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Removal of Trace Concentrations of Heavy Metals Using Complexing Ion-Exchange Resins

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Abstract: Oak Ridge National Laboratory is examining potential new technologies for treating radiologically-contaminated process wastewater. The current treatment facility is aging and is optimized to remove ^{90}Sr, but future wastewaters are likely to contain mostly activated metals, such as ^{51}Cr and ^{64}Cu. Other low-volume wastewaters may contain trace concentrations of Hg and U. Complexing ion-exchange resins and other specialized sorbents were tested for removing trace concentrations of heavy metals. Short-term column tests and batch loading tests were conducted using a surrogate wastewater and various sorbents. These tests showed that metal uptake was very rapid, and that good removal and relatively high loadings could be achieved from a very dilute wastewater surrogate. Forager M-TU (Dynaphore, Inc.) showed the best overall results, removing 91.9% of the Cr, 99.3% of the Cu, >99.7% of the Hg, and >99.9% of the U with a contact time of 120 seconds in a short-term column test.

Keywords: Wastewater, treatment, ion exchange resin, mercury, uranium, radionuclides

INTRODUCTION

Oak Ridge National Laboratory (ORNL) is considering building a new treatment facility for radiologically-contaminated process wastewater. The current facility, the Process Wastewater Treatment Complex, is aging, is very large (~150 gallons per minute (gpm)) and is optimized to remove ^{90}Sr. Most of the current wastewater comes from contaminated groundwater,

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which future environmental remediation work should greatly reduce. The primary future sources of radiological process wastewater will be the High Flux Isotope Reactor (HFIR) and the Spallation Neutron Source (SNS), which will produce water containing trace quantities of activated metals, such as ^{51}Cr and ^{64}Cu. The flow rate from these sources is expected to be in the range of 5–10 gpm. Other low-volume wastewaters, such as burial ground leachate, may contain trace concentrations of Hg and U. Complexing ion-exchange resins and other specialized sorbents were tested for removing trace concentrations of heavy metals.

MATERIALS AND METHODS

Surrogate wastewater was prepared by adding small amounts of analytical standard solutions to tap water, to give nominal concentrations of 10 μg/L of Cu, Cr and Hg, and 300 μg/L U, plus 55 mg/L Ca, 16 mg/L Mg, and 8 mg/L Na... These concentrations correspond to measured or predicted concentrations for wastewaters that will be generated in the future at ORNL. Four different sorbents were initially tested, including ion-exchange resins with iminodiacetic and methylenethiol active sites, and specialized sorbents with polyamine/polyamide, and dithiocarbamate groups. A fifth sorbent with humic acid groups was tested later (See Table 1). These sorbents are designed to be much more selective for transition group heavy metals than for the common alkaline and alkaline-earth metals (1–3). Several of these sorbents have been tested in the past for removing trace concentrations of mercury from water (4, 5).

Short-term column tests were performed using a 1.3-cm I.D. by 25-cm tall clear PVC column. About 7 cc of sorbent was weighed, slurried in water, and poured into the column. Surrogate solution was pumped down through the column for several minutes, and then the sorbent height was measured and the settled volume was calculated. The flow rate was measured by collecting effluent in a graduated cylinder. A sample was taken for metals analysis and then the pump speed was adjusted and a new sample was taken after several bed volumes of surrogate had been pumped through the column. These short-term column tests were designed to determine the relative performance

Table 1. Description of sorbents tested

Sorbent	Active site	Company
Amberlite IRC-718	Iminodiacetate	Rohm & Haas
Forager M	Polyamine/Polyamide	Dynaphore, Inc.
Forager M-TU	Dithiocarbamate	Dynaphore, Inc.
Ionac SR-4	Methylenethiol	Sybron Chemicals
Humasorb	Humic acid	Arctech, Inc.

of the sorbents, and to determine the minimum residence time required to meet treatment requirements. Because of the low metal concentrations in the surrogate solution, running the columns to breakthrough would have required very long run times, and were beyond the scope of these tests.

Batch loading tests were conducted using Forager M-TU sorbent, which showed the best results in the column tests, and Humasorb, which was received after the column tests were completed. Various ratios of surrogate solution and sorbent were measured into polyethylene bottles, which were placed on a roller for 4 days to gently mix the slurries. Then samples of the solution were removed, filtered using 0.2 μm syringe filters, and submitted to the lab for analysis. Chromium, copper, and uranium were analyzed by inductively-coupled plasma—mass spectroscopy (ICP-MS), and mercury was analyzed by cold-vapor atomic adsorption (CV-AA). The analytical laboratory reports the results to three significant figures, with a Standard Error of $\pm 10\%$ of the concentration value.

