawdust. They attributed it to overlap of adsorption sites, arising from overcrowding of adsorbent particles. Also the high adsorbent dose could impose a screen effect of the dense outer layer of the cells, thereby shielding the binding sites from the metal ions [28]. The time for the equilibrium adsorption capacity of the biomass materials for the different adsorbents at pH 4 and optimum biomass load are shown in figure 4.

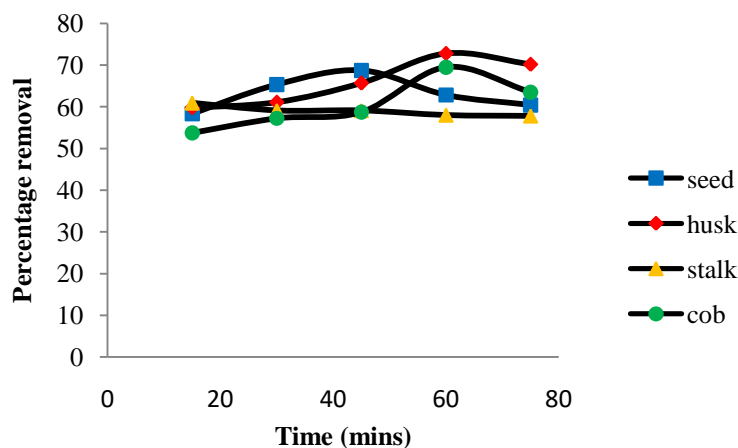


Figure 4: Plot of Contact time vs percentage removal of Zn^{2+} at optimum conditions

Maximum adsorption capacity for the seed chaff was reached in 45 minutes at a biomass load of 0.4 g while the stalk attained this limit in 15 minutes at a load of 0.1 g. The values of percentage removal of Zn^{2+} ions from solution at optimal study conditions for husk, cob, seed chaff and stalk were in the order 72.8 % > 69.5 % > 68.7 % > 60.9 % respectively.

Decrease in percentage removal was observed for all the biomass parts after the time their adsorption capacities were reached. This observation suggests a multilayer adsorption pattern on the biomass surface where weakly held ions desorbed when the concentration of Zn^{2+} ions in solution reduce. This might be as a result of shift in equilibrium to the adsorption process in the direction of releasing some weakly adsorbed ions back into the solution.

IV. Conclusion

The results from this study have shown that the different parts of maize biomass have varying abilities in removing Zn^{2+} ions from aqueous solution. Specific active sites on the different parts of the biomass were responsible for the metal adsorption. Though the same functional groups might be present on some biomass materials, their affinities for specific metal ions vary. The maize husk and cob had greater number of available functional groups than other parts for Zn^{2+} ion removal in aqueous solution. Adsorption of metal ions from solution increases with an increase in the pH of the solution containing the ions. Increase in adsorption capacity of a biomass with increase in biomass load is not a general rule, but depends on what happens to the active sites at such doses.

At optimal pH and adsorbent dose, the maize husk had the highest efficiency in the removal of Zn^{2+} ions from solution relative to the other parts of the plant. This makes it a promising material for industrial scale treatment of water polluted by Zn^{2+} ions.

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