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EVALUATION OF EXTRACTANT-COATED FERROMAGNETIC MICROPARTICLES FOR THE RECOVERY OF HAZARDOUS METALS FROM WASTE SOLUTION

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ABSTRACT

A magnetically assisted chemical separation (MACS) process developed at Argonne National Laboratory is a compact method for the extraction of transuranic (TRU) metals from, and volume reduction of, liquid waste streams that exist at many DOE sites. The MACS process utilized the selectivity afforded by solvent extractant/ion-exchange materials in conjunction with magnetic separation to provide a more efficient chemical separation. Recently, the principle of the MACS process has been extended to the evaluation of acidic organophosphorus extractants for hazardous metal recovery from waste solutions. Moreover, process scale-up design issues were addressed in respect to particle filtration and recovery.

Two acidic organophosphorus compounds have been investigated for hazardous metal recovery, bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex® 272) and

bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex® 301). These extractants coated onto magnetic microparticles demonstrated superior recovery of hazardous metals from solution as compared with data from solvent extraction experiments. The results illustrate the possibility for diverse applications of this technology for dilute waste streams. Preliminary process scale-up experiments with a high-gradient magnetic separator at Oak Ridge National Laboratory revealed the potential for very low microparticle loss rates.

INTRODUCTION

The use of the neutral organophosphorus extractants, CMPO-TBP, coated onto ferromagnetic microparticles has been evaluated for the extraction of TRU metals from acidic solutions (1). In that study, higher distribution coefficients were obtained for Am(III) and Pu(IV) extraction with CMPO-TBP coated microparticles than what was expected from liquid-liquid separation results under similar conditions. The study implied that a synergistic effect existed in this system unlike what was expected from typical solvent extraction recovery systems (1, 2). The identification of the synergistic effect has been difficult due to the chemical complexity of the microparticle support (mean diameter=0.88 μm), which is composed of iron oxide, charcoal, and N,N-methylene bis-acrylamide polymer. With the observed synergism, the application of metal recovery systems to very dilute solutions becomes attractive. The use of solvent-impregnated microparticles offers other advantages that are worthy of further investigation. Separation of phases and subsequent recovery of metal concentrate are facilitated by the absence of problems such as crud formation and solvent losses.[1] From an engineering standpoint, a magnetic filtration system offers a simple, compact, and cost-effective processing unit that can be easily tailored to specific processing goals.

The use of extractant-coated ferromagnetic microparticles has been extended for the evaluation of hazardous metal extraction with commercially

[1] Operating plants with Cyanex 272 report solvent losses of 10-15% from solubility and entrainment.

available bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex® 272), and bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex® 301) as in previous studies (1, 2). Specifically, this paper presents Cd and Zn recovery with the same polymeric support and compares the separation efficiency to solvent extraction measurements in the literature.

Considering the success of extractant-coated magnetic microparticles, preliminary process engineering issues were addressed. The small sizes of these particles preclude the use of conventional filtration and recovery systems. Therefore, magnetic separation is the targeted filtration concept. In this paper, magnetic field requirements and flow rate limitations were addressed using a high-gradient magnetic separator at Oak Ridge National Laboratory.

CMPO-TBP Systems

Previous studies (1) showed that coatings on the magnetic microparticles with 0.75 M CMPO in undiluted TBP had a partition coefficient (K_d) of 3000-5000 mL/g for Am. With the same concentration of extractants, a volume distribution ratio (D) of 240 was obtained with a solvent extraction (A/O=1) system. Based on these experimentally measured D values and the cubic dependency on the CMPO concentration, the predicted (2) K_d values would be about 80 mL/g, in contrast to 3000-5000 mL/g obtained experimentally. Similar behavior was observed with partition coefficients (5000-10,000 mL/g) for Pu which are much higher than predicted by solvent extraction measurements (2). The batch extraction results suggested a synergism between the solvent and complex microparticle support. Exactly how the support influences the metal-ligand separation is yet unknown.

