



Original Paper

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Effect of particle size on adsorption of heavy metals using chemically modified and unmodified fluted pumpkin and broad-leafed pumpkin pods

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ABSTRACT

The effect of particle size on the bioremediation of Pb(II), Zn(II), Cd (II) and Hg(II) ions from synthetic aqueous effluents using unmodified and carboxymethylated fluted pumpkin and broad-leafed pumpkin pods was investigated in a batch system. 1.2 g of adsorbents was used in each sorption experiment at 25 °C and pH 6.5-8.5 for one hour interval. The results showed that the two adsorbents were good for the removal of these metal ions. Unmodified fluted pumpkin pod was found to be better than the other tested adsorbents with removal efficiencies of 92.62%, 81.88%, 75.21% and 49.67% for Pb (II), Zn (II), Cd (II) and Hg (II), respectively. Carboxymethylation decreased the adsorption capacity of the cellulose materials mostly for fluted pumpkin pod. Particle size below 600 µm was found to be the optimum size for unmodified adsorbent, while 600-1000 µm was observed for modified adsorbent. Fluted pumpkin pod was found to be a more effective adsorbent for these metal ions than the broad leafed pumpkin pod especially when unmodified. Therefore these results show that fluted pumpkin and broad-leafed pumpkin pods could serve as very good adsorbents in the treatment of these metal ions from aqueous effluents.

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Keywords: agricultural waste, bioremediation, heavy metals, pollution control, surface chemistry.

INTRODUCTION

Environmental pollution problems caused by heavy metals cannot be over emphasized. Heavy metals are very toxic and pose a threat to man and the environment. High concentration of heavy metal in the environment can be detrimental to a variety of living species (Onundi et al., 2010). Some heavy metals normally occurring in nature are not harmful because they are only present in very small amounts. Living organisms require trace amounts of some of these heavy metals including iron, cobalt, copper, manganese, molybdenum, vanadium, strontium and zinc but excessive levels can be detrimental to the

organisms (Ikhuoria and Omonmhenle, 2006). Whereas, other heavy metals such as mercury, lead, and cadmium have no known vital or beneficial effect on living organisms, their accumulation in the environment causes serious environmental and ecosystem imbalance, hence results to different kinds of adverse health conditions (Issabayeva et al., 2007; Onundi et al., 2010) Carcinogenesis, kidney damage, neurological disorder, blindness, damage to aquatic resources, nervous disorder, and so on are some of the problems caused by these bioaccumulating and non-biodegradable heavy metal pollutants. It has been reported that excessive

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DOI : <http://dx.doi.org/10.4314/ijbcs.v7i2.40>

ingestion of these metals by humans can cause accumulative poisoning, cancer, nervous system damage and ultimately death (Issabayeva et al., 2007).

Therefore, the elimination of heavy metals from the environment is important as a result of their high toxicity and at least to protect public health (Abdel-Ghani and El-Chaghaby, 2007; Abdel-Ghani et al., 2009; Resmi et al., 2010). Many researchers have reported the removal of these heavy metals using several physicochemical methods such as chemical precipitation, evaporation, ion exchange, and reverse osmosis (Ikhuoria and Omonmhenle, 2006). However, these conventional technologies appear to be inadequate and expensive. Over the last few years sorption have been shown to be an economically feasible alternative method for removing metal ions (Uzun and Güzel, 2000; Qadeer and Akhtar, 2005; Onundi et al., 2010; Okoye et al., 2010).

As a result of the toxic effects of heavy metals and the disadvantages of conventional methods of removal, a great deal of interest in the research for the removal of heavy metals from industrial effluents (or other sources) have focused on the use of agricultural by-products as adsorbents. The sorption of heavy metal pollutants using agricultural waste is an innovative method which has attracted a lot of attention in the past few years to control and detoxify heavy metal pollutants. Some of the agricultural by-products that have been reported includes maize cob and husk (Igwe and Abia, 2003, 2005; Opeolu et al., 2009), maize tassel (Zvinowanda et al., 2009), sawdust (Urik et al., 2009; Kaczala et al., 2009; Vinodhini and Das, 2009, 2010), cassava waste (Horsfall et al., 2003), coconut fiber (Igwe et al., 2007, 2011), cocoa pod husk (Igwe et al., 2011), boiler fly ash (Okoronkwo et al., 2008). Fluted pumpkin have been reported as an adsorbent for heavy metal ions from aqueous solutions (Ikhuoria and Omonmheale, 2006; Okoye et al., 2010).

