Decontamination of Polluted Water by Treatment with a Crude Humic Acid Blend

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The use of humic acid for contaminant extraction from environmental matrices is an attractive concept because of the natural origin of the material and its low pollution potential. The problem of availability and the need for alkaline extraction were circumvented by the use of an unrefined leonardite humic acid (LHA) material used as received. This mined product has a high humic acid content, is inexpensive, and is available in bulk. LHA, applied without alkaline extraction, was used in the decontamination of water containing organic and inorganic test pollutants. The former included pyrene, difenzoquat, and rhodamine B base, while the latter were comprised of Pb^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Sr^{2+}, Cd^{2+}, As^{3+}, Ag^{+}, and Mg^{2+}. Simulated acidic waste solutions were treated by both batch precipitation and column extraction, with the pollutants applied singly and as mixtures. In the precipitation procedure, commercial lime was used as the coagulant, and virtually complete removal of the metals was achieved. Pyrene and difenzoquat were also removed, but rhodamine B base was not. With LHA column elution, all three organic compounds were fully extracted from waste solutions, including those containing mixed contaminants. Removal of metals by column treatment gave encouraging results, with Pb^{2+}, Cu^{2+}, and Sr^{2+} being extracted most effectively.

Introduction

Leonardite is mined humic material found across North America, with extensive deposits located in New Mexico and North Dakota. It contains major proportions of humic and fulvic acids, with the former predominating. Thus far, the primary use of leonardite has been as a fertilizer and soil conditioner in agriculture and horticulture. The benefits listed include improvements in water retention, cation-exchange capacity, and metal chelation (*1*). The same chemical features that convey these desirable properties to the material also make it a promising candidate for pollution remediation. Being an all-natural substance, it is especially attractive for this use, because its own pollution potential is minimal.

A recent patent by Zanin and Boetti (*2*) reports the use of humic acid for the removal of heavy metals, chlorinated organics, phosphorus, and nitrogen from wastewater. In the described procedure, however, an alkaline extract of humic acid is used, and only batch precipitation with an aluminum salt is employed. In the work described below, a leonardite blend was used in its crude form, dissolved in water for batch precipitation, and packed as a solid for column extraction.

Both approaches minimize preparation expenses and waste generation, but emphasis was given to continuous column extraction as a more attractive option for the decontamination of large volumes of water. The bulk availability of leonardite makes it a choice material for both treatment approaches. A portion of the contaminant extraction work was done on acid (pH 2.5) solutions in order to mimic acidic mine runoff streams and high-volume polluted pools such as the one at the Berkeley Pit Superfund site in Butte, MT.
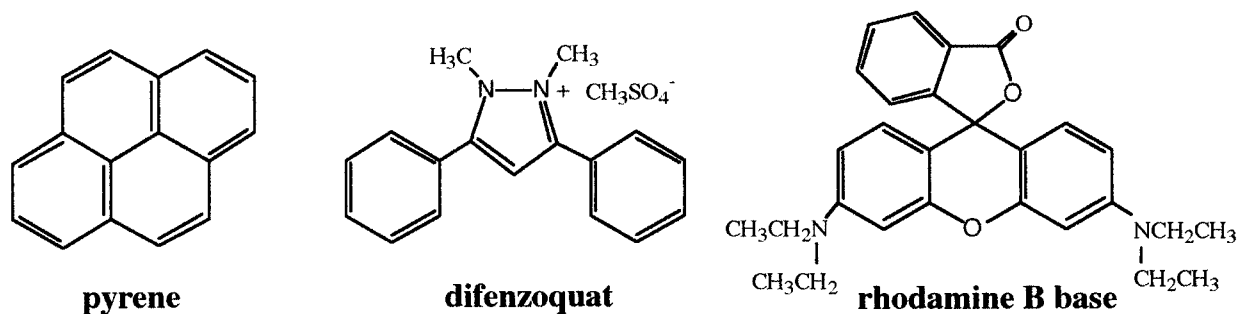
Materials and Methods