Support-Extractant Interactions

Support-extractant interactions have been identified in previous investigations. Hydrometallurgy studies on solvent extractants impregnated into polymeric supports have identified the possible role of the polymeric support in the extraction of heavy metals (3-5). Also, Alexandratos and Miller (6) pointed out the influence of a polymeric support on the efficacy of covalently bonded (dialkylamino) pyridine ligands. The efficacy was maximized when the functionalization was less

than 50% due to an increased hydrophobicity surrounding each ligand. Their study suggested that the microenvironment surrounding the extractant played a role in metal-extractant complexation. Studies have established the influence of the polymeric support on the ligand-molecule interactions postulating that the polymeric support provided mechanisms to enhance the ligand specificity toward the metal ion (7,8). Furthermore, polymeric supports containing two different ligands can act in a cooperative manner to yield a higher level of complexation than can be attained from either ligand alone. This selectivity is obtained by coupling an access mechanism which serves to bring the metal ions into the polymeric support in a cooperative fashion (9). One example of this cooperative mechanism is a bifunctional polymer containing a phosphinic acid and quaternary ammonium salt (10). The synergistic cooperation allowed one ligand to bring the metal ion near the second ligand,which interacts selectively with the metal ion. This mechanism can also serve to dehydrate the metal ions (e.g., actinides), which thermodynamically (11) favors the metal-extractant complexation. Although the currently studied system has only one functional group on the support [acrylamide, $-CH_2CH(CONH_2)-$] the sorption of extractants on the microparticle can produce multi-functionality with the other matrix components. The actinides have both soft and hard characteristics (12), and the currently used N,N-methylene bis-acrylamide polymer provides a preorganization of soft and hard donor sites in near proximity that can aid in hydrogen bonding. Furthermore, the nitrogen in an amide has some characteristics of the ammonium ion,except the amides are far less basic. Thus, the sorption of the organophosphorus extractant onto the polymer support would increase the functionality of the microparticle. In addition, the interactions of the iron oxide and charcoal can affect the orientation of the metal ion and possibly aid in bringing the metal ion closer to the selective extractant. The systematic studies of different extractants other than CMPO and TBP provide some information toward the effect the complex support may have on the separation of transuranic and hazardous metals from solution.

EXPERIMENTAL

Reagents and Equipment

Metals were obtained as A.C.S.-grade sulfate salts and the extractants from commercial sources. Stock solutions were prepared by diluting concentrated

solutions.[2] The pH was adjusted with microliter quantities of dilute H_2SO_4 and monitored with an Accumet™ Model 10 pH meter from Fisher Scientific. The Cyanex 272 and 301 solvents were obtained from American Cyanamid Co. without further purification. The extractants were prepared by dissolving the appropriate amount in 0.5M di-(2-ethylhexyl) phosphoric acid (D_2EHPA) and ethanol. All the radiotracers were obtained from the Chemical Technology Division at Argonne National Laboratory. Metal analysis was done with inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The ferromagnetic microparticles consist of 1:1:1 N,N-methylene bis-acrylamide[$(H_2C{=}CHCONH)_2CH_2$], iron oxide,[3] and charcoal (Cortex Biochem, Inc.) with microparticle sizes between 0.1 and 25 μm and an average apparent diameter of 0.88 μm. Coated microparticles were prepared as described previously with an extractant-microparticle ratio of 2.5 mL:1 g and ethanol as the volatile diluent (13).

The bench-scale magnetic filtration experiments were conducted at ORNL with the uncoated magnetic microparticles.

PROCEDURE

Equilibrium Partition Coefficient Measurements

Contacts were performed in test-tube experiments with 2 mL of metal solution and approximately 3 mg of microparticles. The pH was adjusted by adding microliter quantities of dilute H_2SO_4. The test tubes were placed in an ultrasonic bath for 3-5 minutes to promote microparticle dispersion. Then, the samples were mixed vigorously for 3 minutes followed by placement in a 25°C bath for 3 minutes. This step was repeated twice more before the test tubes were placed in a magnetic rack where permanent magnets in the wall cause the particles to aggregate to one side of the test tube. The supernatant was withdrawn, and the pH was measured and the solution diluted with deionized water for ICP-AES analysis or prepared for gamma or liquid scintillation analysis. The equilibrium partition coefficient, K_d, is expressed in Eq. 1 as

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[2] Approximately 5 and 10 ppm for Cd(II) and Zn(II), respectively.

