

Full Length Research Paper

Removal of some metal ions from aqueous solution using orange mesocarp

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Accepted 23 July, 2008

In this study, the use of orange mesocarp residue biomass (modified and unmodified) as a cost-effective and environmentally safe technique to remove Mg^{2+} , Zn^{2+} , Cu^{2+} , Pb^{2+} from aqueous solution was investigated. The results showed that unmodified orange mesocarp residue bound 56% of Mg^{2+} , 81% of Zn^{2+} , 71% of Cu^{2+} , 73% of Pb^{2+} , and 85.05% of Cd^{2+} . In the case of modified orange mesocarp residue, it was able to bind the following amount of metal ions: 63.05% of Mg^{2+} , 37.0% of Zn^{2+} , 43.25% of Cu^{2+} , 33.05% of Pb^{2+} and 86.45% of Cd^{2+} . These results show that orange mesocarp residue biomass can be effectively used to adsorb heavy metals from aqueous solution.

Key words: Orange mesocarp, heavy metals, adsorption, biomass.

INTRODUCTION

Natural waters have been found to be contaminated with several heavy metals, arising mostly from mining waste and industrial discharges (Baig et al., 1999). These contaminants cause problem to the ecosystem. Although some heavy metals are necessary for the growth of plants, after certain concentration, they become poisonous to both plants and microorganisms. Sometimes, these heavy metals are held in soil as a result of adsorption, chemical reaction and ion exchange (Uzun and Guzel, 2000).

It has been established that various metal ions hinder various enzymes responsible for mineralization of organic compounds to the soil (Uslu and Turklamen, 1987). The effect of heavy metals on man cannot be neglected because exposure to these contaminants even at low concentration in the environment can cause severe dysfunction in the renal, reproductive and central nervous systems (Manaham, 2004).

As a result of the increasing environmental concern for these contaminants, there has been serious interest in removal of heavy metals from contaminated soil and waste water. A number of technologies have been developed over the years to remove toxic metals from water.

The most important of these methodologies include chemical precipitations, electroflotation, ion exchange, reverse osmosis and adsorption on activated carbon (Gaikward, 2004). These methods of water treatment are expensive and sometimes ineffective especially when metals are present in solution at very low concentration (Baig, et al., 1999). An emerging field of interest is employing agricultural by-products as adsorbents for the removal of heavy metals from aqueous solution. Many agricultural wastes that are available at low cost have been reported to be capable of removing substantial amounts of metal ions from aqueous solutions (Igwe et al., 2005; Abia et al., 2000; Herrera et al., 2003; Gardea-Torresdey et al., 1998).

These agricultural waste materials remove toxic heavy metals from aqueous solutions by adsorption, chelation and ion exchange (Gardea-Torresdey et al., 1999). The exchange properties of these agricultural wastes can be attributed to the presence of carboxylic, phenolic, hydroxylic, cyano groups, etc. These functional groups attract and sequester metal ions (Abia et al., 2002). Orange mesocarp residue possesses these chemical characteristics and it is inexpensive and environmentally friendly. It was therefore explored in the present study as an adsorbent for the removal and recovery of heavy metals from contaminated water.

The performance of a biomass can further be improved

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Table 1. Percentage of metal ion removal by orange mesocarp residue and modified orange mesocarp residue.

Adsorbent	Zn ²⁺	Cu ²⁺	Pb ²⁺	Cd ²⁺	Mg ²⁺
Orange mesocarp residue	81.0	71.0	73.0	85.05	56.0
Modified orange mesocarp residue	37.0	43.25	33.05	86.46	63.05

by various physical and chemical treatments. The pre-treatments modify the adsorbent either by removing or masking the groups or exposing more metal binding sites (Gupta et al., 2000).

Orange is one of the important fruits in Nigeria, because it is a source of vitamin C. It produces large volumes of wastes, which has caused environmental nuisance in the region. The objective of this study is, therefore, to develop inexpensive and effective metal ion adsorbents from orange mesocarp, an agricultural waste which is available in Nigeria. If such an adsorbent is developed, it may replace the existing commercial adsorbents which are expensive.

MATERIALS AND METHODS

Sample collection

Oranges were bought from the local market in Port Harcourt. They were washed with deionized water and peeled to obtain the mesocarp. The mesocarp was air dried, ground and sieved using 1.00 mm mesh size sieve.

Extraction of rutin from orange mesocarp

The bioflavonoid rutin in the orange mesocarp was extracted with methanol. The rutin obtained from the extract was washed with cold methanol and air dried. The residue left was also collected and air dried.

