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Effect of pH on the removal of metal ions from industrial wastewater/ effluent from peacock paint Nigeria by coconut coir dust, maize cob and the modified coir extracts

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ABSTRACT

Early studies on the adsorption and ion exchange potential of coconut coir dust (*Cocos nucifera L.*) has great proficiency for removal of trace metal ions from waste water and industrial effluents. Several factors influence the process of waste water detoxification by ion exchange using agricultural biomass. In this paper the effect of pH on the removal of metal ions by ion exchange has been studied by batch process for Pb(II), Cu(II), Ni(II), Cd(II) and Zn(II) Using Native Coir dust (CD), Maize Cob (MC) and Carboxylated (CTR) and Sulphonated (STR) acetone modified extract of native coir dust. The amount of metal ions adsorbed increased with increase in pH of solution. Coir dust and Maize Cob removed more metal ion than carboxylated resin while the sulphonated resin removed the least i.e MC > CD > CTR > STR. At pH 4.5, the maize cob removed 94.53% of Pb(II), 95.92% Zn(II), 92.26% Cu(II) and 86.11% Cd(II). While at pH 6.5, it removed 92.56% Pb(II), 97.89% Zn(II), 92.45% Cu(II) and 89.44% Cd(II) respectively while the coir dust removed Pb(II): 72-33%, Zn(II):85.79%, Cu(II), 71.69% and Cd(II) 76.67% at pH 4.5 and 97.44%, 95.39%, 96.98% and 87.22% of Pb, Zn, Cu, and Cd respectively at pH 6.5. With adsorbent dosage of 0.1 - 0.30g, the % adsorption of metal ions varied in the following order: CD > MC > CTR > STR

Introduction

Over the years, enhanced industrial activities has led to the discharge of unprecedented volumes of waste waters and effluents into the environment. The various activities associated with environmental pollution are mining operations, ore-processing and smelting, urbanization, metal-plating, tanneries and agriculture-related processes (Okieiman et al, 1991; Raji et al, 1997). These metal contaminants are not biodegrable but accumulate in living organisms becoming a permanent burden on the ecosystem (Balasubramaniam and Ahamen, 1998). Their presence in the environment even at low concentration has therefore the potential of becoming a cause of toxicity to humans and other forms of life (Langmiur, 1918). Industrial effluents and drinking water loaded with metals is thus a serious public health problem (Faisal and Hasmain, 2004). Over-abundance of the essential trace elements and particularly their substitution by non-essential ones, such as Cd, Ni, Ag can also cause toxicity symptoms.

From the ecotoxicological point of view, metals such as Cd, Hg and Pb, the so-called family of "big three", are highly toxic and are included in the 'Red List' of priority pollutants published by the Department of the Environment, United Kingdom and in List 1 of European Economic Commission (EEC) Dangerous substances directive (Sekar et al, 2004). The same directive lists Cu, Ni, Sn and Cr in "List II", which contains pollutants of less toxicity. These metals, nevertheless, create environmental pollution problems since, although not necessarily toxic at low concentrations, can accumulate in the food chain and upon entry into human body are not excreted.

Hence, from environmental and human safety point of view, it is of the utmost importance that metal contaminants are removed from industrial wastewaters before their release into the environment. The method through which these are removed are varied from different media. These processes includes adsorption, ion exchange, reverse osmosis etc.

Adsorption is a process that occurs when molecules of gas or liquid solute are attracted, and accumulated on the surface of a solid or liquid (adsorbent), forming a molecular or atomic film (the adsorbate). This given rise to a higher concentration of any particular component at the component at the surface of solid or liquid phase than present in the bulk of the solution (Atkins, 1979). Adsorption is different from absorption in which a substance diffuses into a solid or liquid to form a solution.

Ion exchange chromatography is a reversible process in which ions are released from an insoluble material (usually polymer matrix) in exchange for other ions in a surrounding solution. The direction of the exchange process depends on the affinities of the exchanger for the ions on it and the concentration of ions in the solution. The solid material is known as the ion exchanger. Many substances both natural and artificial (synthetic) e.g clay mineral, polymer matrix and other adsorbents have ion exchanging properties. Any ion exchanger (usually resin) consists principally of two parts, namely, the structural portion (polymer matrix or resin) and function all portion (ion active group).

The value of the pH of the reaction strongly influence not only the site dissociation of the adsorbent/resin surface but also the solution chemistry of the metal ions.

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The surface charge of the adsorbent/ion-exchanger, degree of dissociation and specie of adsorbate is determined by the pH value of the system.

Several efforts targeted at reducing and/or removing these harmful substances demands harnessing the pH of the system in order to achieve optimum result hence the burden of this research.

