Full Length Research Paper

Adsorption of metal ions by dye treated cassava mesocarp

G. O. Agiri[1]* and O. Akaranta[2]

[1]Industrial Safety and Environmental Technology Department, Petroleum Training Institute, Effurun, Delta State, Nigeria.
[2]Department of Pure and Industrial Chemistry, University of Port Harcourt, Port Harcourt, River State, Nigeria.

The ability of dyed cassava mesocarp to remove Cu (II) and Zn (II) ions from single ion solutions (10 mg/l) has been studied. The experiments were carried out using dyed cassava mesocarp (1.0 g). The amount (mg/g) of Cu (II) adsorbed by dyed cassava mesocarp of different particle sizes 0.40 mm (DCMI) and 0.63 mm (DCMII) at the contract time of 30 min was 389 and 248.5 respectively. The amount (mg/g) of zinc (II) adsorbed by DCMI and DCMII was 45.5 and 28.5 respectively. Furthermore, the residual amount of the metal ions solution decreased as the time of agitation increased. This results show that the dye-treated cassava mesocarp (1.0 g) has the ability to remove metal ion from aqueous solution. The modification of the adsorbent as a result of dyeing with reactive dye was helpful in the removal of metal ion from aqueous solution.

Key words: Adsorption, dyed cassava mesocarp, particle sizes, contacts time.

INTRODUCTION

The investigation on the use of agricultural by-products for the removal of heavy metals from aqueous solutions has been on the increase. Some of the reasons for the use of these waste materials are that; they are available at little or no cost, naturally occurring, stable and require minimum care or maintenance. Metal ions produced and released during industrial activities may pose a serious threat to the environment. These metal ions when present in sufficient quantity can be harmful to aquatic life and human health. Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of fresh water and marine environment (Balkose and Baltacioglu, 1992).

Several studies have been carried on the use of modified agricultural products for adsorption of heavy metal from aqueous solution such as; modified chitosan (Saucedo et al., 1993); walnut waste (Randall et al., 1974); peanut skin (Randall et al., 1975, 1975a); cotton (Kumar and Dara, 1982); coffee grounds (Macchi et al., 1986); apple waste (Maranon and Sastre, 1991); wool fibre (Balkose and Baltacioglu, 1992); green algae and rice hull (Rey et al., 1993); cotton seed hulls (Marshall and Champagne, 1995); linseed flax straw (Taylor et al.,

1994); cotton stalk and apricot seed (Kahraman et al., 2008); barks of trees and other cellulosic materials. Recently, more effort has been put to develop new adsorbents and improve existing ones like: cassava waste (Horsfall et al., 2003); Chitosan (Karthikeyan et al., 2004); modified coconut pollen grains (Agiri et al., 2007).

In Nigeria, the annual production of cassava tuber is on the increase as it constitutes one of the major staple foods and presently being cultivated for the production of biofuels. Consequently, large quantities of cassava wastes are produced and may constitute environmental nuisance as a result of lack of proper disposal of the wastes. And until the present work cassava wastes have not been put into important use. Conversion of these low value cassava wastes into adsorbent that can remove toxic and valuable metals from industrial wastewater would increase their market value and ultimately benefit the million of cassava starch, garri and foo-foo producers.

The objective of the present study is to produce dyed cassava mesocarp (adsorbents) from dyeing cassava mesocarp with reactive dyes, examine the adsorption of heavy metal on dyed cassava mesocarp and determine the suitability of cassava mesocarp treated with reactive dyes as adsorbents for heavy metals such as copper and zinc, elucidate the mechanisms of heavy metal adsorption on the dyed cassava mesocarp.