Chemicals. Studies were performed with a crude leonardite humic acid (LHA), obtained under the trade name Agri-Plus from Horizon Ag-Products (Kennewick, WA). This is a mined material, subjected to minimal milling, and was used as received. It is a dark brown powder, with particle diameters in the 0.1–0.6 mm range and a density of 0.78 g/cm³. It was reported by the purveyor to contain ≥80% humic acid, ≤5% fulvic acid, 15% clay, shale, gypsum, silica, and fossilized organic matter and to have a cation exchange capacity of 400–600 mequiv/100 mg (*1*). The ash content was determined to be 13.37 ± 0.05%. The carbon, hydrogen, and nitrogen contents, determined at the University of Idaho Analytical Sciences Laboratory, were 50.0, 4.9, and 1.1%, respectively. The metal content, determined according to the method reported by Pawluk (*3*), was found to be 140 ppm Mg, 269 ppm Ca, and 40 ppm Cu. Pb, Sr, Cd, and Zn were not detected. In view of the crude nature of the material, variability between batches must be anticipated for all these parameters. Pyrene (98%) was purchased from Sigma (St. Louis, MO), recrystallized from absolute ethanol, and sublimed onto a cold finger. All pyrene solutions were 1.0×10^{-7} M and were prepared by adding the appropriate amount of 0.02 M ethanolic pyrene to a volumetric flask, evaporating the ethanol, adding the aqueous solvent, and sonicating for 2 h. Difenzoquat (98.1%; American Cyanamid Corp, Princeton, NJ), sold under the trade name Avenge, and rhodamine B base (Sigma) were used without further purification. $CdCl_2$, $Pb(NO_3)_2$, $NaNO_3$, and $ZnCl_2$ (Aldrich, Milwaukee, WI); $CuCl_2$, $Cu(ClO_4)_2$, $Sr(NO_3)_2$, and $MgCl_2$ (J. T. Baker, Phillipsburg, NJ); $AgNO_3$ (High Purity Chemical Inc., Portland, OR); washed sea sand, and HNO_3 (Fisher, Pittsburgh, PA) were all used as received. All aqueous solutions were prepared with doubly deionized water treated with a 0.22 μm Millipore filter to a minimum resistivity of 16 MΩ cm. The lime was purchased locally from a garden supply store.

Instrumentation. Atomic absorption measurements were taken with a Varian AA-875 spectrometer using an air/acetylene flame. Slit width, lamp current, and wavelength were adjusted to values suggested by the manufacturer for the element in question. Fluorescence measurements were obtained with a Hitachi F-4500 fluorescence spectrophotometer equipped with a thermostated cell holder set at 20 ± 0.5 °C. Absorbance values were measured with a Hitachi U-3000 spectrophotometer equipped with a thermostated cell holder set at 20 ± 0.5 °C. Ion selective electrodes (ISEs) were supplied by pHoenix Electrodes (Houston, TX), and used in conjunction with a Chemtrix (Hillsboro, OR) pH/mV meter.

Procedures. *Precipitation.* Aqueous LHA solutions were prepared by adding 20 g of LHA to 250 mL of water and agitating on a reciprocating shaker for 3 days. The solution was then centrifuged at 4500 rpm for 15 min, and the supernatant was decanted and stored in glass. The resulting concentration of LHA was 300 ± 25 ppm, determined by

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CHART 1

pyrene **difenzoquat** **rhodamine B base**

evaporating 25 mL of the solution at 100 °C and weighing the residue. Precipitation studies were conducted on 1.0×10^{-5} M metal solutions prepared by adding 25 μL of a 1.00×10^{-2} M aqueous metal stock solution to 25-mL volumetric flasks and filling to volume with LHA stock solution. Experiments were conducted in triplicate for each metal. LHA was precipitated by saturating the solution with lime or by addition of 1.00 M $Mg(NO_3)_2$ to a final concentration of 0.01 M. Both methods required approximately 24 h for complete precipitation. Using UV−Vis absorption spectroscopy, it was determined that the supernatant contained less than 5 ppm humic acid. Its metal content was determined by atomic absorption spectrometry.

