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Removal of Some Metal Ions from Aqueous Solution Using Coconut Coir Dust and Modified Coconut Coir Dust Extract Resins

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Abstract: Coconut coir dust and its modified (carboxylated and sulphonated toluenediisocynate) extract resins (CTR and STR) have been used to remove Pb, Cu, Zn and Ni ions from aqueous solution. The coconut coir dust removed more of these metal ions than the CTR and STR. The adsorption of the metal ions decreased in descending order of Pb>Ni>Cu>Zn for the coir dust, Cu>Pb>Ni>Zn for the CTR while that for STR followed the Cu>Pb≈Ni>Zn. The efficiency of the adsorbents depended on their cation exchange capacities and $pH_{(pzc)}$. The higher the Cation Exchange Capacity (CEC) and $pH_{(pzc)}$ the higher the rate of adsorption of the metal ions. The functional groups on the adsorbents are responsible for metal ion removal include the carboxylic, hydroxyl and sulphonic groups as revealed by their infra-red spectra. Hence, coconut coir dust and its modified extract resins are efficient for the removal of metal ions from aqueous solution.

Key words: Coconut coir dust, modified adsorbents, carboxylated and sulphonated toluenediisocynates, metal ions, Nigeria

INTRODUCTION

Over the years, industrial activities has led to the discharged of unprecedented volumes of waste water and effluents into the environment. The various activities associated with this environmental pollution are mining operations, ore-processing and smelting, urbanization, metal-plating, tanneries and agriculture-related processes (Pagnanelli *et al*., 2002; Puranik and Paknikar, 1997). These contaminants cause unthinkable problems to the ecosystem. Although, some heavy metals are necessary for the growth of flora and fauna, at certain concentration, they become toxic, even to microorganisms. It has been established that various metal ions hinder various enzymes responsible for mineralization of organic compounds to the soil (Uslu and Turkmen, 1987). Also, the effect of heavy metals on man cannot be neglected because of the 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).

There has been serious interest in the removal of heavy metals from contaminated soil and waste water in recent times. A number of technologies have been developed over the years to remove toxic metals from water. Some important technologies include chemical precipitation, reverse osmosis, electrodialysis, electrofloatation, ion exchange and adsorption on activated carbon (Kratochvil and Volesky, 1998; Chong *et al*., 2000; Sud *et al*., 2008). 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 the use of agricultural by-products as adsorbents for the removal of heavy metals from solutions. 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 (Bailey *et al*., 1999; Mckay, 1996; Pollard *et al*., 1992; Abia *et al*., 2002). These agricultural waste materials remove toxic heavy metals from aqueous solution by adsorption, chelation and ion-exchange (Gardea-Torresday *et al*., 1999). The exchange properties of these agricultural by-products can be attributed to the presence of carboxylic, phenolic, hydroxylic cyano groups etc; these functional groups attract and remove metal ions (Abia *et al*., 2002). Coconut coir dust possesses these chemical characteristics apart from being 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. Its performance can further be enhanced by various physical and chemical treatments. Pre-treatments procedures are employed to modify the adsorbent either by removing or blocking the groups or exposing more metal binding sites (Fourest and Volesky, 1996; Park *et al*., 2005; Tsekova *et al*., 2006).

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Coconut coir dust used here is a by-product of the coir processing industry which was discarded as waste in the environment. Large volumes of coir dust are stockpiled at coir processing centers which caused environmental nuisance in Nigeria. The objective of this study is therefore, to develop an inexpensive and effective metal ion adsorbents from coir dust, an agricultural waste which is available in the environment for adsorption process. If such an adsorbent is developed, it may replace the existing commercial adsorbents which are expensive, toxic and environmentally unfriendly.

MATERIALS AND METHODS

Sample collection: Coconut coir dust was obtained from a local processing coir mill in Uyo, Nigeria. It was air-dried for 24 h and in an oven at 60°C to constant weight. The dried coir dust was sieved using 1.00 mm mesh size sieve.