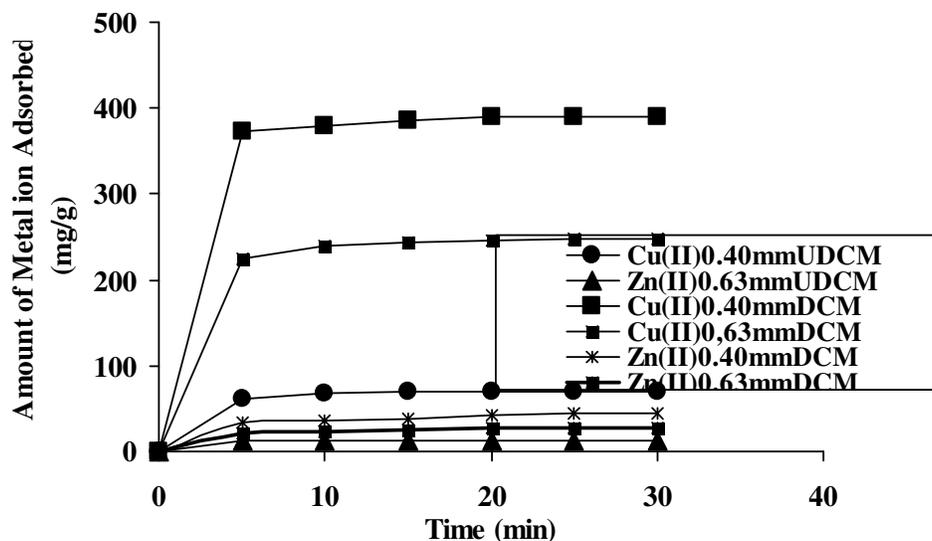*Corresponding author. E-mail: otasgiri@yahoo.co.uk.

Figure 1. Plot of contact time against adsorption of Cu (II) and Zn (II) ions form 10 mg/l aqueous solution on dyed cassava mesocarp.

MATERIALS AND METHODS

Cassava mesocarp utilized for this study was obtained from cassava mill factory in Effurun, Nigeria. The epicarps of the peels were carefully removed and the mesocarp thoroughly washed with water and then reduced to chips. The chips were air dried for five days and stored in a polyethylene bag. The dried cassava mesocarp chips were reduced to powder using a manual grinding mill. The resultant product (powder) was sieved to obtain 0.40 and 0.63 mm particle sizes, stored in plastic containers and labeled as undyed cassava mesocarp (UDCM). About 20 g each of these were dyed with a reactive dye (2,7-napthalene disulphonic acid-5-[(4,6-dichloro 1, 3, 5-triazine-2-yl)amino]-4-hydroxyl-(1,3-disulpho-7-napthalenyl) azo-tetra sodium salt), according to the method given by Suemitsu et al. (1986) and adopted by Agiri et al. (2007) and labeled dyed cassava mesocarp (DCMI and DCMII.) respectively. All the chemicals including copper nitrate, zinc sulphate, sodium chloride, hydrochloric acid and sodium carbonate employed for the analysis were AnalaR high purity grade and used without further purification. The experiments were performed using distilled ionized water. From the stock solution containing 1000 mg/l of copper ions and 1000 mg/l of zinc ions, volumes of the adsorbate containing 20 mg/l of copper and zinc ions were prepared. All batch experiments were performed at a temperature of 30 °C on a gyratory shaker at 200 rev/min. The adsorption studies were conducted by placing one gram of dyed cassava mesocarp in 250 ml stopper Erlenmeyer flasks. This was followed by the addition of 50 ml pre-determined metal ion stock solution containing 10 ppm copper and zinc solutions. The flask was then shaken for a given time interval in vibratory shaker. At the end of the shaking period the solution was filtered through a glass wool at preset time intervals (5 min) and the residual metal ion concentrations were measured using the Buck scientific atomic absorption/emission spectrophotometer 200 A.

The amount of metal ion adsorbed on the adsorbent was com- computed using the following equation:

$$q_e = \frac{(C_i - C_t)v}{m}$$ (1)

Where q_e = the amount of adsorbate adsorbed on adsorbent after adsorption at time, t per unit mass of adsorbent (mg adsorbate/g adsorbent)

C_i = initial concentration of adsorbate in solution, mg/l

C_t = concentration of adsorbate in solution after adsorption time t, (mg/l)

v = volume of liquid in the reaction vessel, l.

m = mass of adsorbent, g.