Column Extraction. LHA columns used for the removal of metals and mixed waste from aqueous solution were prepared by dry-packing a mixture of 1.66 g of LHA (2.1 cm³) and 3.33 g of washed sea sand into a 50×1.5 cm glass column to a depth of 6.0 cm. This bed was covered with a further layer of 0.50 g of washed sea sand and retained in the column by a plastic cap with a 2-mm hole overlaid with glass wool. Solutions (50 mL) were allowed to drain freely through the column and required approximately 1 h for complete elution. For the organic compounds studied, a 22×0.75 cm column was used, packed in a similar manner with about 10% of the quantity of material used for the larger column. It produced a flow of approximately 40 mL/h. After preparation, the columns were washed with three 50-mL aliquots of a pH 2.5 nitric acid solution. Less than 1 ppm humic acid, determined by absorption at 450 nm, was detected in the final rinse solution, indicating that the LHA was minimally soluble at pH 2.5. After acid washing, a 50-mL aliquot of a 1.0×10^{-4} M solution of a metal at pH 2.5 was eluted through the column, and the metal content of the eluent was monitored. For the studies with organic pollutants, 50-mL aliquots of 1.0×10^{-7} M pyrene, difenzoquat, and rhodamine B base solutions at pH 2.5 were eluted until amounts great enough to be detected by fluorescence measurements were observed in the eluent. The following excitation (ex), emission (em), and band-pass (bp) values were used (all nm): pyrene, ex 240 (bp 2.5), em 372 (bp 5); difenzoquat, ex 256, em 366, bp 5; rhodamine B, ex 260 em 590, bp 2.5. Experiments for each set of analytes (metals, organics, and mixed waste) were run in triplicate.

Binding Constants. Experimental procedures for determining metal binding constants were similar to those used by Stevenson et al. (*4*). Measurements were carried out in a 50-mL glass vessel fitted with a lid to accommodate reference and working electrodes, gas inlets for N_2 sparging and blanketing, a micropipettor, and a thermometer. A batch method was used to determine binding constants for LHA and metals. A series of solutions was prepared with varying metal ion content and a constant LHA concentration of 300 ± 25 ppm. All solutions were brought to a pH of 4.5 with nitric acid and were allowed to equilibrate for 24 h. The solutions were then sparged with N_2 for 10 min and subsequently blanketed with a continuous flow while the

electrode response was measured. The ionic strength was adjusted to 0.1 M with $NaNO_3$.

Difenzoquat and pyrene association constants with LHA were determined by a fluorescence quenching method as described by Gauthier et al. (*5*). Equilibrium dialysis techniques were not usable because of extensive adsorption of pyrene by the membrane and other system components. A 3.0-mL volume of a 1.0×10^{-7} M aqueous pyrene solution was placed in a quartz cuvette, and the fluorescence was monitored at 372 nm (ex 240 nm) until no further signal reduction due to pyrene adsorption and various quenching events was observed. A 1-h period was found to be adequate for this. A 10-μL volume of aqueous LHA was then added to the cuvette, and the fluorescence was monitored until a minimum was reached. Similar additions were continued until the fluorescence intensity was reduced to approximately one-half of its original value. A similar procedure was followed with measurements of difenzoquat fluorescence quenching, except that its concentration was 1.0×10^{-5} M.

Results and Discussion

The organic test compounds—pyrene, rhodamine B base, and difenzoquat—were chosen because of their different water solubilities, which is an important parameter in the assessment of a water decontamination technique. They are also all fluorophores and can be determined at low concentrations (see Chart 1). The metal ions studied—Cu^{2+}, Cd^{2+}, Pb^{2+}, Ag^+, Sr^{2+}, Zn^{2+}, Ni^{2+}, and As^{3+}—are typically present in mine water runoff and are prevalent at the Berkeley Pit site. Mg^{2+} was added at a somewhat higher concentration to represent the ubiquitous alkaline earth metals in environmental matrices. To clarify the extent of interaction between LHA and these types of pollutants, association constants for pyrene and difenzoquat, Cu^{2+}, Cd^{2+}, Mg^{2+}, and Pb^{2+} were determined.

Organic Associations. Fluorescence quenching methods are commonplace in the determination of association constants for humic acids and fluorescent probe molecules (*5−10*). The validity of this practice is in some question, in view of both the mechanism of interaction between the species in question and the kinetics of the processes involved (*9−13*). Irrespective of these considerations, however, the values arrived at by the fluorescence quenching method have a relative value and can be used to assess behavior patterns of comparable systems. In the present case, experimental fluorescence measurements were corrected by the method developed by Gauthier et al. (*5*), which incorporates the absorbances at the wavelengths of interest:

$$\frac{F_{corr}}{F_{obsv}} = \frac{2.3dA_{ex}}{1 - 10^{-dA_{ex}}} 10^{gA_{em}} \frac{2.3sA_{em}}{1 - 10^{-sA_{em}}} \qquad (1)$$