Extraction of tannins from coconut coir dust: The tannin in the coconut coir dust was extracted using acetone. A detailed procedure for this extraction is described by Isreal *et al.* (2011).

Phytochemical screening of acetone extract: About 30 mg of the acetone coir extract was dissolved in 20 mL of deionised water at room temperature with stirring and the resulting solution was used for phytochemical screening (Roux, 1951; Sofowora, 1984).

Modification of tannins extracted from coir dust into resins: The catechin obtained from the coir extract was modified into resins: carboxylated toluene diisocyanate coir (CTR) and sulphonated diisocyanate coir resin (STR), respectively.

Synthesis of the modified coir extracts resins: About 1.445 g coir extract was first dissolved in a minimum quantity of 8.0 mL acetone in a beaker placed on a hot plate and stirred with a magnetic stirrer until the mixture was homogeneous and divided into two potions.

For CTR: To a portion of the homogeneous mixture above was added 0.609 g 4-hydroxybenzoic acid dissolved in acetone. This was followed by a dropwise addition of 1.45 mL of Toluene Diisocyanate (TDI). The mixture foamed and became viscous with evolution of heat (exothermic). The light brown solid formed was allowed to cool and air-dried overnight. The air-dried solid was separated into different particle sizes ranging from (100-106 μm) and stored in air-tight lid containers.

For STR: To the other portion of the homogeneous mixture prepared, dropwisely, 0.65 mL of phenol-4-sulphonic acid was added then 1.45 mL of toluene diisocyanate and stirring was allowed to continue until the mixture foamed and turned brownish and hot then became very viscous. The brownish solid residue formed, being the proposed resin was air-dried overnight. The dried Sulphonated Toluene diisocyanate coir Resin (STR) was separated into different particle sizes ranging from 100-106 μm and stored in air-tight lid container (Fig. 1a, b).

Characterization of coir dust, CTR and STR adsorbents: The coir dust was characterized for moisture, ash, lignin,

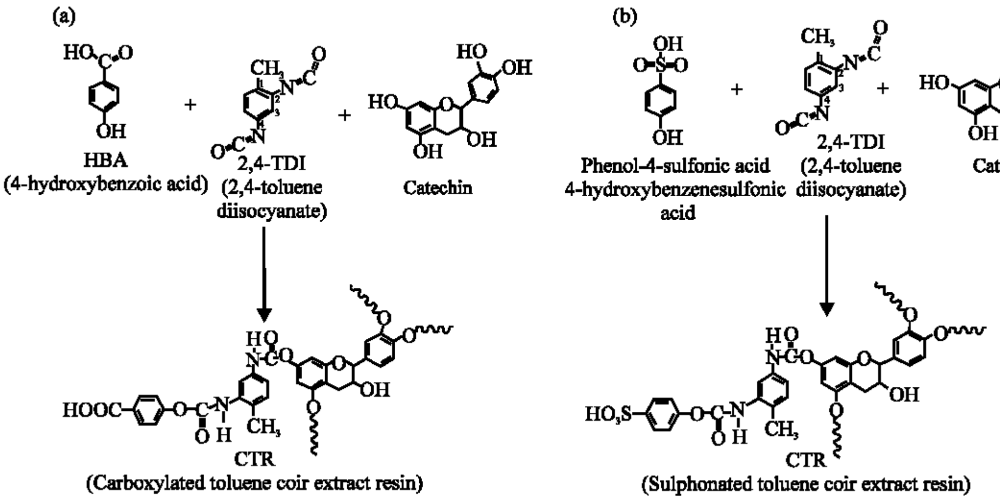

Fig. 1: The formation of CTR and STR and their proposed structures

cellulose contents, pH, cation exchange capacity, degree of swelling, solubility in some solvents according to standard methods (Isreal *et al*., 2011). The CTR and STR were characterized for physical characteristics, solubility in water, cation exchange capacity, zero point charge ($pH_{(zpc)}$), infra red spectroscopy according to standard methods (AOAC, 1975; Tanigami *et al*., 2007; Silverstain *et al*., 1981).

