RESEARCH NOTE

SORPTION OF HEAVY METAL IONS ON WOOD CELLULOSE MODIFIED WITH UREA AND THIOUREA

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Abstract

Adsorption chromatography of some heavy metal ions on wood cellulose of saw dust (wood waste dust) modified with hydrochloric acid, urea and thiourea was studied. Atomic absorption spectrophotometry (AAS) was used to determine the initial concentration of solutions of Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Fe^{3+} metal ions. The solutions were allowed to pass separately through column chromatography packed with different modified adsorbents. The concentrations of the filtrates as well as amount of metal ions sorbed in each case were determined. The percentage of the sorbed metal ions by the unmodified substrate are in the range of 6.57-75.08 % while those modified with dilute HCl was found to be in the range of 69.82-86.48 %. Higher percentages were obtained on further modification of the HCl acid treated wood cellulose and was in the range of 71.98-87.03 % and 76.75-89.86 % for urea and thiourea respectively. Thus, the possibility of using sawdust as a support for the sorption of heavy metal ions may provide effective and economic means of removing valuable or toxic metal ions from sewage, industrial and mining wastewaters.

Keywords: Wood cellulose, metal ions, Chemical Modification, column adsorption method.

1. Introduction

Recovery of valuable metal ions from mixtures as well as removal of toxic ones from waste and industrial effluents are very much desired in this recent time of much technological industrial activities. An effective and economical method of achieving this becomes necessary. Sorption of the heavy metals on modified cellulose of agricultural wastes has been focused on recently.

Basset *et al.,* (1986) observed that due to the availability of small amount of carbonyl groups on cellulose, adsorption processes might contribute tremendously to the partitioning mechanism that effects the separation of metal ions or effect their removal from waste and industrial effluents. The ionizable carboxylic acid groups are known to contribute to metal ion sorption (Reddad *et al.,* 2002). It was also noted that the mobility of different metal ions on the unmodified cellulose depend on factors that enhance their mobility in the organic phase and those that retain the components of the mixture in the stationary aqueous phase of the cellulose. Bark *et al.*, (1960) in theirstudy found that methyl-substituted phenoxyacetic acids could be paper chromatographed using two solvent mixtures. The chromatography of metal ions on thin-layer of cellulose and silica gel impregnated with tributylphosphate was reported by Bark *et al.* (1967). Kumar *et al.,* (1981) also reported that red onions skin is highly effective for binding heavy metal ions from aqueous solution. Column chromatography separation of some divalent ions (Mn^{2+}, Fe^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, and Cu^{2+}) using silica modified with pyridin-2-carboxyaldehydephenyl hydrazone as the stationary phase was studied by Simontadeh *et al.* (1988). In another study, Valasköva (1988), Compared the separation of alkali metal and alkaline -earth metal cations by isotachone as with N- hydroxy ethyl iminodiacetic acid. The sorption of metal ions by use of agricultural products such as tree bark, peanut skins, walnut expeller meal, wool, cotton, paddy husks, onions skin, sugar cane bagasse and wheat flour waste has been studied by several workers (Friedman *et al.*, 1973; Randall *et al.*, 1975, 1978 and Kumar *et al.*, 1979, 1981; Acemioglu and Alma, 2001). Basso *et al.* (2002) reported the use of saw dust for the remopval of cadmium from aqeous solution

Cheaper and biodegradable agriculture wastes like saw dust (wood cellulose) that are being burnt away all over the nations especially third world countries need to be converted to useful product for separation and removal of metal ions. The chromatographic behavior of urea and thiourea modified surfaces towards metal ions removal have not been studied. Therefore, there is need to focus on the use of chromatographic method for heavy metals removal using modified cellulose waste material.

2. Experimental

(a) Reagents.

All reagents used were of analytical grade unless otherwise specified. The stock solution of Zn^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+} and Fe^{2+} were prepared from either their nitrate or sulphate salts using deionised water to give 0.1M solutions.

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(b) Sample Collection and Processing:
The sawdust was collected from a local sawmill at Ilorin, Nigeria. It was sieved using 0.500 mm and 0.250 mm mesh screens to obtain fine particles of sawdust substrate.