Also, several parameters have been investigated as factors in adsorption studies, such as effect of initial concentration of adsorbates, effect of contact time of sorption, and so on. Therefore, in this work, we report

on the effect of particle size of adsorbent on the sorption capacities of modified and unmodified fluted pumpkin and broad-leafed pumpkin pods.

MATERIALS AND METHODS

Materials

Fluted pumpkin (*Telfairia occidentalis*) and broad-leafed pumpkin (*Curcubita* sp.) pods were collected from a local farm in Isiala Ngwa south, Abia State, Nigeria and was properly identified at the Department of Plant Science and Biotechnology, Abia State University, Uturu, Nigeria. Lead nitrate ($Pb(NO_3)_2$); mercury (II) chloride ($HgCl_2$) 98%; hydrated zinc sulphate ($ZnSO_4 \cdot 7H_2O$) 99% and hydrated cadmium chloride ($CdCl_2 \cdot 2H_2O$) 99% were used to prepare the respective metal ions solutions. All chemicals used were analytically grades, purchased and used without further purification.

Methods

Adsorbent preparation

The adsorbents were washed, cut into small pieces, air dried and powdered in a grinder. The meal obtained were air-dried and each was first sieved through 1200 μm mesh; secondly through 850 μm ; thirdly through 600 μm and then through 400 μm size. The meal retained between the particle size ranges of 1200-850 μm , 850-600 μm and 600-400 μm was used. Each of them was soaked in dilute acid solution (HNO_3 , 2% v/v) for 24 hrs at room temperature. After that, each of the adsorbents were rinsed with deionized water, air-dried and divided into two parts, one part was stored for use and the second part was modified by carboxymethylation.

One portion of the activated adsorbents was modified by carboxymethylation (Ragheb et al., 1989). 100 g of the adsorbent were added to a mixture of 650 ml ethyl alcohol and 554 ml toluene, a 50% solution of sodium hydroxide (33 ml) was added in 1 min and followed by gradual addition of 25 g of monochloroacetic acid. The reaction mixture was kept at 65 °C for 70 min with agitation and left over night. The excess sodium hydroxide solution was neutralized with glacial acetic acid. The carboxymethylated

adsorbents were filtered, washed with ethyl alcohol and purified by extraction with ethyl alcohol.

Sorption of metal ions

The sorption of the metal ions was carried out with initially prepared concentration of 100 mg/l of the metal ions (Pb (II), Zn (II) Cd (II) and Hg (II)) solutions. It was put into reagent bottles containing 1.2 g of adsorbent. The reagent bottles were corked and constantly shaken in a rotary shaker for 1 hr at pH of 7.5 and temperature of 25 °C. Thereafter, the contents of the reagent bottle were centrifuged at 3500 rpm and the supernatant rapidly filtered through a Whatman No. 41 filter paper into sample bottles for analysis. The same procedure was used with all the four metal ions solutions with modified and unmodified adsorbent of the different particle sizes. The metal ion contents of all the filtrates, the four initial prepared concentrations of metal ions solutions and blank metal ions solutions without the adsorbents, were analyzed with the aid of an Atomic Absorption Spectrophotometer (AAS) UNICAM 919 model. The concentrations of each metal ions adsorbed by each adsorbent were calculated from the difference between the analyzed initial metal ion concentration of each prepared metal ion solution (C_o) and the concentration after adsorption (C_e).

