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Removal Efficiency of Heavy Metals Using Various Resins and Natural Materials

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Abstract: Heavy metals found in local water are an environmental concern. These metals are potentially harmful since they can bio-accumulate in organisms and have been classified as toxic and/or carcinogenic. In this study, water was collected from a shipyard located on a bayou. Various materials (chitosan, mixed bed and amphoteric resins) were tested to determine their efficiency for metal remediation. Inductively coupled plasma mass spectrometry (ICP/MS) was used to quantify the efficiency of the materials examined. Overall, amphoteric resin was found to be the most efficient for a greater number of metals examined (Al, Co, Cu, Fe, Mn), followed by mixed bed which most efficiently removed As and Fe. Chitosan showed the poorest efficiency for metal removal.

Key words: Environmental pollution, metal chelating agent, remediation technology, toxic materials

INTRODUCTION

Clean water is a primary concern as populations grow exponentially and demands for water overburden our current supply. Heavy metal remediation poses a significant environmental challenge. Trends for global production and consumption of heavy metals have steadily increased from 1850 to present (Jarup, 2003). Exposure to these metals comes from the air, water and food sources and many of these elements accumulate in the body and lead to organ and tissue damage.

The main threats to human health from heavy metals come from cadmium, lead and arsenic exposure (Jarup, 2003). The most common source of human cadmium exposure is through cigarette smoking, however, it is also present in phosphate fertilizers (Jarup, 2003). Long term cadmium exposure contributes to kidney damage and loss of bone density (Satarug and Moore, 2004). Of course the impacts of lead exposure in humans have been known for some time. Children are perhaps more susceptible to the neurotoxic effects of lead with lead crossing the blood-brain barrier, substituting for Ca^{2+} ions and interfering with enzyme function (Lindsay and Schneider, 2003). Human exposure to arsenic comes mainly through food and drinking water consumption (Jarup, 2003). Arsenic pollution mainly comes from two industrial processes: smelting of non-ferrous metals and energy production from fossil fuels. Arsenic is also found in wood preservatives and some pesticides (Jarup, 2003). In a recent study, arsenic exhibited oxidative DNA damage to mouse brain tissue at the 1-2 ppm level commonly observed in environmental systems (Piao *et al.*, 2005).

A good review of chromium toxicity was found by Dayan and Paine (2001), they indicated the human lethal oral dose as $50\text{-}70 \text{ mg kg}^{-1}$ body weight. Long term exposure to chromium may result in liver and kidney disease (Dayan and Paine, 2001). Aluminum increases iron-induced oxidative damage in living tissue (Yokel, 2000). Although copper is necessary for proper nutrition and is present in biologically important enzymes, it can contribute to oxidative stress in cellular systems through the production of reactive oxygen species such as superoxide, hydroxyl radical and hydrogen peroxide (Gaetke and Chow, 2003).

Previously, various natural materials have been examined for their ability to remove metal contaminants. For example, chitin, a naturally occurring component of crab shells is converted to chitosan when it undergoes deacetylation. Chitosan has been investigated as a potential cationic polymer for use in water remediation (Huang *et al.*, 2000; Rana *et al.*, 2009).

Peat has been examined as an inexpensive alternative with efficiency being determined as a function of pH and in the presence competing metals (Brown *et al.*, 2000). Yan and Viraraghavan (2003) investigated the heavy metal absorption capacity of a both live and dead fungus, *Mucor rouxii*. The fungus was found to be most efficient for the removal of Pb, Cd, Ni and Zn with an optimal sample pH >6. Sawdust was also found to be efficient for the removal of Pb and Cu (Yu *et al.*, 2001). Various lignocellulosic materials, including aged hardwood bark, were found to have efficient removal of chromate when it was first reduced to chromite prior to column treatment (Harman *et al.*, 2007). Strains of *Bacillus* were studied

for their ability to grow in media with high chromium concentrations. These strains could remove up to 10% of Cr⁶⁺ in an industrial effluent (Qazilbash *et al.*, 2006). Various plant species were found to be effective in the phytoremediation of lead and zinc. Several perennial plants, *Alternanthera philoxeroides*, *Sanvitalia procumbens* and *Portulaca grandiflora*, were determined to effectively remove Pb from contaminated soil by 30-80% (Cho-Ruk *et al.*, 2006). In another study, cultured *Solanum nigrum* (black nightshade) was found to remove Zn in contaminated natural waters (Subroto *et al.*, 2007).