RESULT AND DISCUSSION

Effect of particle size on metal ion adsorption on dyed cassava mesocarp

The adsorption rate of metal ions on the dyed cassava mesocarp (0.40 and 0.63 mm) is as illustrated in Figure 1 and the values are given in Table 1. It is evident from the table that the concentration of metal ion adsorbed increased with a decrease in the particle size of the DCM explaining the increased adsorption rate with small dimensions which is attributable to the availability of more specific surface area on the adsorbent.

According to Weber and Morris (1963) the breaking of larger particles tends to open tiny cracks and channels on the particle surface of the material resulting in more accessibility to better diffusion, owing to the smaller particle size.

Therefore, the different particle sizes have different removal abilities as 0.40 mm, particle size showed highest removal ability for metal ion than 0.63 mm.

Time dependency experiment

Figure 1 shows a plot of contact time against metal ions adsorbed by the different type of the dyed cassava mesocarp. This plot represents the adsorption efficiency of the metals on various adsorbents. As can be seen, the adsorption curves exhibit initially a linear portion followed

Table 1. Effect of contract time on metal adsorption on dyed cassava mesocarp.

Time (min)	UDCM		Dyed Cassava Mesocarp			
	Cu(II)mg/g	Zn(II)mg/g	Cu(II)mg/g		Zn(II)mg/g	
	0.40mm	0.63 mm	DCM I	DCM II	DCM I	DCM II
0	0	0	0	0	0	0
5	63	12	372.5	224	34	21
10	67.5	12	379	238.5	36.5	23.5
15	70	12	385	243	39	24.5
20	70	12	389	246.5	41.5	27.5
25	70	12	389	248.5	45.5	28.5
30	70	12	389	248.5	45.5	28.5

UDCM = Undyed cassava mesocarp, DCM = Dyed Cassava Mesocarp, initial concentration of copper solution = 10 mg/l.

Table 2. Residual concentrations of Cu (II) and Zn (II) ions adsorbed on Dyed cassava mesocarp.

Time (min)	UDCM		Dyed Cassava Mesocarp			
	Cu(II)mg/g	Zn(II)mg/g	Cu(II)mg/g		Zn(II)mg/g	
	0.40mm	0.63 mm	DCM I	DCM II	DCM I	DCM II
0	0	0	0	0	0	0
5	437	488	127.5	276	466	479
10	432.5	488	121	261.5	463.5	476.5
15	430	488	115	257	461	475.5
20	430	488	111	253.5	458.5	472.5
25	430	488	111	251.5	454.5	471.5
30	430	488	111	251.5	454.5	471.5

by plateau region at longer times. This shows that the adsorption of metal ions on the DCM I and DCM II was fast for the first 5-10 min depending on the types of metal ions adsorbed on a given dyed cassava mesocarp and equilibrium was attained in different times at which peak adsorption reached its maximum value.

By comparing the results of the experiments presented in Figure 1 show that the adsorption efficiency is dependent on the type of metal. These values represent the amount of Cu (II) and Zn (II) adsorbed on the adsorbents as a function of increasing time. The overall adsorption behaviours of Cu (II) on the adsorbent were similar with differences in the amounts adsorbed. The amounts of Cu (II) ions (mg/g) adsorbed on UDCP, DCMI and DCMII (1.0g) in 5 min were: 63, 375.5 and 224 respectively. This increased to the following amounts (mg/g), 70, 389 and 248.5 in 30 min. It can be shown that the adsorption rate of Cu (II) on DCM I and DCM II was fast and in five min, 375.5 mg/g of Cu (II) was adsorbed compared to 63 mg/g adsorbed on UDCP from aqueous copper (II) solution of initial concentration, 10 mg/l. The amount of Zn (II) ions (mg/g) adsorbed in 5 min on UDCM, DCMI and DCMII (1.0g) were: 12, 34 and 21 respectively. This increased to the following amount 12, 45.5 and 28.5 in 30 min.