The soaking of the adsorbent in 2% (v/v) nitric acid served to activate the adsorbent and wash of any soluble biomolecules that may interfere with adsorption process. The amount of metal ions adsorbed was calculated by a modified mass balance equation as follows (Chu and Hashim, 2001; Ho and Wang, 2004): $q_e = V(C_o - C_e)/m$ (1) where q_e is the equilibrium amount adsorbed (mg/g); C_e is the equilibrium amount (mg/l) remaining in solution; C_o is the initial concentration (mg/l) of metal ion solution; V is the volume (ml) of metal ion solution used and m is the mass (g) of adsorbent used. Then, the percentage of the metal ions adsorbed was

calculated from the equation below:
 $\%q_e = 100 \times (C_o - C_e)/C_o = 100 \times q_e/C_o$ (2)

The prepared stock solutions of the metal ions were analyzed and the initial concentration of the metal ion solutions (C_o mg/l) of Pb(II) Zn(II) Cd(II) and Hg(II) was found to be 92.50 mg/l, 89.87 mg/l, 93.25 mg/l and 94.35 mg/l respectively. The difference between the 100 mg/l prepared and the values obtained above may likely be due to impurities in the individual metal salts, the sensitivity of the AAS or the error in weighing and preparing the stock solutions. The percentage amount adsorbed ($\% q_e$) was calculated from the initial (C_o) and final (C_e) concentration analyzed using AAS.

RESULTS

The effect of particle size on adsorption of the metal ions onto the adsorbents, unmodified fluted pumpkin pods (UFPP), unmodified broad leafed pumpkin pods (UBLPP), modified fluted pumpkin pods (MFPP) and modified broad leafed pumpkin pods (MBLPP), are shown in Figures 1- 4 respectively. The particle size varies with surface area, and with the number of micropores. Since sorption is particle diffusion controlled, the increase in micropore increases the number of accessible sites, hence increases the amount adsorbed.

The amounts adsorbed follow the order 400-600 > 600-850 > 850-1200 μm for unmodified adsorbents with few variations. Pd(II) ions were adsorbed more on UFPP of particle size 400-600 μm . For the modified adsorbent, Zn (II) was adsorbed more than the other metal ions. For modified adsorbents, the amount of metal ions adsorbed follow the order Zn (II) > Pb(II) > Cd(II) > Hg(II), while for the unmodified adsorbents the trend is Pb(II) > Zn(II) > Cd(II) > Hg(II). The results indicated that the amount adsorbed by each individual particle size showed that 400-600 μm particle size give optimum condition for effective adsorption on unmodified adsorbent, while for the modified adsorbent; 850-1200 μm particle size gave higher sorption capacity.

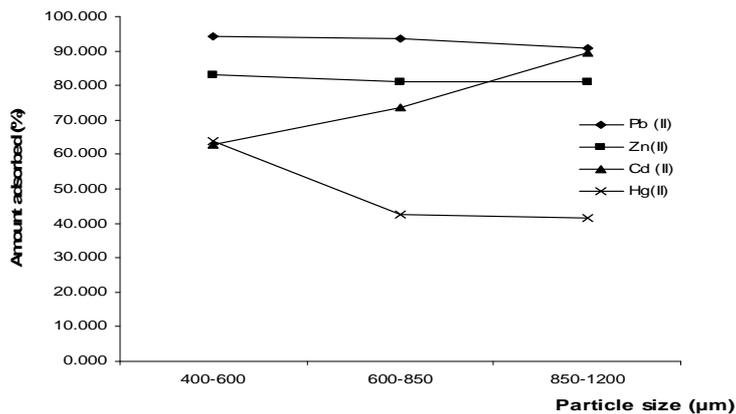


Figure 1: Percent adsorbed % against particle size (μm) for adsorption of Pb (II), Zn (II), Cd (II), and Hg (II) onto unmodified fluted pompkin pods (UFPP).

