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**REMOVAL OF TOXIC HEAVY METAL IONS IN
RUNOFFS BY MODIFIED ALFALFA AND
JUNIPER**

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ABSTRACT

A series of batch isotherm tests was performed with alfalfa and juniper fibers to evaluate the effectiveness in filtering toxic heavy metals from stormwater. The adsorption of the heavy metal ions on the alfalfa and juniper fibers was strongly dependent on the equilibrium pH value of the solution. The change in sorption rate over time showed that two different sorption processes occurred a fast ion exchange followed by a chemisorption. Heavy metals were less sorbed when they are in solution together than when they exist alone in solution; however, the total adsorptive capacity of the adsorbent in multi-component phase was larger than that in a single compound phase. The sorption order based on mass of adsorbed ion is Cu>Cd>Ni, Zn. Sulfonation modification increased more than 250% of the sorption capacity of juniper fiber.

INTRODUCTION

Agro-based fibers such as kenaf, roselle, and tobacco have been shown to be effective in removing heavy metal ions through sorption. In contrast, most wood-based fibers have a relatively low sorption capacity for heavy metals (Han et al., 1995; Han et al., 1999). Researchers have tried to increase sorption capacity of lignocellulosic fibers through chemical modification; yet more success was achieved in bark and marine fibers (Morita et al, 1987; Laszlo and Dintzis, 1994; Vazquez et al., 1994; Muni et al., 1995; Aderhold et al., 1996; Mun et al., 1995; Simkovic et al., 1996; Seki et al., 1997). However, this process has either been too expensive or it has caused other problems, such as bleeding of excessive quantities of colored organic compounds, odor, or further pollution through the use of toxic chemicals. It is important to understand that lignocellulosic materials are not pure polymers. Their main constituents are cellulose, lignin, hemicellulose, and extractives. Except for cellulose, the chemical structure of these components can differ widely. Consequently, removal of heavy metals can be governed by any of four basic mechanisms: absorption, adsorption, ion exchange, and chelation. The most probable mechanism may be ion exchange.

The objectives of this study were to estimate heavy metal sorption capacity of alfalfa and juniper; to assess the effects of pH, competition between ionic species, and interference caused by calcium; and to evaluate the performance of the filter consisting of either alfalfa or juniper for heavy metal removal from stormwater runoff. It was anticipated that filters constructed with agro- or wood-based fibers would effectively remove heavy metals in stormwater runoff at a low cost. In order to compare one type of fiber to another, it was necessary to pulverize the comparing media to an equal particle size and to expose to high concentration to estimate the maximum sorption rates.

EXPERIMENTAL METHODS

Alfalfa and juniper samples were ground to pass through 0.18-mm (30-mesh) screen using a Wiley Mill and any fines less than 0.18 mm (80 mesh) was removed. Fibers were oven dried for 24 h at 40°C. Sulfonation was performed for chemical modification of fibers so as to increase sorption capacity by dissolving 168 g of sodium sulfite and 19 g of sodium bicarbonate in 1 L water (stock solution); 10 mL of this mixture was added to 10 g fiber in 1 L of water, stirred, and heated to 70°C for 2 hours. Adjustment of pH was made using NaOH and HCl. Samples were analyzed by atomic absorption spectrophotometry.

RESULT AND DISCUSSION

Isotherm tests

The Freundlich and Langmuir isotherm tests were performed by exposing 0.01g, 0.2g, 1.0g and 2.0g of alfalfa fiber to 10 mg/L Zn solution (pH 2.73).

$$\text{Freundlich Isotherm equation: } q_e = k_f C_e^n \quad (1)$$

where: q_e = Equilibrium solid-phase solute concentration (mg/g);
 K_f = Freundlich isotherm constant (L/mg);
 C_e = Equilibrium liquid phase solute concentration (mg/L); and
 n = a constant.

$$\text{Langmuir isotherm equation: } q_e = \frac{X}{M} = \frac{Q \cdot a \cdot C_e}{1 + a \cdot C_e} \quad (2)$$

where a = Langmuir isotherm constant (L/mg);
 X = Mass of heavy metal adsorbed by fiber (mg);
 M = Mass of heavy adsorbent (g);
 Q = Langmuir monolayer capacity (mg/g); and
 $Qa = K$ = Langmuir isotherm constant (L/mg)

Isotherm constants are summarized in Table 1. The Langmuir model appeared to have a better fit to the experimental data than the Freundlich model for alfalfa-Zinc ion systems.

Freundlich isotherm				Langmuir isotherm			
M Range (g)	n	K_f (L/mg)	Correlation coefficient, R^2	M Range (g)	K (L mg ⁻¹)	a (L mg ⁻¹)	Correlation coefficient, R^2
0.01-2.0	2.433	6.28348	0.9205	0.01-2.0	10.45	0.608	0.9496