The goal of this study was to determine and directly compare metal removal efficiencies for several, easily accessible materials. Natural water samples were collected from a nearby shipyard located on Bayou Chico Bay, Pensacola, Florida. Samples were then remediated using resins and natural materials to determine removal efficiencies for various elements. Metals of interest in this study included: aluminum, arsenic, chromium, cobalt, copper, iron, manganese and vanadium. The materials selected for study were chitosan, mixed bed and amphoteric resins. Metals were quantified using inductively coupled plasma mass spectrometer (ICP-MS).

MATERIALS AND METHODS

Materials: Water samples from Bayou Chico were collected, treated and analyzed on 3/29/11, 4/5/11 and 4/12/11 (Experiments 1, 2 and 3, respectively). Materials for metal remediation treatment were chitosan-low molecular weight from blue waters crab shell (Sigma-Aldrich), mixed bed resin (Rexyn I-300; Fisher Scientific, analytical grade) and Dowex Retardion 11A8 (Sigma Aldrich) an amphoteric substance containing both carboxylic and amine groups. Ultratrace nitric acid was obtained from JT Baker. Samples were analyzed using a Varian 820 ICP/MS and calibration standards Var-Cal-2 (calibration standard) and Var-IS-1 (internal standard) were obtained from Inorganic Ventures, Inc. Lakewood, NJ.

Sample preparation: Bayou Chico water samples (pH 7.9) were collected on three separate days in plastic bottles and pre-filtered using a 0.45 µm Millipore mixed cellulose ester filter prior to processing through each column to determine the level of metal remediation achieved by each material type. For each experiment, three separate columns of each remediation material were constructed by adding deionized (DI) water and the slurry was transferred to a burette with a glass wool plug. The amount of remediation material used for each experiment was 14.6 g (Experiment 1), 7.0 g (Experiment 2) and 10.0 g (Experiment 3). Filtered

Bayou water (100 mL) was collected via gravity feed through the column into a clean HDPE bottle containing 1 mL Ultratrace nitric acid. Solvent blank samples were 1% v/v HNO₃.

ICP/MS analysis: A Varian 820 ICP/MS was calibrated for each element in the range of 0.01-100 ppb (Var-Cal-2 calibration solution) on high attenuation with a 50 ppb Var-IS-1 (internal standard). All samples and standards were analyzed in 1% v/v HNO₃. Each sample value reported from the instrument was a result of an average of 5 replicate scans for three separate samples of each type of remediation material.

Data and statistical analysis: Each treatment was repeated with 3 separate columns to ensure reproducibility. An ANOVA statistical analysis was performed for sorption capacities (q) with a Tukey HSD *post hoc* test to determine significance at p<0.05. All statistical calculations were completed using SPSS Statistics 19 software and Microsoft Office Excel. Metal speciation determinations were completed using Visual MINTEQ ver. 3 (Gustafsson, 2011).

RESULTS AND DISCUSSION

Pre-filtration of whole water samples removed less than 5% of all metals examined. Detection limits were defined as three standard deviations above the mean of 10 replicate solvent blanks (Table 1) (Wang, 2010). For the elements examined in this study, Cd, Zn and Ni fell below the instrument detection limits in filtered water samples.

Table 2-4 show concentrations and removal efficiencies (% Δ) for metals above detection limits pre and post treatment for Experiments 1-3. Filtered water values represent initial metal concentrations. Removal efficiencies were calculated using Eq. 1 C₀ is the initial metal ion concentration (µg L⁻¹) and C is the final concentration of metal in µg L⁻¹:

$$\Delta(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Table 1: Detection limits of the metals in the instruments

Metals	Detection limits ICP/MS (ppb)
²⁷ Al	0.196
⁷⁵ As	0.326
¹¹¹ Cd	0.149
⁵⁹ Co	0.009
⁵² Cr	0.038
⁶⁵ Cu	0.038
⁵⁷ Fe	7.580
⁵⁵ Mn	0.005
⁶⁰ Ni	0.022
⁵¹ V	0.027
⁶⁶ Zn	0.253

Table 2: Metal concentrations and their removal efficiency in experiment 1

	Conc. (ppb)							
	As	Al	Co	Cu	Cr	Mn	V	Fe
Filtered water	65.39	4.08	0.38	6.18	0.53	9.66	2.99	1448.85
Amphoteric	37.21 (43)	0.95 (77)	0.04 (89)	2.53 (59)	0.42 (21)	0.52 (95)	2.05 (31)	0.78 (100)
Mixed Bed	7.47 (89)	13.20 (-223)	0.00 (100)	4.57 (26)	2.21 (-317)	2.06 (79)	1.03 (66)	18.54 (99)
Chitosan	62.33 (5)	2.51 (39)	0.32 (14)	4.65 (25)	2.13 (-302)	162.67 (-1584)	2.29 (23)	1373.87(5)