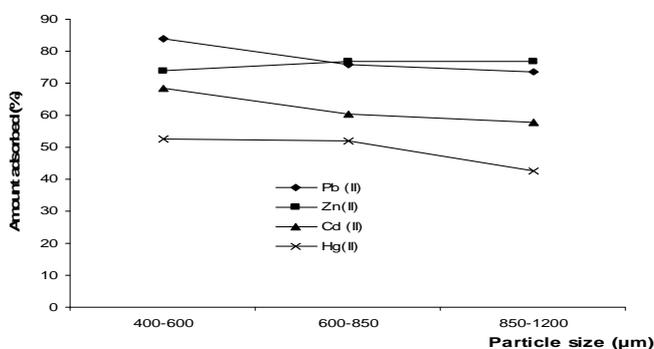


Figure 2: Percent adsorbed % against particle size (μm) for adsorption of Pb (II), Zn (II), Cd (II), and Hg (II) onto unmodified broad leafed pompkin pods (UBLPP).

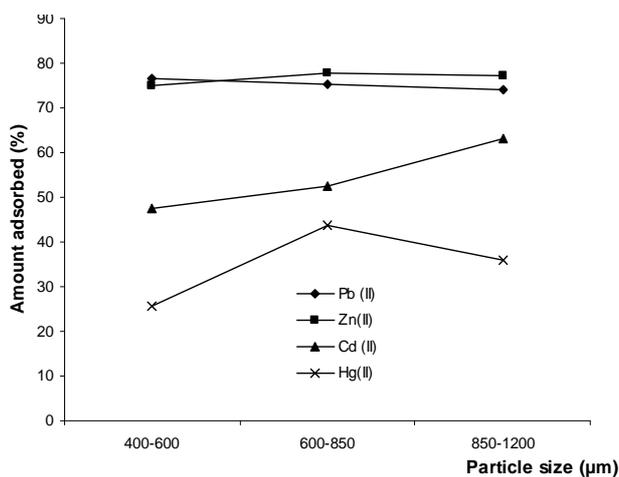


Figure 3: Percent adsorbed % against particle size (μm) for adsorption of Pb (II), Zn (II), Cd (II), and Hg (II) onto modified fluted pompkin pods (MFPP).

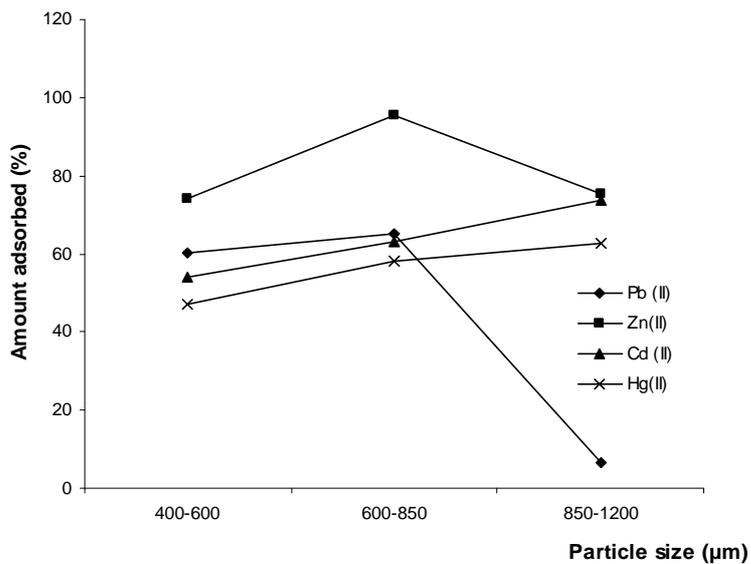


Figure 4: Percent adsorbed % against particle size (µm) for adsorption of Pb (II), Zn (II), Cd (II), and Hg (II) onto modified broad leafed pompkin pods (MBLPP).