The experimental results show that the removal rate of Cu (II) and Zn (II) ions from the solution by the dyed cassava mesocarp occurs quickly, seemly reaching equilibrium within the first 5 min. This can be explained in terms of dying with reactive dyes which help in modifying the adsorbent by the introduction of sulphonic acid groups. Therefore, adsorption by the dyed cassava mesocarp depended on its properties such as the hydrophilicity of the sulphonic acid groups, high cross linking of the adsorbents structure afforded by dyeing and eases of displacement of the counter hydrogen ion. Therefore, removal of metal ions by dyed cassava mesocarp could be due to two different sorption processes, a fast ion exchange followed by chemisorptions as suggested by (Low et al., 1993) in their earlier work on dye-treated oil-palm fibres.

In general, the dyed cassava mesocarp adsorbed more Cu (II) and Zn (II) than the undyed cassava mesocarp. Therefore, the series of batch experiments showed that dyed cassava mesocarp has the ability to bind metal ions and remove them from solution remaining after adsorption.

Table 2 and Figure 2 shows the amount of the residual concentration of the metal ion solution remaining after
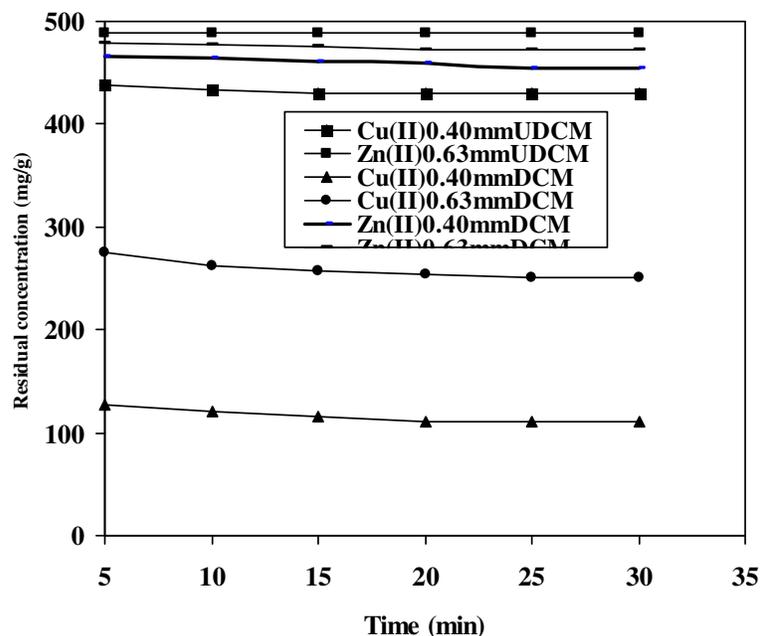
Figure 2. Plot of residual concentrations of Cu (II) and Zn (II) ions adsorbed on dyed cassava mesocarp.

Table 3. Copper (II) ion initial concentration after adsorption.

Cu (II) Ion initial Concentration (mg/l)	Adsorption in 20 min					
	DCM I (0.40mm)			DCM II (0.40mm)		
	C_t(mg/l)	X(mg/l)	%	C_t(mg/l)	X(mg/l)	%
5	2.08	2.92	58.4	1.95	3.05	61
10	2.82	7.18	71.8	2.42	7.58	75.8
20	7.29	12.71	63.6	5.69	14.31	71.6
30	14.83	15.17	50.6	13.52	16.28	54.9

adsorption. Certain amount of copper and zinc ions were left in the solution after contact with UDCM for 30 min. A significant amount of copper ion was removed hence the lower residual concentration recorded for copper ion after contact with DCM I and DCM II as compared to the zinc ion. Cations with smaller ionic radii Cu (II) 0.071nm, Zn (II) 0.074 nm have greater chance to be adsorbed on cation exchanger (Huheey, 1978; Okiemen et al., 1990). This trend in smaller ionic size was observed for Cu (II) with high percentage adsorption than Zn (II) on other biological adsorbents as earlier reported (Abia et al., 2003; Horsfall et al., 2003). Therefore, the smaller the ionic size the greater its affinity to reactive sites, namely hydroxyl and sulphonic acid groups in the dyed cassava mesocarp. The results show that the adsorption of cations with larger ionic radii would be less likely compared with smaller ionic radii.