where F_{corr} and F_{obsv} are the corrected and observed fluorescence intensities, respectively; A_{ex} and A_{em} are the absorbance per centimeter of solution at the excitation and
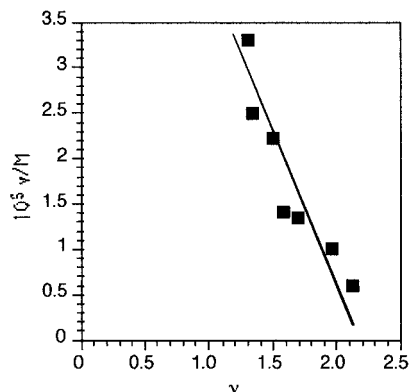
FIGURE 1. Scatchard plot for the association of Cu^{2+} with crude LHA.

TABLE 1. Conditional Stability Constants of Metal Ions with Crude LHA

cation	log K_o	cation	log K_o
copper(II)	5.47	magnesium(II)	4.61
cadmium(II)	4.77	lead(II)	5.32

TABLE 2. Removal (%) of Metal Ions by Batch Precipitation

metal	(Mg(NO₃)₂/LHA	lime/LHA	lime
copper(II)	57.5 ± 7.2	BDL[a]	BDL
cadmium(II)	35.2 ± 1.4	BDL	BDL
lead(II)	58.7 ± 3.0	BDL	BDL
silver(I)	9.52 ± 0.51	BDL	BDL
strontium(II)	BDL	BDL	89.8 ± 4.4

[a] BDL, below detection limit.

emission wavelengths, respectively; d is the inner width of the cuvette; g is the distance between the edge of the excitation beam and the inside wall of the cuvette; and s is the width of the excitation beam (all in cm). This treatment corrects for absorption at both the excitation and emission wavelengths. The fluorescence intensities obtained were used to generate a Stern−Volmer plot, based on

$$\frac{F_o}{F} = 1 + K[Q] \qquad (2)$$

where F_o and F are the fluorescent intensities in the absence and presence of quencher, respectively; Q is the quencher (i.e., LHA), and K (ppm^{-1}) is the Stern−Volmer quenching constant. This constant is the parameter of interest and will be reported as such, without mechanistic implications. At low LHA concentrations, a plot of F_o /F vs [LHA] was found to give a straight line with the requisite slope of K. At higher humic acid concentrations (>20 ppm), the plot showed an upward curvature, and this region was therefore avoided. The Stern−Volmer constant obtained for pyrene/LHA was $(6.39 \pm 0.23) \times 10^{-2}$, and for difenzoquat/LHA, it was $(3.26 \pm 0.35) \times 10^{-2}$. No value could be obtained for rhodamine B base since its fluorescence was not notably quenched by LHA. Despite this, its removal from aqueous solution could be achieved by column treatment, as is described below.

Metal Binding. Potentiometric measurements with ISEs are commonly employed to determine metal−humic acid binding constants. This involves the addition of a known amount of metal ion to a standard humic acid solution and, after an appropriate equilibration period, the ISE measurement of uncomplexed metal remaining in solution. Scatchard plots are then used to determine the binding constant. The Scatchard equation is

$$\frac{\nu}{[M^{x+}]} = nK_o - \nu K_o \qquad (3)$$

where ν is the concentration ratio of bound metal ion to humic acid, n is the total number of reactive sites, K_o is the overall binding constant, $[M^{x+}]$ is the concentration of free metal ion of charge x in solution. A plot of $\nu/[M^{x+}]$ vs ν yields K_o as the slope. These plots tend to deviate from linearity because of the range of metal binding sites present in the humic polymer. The plots can, however, generally be divided into two linear regions, corresponding to carboxylic (lower ν) and phenolic (higher ν) sites. In the present study, only the regions of lower ν values were considered, because the strong interactions involving these sites are especially relevant to a practical decontamination process. A representative Scatchard plot for Cu^{2+} is shown in Figure 1. The LHA binding constants, summarized in Table 1, follow the trend (Cu^{2+} >

$Pb^{2+} > Cd^{2+} > Mg^{2+}$) reported for humic acids in the literature (*14, 15*).