Materials and Method

The metal ions composition of the wastewater at initial pH of 2.90, at 30°C were Pb(II): 8.60mg/L, Cu(II): 5.30mg/l, Cd(II): 1.80mg/l, Zn(II): 7.6mg/l respectively. The pH of the wastewater was adjusted using 0.1MHCl and 0.1MNaOH solution to pH values of 4.5 and 6.5 respectively. $0.2g$ of particle size $(100 - 106\mu m)$ of each adsorbent (CD, MC, CTR ad STR) were used.

Each adsorbent $(0.2g)$ CD, MC, CTR and STR resins were used to evaluate various percentage uptakes of the metals. The amount of adsorbent was taken into $30\ mL$ solution of waste water from Peacock paint Uyo containing various concentrations of Pb(II), Cu(II), Zn(II) and Ni(II) each and of pH 4.5 and 6.5. The different samples were taken in conical flasks containing the metal ion and shaken on a rotatory shaker at $140\ \dfrac{rev}{min}$ for a given time of 120 minutes.

Result And Discussion

Tables 1 show the efficiency of the adsorbents-coir dust, maize cob, carboxylated and sulphonated resin for the removal of metal ions from industrial wastewater/effluent from Peacock Paint, Uyo, Nigeria.

The results show that the natural adsorbents-coir dust and maize cob removed more metal ions than the synthetic adsorbents of carboxylated and sulphonated resin (Table 1).

At pH 4.5, the maize cob removed 94.53% of Pb(II), 95.92% Zn(II), 92.26% Cu(II) and 86.11% Cd(II). While at pH 6.5, it removed 92.56% Pb(II), 97.89% Zn(II), 92.45% Cu(II) and 89.44% Cd(II) respectively while the coir dust removed Pb(II): 72-33%, Zn(II):85.79%, Cu(II), 71.69% and Cd(II) 76.67% at pH 4.5 and 97.44%, 95.39%, 96.98% and 87.22% of Pb, Zn, Cu, and Cd respectively at pH 6.5 (Table 1). The maize cob removed more Zn(II) ions, Cd(II) ions, less Pb(II) ions at higher pH 6.5. There was no significant change in the removal of Cu(II) ions by maize cob at the two pH values of 4.5, (92.26%) and pH 6.5 (92.45%). For the coir dust the removal of all the metal ions increased with increasing pH.

The percentage amounts of Pb(II), Zn(II), Cu(II) and Cd(II) adsorbed on coir dust increase from 72.33%, 85.79%, 71.69% and 76.67% at pH 4.5 to 97.44%, 95.39%, 96.89% and 87.22% at pH 6.5 respectively. The increase in the removal of the metal ions at higher pH 6.5 is attributed to the fact that at low pH, most of the surface functional groups of the adsorbent are undissociated and also the presence of H^+ ions repels the attachment of the metal ions which hinders its adsorption. However at higher pH value (6.5) most of the surface functional groups (carboxylic acid) becomes diassociated, the surface of the adsorbent becomes more negative and more metal ions are hydrated and hydrolysed. These factors enhances adsorption of the metal ions from solution onto the sorbents. Coir dust removed more of the four metal ions- Pb(II), Zn(II), Cu(II) and Cd(II) ions at higher pH than the maize cob. The unique properties of coir dust as an efficient adsorbent has been reported (US Patent 2006, Tejano et al., 1985, Meerow, 1994). The synthetic adsorbents of carboxylated and sulphonated resins

removed less amount (in percentages) of the metal ions compared to the natural adsorbents-maize cob and coir dust (Table 1). The two resins removed less than 90% of all four metal ions (Pb, Zn, Cu, Cd) at both lower (4.5) and higher (6.5) pH values. The amount of Pb(II), Zn(II), Cu(II) and Cd(II) adsorbed on the carboxylated resin at pH 4.5 were 70.0%, 84.61%, 72.0%, 69.44% while at pH 6.5; 76.16%, 87.36%, 80.20% and 83.33% were adsorbed respectively. The adsorption increased with increase in pH values for the reasons explained above. The same increase in % adsorption of the metal ions with increase in pH value was observed with the sulphonate resin except for Pb(II) ions. At pH 4.5, the amount of Pb(II) ions adsorbed (76.0%) was higher than the amount (73.0%) adsorbed at higher pH of 6.5. This reduction in adsorption for Pb(II) ions may be due to the electrostatic interaction between the adsorbent and the metal ion species present in the solution.

Table 2 showed the selectivity coefficients (K_s) of the different metal ions on the adsorbent at pH 4.5 and 6.5 respectively at 30°C.

Distribution coefficient is the ratio between the concentration of species in resin phase and in the solution phase. Dilution of the external solution has a slight effect upon selectivity coefficient. Selectivity is dependent upon total ion concentration in the resin phase, and decrease with increase in degree of crosslinking, and chemical structure of resin matrix. The ions with the highest affinity for the resins give the least swelling and external solution affect the composition of resin phase and concentration on selectivity.