[3] The ferromagnetic microparticles will be referred to as magnetic microparticles.

$$K_d = \frac{V}{m}\frac{(C_i - C_f)}{C_f}, \qquad (1)$$

where V is the volume of the aqueous phase, m is the mass of microparticles, C_i and C_f are aqueous metal concentration before and after microparticle contact.

Magnetic Filtration Experiments

The microparticles were washed of preservatives with deionized water several times and dried prior to flocculation. Flocculation occurred in a standard stirred cell of 100 mm diameter, 142.2 mm height, and equipped with four baffles, each 10 mm wide. The initial volume of the suspension used in each experiment was 0.6 L with a flow rate between 6-51 L/hr. The magnetic filtration process was started 5 or 10 minutes after flocculation was initiated and ranged in magnetic field from 0.1-0.8 Tesla. Additional details are provided elsewhere (14).

RESULTS AND DISCUSSION

TRU Separation

In order to quantify the efficiency of solvent-coated microparticles, the results were compared to solvent extraction literature data. The partition coefficients, K_d, were converted to volume distribution ratios with similar conversion factors used in extraction chromatography, where the density, ρ, and weight percent of the extractant sorbed on the resin, wt %, are incorporated into the conversion factor,

$$D_{eq} = K_d \frac{100}{wt\%} \rho \cdot \qquad (2)$$

Magnetic microparticles were generally loaded to approximately 30% for CMPO-TBP and 1-5% for other extractants tested to date. These loadings generate a conversion factor of approximately 3 for CMPO-TBP particles and approximately 25 for other extractant-coated microparticles. In comparison, typical extraction chromatography resins are loaded to 10-40%. Partition (K_d) results from magnetic microparticle measurements with CMPO-TBP were presented elsewhere (2) but are summarized along with the calculated distribution ratios (D_{calc}) in Table 1. The relative efficiency,

Table 1. Americium and plutonium distribution ratios, D_{SX}, partition coefficients, K_d, and calculated distribution ratios, D_{calc}, for CMPO-TBP coated microparticles. Data taken from (2) using the exact solvent as in partitioning experiments except where indicated.

TRU metal	Solvent type (individual TBP)	Acid	D_{SX}	K_d (mL/g)	D_{calc}	ε
Am	1.2 M CMPO	4.9 M HNO_3	1200 (16)**	2790	8370	7.0
Am	1.2 M CMPO	2 M HNO_3	1700	4000-5000	12,000-15,000	7.1-8.8
Pu	1.0 M CMPO	PFP*	1400	18,000	54,000	39
Pu	1.0 M CMPO	8.0 M HCl	1600	26,000	78,000	49

*Plutonium finishing plant simulant.
**Extrapolated from solvent extraction with CMPO in 0.5 M TBP

ε, is defined here as the ratio of D_{calc} to the solvent extraction distribution ratio, D_{SX}. The relative efficiency for americium separation is 7-8.8 and 39-49 for Pu for the systems tested. The MACS particles coated with CMPO-TBP display a superior separation of americium and plutonium than would be expected from solvent extraction experiments. Therefore, it is postulated that there may exist a synergistic effect between the extractant and the particle material.

A possible explanation for the observed synergism may be the concept of extractant preorganization with the polymeric support as mentioned earlier. The microparticle constituents (either the charcoal, iron oxide, or N,N-methylene bis-acrylamide polymer) may interact with the metal by either dehydrating or partially dehydrating the metal or by retaining the metal in the proximity of the extractant until the extractant-metal reaction can take place. Sorption onto the charcoal by the chain group of the extractant would make the extraction independent of chain length. It is unclear how the iron oxide interacts with the extractant or aids in the separation. However, actinides and other radionuclides are known to sorb onto iron oxides, especially at alkaline pH values (17, 18). Studies of the uncoated microparticle support showed negligible partitioning of the metal onto the magnetic microparticles. If the polymeric support aids in extraction, one would expect that excessive solvent loading on the particle, with subsequent non-

participation by the particle support, would result in a decrease in the synergistic effect. This is precisely what has been observed (1, 13). These trends show that there is an optimum amount of extractant necessary for highest efficiency in separation. The reduction in the partition coefficient above the optimum amount may be partially attributable to the increase in aqueous solubility of the extractant (19).