Determination of pH of zero charge (pH_{pzc}): The points of zero charge ($pH_{(zpc)}$) were also investigated to explain the effect of pH of adsorbent adsorption using the method described by Lu *et al*. (2010). About 50 mL of 0.01M NaCl solutions was placed in Erlenmeyer flasks. The initial pHs of the solutions were adjusted to 2, 4, 6, 8, 10 and 12 by adding 0.1M HCl or 0.1M NaOH solutions. The 0.1g of adsorbent was then added to each flask and agitated at 30°C for 48 h and the zeta potential (mV) of the solutions was plotted against the initial pH to obtain the pH at point of zero charge (pH_{pzc}).

Spectroscopic analysis using Infra-Red spectroscopy (IR): Infrared spectroscopy analysis of the coir dust, carboxylated coir extract resin (CTR) and sulphonated coir extract resin (STR) were carried out with KBr pellet using Buck Scientific M500 IR spectrometer.

Preparation of synthetic metal ion solution: The 1.599 g of Pb^{2+} (Pb $(NO_3)_2$, 3.803 g of Cu^{2+} ($Cu(NO_3)_2.3H_2O$, 4.5490 g of Zn^{2+} ($Zn(NO_3)_2.6H_2O$ and 4.951 g of Ni^{2+} (Ni $(NO_3)_2.6H_2O$) were each dissolved in a litre of de-ionized water, respectively. Researching standard solution of 10 ppm of each of these ions was prepared by appropriate dilution.

Removal of metal ions from solution: About 0.2 g each of coconut coir dust and modified coir extract resins (CTR/STR) were soaked in 30 mL of each of the standard solution of metal ions of initial concentration 10 mg L^{-1}. The suspensions formed were agitated for 90 min. The samples were filtered rapidly and the filtrates were analysed using Atomic Absorption/Emission Spectrophotometer (AAES) Model 250. The amount of the metal ions adsorbed was obtained by the difference between the initial metals ion concentration and that of the supernatant.

RESULTS AND DISCUSSION

Phytochemical screening of coir extract: Phytochemical screening of acetone extract of the coir dust presented in Table 1 shows the presence of active ingredients such as tannins, flavonoids, polyhenols and phlobatannins. The presence of tannins of the epicatechin type which are polyphenols have been reported in coir dust (Tejano, 1985; Joseph and Sarma, 1997). Tannins are major polyhydroxy compounds extractable from plants materials, barks, fruits, leaves, seeds and roots using polar, non-polar or mixed solvent systems. These compounds are not pure chemicals with known structures but contain numerous components with phenolic moieties such, as catechol and pyrogallol condensed into a complicated polymeric structure (Kantz and Singleton, 1991). The tannins in coir dust are polymers of primarily flavan-3-ols (catechin and epicatechin) along with anthocyanin pigments. These polymers can be formed through linkages just between the C-4 position and C-8 position of the adjacent epicatechin units (Garro-Galvez *et al*., 1997).

Table 1: Phytochemical screening of acetone extract of coconut (*Cocos nucifera* L.) coir dust

Test	Observation	Inference
Tannins		
Acetone extract filtrate (10 mL)+few drops of $FeCl_3$ reagent	Blue-black precipitate	Tannins present
Filtrate from acetone extract (5 drops)+10 mL of deionized water+3 drops of bromine water	Brownish colour of filtrate was decolorized	Tannins confirmed
Flavanoids		
A few pieces of magnesium ribbon+5 mL of filtrate+3 drops of conc. HCl	Red coloured solution	Flavaniods present
Polyphenols		
Filtrate from acetone extract (1 mL)+2 drops of mixture of 1mL 1%$FeCl_3$ solution with 1 mL of 1% Potassium ferricyanide	Green-blue coloration	Polyphenols present
Phlobatannins		
Filtrate from acetone extract (2 mL) + 1 mL dil. HCl and boiled for 2 min in a test tube	Pale yellow colour	Phlobatannins present
Anthraquinone		
Filtrate from acetone extract (2 mL) + 2 drops of 3% NH_4OH	No red coloration	Anthraquinone absent
Saponnins		
Frothing test: Filtrate from acetone extract (1 mL) shaken vigorously	No formation of lather	Saponnins absent
Emulsion test: Two drops of olive oil were added to the mixture in frothing test above	No emulsion formed	Saponnins absent