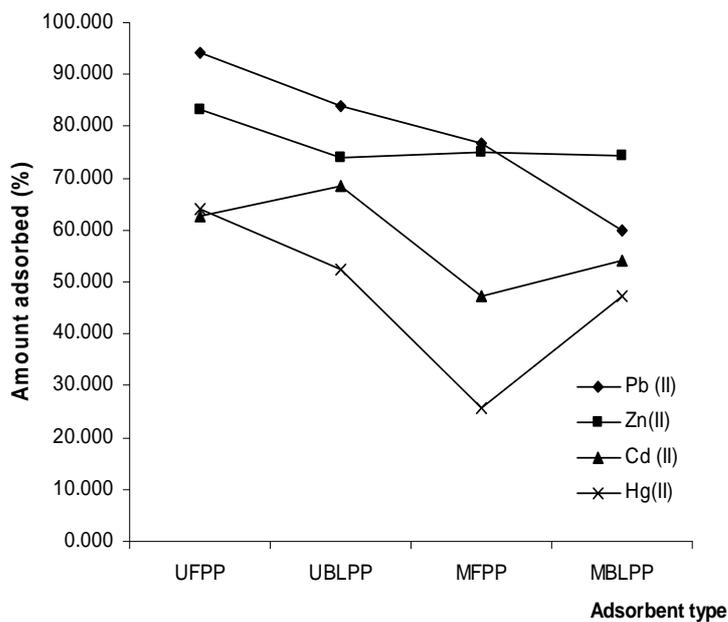


Figure 5: Percent adsorbed % for adsorption of Pb (II), Zn (II), Cd (II), and Hg (II) onto the different adsorbent types for particle size of 400-600 µm.

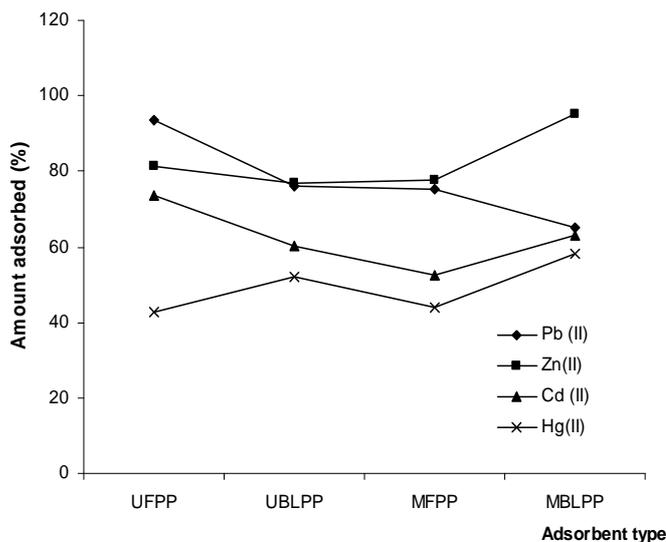


Figure 6: Percent adsorbed % for adsorption of Pb (II), Zn (II), Cd (II), and Hg (II) onto the different adsorbent types for particle size of 600-850 µm.

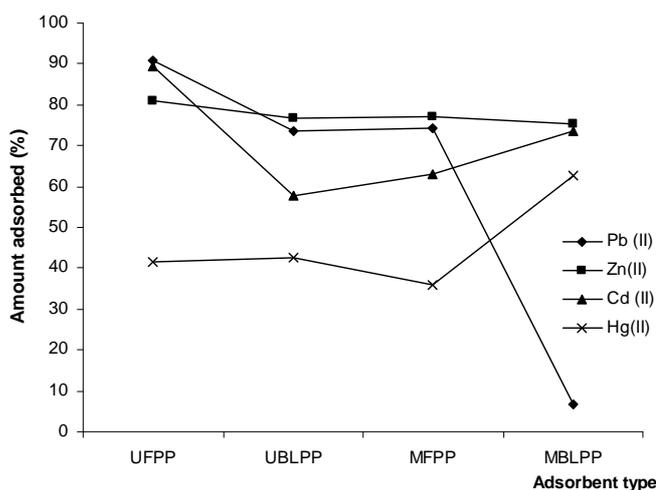


Figure 6: Percent adsorbed % for adsorption of Pb (II), Zn (II), Cd (II), and Hg (II) onto the different adsorbent types for particle size of 850-1200 µm.