About of 250 mL of de-ionized water was added to 25 g of the raw sawdust substrate in a 500 mL flat bottom flask. The mixture was thermostated at 98°C for 6 hours, after which it was filtered and the residue thoroughly washed with de-ionized water. The residue was then dried at 50 °C in an oven. This gave the unmodified substrate (UMS). Three categories of modified substrate were then prepared:

(i) A 250 mL of 1% (v/v) aqueous HCl was added to 25 g of the raw sawdust substrate in a container. The mixture was thermostated at 98 °C for 6 hours, filtered and residue obtained, thoroughly washed with deionized water. The residue was then dried in a Gallenkamp oven at 50 °C for 24 hours to give the acid modified substrate (AMS).

(ii) Refluxing the acid modified substrate, AMS at 98 °C with 50 mL of 7.8% urea and 200 mL of 0.2 M HCl for 2 h further modified a 10.0 g of the acid modified substrate. The mixture was filtered and washed thoroughly with distilled water until the pH was between 4 and 5. The residue was also dried in the oven at 50°C for 24 h to give urea-modified substrate (RMS).

(iii) For the modification of acid modified substrate with thiourea, the above procedure was repeated with thiourea instead of urea to give thiourea modified substrate (TMS).

Column experiments were carried out by subjecting the metal ions to dynamic sorption on the four wood substrate types. About of 10 g of each of the dried unmodified wood cellulose, acid modified wood cellulose, wood cellulose impregnated with urea, and wood cellulose impregnated with thiourea substrates were differently packed in a 50 mL burette column, wetted slowly with deionized water. A 20 mL of each of the 0.1M metal ions solution were then separately allowed to pass through the column and eluates were obtained. The amounts of each of the heavy metal ions in the eluates were determined using Atomic Absorption Spectrophotometer.

3. Results and Discussion

The results of the studies of chromatographic sorption of metal ions on the four different wood substrates are shown in Tables 1, 2, and Figure I. The initial and final concentrations of metals adsorbed on the adsorbents are shown in Table I while the amount of sorbed metal ions in percentage by each of the substrate is presented in Table 2. The Zn^{2+} ion sorbed onto wood cellulose impregnated with thiourea had the highest percentage of 89.86 % of ion sorbed while the least is 6.57 % of Fe^{3+} ions sorbed by the unmodified substrate. The percentage metal ions sorbed onto the substrate are mean values of duplicates results. Means within columns with different letters are significantly different ($p \leq 0.05$).

From the results obtained in Tables 1 and 2 for the chromatography column studies of sorption of metal ions on each of the sawdust substances, it is observed that the final concentrations of these metal ions are lower than their initial values. This indicates that a definite amount of each of the metal ions was sorbed onto the substrates. Table II shows the mean percentage of sorbed metal ions by each of the adsorbents. The unmodified wood cellulose adsorbed 75.08, 50.19, 65.75, 74.58 and 6.57 % for Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Fe^{3+} ions respectively. The value of 86.48, 69.82, 83.59, 81.41, 83.63 % for Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Fe^{3+} respectively are obtained for acid modified substrate. Higher percentage of 87.03, 71.98 and 82.65 % were obtained for Zn^{2+}, Cu^{2+} and Pb^{2+} respectively by sawdust substrate impregnated with urea. The percentage of 89.86, 76.75, 85.61 and 83.06% for Zn^{2+}, Cu^{2+}, Ni^{2+} and Pb^{2+} metal ions sorbed by the substrate impregnated with thiourea were found to be higher than both the acid modified as well as urea modified substrates.

Consequently, the amount of divalent metal ions sorbed onto the different substrates could be ranked in the order of increasing sorbing ability for the studied metal ions as:

*un*mod*ified* < *acid*mod*ified* <
wood cellulose *wood cellulose*

wood cellulose < *woodcellulose*
impregnated with urea *impregnatedwiththioure*

The amount of sorbed divalent metal ions on to other substrates follows similar trend. Thiourea impregnated substrates sorbed the largest amount of the divalent metal ions while the unmodified sorbed the least amount of the divalent metal ions. However, the amount of Fe^{3+} ions sorbed by different substrates did not follow similar trend as those of divalent metal ions. The acid modified substrate sorbed the largest Fe^{3+} ions (83.63 %) while the unmodified substrate sorbed the least amount of Fe^{3+} ions (6.57 %). The order of increasing sorbing ability of these modified wood cellulose substrates for Fe^{3+} ions are:

*un*mod*ified* < *wood cellulose* <
wood cellulose *impregnated with thiourea*

wood cellulose < *acid*mod*ified*
impregnated with urea *wood cellulose*

Table 1: Initial and final concentrations of the metal ions adsorbed onto adsorbents.