Table 2: Characteristics of coir dust and modified coir extract resins

Resins	Appearance	Yield (%)	Melting point (°C)	Cation exchange capacity (Mmol g^{-1})
Carboxylated TDI coir extract resin (CTR)	Brown	65.40	233.234	0.50
Sulphonated TDI coir extract resin (STR)	Dark brown	54.00	220-222	0.25
Coconut coir dust (CD)	Light brown	-	-	2.39
Solubility tests				
Resin	Solubility in cold water	Solubility in hot water		
STR 111	Partially soluble	Sparingly soluble	-	-
STR 112	Partially soluble	Partially soluble	-	-
CTR 111	Partially soluble	Partially soluble	-	-
CTR 112	Partially soluble	Partially soluble	-	-

Characterization of the adsorbents: The coir dust was characterized by standard methods (AOAC, 1975; Browning, 1990; Abad *et al*., 2002) and the results are shown in Table 2. The moisture, cellulose, lignin, ash contents, water and dilute acid (HCl) extractables were 25.20, 365.99, 53.50, 9.00, 28.20 and 41.30%, respectively. Solubility of coir dust in aqueous NaOH solutions 1 and 18% were 27.5 and 41%, respectively while solubility in cold and hot water were 25 and 31%. The pH of the coir filtrate and cation exchange capacity were 6.40 and 2.39 mmol g^{-1}, respectively. The high lignin and cellulose with low ash contents of coir dust are characteristics of agricultural by products generally referred to as lignocellulsoic materials. These findings are in accordance with earlier studies on coir dust (Tejano, 1985; Festin and Jose, 1980; Abad *et al*., 2002). The high lignin and cellulose content of coir dust contributes to its physical stability which does not change markedly with moisture content.

Lignin and cellulose are biopolymers bearing multiple phenolic hydroxyl, carboxyl and amino groups admittedly associated to be responsible for the removal of heavy metals ions and other contaminants from waste water/effluents (Tan *et al*., 1993; Gaballah *et al*., 1997). The low ash content (9.0%) of coir dust suggests that it contain low extractables with little or no waxes or resin when compared with other non-woody lignocellulosic materials such as plantain stem (Umoren *et al*., 2004).

The physical characteristics such as appearance and cation exchange capacity of coir dust, melting points, yield%, cation exchange capacities and solubility test of the synthesized resins are shown in Table 2. The colour of the coir dust, CTR and STR ranges from dark brown to light brown in appearance. The melting point of the CTR was 233-234°C while that of STR was 220-222°C, respectively. The cation exchange capacities (mmol g^{-1}) of the coir dust, CTR and STR were 2.39, 0.50 and 0.25, respectively.

Cation exchange capacity of a resin in the total quantity of metal ions equivalent absorbed per gramme of the resin. The highest exchange capacity of the coir dust (2.39 mmol g^{-1}) compared to those of the coir extract resins-0.50 mmol g^{-1} for CTR and 0.25 mmol g^{-1} for STR is due to number of exchangeable ions which is higher in the coir dust compared to the CTR and STR, respectively. This may be attributed to the fact that coir dust is a lignocellulosic material with lignin and cellulose contents of up to 90% (Benzon and Valesco, 1982) while CTR and STR are non-lignocellulosic being derived from tannin. It has been reported that acetone can only extract tannins which are polyhydroxy compounds from coir dust (Pansera *et al*., 2004; Giner, 1996). The coir dust has more exchangeable sites because of lignin, cellulose and extractables with the CTR and STR which are synthesized from only its extractables. The result also shows that the coir dust, CTR and STR are all partially soluble in water (hot/cold) which indicates their high molecular weight and consequent stability. This makes them useful resins in aqueous medium since stability and partial solubility are essential requirements for material to be used as ion exchangers/adsorbents.