Hazardous Metal Recovery

The commercially available extractants Cyanex 272 and Cyanex 301 were chosen because of their importance in industrial applications and their low aqueous solubilities. The overall reaction for divalent extraction by acidic organophosphorus reagents occurs according to the reaction

$$M^{2+} + \overline{(p+2)(HX)} \xleftrightarrow{\beta_{2p}} \overline{MX_2(HX)_p} + 2H^+, \qquad (3)$$

where HX denotes the extractant and β_{2p} the equilibrium constant (20). For extraction by Cyanex 272, p=2 for Cu, p=2 and p=1 for Zn, and p=2 and p=3 for Cd (20). Following from above, the graphical analysis for log K_d vs pH plots should produce data lines of slope 2 to correspond with the thermodynamic equation (Eq. 3).

Initially microparticles were prepared by sorbing a mixture of 0.25, 0.5, or 1.0M Cyanex solvent in 0.5M D_2EHPA, and ethanol. Figure 1 indicates concentration dependency curves for Zn recovery by Cyanex 272-coated microparticles,[4] and is representative of all extractants tested to date. Also, since the coating process has not been optimized, data scatter is observed. The K_d values decrease as a function of increased extractant concentration, which is contrary to solvent extraction studies (20). With consistency, partitioning was favored for microparticles prepared with the more dilute solvent. This is also consistent with previous coatings prepared with a variation of the TRUEX[5] solvent (13), where increased CMPO loading reduced TRU partition coefficients. This may be a direct result of the diminishing role (synergism) of the microparticle support when the solvent is overloaded onto the support.

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[4] Curve fits expressed herein are smooth correlations and not least-squares fit.

[5] Transuranic Extraction.

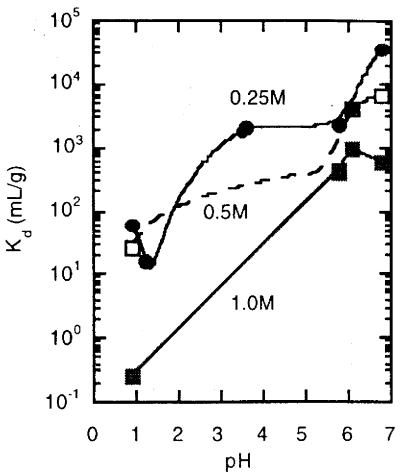

Figure 1. Concentration dependence for Zn recovery with microparticles coated with 0.25M, 0.5M, and 1.0M Cyanex 272 and 0.5M D_2EHPA diluted by ethanol at 20°C.

Cyanex 272

Cyanex 272, bis (2,4,4-trimethylpentyl) phosphinic acid, is a well known extractant that has received much attention in the selective recovery of Co over Ni from sulfate and chloride media, and the recovery of other notable hazardous metals (e.g., Zn, Cu, Cd) over alkaline earths such as Ca (21). The latter feature is highly advantageous for industrial applications due to loading considerations and subsequent gypsum formation upon stripping (21). The behavior of the Cyanex 272-coated microparticles with respect to Cd and Zn recovery is displayed in Figure 2 and Figure 3.

Figure 2 shows the percent extraction for Zn and Cd with the coated microparticles and the reported solvent extraction data (20). Zinc is extracted well at pH>4 while Cd(II) is extracted at pH>6. Solvent extraction measurements indicate that quantitative extraction of Zn(II) and Cd(II) occurs at pH>3 and pH>4, respectively, as indicated by the dashed lines in Figure 2. The shift is likely due to differences between the organic phase composition (diluent).