Synthesis of 2,4-dichloro-6-(phenoxy-4-sulphonic acid)-1,3,5-triazine (DPS resin)

A solution of 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) (9.5 g) in acetone (50 ml) was poured into a stirred mixture of water and crushed ice (300 ml). After 15 min, 2 M HCl (2 ml) was added and the temperature was kept at 4°C. The resultant suspension was allowed to stand for 20 min at 4°C.

A solution of phenol-4-sulphonic acid (13.0 g) in water (80 ml) was added to this suspension at the temperature of 2°C. The mixture was made slightly alkaline by adding 10 ml of an aqueous solution of 2 M Na₂CO₃ still with stirring at 2°C. Thereafter 20 ml of the 2 M Na₂CO₃ solution was added drop wise over a one hour period with constant stirring at 2°C. It was then allowed to stand for another 20 min with stirring. The product was washed with distilled water to a pH of 7. It was dried at 50°C for 2 h (See reaction scheme in Figure 1).

Coupling of orange mesocarp residue with dps resin

DPS resin (1.0 g) was suspended in 30 ml of acetone. Orange mesocarp residue (3.0 g) was added to the suspension and the mixture was agitated for 30 min. The mixture was made alkaline

(pH 9) by adding aqueous Na₂CO₃ solution (2 M) and the agitation was continued for another 30 min. The reaction mixture was allowed to stand for one hour and the product was collected by filtration, washed with distilled water to pH 7 and air dried.

Preparation of synthetic metal ion solution

0.44 g of Zn²⁺ (ZnSO₄·7H₂O), 0.25 g of Cu²⁺ (CuSO₄), 0.16 g of Pb²⁺ [Pb(NO₃)₂], 0.23 g of Cd²⁺ (CdSO₄·8H₂O) and 0.5 g of Mg²⁺ (MgSO₄) were each dissolved in a litre of de-ionized water, respectively. Working standard solution of 2 ppm of each of these ions was prepared by appropriate dilution. In the case of Cu²⁺, 4 ppm was used.

Removal of the metal cation

A 0.3 g each of modified orange mesocarp residue and orange mesocarp residue was soaked in 30 ml of each of the metal ion solutions of initial concentration 1000 mg/L. The suspensions were agitated for 1 h. The samples were filtered rapidly and the filtrates were analysed using Atomic Absorption/Emission Spectrophotometer (AAES) model 200A. The amount of the metal ions adsorbed was obtained by the difference between the initial metal ion concentration and that of the supernatant.

RESULTS AND DISCUSSION

From Table 1, orange mesocarp residue bound 85.05% of Cd²⁺, 81% of Zn²⁺, 73% of Pb²⁺, 71% of Cu²⁺ and 56% of Mg²⁺. Apart from Mg²⁺, orange mesocarp residue has higher adsorption capacity on the chosen metal ions. In the case of modified orange mesocarp residue, it bound 86.45% of Cd²⁺, 63.05% of Mg²⁺, 43.25% of Cu²⁺, 37.0% of Zn²⁺ and 33.05% of Pb²⁺. It was observed that modification by coupling reaction decreased the adsorptive capacity of the cellulosic material on some ions. The decrease in the amount adsorbed on modification indicates that DPS resin blocks some adsorption sites, on which the metal ion would have bound to. The proposed mechanism for DPS resin coupling is as shown in Figure 2.

Magnesium ion (Mg²⁺) shows a different trend with modified orange mesocarp residue. This could be as a result of the small ionic radius of the ion and the fact that Mg is not a heavy metal. Magnesium has a chemistry intermediate between that of beryllium and the heavy metals. The ionic radii of the metal ions are Zn²⁺ (0.74Å^o), Cu²⁺ (0.73Å^o), Pb²⁺ (1.19Å^o), Cd²⁺ (0.97Å^o) and Mg²⁺ (0.72Å^o). Due to the small size of Mg²⁺ and its nature, it was able to penetrate to the other adsorption sites. In that case, ion-exchange and surface adsorption take place. This probably explains why modified orange mesocarp