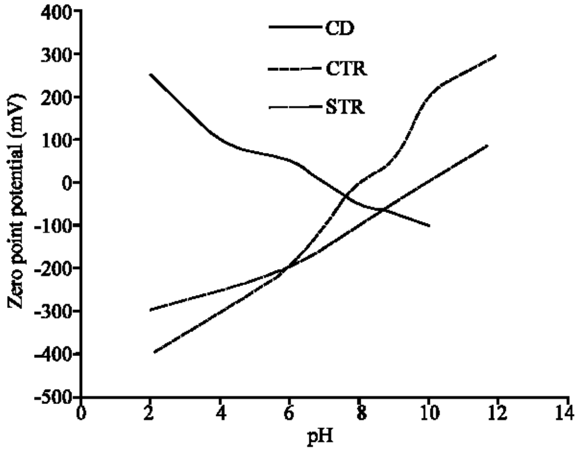

Fig. 2: Plot of zero point potential (mV) versus pH for the three adsorbents coconut coir dust, carboxylated resin and sulphonated resin

pH of zero charge (pH_{pzc}) of the adsorbents: The effect of pH on the cation exchange reaction which can be described in terms of pH_{pzc} of the coir dust, CTR and STR and the metal ions species (Pb, Cu, Zn and Ni) was studied. Figure 2 shows the pH of zero charge of the coir dust, carboxylated and sulphonated coir extract resins.

At the zero point charge (zpc), the surface of the adsorbent/cation exchanger is neutral. At a pH greater than pH_{pzc}, the surface becomes negative and cations are attracted to it and exchanged/adsorbed by the exchanger. However, at pH lower than pH_{pzc}, the surface becomes positive which inhibits the approach of positively charged cations. In this, study the pH_{pzc} were 7.5, 7.8 and 10.5 for the coir dust, carboxylated coir extract (CTR) and sulphonated coir extract resin (STR), respectively. There is a relationship between the pH_{pzc} of adsorbents and their adsorptive capacity (Lu *et al.*, 2010; Adedirin *et al.*, 2011). It was observed from the results that the adsorption of the metal ions were higher at pH values greater than pH_{pzc} of these adsorbents (coir dust, CTR/STR). The coir dust with pH_{pzc} of 7.5 adsorbed more metal ions than CTR with pH_{pzc} of 7.8 while the STR with pH_{pzc} of 10.5 which adsorbed the least. This is in agreement with other finding (Rivera-Utrialla *et al.*, 2003; Borah *et al.*, 2007).

Infrared spectrophotometry: Figure 3-5 show the infrared spectra of the coir dust, carboxylated coir extract resin (CTR) and sulphonated coir extract resin (STR), respectively. These spectra show the presence of adsorption bands for the $OH_{stretch}$ at 3424 cm^{-1} in coir dust, 3310 cm^{-1} in CTR and 3360 cm^{-1} in STR which is indicative of the hydroxyl groups of the polyhydroxy compounds (Sud *et al.*, 2008).