DISCUSSION

The differences in the adsorption of the metal ions from aqueous solutions have been ascribed to some factors (Ho et al., 1995): (i) sizes of metal ions, (ii) affinity of the metal ions for some active groups on the biomass and (iii) nature of anions of the salt of the metals. It could be seen from the results of this work that the interplay of these factors has not produced a common trend for the

metal ions on the adsorbents. The effect of particle size on adsorption of the metal ions from aqueous solutions has been reported by previous workers (Kuyucak and Volesky, 1989; Yang and Volesky, 1999). Eneida et al. (2002) reported that the size grading of ground biomass particles by standard sieves works on the length and width dimensions. Hence, the result of opposite trends on particle size effect. Similar to the results of this work,

it has been found that smaller particle sizes gave higher adsorption capacities (Ho et al., 2002; Saueprasearsit et al., 2010). This may be attributed to the higher external surface available with smaller particles at a constant total mass.

Besides adsorption at the outer surface of the adsorbent, there is also the possibility of intraparticle diffusion from the outer surface into mass transfer, which is greater for large particles. As a result of various factors, such as diffusion part length or mass transfer resistance, contact time and blocked sections of the particle may not be utilized for adsorption, therefore, the adsorption capacity of large particles may be low (Romero-Gonzalez et al., 2001; Shukla et al., 2002; Ngeontae et al., 2007).

For effect of modification on the sorption processes, Figure 5 shows the percent adsorbed versus the different adsorbents for particle size of 400-600 μm while Figure 6 and Figure 7 shows that for particle size of 600-850 μm and 850-1200 μm respectively. It could be seen that modification by carboxymethylation decreased the adsorptive capacity of the adsorbents. Modification of adsorbent has been reported to alter the surface characteristics of the adsorbent (Horsfall et al., 2003; Chen and Yang, 2005). Although most modifications are known to improve the sorption capacity of the adsorbent, some modifications result in masking or inhibitory tendencies and thereby reduce the sorption capacity. Therefore, the modification of the adsorbent by carboxymethylation which introduced the group $-\text{COCH}_3$ onto the surface of the adsorbent reduced the sorption capacity. The reduction in the amount adsorbed as affected by modification means that the carboxymethyl group blocks some of the micro pores, making it difficult for the metal ions to reach the adsorption sites. This is similar to the result obtained with maize cob and husk (Igwe et al., 2005). Other modification methods have also been reported such as; EDTA (Igwe and Abia, 2007), thiolation (Abia and Asoquo 2006; Akaninwor et al., 2007; Igwe et al. 2008), formaldehyde, glutaraldehyde and HCl (Chen

and Yang, 2005), Urea and ferric Fe (III) oxhydroxides (Urik et al., 2009).

Conclusion

Fluted pumpkin and broad leafed pumpkin pods are all agricultural wastes and cause environmental pollution. They have been found to be good adsorbent for the removal of Pb^{2+} , Cd^{2+} , Zn^{2+} and Hg^{2+} from aqueous effluents. It was seen that modification by carboxymethylation decreased the adsorptive capacity of the cellulose materials mostly in fluted pumpkin pod. Also when unmodified, the adsorbent with particle size 400-600 μm adsorbed more but when modified, the particle size of 850-1200 μm adsorbed more. Furthermore, fluted pumpkin pod is more effective than broad – leafed pumpkin pod especially when unmodified. This was attributed to its high degree of micropores and very low weight per volume ratio. The increasing order of adsorbitivity based on each particular metal ion is as follows:

Pb (II) ion: UFPP> UBLPP> MFPP> MBLPP

Zn (II) ion: UFPP> MFPP> UBLPP> MBLPP

Cd (II) ion: UFPP> MPLPP> UBLPP> MFPP.

Hg (II) ion: MBLPP> UFPP> UBLPP> MFPP. Therefore, this innovative method of detoxifying/treating non-biodegradable pollutants (heavy metals) is found to be a good means of getting rid of heavy metal bearing effluent and that particle size affected the sorption capacity.

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