Values in parenthesis are removal efficiencies (% Δ)

Table 3: Metal concentrations and their removal efficiency in experiment 2

	Conc. (ppb)							
	As	Al	Co	Cu	Cr	Mn	V	Fe
Filtered water	74.21	2.39	0.47	6.75	0.59	18.65	3.07	1637.54
Amphoteric	54.26 (27)	1.51 (37)	0.17 (64)	4.01 (41)	0.58 (2)	4.37 (77)	2.95 (4)	510.28 (69)
Mixed bed	29.71 (60)	10.85 (-354)	0.17 (64)	7.48 (-11)	2.00 (-239)	9.96 (47)	1.96 (36)	421.95 (74)
Chitosan	70.87 (5)	2.43 (-2)	0.43 (9)	4.71 (30)	1.63 (-177)	86.60 (-365)	2.42 (21)	1578.87 (4)

Values in parenthesis are removal efficiencies (% Δ)

Table 4: Metal concentrations and their removal efficiency in experiment 3

	Conc. (ppb)							
	As	Al	Co	Cu	Cr	Mn	V	Fe
Filtered water	84.46	5.32	0.53	10.64	1.08	12.30	0.44	1789.25
Amphoteric	49.94 (41)	1.14 (79)	0.08 (85)	3.95 (63)	1.02 (6)	1.24 (90)	1.08 (-145)	260.20 (85)
Mixed bed	24.00 (72)	15.20 (-186)	0.17 (68)	8.41 (21)	3.58 (-231)	5.78 (53)	1.43 (-225)	256.00 (86)
Chitosan	78.45 (7)	3.49 (35)	0.51 (4)	6.12 (42)	3.49 (-223)	63.88 (-419)	1.60 (-263)	1705.71 (5)

Values in parenthesis are removal efficiencies (% Δ)

Comparing the metal concentrations between each sample from Bayou Chico prior to remediation treatment, iron was consistently present in the highest initial concentration ranging from 1448.85 ppb (Table 2) to 1789.25 ppb (Table 4). Arsenic was second highest ranging from 65.39 ppb (Table 2) to 84.46 ppb (Table 4).

From experiment 1 (Table 2), amphoteric resin showed the greatest removal efficiency for Fe (100%), Mn (95%) and Co (89%). Chromium (total of all soluble species) was the least effectively removed metal (21%) by amphoteric resin. Mixed bed resin efficiently removed Co (100%), Fe (99%) and As (89%) but mixed bed resin appeared to contaminate the samples with Al and Cr resulting in higher metal concentrations post treatment (i.e., a negative removal efficiency). Chitosan was most effective at removing Al with a 39% removal efficiency but showed Cr and Mn contamination post treatment as well.

In experiment 2 (Table 3), amphoteric resin was most effective at removing Mn (77% removal efficiency), followed by Fe (69%) and Co (64%). Mixed bed resin removed 74% of Fe and appeared to show Al, Cu and Cr contamination. Chitosan most effectively removed Cu (30%) and showed Al, Cr and Mn contamination.

For experiment 3 (Table 4), amphoteric resin had greatest removal efficiency for Mn (90%), Fe (85%) and Co (85%) and it was least efficient in removing Cr (6%). Mixed bed resin was most efficient for Fe removal (86%) and showed Al, Cr and V contamination.

Chitosan was most efficient for the removal of Cu (42%) and showed Cr, Mn and V contamination.

The previous discussion compared efficiencies within each experiment. However, in order to account for the different amounts of material used in each experiment, sorption capacity values (q) were determined for each material using equation 2 where q (µg metal ion per g adsorbent), C₀ is the initial metal ion concentration (µg L⁻¹), C is the final concentration of metal ion (µg L⁻¹), m is the amount of material used (g) and V is the volume of sample used (L) (Hui *et al.*, 2005; Zhu *et al.*, 2007):

$$q = \frac{C_0 - C}{m} V \tag{2}$$

Sorption capacity values obtained from all three experiments were calculated for each material (Table 5). Overall, mixed bed and amphoteric resins had the highest and equivalent q values for Fe (14±3 µg g⁻¹).