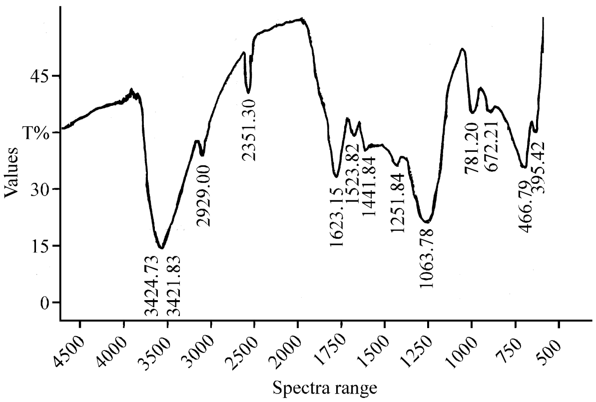

Fig. 3: Infrared spectrum of unmodified coir dust

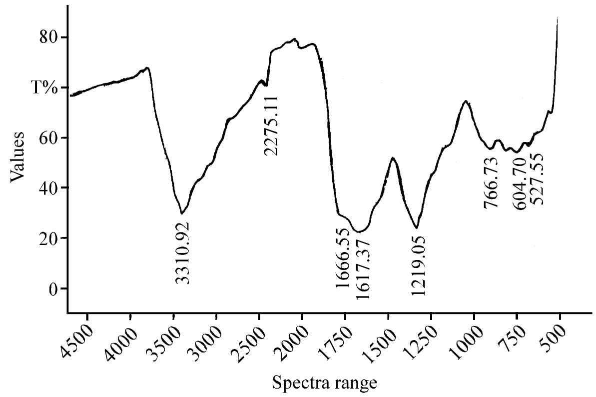

Fig. 4: Infrared spectrum of carboxylated coir extract (CTR)

These carboxylic groups in the compounds are indicated by the bond at 1633 cm^{-1} in coir dust, 1666-1617 cm^{-1} in CTR and 1613 cm^{-1} in STR responsible for metal ion adsorption. The carboxylic group contained other minor group vibrations: $Oh_{stretching}$, $O\text{-}H_{bending}$ and $C\text{-}O_{stretching}$ vibrations (Pavasant *et al.*, 2006). The hydroxyl (-OH) and carboxylic groups (C = O) are believed to be responsible for metal ion binding sites in these adsorbents. The wave bands at 2275 and 2280 cm^{-1} in both the CTR and STR probably arise because of new bonds formed between the coir extract and the crosslinking agent (Toluene Diisocyanate, TDI) resulting in the resin formation from their precursors.

Removal of metal ions by adsorbents: The chemical constituents of coir dust significantly include cellulose, hemicellulose and extractables such as tannins and pectins (Tejano, 1985; Abad *et al.*, 2002). These constituents make coir dust a useful natural ion exchanger because of the presence of the hydroxyl and carboxylic functional groups in the bulk of the material matrix. Table 3 shows the percentage metal ion removal by coir dust and the modified coir extract resins-CTR and STR, respectively. The results show that coconut coir dust bound 99.90% of Pb^{2+}, 95.0% of Cu^{2+}, 85.0% of Zn^{2+} and 96% of Ni^{2+}. Apart from Zn^{2+}, the coir dust adsorbed the

Table 3: Percentage of metal ion removal by coir dust and modified coir extract resins (CTR and STR)

Adsorbent	Pb^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}
Coir dust	99.9	95.0	85.0	96.0
CTR	36.9	44.9	5.1	34.3
STR	21.8	57.0	21.7	15.6

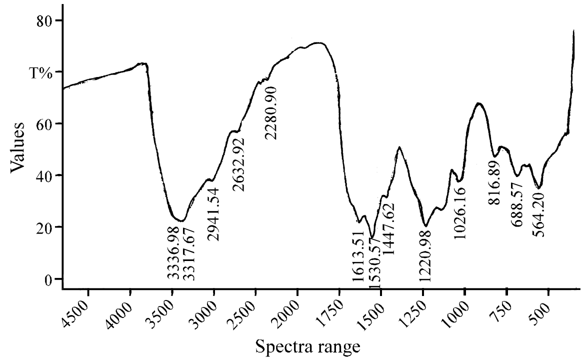

Fig. 5: Infrared spectrum of sulphonated coir extract resin (STR), respectively

other metal ions >90%. In the case of the Carboxylated coir extract resin (CTR), it bound 36.90% of Pb^{2+}, 44.90% of Cu^{2+}, 5.10% of Zn^{2+} and 34.30% of Ni^{2+}. It was observed that modification of the coir extract decreased the adsorptive capacity of the adsorbent. The decrease in the amount adsorbed on modification indicates that the Carboxylic group (-COOH) and the Sulphonate group ($-SO_3H$) blocks some adsorption sites, on which the metal ion would have to be bound to.