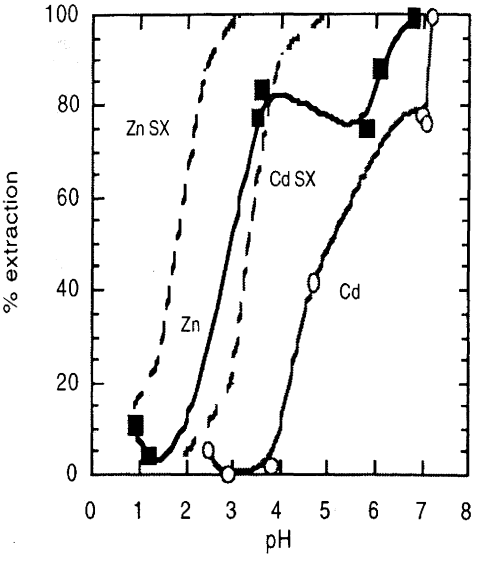

Figure 2. Percent recovery of Zn and Cd as a function of pH. Microparticles coated with 0.25M Cyanex 272 and 0.5M D_2EHPA diluted by ethanol at 20°C. Solvent extraction (SX) was performed with 0.6M Cyanex 272, 10v/o p-nonylphenol in Kermac 470B diluent at 50°C and O/A=1 (23).

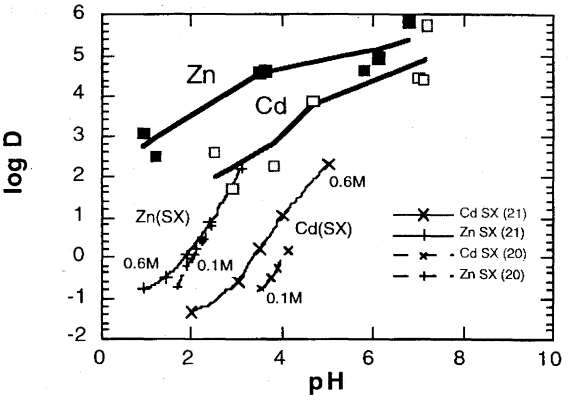

Figure 3. Partition coefficient curves for Zn and Cd with microparticles coated with 0.25M Cyanex 272 and 0.5M D_2EHPA diluted by ethanol at 20°C. Solvent extraction data (SX) was borrowed from two sources. The 0.6M Cyanex 272 data was carried out with the extractant in 10v/o p-nonylphenol in Kermac 470B diluent and 0.015M metal with O/A = 1 (21). The 0.1M Cyanex 272 data was carried out with the extractant in Isopar-H and 10^{-4} M metal with O/A = 1 (20).

Figure 3 illustrates the partition coefficients (converted to the volume distribution coefficient) with magnetic microparticles and includes solvent extraction data from Sastre et al. (20) and Cyanamid (21). Slope analyses of the above data were hindered by curvature of the data above pH~4 and high degrees of uncertainty associated with the analyses of the very dilute solutions. This problem is especially evident at low pH where small variations in the metal concentration can translate to order-of-magnitude differences in the calculated K_d and, consequently, flattened curves translate into a slope of 0.8 and not 2 which is expected from the solvent extraction studies (20). Nevertheless, the above data illustrates the superior extraction capabilities of microparticles coated with Cyanex 272 and D_2EHPA as opposed to conventional solvent extractions systems for the recovery of Zn and Cd.

Cyanex 301

Cyanex 301, bis (2,4,4-trimethylpentyl) dithiophosphinic acid, utilizes a sulfur atom as the anionic donor atom, which increases the acidity and facilitates extraction of metals at lower pH value. It has been shown to be less selective between transition metals at low pH (< 2) but extremely selective between heavy metals and alkaline earths. It displays a greater selectivity for Zn over Ca than Cyanex 272 (21). It has received attention as a possible replacement for Cyanex 272 for recovery of Co from Ni sulfate solutions.

Figure 4 shows Cd does not extract well in acidic to neutral media. This is rather surprising considering the soft character of Cd(II) and the softness of the donor sulfur. Although no Cd data were available for direct comparison, 5% Cyanex 301 in dodecane is known to quantitatively remove 100 mg/L of Cd at pH 1 (22). Also, it has been shown to remove Cd from wet-process phosphoric acid (23). The data on Zn extraction show similarities to Cyanamid Company solvent extraction data (21), which reports quantitative extraction of Zn at pH<2.3. However, slope analysis was difficult because of the low pH of extraction (24). According to Sole et al. (24) extraction of Zn from sulfate media follows as expected from Eq. 3. These data are presented in Figure 4 for comparative purposes. The increased extraction efficiency with magnetic particles is evident.