Factors affecting heavy metal sorption

Effect of pH on sorption of heavy metals: The adsorption tests, measuring the effect of pH on removal rates of heavy metals, was performed at room temperature. The reaction mixture consisted of 1 g of fiber exposed to 50 mL of a solution containing 10 mg/L (PH 2.51) of each Ni, Cu, Zn, and Cd. The different initial pH values were achieved by adding either 0.1 M NaOH solution or 0.1 M HCl solution to the reaction mixture before adding Alfalfa or juniper fibers to the reaction mixture. The reaction mixture was placed in a closed glass bottle and agitated in a shaker for 12 hours. At the end of this 12-hour period, the bottles were removed from the shaker, and contents were filtered through Whatman No. 1 filter paper. The samples were then analysed for each of the four heavy metals. The adsorption of the heavy metal ions on the alfalfa and juniper fibers was strongly dependent on the equilibrium pH value of the solution between 2 and 4 but not affected much between pH of 4 to 8. The metal ions were not absorbed much by alfalfa and juniper fibers at pH of 2. At pH values of < approximately 3, very little sorption occurred for both types of fiber. This lack of sorption ability at low pH could be ascribed to the hydrogen ions competing with the heavy metal ions for sorption sites (Low, 1993).

Effect of reaction time: The sorption rate was almost constant for the first 15 minutes, sharply increased for 10 minutes, and then reached a maximum sorption capacity. This change in uptake rate could be attributed to two different sorption processes, namely a fast ion exchange followed by a chemisorption (Low, 1993).

Multi-component phase: Since stormwater consists of various pollutants, competition of various ions for limited sorption site available in fibers must be evaluated. The fiber-heavy metal partition coefficient (L/kg) was estimated by taking the ratio of solid-phase concentration (mg/kg) to solution-phase concentration (mg/L). The estimates of the

fiber-heavy metal partition coefficients for the single and multi-solute tests are summarized in Table 2. There was a decrease in the adsorptive capacity of any individual compound in the multi-component phase; however, the total adsorptive capacity of the adsorbent was larger than that in a single compound phase. The amount of inhibition due to competing adsorbate was related to the size of the molecules being adsorbed, their adsorptive affinities, and their relative concentration (Crittenden and Weber, 1978). Ionic data for metals are summarized in Table 3. The sorption capacities of four ions were not clearly related to their atomic weights, ionic radii, electronegativities, or ionization energies as a whole; however, only one or two factors will dominate regardless of the other factors. For example, Han et al. (1999) showed that Cd was most sorbed ionic species among Cu, Zn, Ni. Cd had highest atomic weight and ionic radius. In juniper and alfalfa, Cu with highest electron gravity and ionization energies was dominating species.

Initial concentration (mg/L)	Fiber-heavy metal partition coefficient (L/kg)			
	Zn	Ni	Cu	Cd
10(single)	747	-	-	-
10(multi)	32	46	402	100
20 (single)	245	-	-	-
20(multi)	2	10	100	14

Oxidation status	Ni		Cu		Zn		Cd	
	(+1)	(+2)	(+1)	(+2)	(+1)	(+2)	(+1)	(+2)
AtomicNo.	28		29		30		48	
Atomic weight	58.7		63.54		65.37		112.4	
Ionic radius A	0.69		0.96	0.72	0.88	0.74	1.14	0.97
Electronegativity	1.8		1.9		1.6		1.7	
Ionization energies	7.63	18.2	7.724	20.3	9.391	17.96	8.991	16.9

Based on these observations, the ionization energies and atomic weight of ions appear to have an effect on sorption capacity. The reason why any of four physical properties play the major role in a given fiber can be explained by the fact that the lignocellulosic materials are heterogeneous substrates where chemical and physical properties of fibers interact with ionic properties and resulting complexity.

Chemical modification: The effect of sulfonation of fiber on sorption capacity is shown in Figure 1. Sulfonation modification increased more than 250% of the sorption capacity of juniper fiber.

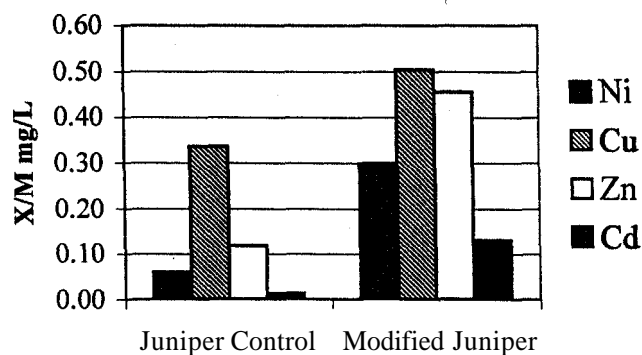


Figure 1. The effect of heavy metal adsorption by sulfonation at 50 mg/L.

CONCLUSIONS

From the adsorption isotherm test and laboratory-scale experiment, the following conclusion can be drawn:

- (1) Alfalfa fiber had slightly higher sorption capacity than juniper fiber except cadmium ion.
- (2) The Langmuir model fitted better to the experimental data than the Freundlich model for alfalfa-zinc ion system.
- (3) The adsorption of the heavy metal ions on the alfalfa and juniper fibers was strongly dependent on the equilibrium pH value of the solution.
- (4) The sorption of heavy metals onto fibers occurred through ion exchange and chemisorption.
- (5) Heavy metals were less sorbed when they are in solution together than when they exist alone in solution; however, the total adsorptive capacity of the adsorbent in multi-component phase was larger than that in a single compound phase. The sorption order based on mass of adsorbed ion is $Cu > Cd > Ni, Zn$.
- (6) Sulfonation modification increased more than 250% of the sorption capacity of juniper fiber.

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