Chitosan showed large variability in q values for the removal of Al (0.003±0.02) resulting in standard deviations greater than the sorption capacity value due to contamination in experiment 2. Mixed bed resin exhibited a similar response for Cu (0.01±0.01). The large variation in the mixed bed resin results is most likely due to Cu contamination in experiment 2 which did not appear in experiments 1 and 3. Amphoteric resin had low, negative q values for Cr (-0.0002±0.002) indicating either contamination by the resin or initial concentrations near the detection limit. The mixed bed resin showed Al

Table 5: Sorption capacity (q)

	q (µg g ⁻¹)							
	As	Al	Co	Cu	Cr	Mn	V	Fe
Amphoteric	0.28±0.06 ^a	0.030±0.01 ^a	0.0040±0.001 ^a	0.04±0.01 ^a	-0.0002±0.002 ^a	0.14±0.06 ^a	0.0020±0.006 ^a	14.0±3.0 ^a
Mixed Bed	0.59±0.09 ^b	-0.090±0.05 ^b	0.0035±0.0009 ^b	0.01±0.01 ^b	-0.019±0.006 ^b	0.08±0.03 ^a	0.0100±0.010 ^a	14.0±3.0 ^a
Chitosan	0.04±0.03 ^c	0.003±0.02 ^a	0.0004±0.0009 ^b	0.03±0.02 ^{ab}	-0.017±0.008 ^b	-0.80±0.30 ^b	0.0008±0.010 ^a	0.7±0.3 ^b

Values are Mean±SD, Values followed by different superscripts are significant Tukey group

Table 6: Speciation calculated using Visual MINTEQ software

Element	Species	Total conc. for given element (%)
As	HAsO ₄ ²⁻	89.1
	H ₂ AsO ₄ ⁻	10.9
	H ₃ AsO ₄ , AsO ₄ ³⁻	All<0.1
Al	Al(OH) ₃	97.4
	Al(OH) ₃ (aq)	2.5
	Al(OH) ₂ ⁺ , Al ³⁺ , Al ₂ (OH) ₂ ⁴⁺ , Al ₃ (OH) ₄ ⁵⁺ , AlOH ²⁺	All<0.1
Co	Co ²⁺	98.3
	CoOH ⁺	1.6
	Co(OH) ₂ (aq), Co(OH) ₂ ⁻ , Co ³⁺ , Co ₄ (OH) ₄ ⁴⁺ , CoOH ²⁺	All<0.1
Cr	Cr(OH) ₃ (aq)	97.2
	Cr(OH) ₂ ⁺	2.7
	Cr(OH) ₄ ⁻ , Cr ³⁺ , Cr ₂ (OH) ₂ ⁴⁺ , Cr ₃ (OH) ₂ ⁵⁺ , CrOH ²⁺	All<0.1
Cu	CuOH ⁺	64.1
	Cu ²⁺	25.6
	Cu(OH) ₂ (aq)	9.4
	Cu ⁺	0.7
	Cu ₂ (OH) ₂ ²⁺	0.2
	Cu(OH) ₃ ⁻ , Cu(OH) ₄ ²⁻ , Cu ₂ OH ²⁺ , Cu ₃ (OH) ₄ ²⁺	All<0.1
Fe	Fe(OH) ₂ ⁺	85.1
	Fe(OH) ₄ ⁻	6.0
	Fe ²⁺	4.9
	Fe(OH) ₃ (aq)	3.8
	FeOH ⁺	0.2
	Fe(OH) ₂ (aq), Fe(OH) ₃ ⁻ , Fe ³⁺ , Fe ₂ (OH) ₂ ⁴⁺ , Fe ₃ (OH) ₄ ⁵⁺ , FeOH ²⁺	All < 0.1
Mn	Mn ²⁺	99.8
	MnOH ⁺	0.2
	Mn(OH) ₄ ²⁻ , Mn ³⁺ , Mn ₂ (OH) ₃ ³⁺ , Mn ₂ OH ³⁺ , MnO ₄ ⁻ , MnO ₄ ²⁻	All < 0.1
	V(OH) ₃ ⁺	99.3
V	VO ²⁺	0.6
	VO ³⁺	0.6
	H ₂ V ₂ O ₄ ²⁺	< 0.1

(-0.09±0.05) and Cr (-0.019±0.006) contamination in all three experiments as indicated by a negative sorption capacity in Table 5.

To determine significant differences between q values for each material, a comparison of means using one way ANOVA with Tukey HSD *post hoc* test (p<0.05) was performed. Statistically different results are indicated as separate Tukey groups (a, b, c) in Table 5. For example comparison of q values for As alone showed all three materials to be statistically different (groups a, b, c). For Al, amphoteric and chitin were similar (group a) and mixed was different (group b).