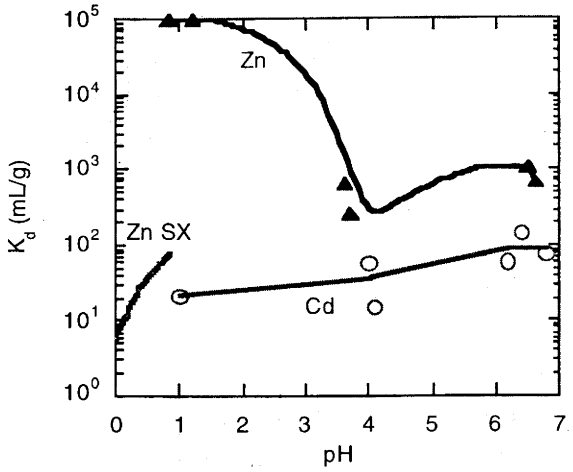

Figure 4. Partition coefficient curves versus pH for Zn and Cd with microparticles coated with 0.25M Cyanex 301 and 0.5M D_2EHPA diluted by ethanol at 20°C. Solvent extraction (SX) data from Sole et al. (24) was collected for 1 mM $ZnSO_4$ in 0.5M Na_2SO_4 with 0.1M Cyanex 301 in xylene and O/A = 0.5.

With regard to recovering Cd, Figure 5 illustrates that Cyanex 301 is more effective than Cyanex 272 at pH <3.5, while at higher pH Cyanex 272 is more effective. For Zn recovery, as presented in Figure 6, Cyanex 301 is highly effective at pH<3 while at higher pH Cyanex 272 is more effective.

The results obtained on extractant-coated microparticle systems are encouraging. The current experimental plan was not attempting to decouple the contributions from the various magnetic microparticle components. The attempt of this study was to identify a similar synergistic effect with a variety of extractants on the same supporting matrix. The synergistic effect was evident for Cyanex 272 extraction of Zn and Cd and for Cyanex 301 extraction of Zn. Extraction of Cd with Cyanex 301 could not be ascertained because of the lack of available solvent extraction distribution measurements for the metal. Future investigations will determine adsorption mechanisms and loading capacities, stripping efficiencies, and solvent losses, as well as other solvent-microparticle systems.

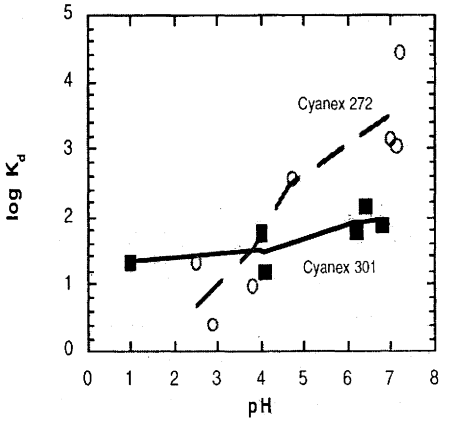

Figure 5. Cadmium partition coefficient curves with microparticles coated with 0.25M Cyanex 272 and 301 and 0.5M D_2EHPA diluted by ethanol at 20°C. Note the ordinate axis is expressed in log format.

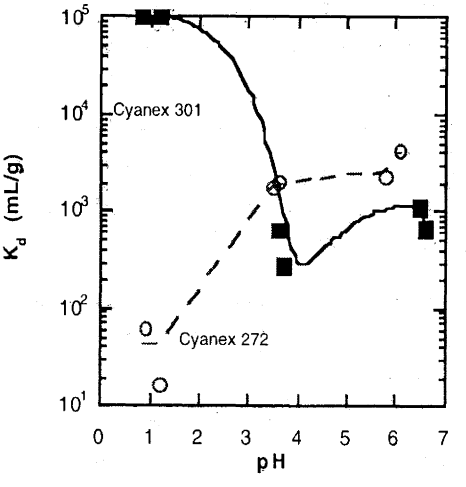

Figure 6. Zinc partition coefficient curves with microparticles coated with 0.25M Cyanex 272 and 301 and 0.5M D_2EHPA diluted by ethanol at 20°C.