Another important factor used in describing the uptake capacity of metal ion on adsorbent is the hydrolysis constant pk_h. Metals with smaller hydrolysis constant pk_h have increasing tendency to hydrolyze because of larger charge size function (Z^2/r) and electronic structure (Huheey,

1983). Charge size values of these metal ions are: Cu (II) = $14.1C^2 m^{-1} \times 10^{28}$ and Zn (II) = $13.7 C^2 m^{-1} \times 10^{28}$. The pk_h values of these metals are: Cu (II) = 7.53 and Zn (II) = 9.60. Therefore, the extent of hydrolysis of these metals indicates that Cu (II) hydrolyzes to a greater extent than Zn (II) indicating a higher binding for Cu (II) than Zn (II).

Therefore, the greater affinity for these metals by dyed cassava mesocarp is attributed to the presence of sulphonic acid groups in the dyed treated adsorbents in addition to the carboxylic, phenolic and hydroxyl group in the natural cellulosic materials. This pattern of sorption was also noted in the sorption experiments using dyed treated palm oil fibre and moss, *Calyperes deleeserta* (Low et al., 1993).

Effects of metal ion initial concentration on Cu (II) adsorption on dyed cassava mesocarp

Table 3 shows the metal ions concentration (C_i), the metal ions concentration after contact (contact time 30 min) with the dyed cassava mesocarp samples (C_t), the
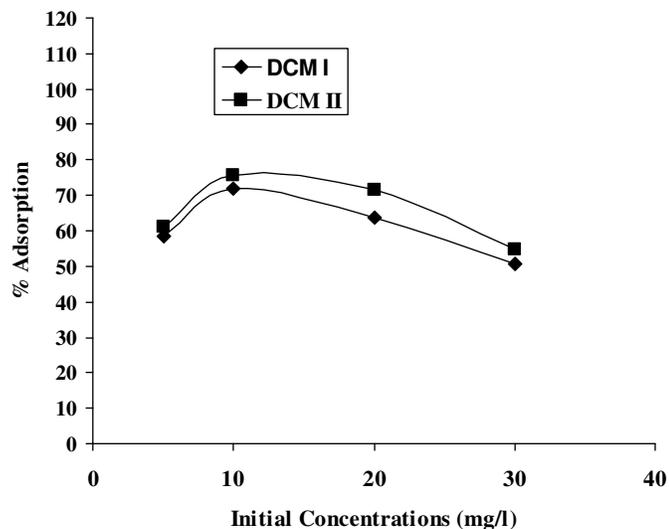
Figure 3. Effect of initial concentration of ion in aqueous solution on Cu (II) adsorption on DCMI and II (0.40 mm particle size).

amount metal ions adsorbed (x), calculated from the difference between the two concentration data. Therefore, the removal efficiency (RE) % Adsorption of the adsorbent is defined as RE (%) = $[(C_i - C_t) / C_i]$ x 100, where C_i and C_t are the initial and concentration of metal ions (mg/l) after contact time t. A plot of initial metal ion concentration against the % adsorption is shown in Figure 3. The result indicates that as concentration of metal ion in aqueous solution increases the amount of ion adsorbed decreases. The result also show that highest amount of metal ions was adsorbed from metal ion initial concentration of 12 mg/l.

Conclusion

In the present study it is observed that an optimum contact period of about eight minutes is required for the maximum removal of zinc (II) by dyed cassava mesocarp. The adsorption mechanism also depends upon the particle size of the adsorbent, contact time, initial concentration of the metal ion. And so, the adsorption of metal ion increases with decrease in particle size. The results obtained in this paper for the mechanisms involved in heavy metal removal can be considered as a fundamental step for the representation of the experimental behavior and for development of process design.