Types of Metal ion	Initial concentration x 10^3 (mg/l)	Final concentrations x 10^3 (mg/l)			
		UMS	AMS	RMS	TMS
Zn^{2+}	6.538	1.581	0.879	0.853	0.660
	6.538	1.678	0.891	0.843	0.666
Cu^{2+}	6.355	3.161	1.914	1.773	1.466
	6.355	3,170	1.922	1.789	1.490
Ni^{2+}	5.870	2.010	0.958	0.985	0.847
	5.870	2.013	0.958	0.985	0.847
Pb^{2+}	20.720	5.284	3.814	3.638	3.524
	20.720	5.253	3.893	3.554	3.496
Fe^{3+}	5.585	5.263	0.930	0.994	1.072
	5.585	5.173	0.899	0.994	1.080

Table 2: Percentage of sorbed metal ions on the differently modified wood cellulose substrates

Wood Substrates	Metal ions				
	Zn^{2+} (%)	Cu^{2+} (%)	Ni^{2+} (%)	Pb^{2+} (%)	Fe^{3+} (%)
UMS	75.08 ± 1.05^a	50.19 ± 0.10^a	65.75 ± 0.06^a	74.58 ± 0.11^a	6.57 ± 1.15^a
AMS	86.48 ± 0.11^b	69.82 ± 0.05^b	83.59 ± 0.13^b	81.41 ± 0.27^b	83.63 ± 0.39^c
RMS	87.03 ± 0.10^b	71.98 ± 0.18^c	83.36 ± 0.19^b	82.65 ± 0.29^c	82.33 ± 0.18^{bc}
TMS	89.86 ± 0.06^c	76.75 ± 0.28^d	85.61 ± 0.04^c	83.06 ± 0.10^d	80.74 ± 0.10^b