Precipitation Studies. It is well-known that humic acids precipitate when the ionic strength of the solution is increased (*4, 16, 17*). The resulting precipitate is an agglomerate of humic acid molecules and bound metal ions. Preferential binding of certain cations by humic acid can be used as an effective means of removing problematic and potentially harmful metals from aqueous media. In such a process, the coagulated material, incorporating the metal ions as well as organic contaminants, settles as a sludge to the bottom of the vessel and can be isolated. It is however rarely the case that the contaminant ions are sufficiently plentiful to serve as the coagulant for the humic acid. This necessitates the addition of a further source of ions, which should not itself constitute a pollutant. In the present case, the LHA decontaminant was precipitated with commercial lime, which was chosen for its moderate cost and low environmental impact. The addition of lime does, of course, raise the pH of the solution—in the present case above 10. This is in itself sufficient to precipitate a majority of heavy metals as their hydroxides. The benefit of LHA in the process was however demonstrated by the inclusion of Sr^{2+} among the metal pollutants. $Sr(OH)_2$ has a solubility of 0.41 g/100 mL in water and cannot be removed by simple liming. Moreover, in the presence of LHA, all precipitated material (including metal hydroxides and organics) was incorporated in the sludge formed in the process. This made quantitative removal of all metal-containing residues possible. The results in Table 2 show that the lime/LHA treatment led to the complete removal of Sr^{2+} from the solution. Also included in Table 2 are the results of a series of experiments in which $Mg(NO_3)_2$, a neutral coagulant, was used to precipitate LHA. While heavy metal extraction was modest in this treatment, Sr^{2+} was completely removed. The results clearly show that the lime/LHA system is most effective for complete metal decontamination by precipitation.

Pyrene is a polyaromatic hydrocarbon with a water solubility (S) of 5×10^{-7} M and an octanol−water partition coefficient (K_{ow}) of 2×10^5; difenzoquat is a positively charged pesticide ($S = 2.1 \times 10^{-3}$ M; $K_{ow} = 0.14$); rhodamine B base is neutral dye ($S = 1.0 \times 10^{-2}$ M; $K_{ow} = 125.9$). Treatment of 1.0×10^{-7} M pyrene and difenzoquat solutions with both lime/LHA and $Mg(NO_3)_2$/LHA decontaminants resulted in their complete removal from water. In view of the micellar model of humic acid, this can be ascribed to the ability of dissolved LHA to sequester solution borne hydrophobic species. It has been shown (*11, 18, 19*) that many metal ions (notably Ca^{2+} and Mg^{2+} present in lime) effectively enhance the detergent character of humic acid. The attendant model suggests that these cations expedite the formation of

TABLE 3. Column Capacity for Metals (Single Solute)

metal ion	quantity retained (mg of metal/g of LHA)
lead(II)	2.22
magnesium	0.03
zinc	0.17
copper(II)	0.94
strontium	0.26
cadmium	0.34
arsenic(III)	0.30
nickel(II)	0.17
silver	0.15

TABLE 4. Column Extraction of Metal Mixture[a]

metal ion	metal/g of LHA	
	mg	mmol $\times 10^2$
lead(II)	0.30	1.1
magnesium	0.01	0.12
zinc	0.08	0.26
copper(II)	0.23	1.5
strontium	0.20	0.30
cadmium	0.08	0.30
arsenic(III)	0.28	0.40

[a] 50 mL containing 10 ppm of each; 25 ppm of Mg^{2+}.

TABLE 5. Column Capacities for Organic Test Compounds

compound	capacity (μmol/g of LHA)
pyrene	29.0 ± 1.8
difenzoquat	28.7 ± 0.7
rhodamine B	5.4 ± 1.3

TABLE 6. Column Extraction of Mixed Waste

contaminant	% removal	contaminant	% removal
pyrene	100	cadmium	25.6 ± 1.2
difenzoquat	100	copper(II)	79.9 ± 2.5
rhodamine B	100	strontium	97.3 ± 0.4
lead(II)	100	magnesium	5.0 ± 0.7
zinc	25.0 ± 0.3		

hydrophobic domains (pseudomicelles) in dissolved humic acid by partially neutralizing the negative charges on functional groups (mostly -COO$^-$) and drawing various chains of the polymer together through bridging interactions. This produces a contracted, micelle-like microenvironment with a relatively nonpolar interior and a polar surface. Hydrophobic species such as pyrene partition into these regions, are isolated there, and are carried down with the humic precipitate when the ionic strength is sufficiently increased. A similar mechanism may be operative in difenzoquat removal, although it is undoubtedly supplemented by electrostatic sorption of the positively charged herbicide to the negative humic matrix. Rhodamine B base, an uncharged soluble lactone, was neither sequestered nor sorbed, and virtually none was removed from solution by precipitation with LHA. The results obtained for difenzoquat and rhodamine do not follow their K_{ow} values (vide supra), which is probably partially due to the electrostatic interactions noted for difenzoquat.