Mathematically, selectivity/distribution coefficient is expressed as:

$$K_D = \frac{\text{conc. of ions in solid phase}}{\text{conc. of ions in aqueous phase}} \text{ or}$$

$$= \frac{\text{mass of ions in solid phase}}{\text{mass of ions in aqueous phase}}$$

Selectivity coefficient values arestrongly dependent on experimental conditions, such as pH, initial concentration, and temperature.

The selectivities of the metal ions by the adsorbents also increase with increase in pH value from 4.5 to 6.5. For the coir dust the selectivity coefficient (K_s) increased with increase in pH from 4.5 to 6.5 from 2.61 to 38.09 for Pb(II) 6.04 to 20.7, Zn(II):2.53 to 32.13, Cu(II): 3.29 to 6.83 and from pH 4.5 to 6.5 for Pb(II), Zn(II), Cu(II) and Cd(II) ions respectively. From Table 2, the increase in selectivities of the metal ions from lower pH (4.5) to high pH (6.5) was more than hundred fold. The increase in selectivity for coir dust increased from 2.61 to 38.09 for pH use of pH 4.5 to pH 6.5 for Pb(II). The results show that the selectivities of the metal ions on the natural adsorbents were higher than those for the synthesized resins. However, higher selectivity coefficients were exhibited by the metal ions for the maize cob than coir dust at lower pH 4.5, while the selectivities of the metal ions were higher for the coir dust than for maize cob at higher pH of 6.5. This is attributable to the differences in the nature of functional groups present in each adsorbent. The increase in the selectivity coefficients of the metal ions for coir dust at higher pH than lower pH supports the fact that carboxylic acid group (−COOH) which becomes dissociated at higher pH than low values is one of the major functional group responsible for metal ion binding in coconut coir dust (Matheickal et al., 1999, Ting et al., 1991).

The selectivities of the metal ions for the synthesized adsorbents were lower than for the natural adsorbents, at both low pH (4.5) and high pH (6.5) (Table 2).

The selectivity coefficient (K$_s$) for Pb(II), Zn(II), Cu(II) and Cd(II) ions at pH 4.5 for the carboxylated resin were 2.33, 5.49, 2.61, 3.39 while at pH 6.5 the selectivity coefficients were 3.19, 6.92 4.05 and 5.21 respectively. For the sulphonated resin at pH 4.5, the selectivity coefficients were 3.17, 4.10, 2.58, 2.27 and 2.69, 7.09, 5.71, 5.00 for Pb(II), Zn(II), Cu(II) and Cd(II) at pH 6.5 respectively. The results showed that the synthesized adsorbents of carboxylated and sulphonated resins were effective in removing metal ions from wastewater though not as efficient as the natural adsorbents. The natural adsorbents with the cellulose, lignin constituents have advantages over the synthesized adsorbents with no lignin nor cellulose in their composition. The high performance of lignocellulosic materials as adsorbent has been reported by several authors (Nada et al., 2002, Kardivelu et al., 2001).

Conclusion

The natural adsorbents with the cellulose, lignin constituents have advantages over the synthesized adsorbents with no lignin nor cellulose in their composition. Coir dust and Maize Cob removed more metal ion than carboxylated resin while the sulphonated resin removed the least i.e MC > CD > CTR > STR. The reason for this being that the MC and CD being natural adsorbent has many vacant site which increase their binding capacity for metal ions.

The increase in the removal of the metal ions at higher pH 6.5 is attributed to the fact that at low pH, most of the surface functional groups of the adsorbent are undissociated and also the presence of H$^+$ ions repels the attachment of the metal ions which hinders its adsorption. However at higher pH value (6.5) most of the surface functional groups (carboxylic acid) becomes diassociated, the surface of the adsorbent becomes more negative and more metal ions are hydrated and hydrolysed.

This study also shows that the average toxicity level of industrial effluent from peacock paint and any other heavy metal containing industrial effluent can be detoxify be carefully regulating the pH and other factors using low cost biomass as adsorbent.

Acknowledgement

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Table 1: Percentage Removal Values of Metal Ions from Waste Water Obtained from Peacock Paint Industry, Uyo on Different Adsorbents

pH	CD				MC				CTR				STR			
	Pb^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}
4.5	72.33	85.79	71.69	76.67	94.53	95.92	92.26	86.11	70	84.61	72	69.44	76	80.39	72.1	77.8
6.5	97.44	95.39	96.98	87.22	92.56	97.89	92.45	89.44	76.16	87.36	80.2	83.33	73	87.63	85.1	82.7

Table 2: Distribution Coefficient Values (Selectivities) of Metal Ions from Waste Water Obtained from Peacock Paint Industry, Uyo on Different Adsorbents

pH	pH	CD				MC				CTR				STR			
		Pb^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}
4.5		2.61	6.04	2.53	3.29	17.29	12.8	11.9	6.2	2.33	5.49	2.61	3.39	3.17	4.1	2.58	2.27
6.5		38.09	20.71	32.13	6.83	12.43	23.5	12.3	7.18	3.19	6.92	4.05	5.21	2.69	7.09	5.71	5