ADSORPTION OF HEAVY METAL IONS ON MODIFIED AGRICULTURAL WASTE (CORN-COBS)

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Abstract

The removal of heavy metal ions, Cd(II), Pb(II) and Zn(II) ions from aqueous solution by agricultural waste, such as corn-cobs modified with thioglycolic acid was examined by equilibrium sorption studies at 29^{o}C. The sorption of the metal ions was studied under various conditions. The parameters being effect of P^{H} and initial concentration. It was found that the rate of sorption was particle diffusion controlled. The present work concludes that modified agricultural wastes have good metal ion binding capacities. The researcher recommends the use of more inexpensive agricultural wastes as a frontier to reducing the environmental load of heavy metal ions in the aqueous effluents.

Introduction

The removal/recovery of toxic and valuable heavy metals from the aqueous effluents have received much attention in the recent years. Industrial and mining waste waters are generally considered to be the major sources of these heavy metals in the environment. There is the added concern of the use and manufacture of fertilizers, particularly phosphate based fertilizers on the environmental load of heavy metals.

These industries pretend not to be aware of the environmental hazards presented by the accumulation of heavy metals because of their huge economic interests.

Incidentally, deteriorating environmental conditions has aroused the need for cost effective and effective methods of using waste to treat waste through the use of agricultural waste materials that may be useful in reducing the levels of heavy metals accumulation in the environment. Many workers have shown that agricultural waste materials can bind substantial amounts of metal ions. These present work reports on the sorption behaviors of cadmium, lead and zinc ions on corn-cobs modified by the introduction of thiogylcollic acid. The practical method used in the removal of these heavy metal ions is "Adsorption". Hence, the relative polarities of the solute and solid stationary phase are determined by the rate of movement that the solute makes through a column of across a surface. It is a situation whereby solid substances, molecules or ions on the surface do not have all their forces satisfied by anion with other particles; they tend to satisfy their residual forces by attracting unto and retaining on their surfaces, be it gas or dissolved substances with which they come in contact with.

The ability of gases, ions or molecules to bind on the surface depends on the surface coverage of the adsorbent. In this case the free and the adsorbed substances are in dynamic equilibrium at a given temperature.

Method

Experimental

Apparatus

The apparatus used for the study are manual grinder, pH meter and molecular sieve.

Reagents

Thioglycollic acid, nitric acid, deionized water and corn-cobs are the reagents used.

Modification of Corn-Cobs

The maize cobs which were obtained from a maize mill were treated with thioglycollic acid.

Procedure

The maize cobs were cut into small pieces, air-dried and powered in grinder. The maize cobs meal was sieved through a 300μm screen. The portion of the maize cobs meal retained on the mesh was soaked in dilute nitric acid solution (2%v/v) over night, rinsed with deionized water and air-dried. The cellulosic material was modified by treating the cobs meal material with thioglycollic acid solution at 29^{o}C. A 25g portion of the maize cobs meal was stirred with thioglycollic acid solution (0.3M and 1.0M) for 24 hours at 29^{o}C in a well ventilated hood. The mixture was filtered and the cellulosic material was thoroughly washed with deionized water. The thiol content of the cellulosic material was determined by reacting 0.5g sample of the thiolated material with excess iodine at neutral pH followed by back titration of the un-reacted iodine with thiosulphate solution.

Sorption of Metal Ions on Modified Corn-Cob

Equilibrium sorption of cadmium, lead and zinc ions on thiolated cellulosic material was carried out using 100ml of various concentrations (10.0mg/100ml-50.0mg/100ml) of the metal ions at constant metal ion-substrate contact period of 1 hour at 29^{o}C. Uptake level of the metal ions from acidic solutions (H^{+} concentration between 0.01M and 0.001M) were examined.

Results and Discussion

The uptake of Cd (II), Pb(II), and Zn (II) ions from solutions containing various amounts of the metal ions by the unmodified and modified thiolated cellulosic materials are shown in Table 1. The results show that the amounts of the metal ions bound by cellulosic substrate depend on the types and level of incorporation of the thiol groups in the substrate. The level of metal ions uptake is Zn > Cd > Pb ion. The difference in the uptake levels of the metal ions can be explained in terms of the difference in ionic size, the nature and distribution of active groups on the substrate and the mode of interaction between the ions and the substrate. The amount of metal ions removed from solution increases with increase in the initial concentration of the metal ions.