Column Extraction. The precipitation methods described above are suitable only for decontamination by batch treatment. While this has potential uses in a number of scenarios, continuous extraction has no doubt a broader scope of application. While the acidity of such media is a distinct drawback for many decontamination techniques, in the case of extraction with humic acid it is actually an enabling factor. The low solubility of humic acids at pH values around 2 makes them a suitable medium for column-based extraction of such solutions. As described under Procedures, it was found that elution of an LHA-packed column with a solvent of pH 2.5 resulted in minimal solubilization of the humic material. The presence of sea sand in the packing mixture improved the wetting characteristics of the column and prevented the LHA fines from floating. A control study was carried out with a column packed only with sand, and this was found to retain none of the contaminants. The results of the column extraction studies with metals are summarized in Table 3. The column showed the greatest affinity for copper and lead, retaining these metals 4−5-fold better than any of the others. Previous work (12, 20, 21) has shown that metal−humic acid complexation rates can be very slow, and it must be inferred that this affects the metal exchange capacity of the column. No kinetic data were gathered in this study, but varying (slowing down) the eluent flow rate is likely to improve the retention characteristics for all metal species. For practical purposes, this means that a compromise between acceptable throughput and degree of contaminant removal would have to be reached.

To assess the extraction characteristics of the LHA column in a situation of competitive metal retention, a solution containing 10 ppm concentrations of Pb^{2+}, Cu^{2+}, Cd^{2+}, Sr^{2+}, and Zn^{2+} as well as 25 ppm Mg^{2+} was eluted. The results are shown Table 4, where the mmoles of each metal retained can be considered a rough indicator of their individual affinities for the column. The highest mole retention for a single solute (1.48×10^{-2} mmol of Cu^{2+} (g of LHA)$^{-1}$) was slightly higher than the combined retention of the mixed metal ions (1.34×10^{-2} mmol of M^{x+} (g of LHA)$^{-1}$). A complete set of data for the assessment of site specificity was not generated in this study, but a general indication was obtained by eluting a 50-mL aliquot of 10 ppm Mg^{2+} through an LHA column that had previously been saturated with Cu^{2+}. The retention of Mg^{2+} on this column was the same as that obtained in the simultaneous elution of the mixture of metal ions. It suggests that a small number of sites was preferentially accessible to Mg^{2+}. A somewhat surprising aspect of the data in Table 4 is that Sr^{2+} was considerably more strongly retained by the LHA column than Mg^{2+}. In view of the size difference between these ions and the previous observation that smaller ions interact more strongly with humic acid (22), this may be ascribed to the fact that the hydrated radii of Mg^{2+} and Sr^{2+} are 8 and 5 Å, respectively (23). Also, Stevenson has pointed out (24) that Mg^{2+} behaves like a monovalent ion in its interactions with humic acids and is easily displaced by other divalent cations.

Retention of the organic test compounds by the LHA column was found to be complete. Elution of 50 mL of a pH 2.5 solution containing 1.0×10^{-7} M pyrene, difenzoquat, and rhodamine B base was found to result in removal below their detection limit. This is especially interesting for the case of rhodamine, which, as noted above, could not be removed by LHA precipitation. Its apparent affinity for LHA in the column, operated under saturated flow conditions, may be ascribed to extensive contact between sorbent and sorbate in the process. A relative column capacity was determined for each compound by sequential additions of their solution to the column until the compound was detected in the effluent. The results are summarized in Table 5, which shows that the capacity for rhodamine B was lowest, while it was similar for the other two test compounds.

Column performance with a mixed waste sample including both metal and organic contaminants is shown in Table 6. The results indicate that the retention values obtained for

the metals (concentrations as in Table 4) were comparable to those obtained with solutions containing no organic contaminants. All three organic test compounds were introduced into the solution at 1×10^{-7} M concentrations and were completely retained.

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