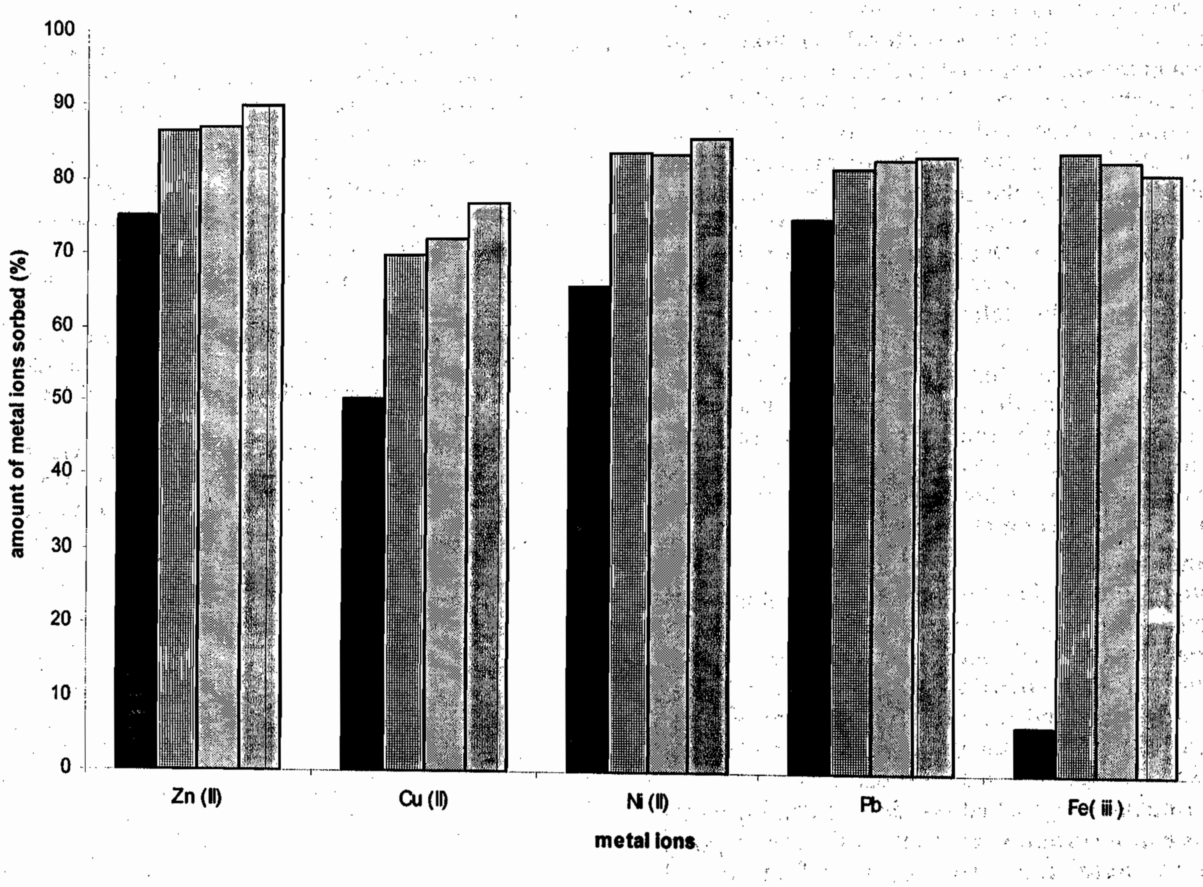

figure1: Sorbing ability of substrate types towards some metal ions

Analysis of variance procedure and Duncan multiple range test of variables with Harmonic mean square size of 2 at $P < 0.05$ were used to separate means and ascertain statistical significant difference in variables for metal ions studied for the variously modified wood cellulose substrates. There is no significant difference in sorbing ability of urea and acid modified substrates for Zn^{2+} and Ni^{2+} ions but are significantly different for TMS and UMS. Table II also indicates that there is significant difference between the unmodified substrate and the modified substrates for each of the metal. The amount of Zn^{2+} and Ni^{2+} ions sorbed by TMS are significantly different from those sorbed by AMS and RMS. All the substrates are significantly different in sorbing ability towards Cu^{2+} and Pb^{2+} ions.

The sorbing of trivalent ion (Fe^{3+}) by these substrates indicate that, urea modified substrate (RMS) is not significantly different from acid modified and thiourea modified substrates.

These findings may be attributed to the nature of urea and thiourea that provided more binding sites within each of their substrates for divalent ions. These observations are in agreement with Basset et al (1986) that noted that partitioning mechanism that effects mobility and retention of metal ions on the substrates are dependent upon the available binding sites on the substrate (stationary aqueous phase) and nature of the modifying agent. The values of divalent metal ions sorbed by thiourea modified wood cellulose are higher than those of wood substrate impregnated with urea and acid modified substrate probably because the nature and structural orientation of thiourea in the substrate makes it have more affinity to hold on the metal ions than the other substrates. The findings agree with suggestions of Lee and Rowell(2004) that the number of available free phenolic groups may play prominent role in the extent of sorbability of metal ions .They opined that treatment of fibers with chemicals might reduce or increase free surface area that determine the extent of accessibility of the cell walls. The sorption of Fe^{3+} ion followed the reverse order of the divalent metal ions on the substrates with exception of the unmodified substrate that still sorbed least amount of metal ion. This may be due to trivalent nature of the metal ion, for more simple molecules like HCl could create more sorption sites than the bulkier thiourea and urea for trivalent metal ions.

4. Conclusion

This study showed that thiourea-modified substrates are better adsorbent for removal of divalent metal ions than urea and acid modified substrates. On the other hand, acid modified substrates was found to be better than urea and thiourea for sorption of Fe^{3+}. Generally there was an improvement in sorption capacity over the unmodified substrates.

These findings suggest that saw dust containing wood cellulose as a sorption can be used for the sorption of heavy metal ions. Hence, an effective and economical removal of valuable or toxic metal ions from sewage and industrial wastewaters may be achieved using these substrates. The substrates are environmentally friendly as they are biodegradable.

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