Considering the success that extractant-coated magnetic microparticles have received, preliminary engineering aspects were considered. Since microparticle loss is the most financially costly issue, the following section addresses microparticle losses with changes in flow rate, magnetic field strength, and filtration geometry.

High-Gradient Magnetic Separation

The target magnetic filtration process for this separation technology is high-gradient magnetic separation (HGMS). An HGMS system is applicable to a wide range of liquid wastes, including groundwater, process waters, and tank supernatants. As described previously (1) mixing will occur in situ or in a flocculation tank. After the appropriate residence time, the microparticles are filtered from the waste water with a magnetic filter. An HGMS system at ORNL was used to perform experiments regarding the filter efficiency. Figure 7 provides a schematic of the magnetic filtration process.

Six experiments were conducted with uncoated magnetic microparticles. The zeta potential of these microparticles was measured at -35.1 mV for a 1000 ppm (or 0.1 wt%) solution in deionized water at pH 6. These microparticles proved to be paramagnetic, with a volume magnetic susceptibility of 5.93×10^{-6} in the 1000-ppm solution. At this magnetic susceptibility, even a relatively modest magnetic field of 0.1 T is capable of removing 98% of the uncoated magnetic microparticles. At a higher field (1.5 T) and a low flow rate (0.6L/h), breakthrough was not measurable. The microparticles were retained in the filter and eventually completely blocked the flow with an approximately 26-psi pressure drop.

As expected, a lower magnetic field (0.1T) results in an earlier breakthrough of <10 minutes opposed to slightly greater than 20 minutes for a magnetic field of 0.8T. At 0.8T, the breakthroughs occur at approximately 50 min., 20 min., and after a few minutes for flow rates of 11.5, 24, and 51 L/h, respectively. The leakage rates (prior to breakthrough) were <2% in all cases and will improve with the increased magnetic field expected for scale-up processing.[6] An interesting result is shown in Figure 8, where the higher packing density of the filter (1.7%) results in earlier

[6]Target magnetic field strength is between 1 and 2T for scale-up unit.

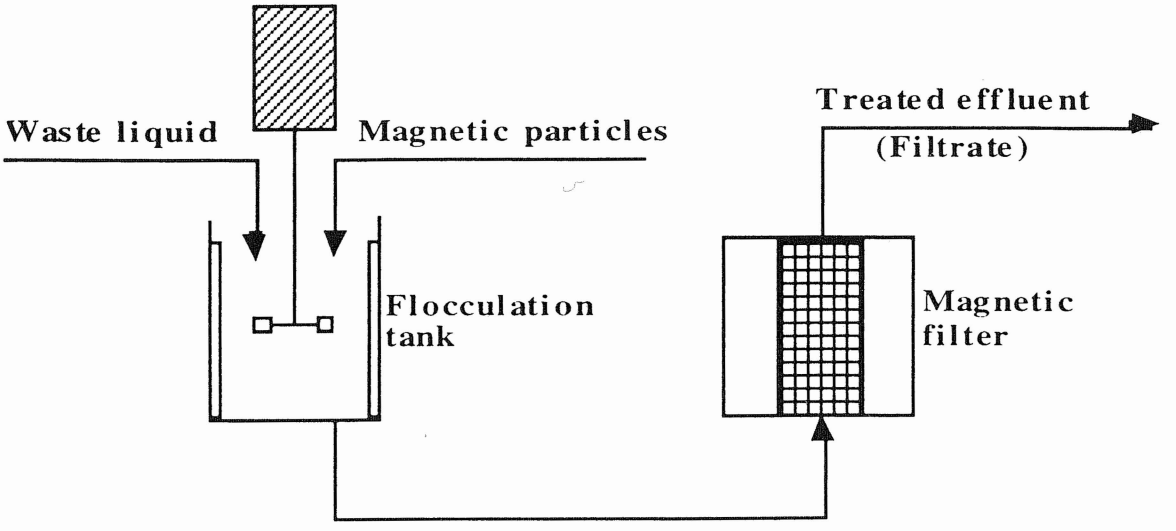

Figure 7. Schematic of magnetic filtration process.