To better predict dissolved species present in the samples, ion speciation calculations were carried out at fixed pH (Table 6) using the chemical modeling software, Visual MINTEQ ver. 3.0 (Gustafsson, 2011). Predominant species were HAsO₄²⁻, Al(OH)₃, Co²⁺, Cr(OH)₃, Cu(OH)⁺, Fe(OH)₂⁺, Mn²⁺ and V(OH)₃⁺ and are listed as percent concentration by element. Other minor species are listed for concentrations <0.1% of the total element concentration.

Overall, amphoteric resin had the best removal efficiencies and sorption capacity values for a larger number of metals (Al, Co, Cu, Fe, Mn) followed by mixed bed showing best removal for two of the metals tested (As and Fe). Chitosan was poorest overall at metals removal.

Water concentrations of As are normally less than 10 ppb which is the maximum exposure level set by the EPA but industrial areas can have higher concentrations. Human exposure to arsenic is mainly through food and drinking water. Drinking water with concentrations of 100 ppb is associated with increased cancer risk (Jarup, 2003). Initial data from the Bayou Chico shipyard show arsenic concentrations as high as 84 ppb. The elevated levels of As seen in our samples is most likely due to the proximity of the sampling location to an abandoned creosote treatment facility.

Sample pH can have a significant effect on removal efficiencies by ion exchangers. When a different amphoteric resin, Fiban AK-22, was tested, the optimal

range of was pH 3-4 (Leinonen, 1999). This may explain the reduced efficiency for Cr removal in this study near pH 8.

The mixed bed resin used in this study contains RSO_3^- functional groups similar to Amberlite IR 120-H. Sapari *et al.* (1996) found 100% removal efficiency for Cr in contaminated industrial wastewater using Amberlite IR 120-H. However, our results show Rexyn I-300 mixed bed resin was not efficient at the removal of Cr for the water samples examined. Hubicki *et al.* (1999) discuss possible difficulties in Cr removal due to soluble Cr complexes present (10-32%) which are not removed by sulfonic cation exchange material.

Amberlite IRC-84 (carboxylic group) contains similar functionality to the amphoteric resin examined in this study. Using Amberlite IRC-84, it was found to effectively remove Cu from ammonia industrial wastewater (Hubicki and Jusiak, 1978). This is consistent with our results for Cu when comparing relative efficiencies of the three resins examined.

The chitin used in this experiment (blue waters crab shell, Sigma-Aldrich) shows similar efficiencies for Co, Fe and Cr to the material tested by Rana *et al.* (2009). However, our observations showed Mn contamination. In contrast, Rana *et al.* (2009) observed that Mn was removed with the highest efficiency. Previously reported studies of chitosan showed decreased efficiency for Cr removal (Rana *et al.*, 2009; Kartal and Imamura, 2005). Despite the different material origin, chitosan from crab shell showed remarkably close similarity in removal efficiency with the only exception being Mn.

In another study, chitin from prawn shell was examined for its ability to remove Cu. After deacetylation to convert to chitosan, Cu solutions were tested at various pH values with removal efficiency increasing at higher pH (Chu, 2002). This pH dependence is perhaps due to protonation of available amine functional groups in the chitosan (Dambies *et al.*, 2000). The number of available amine sites decreases with an increase in proton concentration.

In a study by Nomanbhay and Palanisamy (2005), chitosan was coated onto acid treated oil palm shell charcoal. By coating chitosan on this charcoal, a granular matrix was produced rather than a gel typically observed for chitosan alone at low pH. Using the modified chitosan matrix, effective removal of Cr(VI) was achievable at pH 4-6.

Remarkably, the results of this study show that for a naturally derived material, such as chitin, there was good reproducibility compared to previously published data. This study helped improve our knowledge of the

capacity for certain materials to effectively remove metals from contaminated natural waters. For the materials tested, it was determined that amphoteric resin was the best for metals remediation. Further experiments are needed to test a greater variety of materials. It is suggested that a similar experimental design is used so direct comparisons of removal efficiency can be made. Samples of varied pH should also be tested to determine pH effects on removal efficiency.

CONCLUSION

Various natural and manufactured materials have been examined for metals removal efficiency by using known, defined standards under controlled experimental conditions. This study used natural water samples to compare the removal efficiency and sorption capacity of three commonly available materials. By using natural water samples that contain dissolved organic species and salts, this study provided a more realistic description of the performance of these materials for complex sample matrices. Overall, the amphoteric resin tested here had the highest removal efficiencies and sorption capacities and showed the greatest potential for removal of dissolved metals.

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