RESULTS AND DISCUSSION

Table 2 shows the results of the short-term column tests. A sample of the unused surrogate wastewater contained 10.8 μg/L Cr, 13.9 μg/L Cu, 8.6 μg/L Hg, and 380 μg/L U. All of the sorbents were very good at removing mercury from the water, with all of the effluent samples below

Table 2. Summary of analytical results for short-term column tests

Sorbent	Flow rate (BV/min[a])	Percent removal			
		Cr	Cu	Hg	U
Amberlite IRC-718	1.03	3.7	80.9	>97.7	99.9
	0.51	10.7	81.0	>97.7	99.7
	0.27	10.1	77.6	>97.7	97.3
Forager M	1.00	61.7	93.5	>97.7	>99.9
	0.54	76.5	86.5	>97.7	>99.9
	0.26	90.5	86.9	>97.7	>99.9
Forager M-TU	1.03	73.1	91.0	>97.7	>99.9
	0.51	88.3	97.5	>97.7	>99.9
	0.27	91.9	99.3	>97.7	>99.9
Ionac SR-4	1.06	36.1	86.9	>97.7	52.6
	0.52	51.1	91.2	>97.7	62.4
	0.28	65.9	93.0	>97.7	68.9

[a]Bed volumes per minute, based on the empty-bed volume of the sorbent.

Table 3. Summary of batch loading test results using Forager M-TU sorbent

Solution Volume (mL)	Sorbent weight (g)	Liquid concentrations (μg/L)			
		Cr	Cu	Hg	U
100	0.0	11.1	27.8	5.02	286
100	0.001	8.09	8.63	0.226	167
100	0.0107	6.02	5.12	<0.2	1.48
10	0.0094	2.09	5.01	<0.2	0.10
10	0.1006	1.46	1.20	<0.2	0.01

the detection limit of 0.2 μg/L. All of the sorbents except Ionac SR-4 were also very good at removing uranium. Chromium, which was present as the chromate ion, showed the poorest results for all of the sorbents. Overall, the Forager M-TU sorbent showed the best results, with Forager M a close second. The actual contact time of the surrogate with the sorbents in these tests was very short (30–120 seconds); however, longer contact times would probably be required to fully utilize the capacity of the sorbents for long-term use.

Tables 3, 4, and 5 show the results of the batch loading tests using the Forager M-TU sorbent. A batch loading test using 0.101 g of Humasorb in 10 mL of surrogate showed final liquid concentrations of 8.2 μg/L Cr, 4.1 μg/L Cu, 0.2 μg/L Hg, and 185 μg/L U, which are much higher than the corresponding results for the Forager M-TU.

The test results using the highest ratio of surrogate to sorbent show that fairly high loadings can be obtained from a very dilute wastewater. The uranium concentration in the surrogate solution was at least 10 times higher than for the other metals, and the maximum uranium loading was also much higher on the sorbent. The large increase in soluble uranium concentration and the drop in distribution coefficient for the test with the highest solution-to-sorbent ratio, compared to the second highest, suggest that the

Table 4. Sorbent loading results for batch loading tests using Forager M-TU sorbent

Solution/Sorbent ratio (mL/g)	Sorbent loading (μg/g sorbent)			
	Cr	Cu	Hg	U
100000	300	1900	1200	12000
9346	47	210	110	2700
1063	9.6	24	12	300
99.4	1.0	2.6	1.2	28

Table 5. Distribution coefficient results for batch loading tests using Forager M-TU sorbent

Solution/Sorbent ratio (mL/g)	Distribution coefficient (L/kg)			
	Cr	Cu	Hg	U
100000	37000	220000	2800000	71000
9346	7900	41000	260000	1800000
1063	4600	4800	62000	3000000
99.4	660	2200	6100	2800000

sorbent is reaching its maximum loading capacity for uranium. The manufacturer's data sheet gives maximum expected metal loadings of 3–24 mg/g for the Forager M-TU sorbent, which brackets the measured uranium loading.

REFERENCES

1. Senjupta, A.K., Zhu, Y., and Hauze, D. (1991) Metal(II) ion binding onto chelating exchangers with nitrogen donor atoms: Some new observations and related implications. *Environ. Sci. Technol.*, 25: 481–488.
2. Louriero, J.M., Costa, C.A., and Rodrigues, A.E. (1988) Recovery of copper, zinc, and lead from liquid streams by chelating ion exchange resins. *Chem. Eng. Sci.*, 43: 1115–1123.
3. Janauer, G.E., Gibbons, R.E., and Bernier, W.E. (1985) In *Ion Exchange and Solvent Extraction*; Markinsky, J.A. and Markus, Y. (eds.); Marcel Dekker: Vol. 9, Chapter 2.
4. Hollerman, W., Holland, L., Ila, D., Hensley, J., Southworth, G., Klasson, T., Taylor, P., Johnston, J., and Turner, R. (1999) Results from the low level mercury sorbent test at the Oak Ridge Y-12 Plant in Tennessee. *J. Hazardous Materials*, B68: 193–203.
5. Taylor, P.A. and Klasson, K.T. (1999) *Results of Small-Scale Tests for Removing Mercury from ORNL Process Wastewater*; Oak Ridge National Laboratory: Oak Ridge, TN, ORNL/TM-13763, (OSTI Order Number DE00009041).