The results in Table 2 also show that the metal ion binding capacity of the cellulosic material is remarkably enhanced by the presence of low levels (less than 5%) of thiol groups on the substrate. The improved levels of metal ions uptake by the thiolated cellulosic materials are quite high

Table 1: Equilibrium sorption of Cd (II), Pb (II) and Zn (II) ions from aqueous solutions (pH 6.8 approximately) by corn-cobs meal containing different concentrations of SH-groups (3.3%, 1.7% and 0%) at 29^{o}C using 100ml of the metal ion solutions.

Metal ion concn.	Amount of Metal Ions Adsorbed (meq/g)		
(mg/100ml)	Cd (II)	Pb (II)	Zn (II)
10.0	0.05 : 0.03(0.02)	0.03:0.001(0.01)	0.05:0.003(0.03)
20.0	0.09 : 0.01(0.04)	0.09:0.002(0.02)	0.10:0.014(0.08)
30.0	0.20 : 0.03(0.12)	0.16:0.014(0.05)	0.25:0.058(0.22)
40.0	0.26 : 0.05(0.19)	0.19:0.029(0.10)	0.29:0.084(0.27)
50.0	0.30:0.09(0.29)	0.23:0.044(0.17)	0.33:0.096(0.28)

Levels of metal ions uptake by cellulosic materials containing 3.3%, 1.7% SH-groups. Levels of metals ion uptake by unmodified corn-cobs (0% SH) cellulosic material in bracket

The influence of pH on the sorption of Cd (II), Pb(II) ions by the unmodified and thiolated maize cobs is shown in Table 2. It can be seen that the amount of metal ions removed from solution by the cellulosic materials increases as the pH of the metal ions is increased by arithmetic progression from 2-4. The uptake of the metal ions from the aqueous solutions by the cellulosic materials is usually accompanied by a reduction in the pH of the metal ion solution. This is largely due to the exchange of the hydrogen atoms in the substrate by the metal ions. The extent of hydrogen ion exchange depends on the relative concentration of the medium.

The observed reduction in the levels of metal ions removed from solution by the cellulosic materials is associated with increase in the hydrogen ion concentration of the hydrogen atom exchange to the overall sorption process at these pH values are insignificant. The pH dependence of Cd (II), and Pb(II) ions sorption by corn cobs suggest that a large proportion of metal ions adsorbed may be recovered by using pH of 2.

Table 2: Uptake of Cd (II) and Pb(II) ions from 0.01MHNO_3 (pH 2), 0.001MHNO_3 (pH 3) and, 0.0001MHNO_3 (pH 4) solutions containing 50mg/100ml of the metal ions by corn-cobs meal at 29^oC.

pH of metal Ion Solution	Amount of Metal Ions Adsorbed (meq/g)					
	Unmodified Corn-Cobs		Corn-cobs with 1.7% SH-group		Corn-cobs with 3.3% SH-group	
	Cd (II)	Pb (II)	Cd (II)	Pb (II)	Cd (II)	Pb (II)
2.0	0.21	0.14	0.29	0.16	0.32	0.19
3.0	0.29	0.20	0.31	0.21	0.36	0.20
4.0	0.31	0.25	0.34	0.25	0.39	0.25

Conclusion

The modified agricultural waste with improved levels of metal ion uptake are thought to have resulted from relative ease of exchanging the heavy metal ions at the reactive sites. The modified cellulosic materials have improved binding metal ions capacity which could have come as a result of the incorporation of thioglycollic acid to the corn-cobs which provided the thiol group for exchangeable metal ions.

The unmodified agricultural waste, however, had some degree of binding metal ions capacity, even though the rate of equilibrium may be very slow which may be due to some heavier exchangeable functional groups. Generally, it was observed that at lower pH, the modified agricultural waste was able to sorb about 90% of the metal ions.

The choice of agricultural by products for the removal/recovery of heavy metal ions could be due to their inexpensive nature in contrast to the conventional precipitation and ion-exchange techniques which require the use of expensive chemicals and synthetic resins.

Recommendations

The researcher recommends the use of agricultural wastes, especially the materials which do not have heavy exchangeable functional groups such as carboxylic phenolic and hydroxylic groups which may have low rate of equilibrium. However, the researcher suggests the use of coco-nut shell, natural palm fibre, ground-nut husk etc as veritable replacement of the conventional ion-exchange resins.

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