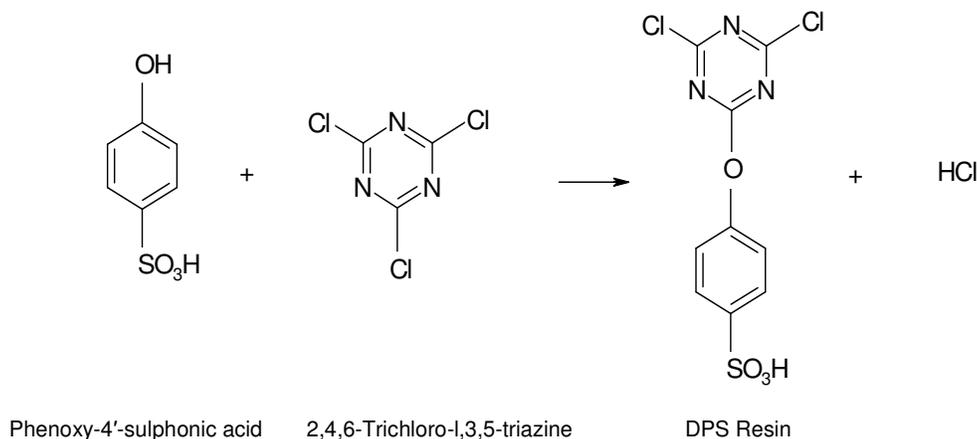


Figure 1. Synthesis of 2,4-Dichloro-6-(Phenoxy-4'-Sulphonic acid)-1,3,5-triazine (DPS Resin).

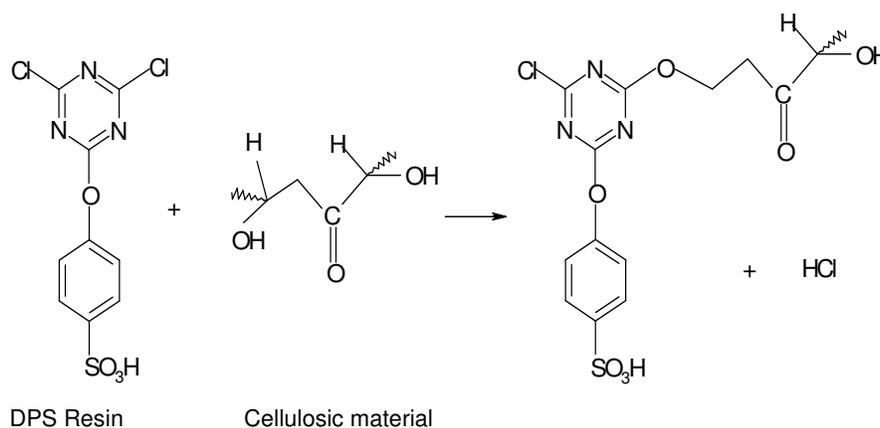
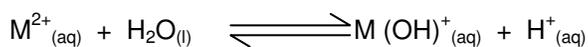


Figure 2. Mechanism for DPS resin coupling.

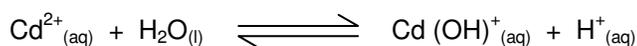
residue was able to bind 63.5% of Mg^{2+} , while orange mesocarp residue bound 56% of Mg^{2+} .

In the case of Cd^{2+} , the difference is not very significant (cf 85.05 and 86.45%). The higher percentage removal may be as a result of hydrolysis of the metal. The hydrolysis of most divalent metal ions can be written as follows:



where M^{2+} could be any divalent metal.

Thus for Cd^{2+}



The monovalent cations $[M(OH)^+]$ and protons generated by this reaction could contribute to the increased acidity of M^{2+} solutions. If $M(OH)^+$ species attach to the biomass, more H^+ will be produced. Hence, the solution becomes more acidic as was evident in the Cd^{2+} solution

mixture (pH 5). The presence of sulphonyl acid group ($-SO_3H$) on the modified biomass could also enhance the acidity of the M^{2+} solution. It could therefore be suggested that $Cd(OH)^+$ was probably adsorbed on the biomass. Hence the percentage removal of Cd^{2+} was the highest in both modified orange mesocarp residue and orange mesocarp residue. Binding unto the substrate depends on the metal ion type and the level of modification.

These results indicate that both modified and unmodified orange mesocarp residue have the capacity to remove metal ions from aqueous solution, and the amount of the metal ions bound by cellulosic substrate depends on the metal ion type and the level of the modification.

Conclusions

Orange mesocarp residue has been shown to be capable of binding several metals ions such as Zn^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} and Mg^{2+} . Metal ion binding was efficient, indicating

that the metal ions were probably adsorbed to the cell walls of the biomass. Chemical modification of the orange mesocarp residue with DPS resin increased the acidity of the solution because of the introduction of sulphonic acid group. This condition favoured the removal of Mg^{2+} in solution. The modification caused a steric hindrance on the adsorption of Zn^{2+} , Cu^{2+} and Pb^{2+} thereby reducing the amount of metal adsorbed while there was no significant change for Cd^{2+} .

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