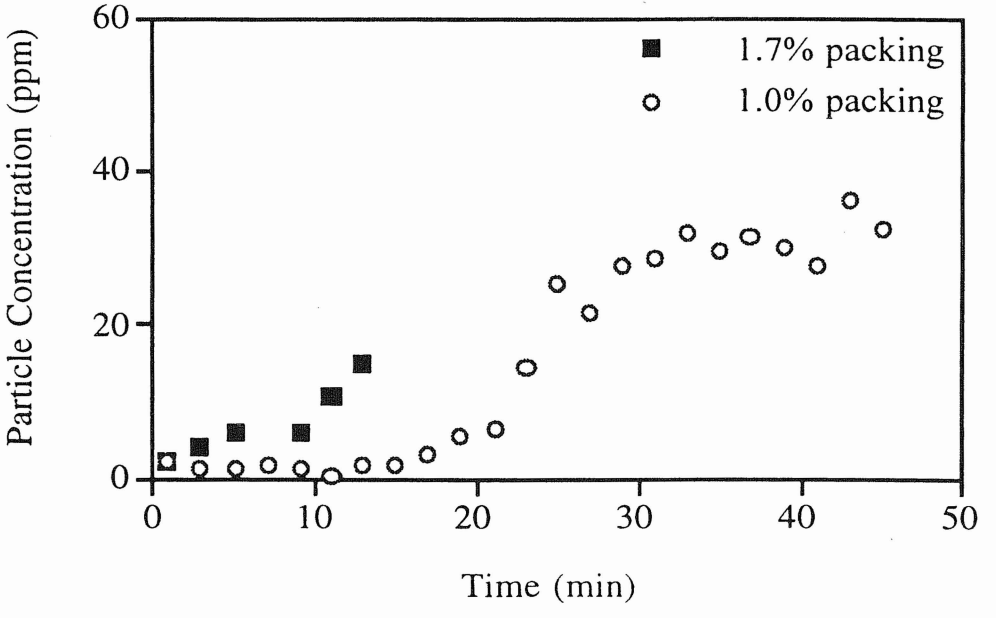

Figure 8. Effect of filter packing density on the breakthrough curve of uncoated magnetic microparticles: 100 ppm uncoated magnetic microparticles in deionized water; Q= 24 L/h, magnetic field,0.8 T.

microparticle breakthrough, after about 10 min., than the 1% packing density after 20 min. This comparison illustrates the contribution of turbulent forces created by the packing. Although local magnetic field gradients are expected to increase as the packing increases, the generation of turbulent flow fields is clearly offsetting the forces generated by the magnetic field. Also, of considerable significance, these magnetic microparticles were successfully modeled to calculate the magnetic filtration with a mathematical approach without empirical fitting coefficients (14).

CONCLUSIONS

The use of extractant-coated magnetic microparticles has been successful with neutral and acidic organophosphorus extractants. The explanation for augmented partitioning may be interactions between the extractant and the complex iron oxide, N,N-methylene bis-acrylamide, and/or charcoal microparticle support. This paper illustrated the strong partitioning of Zn and Cd by Cyanex 272 and Zn by Cyanex 301 from acidic solution. Although important issues need to be clarified, a synergism was observed with Cyanex 272 and 301 greater than measured or predicted by liquid-liquid systems. Along with previous studies, a wide range of solvent extraction systems may be improved upon for the recovery of metals from dilute solutions with solvent extractant-coated magnetic microparticles. Future efforts will seek to elucidate the mechanism of extraction for various extractant particle systems.

Magnetic filtration experiments show losses are slight at low magnetic fields and low flow rates and can be predicted with a mathematical breakthrough model. Increasing magnetic field strength offers a method of achieving quantitative recovery of microparticles, while increasing the packing density can be deleterious depending on the flow characteristics. Future magnetic filtration experiments will focus on separating coated microparticles from actual plating waste solution.

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