This pattern of adsorption behavior has been documented in the literature (Fourest and Volesky, 1996; Park *et al*., 2005). Reduced rate of adsorption caused by modification has been reported for lead adsorption on modified coconut fibre (Igwe *et al*., 2005), Cu adsorption on modified algal carboxyl group in cyamolium caladarium (Gardea-Torresday *et al*., 1990) and Zn adsorption on modified rice husk (Sharma *et al*., 2008), respectively.

The trend of adsorption of these metal ions on coir dust followed decreasing order: $Pb^{2+}>Ni^{2+}>Cu^{2+}>Zn^{2+}$ and that on carboxylated coir extract (CTR): $Cu^{2+}>Pb^{2+}>Ni^{2+}>Zn^{2+}$ while that on sulphonated coir extract resin (STR): $Cu^{2+}>Pb^{2+}\approx Ni^{2+}>Zn^{2+}$, respectively. The differences in the amount of metal ions adsorbed by each adsorbent is being affected by metal solution chemistry, surface morphology of adsorbent, ionic radius, charge, electronegativity, electrostatic strength and covalent index ($\chi_m r$) of the metal ion, χ_m is the electronegativity and r the ionic radius. The greater the covalent index value of the metal ion, the greater is its potential to be adsorbed Nieboer and McBryde (1973). The ionic radii of the metal ions are Pb^{2+} (1.19A°), Cu^{2+}(0.73A°), Zn^{2+}(0.74A°), Ni^{2+}. The electronegativities of the metal ions were Pb (2.33), Cu (1.80), Zn (1.70) and Ni (1.69) have been documented by Purcell and Kotz (1980). The higher sorbability of Pb (II) over the other metal ions may be due to the fact that Pb (II) is hydrolysed in aqueous solution to a greater extent than Cu (II), Zn (II) and Ni (II) rendering it more available for sorption than others (Kongsuwan *et al*., 2006). The hydrolysis of most divalent metal ions can be written as follows:

$$M^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons M\,(OH)^{+}_{(aq)} + H^{+}_{(aq)}$$

where, M^{2+} could be any divalent metal. Thus, for the least adsorbed metal, it means the hydrolysis is not very significant; for example Zn^{2+} :

$$Zn^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons Zn\,(OH)^{+}_{(aq)} + H^{+}_{(aq)}$$

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 is attached to the adsorbent, more H^+ will be produced hence, the solution becomes more acidic. The presence of Sulphonyl acidic group ($-SO_3H$) and Carboxyl (-COOH) group on the modified coir extract could also enhance the acidity of the M^{2+} solution. Binding onto the substrate depends on the metal ion type and the level of modification.

These results indicate that both modified coir extract (CTR/STR) and unmodified coir dust have the capacity to remove metal ions from aqueous solution and the amount of metal ions bound by cellulosic substrate depend on the metal ion type, the solution chemistry the level and type of modification.

CONCLUSION

Coconut coir dust and its modified extract resins have been shown to be capable of binding several metal ions such as Pb^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+}. Metal ion removal from the aqueous solutions was efficient, indicating that the metal ions were probably adsorbed to surface of the adsorbent. Chemical modification of the coir dust extract using phenol-4-sulphonic and 4-hydroxybenzoic acid produced the sulphonated coir extract resin and carboxylated coir extract resin was produced using Toluene Diisocyanate (TDI). The modification caused a steric hindrance on the adsorption of all the metal ions that was the reason the coconut coir dust removed more of these metal ions than the modified resins (CTR and STR).

The adsorption of the metal ions decreased in descending order of Pb>Ni>Cu>Zn for the coir dust, Cu>Pb>Ni>Zn for the CTR while that for STR followed the Cu>Pb≈Ni>Zn. The efficiency of the adsorbents depended on their cation exchange capacities and $pH_{(pzc)}$. The higher the Cation Exchange Capacity (CEC) and $pH_{(pzc)}$ the higher the rate of adsorption of the metal ions. The functional groups on the adsorbents are responsible for metal ion removal include the carboxylic, hydroxyl and sulphonic groups as revealed by their infra-red spectra.

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