REFERENCES

Abia AA, Horsfall MJnr, Didi O (2003). The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn from aqueous solution. Bioresour. Technol. 90: 345-348.

Agiri GO, Akaranta O, Ajayi IO (2007). Equilibrium and kinetics studies of metal ion adsorption on dyed coconut pollens. Afr. J. Biotechnol. 6 (7): 933-938.

Balkose D, Baltacioglu H (1992). Adsorption of heavy metal cations from solutions by wool fibres. J. Chem. Technol. Biotechnol. 54: 393-397.

Horsfall MJnr, Abia AA, Spiff AI (2003). Removal of Cu (II) and Zn (II) ions from wastewater by cassava (*manihot esculenta cranz*) waste biomass. Afr. J. Biotechnol. 2 (10): 360-364.

Huheey JE (1983). Inorganic Chemistry 3rd ed. Haper International SI Edition Publishers, London, pp. 265-266.

Kahraman S, Dogan N, Erdemoglu S (2008). Use of various argicultural wastes for the removal of heavy metal ions. Int. J. Environment Pollut. 34(1-4): 275-284.

Karthikeyan G Anbalagan K, Muthulakshmi N (2004). Adsorption Dynamics and Equilibrium Studies of Zn (II) onto Chitosan. J. Chem. Sci. 116(2): 119-127.

Kumar P, Dara SS (1982). Utilization of Agricultural Wastes for Decontaminating Industrial/Domestic Wastewaters from Toxic Metals. Agric Wastes, 4: 213-223.

Low KS, Lee CK, Lee KP (1993). Sorption of copper by dye treated oil-palm fibres. Bioresour. Technol. 44: 109-112.

Macchi G, Marami D, Tinivanti G (1986). Uptake of Mercury by Exhausted Coffee Grounds. Environ. Tech. Lett. 7: 431- 444.

Maranon E, Sastre H (1991). Heavy Metal Removal in Packed Beds using Apple Wastes. Bioresour. Technol. 38:39-43.

Marshall WE, Champagne ET (1995). Agricultural By products as Adsorbents for Metal Ions in Laboratory Prepared Solutions and in Manufacturing Wastewater. J. Environ. Sci. Health, part A: Environ. Sci. Eng. 3(2): 241- 261.

Okiemen FE, Okundia E, Ogbeifo PE (1990). Sorption of cadmium and lead ions on modified groundnut (*Arachi hypogen*) husks. J. Chem. Technol. Biotechnol. 51: 97-103.

Randall JM, Garret V, Bermann RC, Waiss AC (1974). Removal and Recycling of Heavy Metal Ions from Waste Solutions. Forest Prod. J. 24(9): 80-84.

Randall JM, Garret V, Bermann RC, Waiss AC (1974). Removal and recycling of heavy metal ions from waste solutions. Forest Prod. J. 24 (9): 80-84.

Randall JM, Hautala E, Waiss AC (1975). Binding of heavy metal ion by formaldehyde polymerized peanuts skins. J. Appl. Polym. Sci. 22: 379-389.

Randall JM, Reuter FW, Waiss AC (1975a). Removal of cupric ion from solution by contact with peanut skins. J. Appl. Polym. Sci. 19. 156-171.

Rey D, Greenlaw PN, Shame BS (1993). Adsorption of Heavy Metals by Green Algae and Ground Rice Hulls. J. Environ. Sci. Health. Part A, 28(1):37-50.

Saucedo I, Guibal E, Roussy J, Roulph C, Le Choirec P (1993). Uranium Sorption by Glutamate Glucan. A Modified Chitosan. Part 1. Equilibrium Studies. Water S.A. 19(2):113-118.

Suemitsu R, Uerishe R, Akashi I, Nakano M (1986). The Use of Dyestuff-treated Rice Hulls for Removal of Heavy Metals from Wastewater. J. Appl. Polymer Sci., I:75-83.