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Diethylenetriamine Functionalized Silica Coated Magnetite Nanoparticles for Selective Palladium Ion Extraction from Aqueous Solutions

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Abstract: The extraction of Pd(II) over Cu(II) from aqueous solutions by diethylenetriamine functionalized silica particles with superparamagnetic nanosized magnetite core (FeSiDETA) was compared to that of bare magnetite and silica coated magnetite (FeSi). FeSiDETA was found to quantitatively and selectively (at pH <4) extract Pd(II) ions as compared to the magnetite and FeSi with a considerable improvement in material robustness with regards to iron dissolution. FeSiDETA particles could potentially provide ion exchanger surface areas orders of magnitude greater than conventional ion exchangers and offer alternative novel magnetic processing techniques.

Keywords: Ion exchange, nanosized superparamagnetic extractant, magnetite, silica, amine ligand, PGMs

INTRODUCTION

Superparamagnetic nanoparticles are becoming increasingly important in a variety of different applications such as magnetic storage media (1), catalysis (2), and medical applications (1, 3, 4). Superparamagnetic materials can be magnetized when exposed to an external applied magnetic field but exhibit no hysteresis in their magnetization curve and have zero magnetisation at zero applied field (5). This phenomenon arises

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when particles are sufficiently small and thermal energy is sufficient to overcome magnetic coupling moments through the random fluctuation of atomic magnetic moments (3, 6). In the absence of a magnetic field, the particles exhibit a random distribution of magnetic moments and the particles as a whole have no net magnetization. In an applied field, the moments experience a torque and align in the direction of the field. This essentially allows one to use these materials as conventional "unmagnetized" materials but with the added advantage that one can control and manoeuvre them as required by judicious application of an external applied magnetic field.

Packed columns are often used in industrial ion exchange processes (7). The commercial ion exchanger particles used in the columns generally have diameters ranging from 0.3 to 1.2 mm (8, 9). A compromise in ion exchanger particle size is usually required as small particles display faster ion exchange rates and are less susceptible to abrasion and fragmentation during processing while coarser particles may be required to minimize head loss at high flow rates (7, 8). A nanosized ion exchanger with superparamagnetic properties could provide particles with surface areas orders of magnitude greater than conventional ion exchangers. In addition, the magnetic nature of the ion exchanger could allow for the use of novel processing technologies e.g. magnetic fields could be used for the mixing and extraction of ion exchange particles from solutions. This could eliminate problems associated with pressure drops across packed columns, blockages and potential scale-up issues as experienced when larger diameter commercial ion exchangers are used (9).

Platinum, palladium, and the other platinum group metals (PGMs) are highly valuable, rare precious metals and are used in a number of industrial applications such as auto-catalyst manufacture and jewelry fabrication (10–12). PGM recoveries involve difficult mining conditions and laborious refining processes (13), and increased amounts of costly PGMs are required annually to replace material lost in processing, for increased capacity in industry and for new applications (11). It is for this reason that we have become interested in the improved recovery of PGMs from process streams and effluents.

A variety of bare and functionalized micron and nanosized magnetic particles have been used, for example, in turbidity and color removal (9, 14–16) and cadmium (17), mercury (17), chromium (18), zinc (18), aluminum (19), iron (19), copper (19–21), nickel (22), cobalt (22), and silver (20, 21, 23) extraction through chelating and electrostatic interactions. Although some work has been performed on the extraction of PGMs using nonylthiourea coated magnetite nanoparticles (24), to our knowledge, no investigation into PGM extraction using silica-coated nanosized superparamagnetic ion exchange materials has yet been attempted.

In this paper, preliminary tests are performed using a silica coated, diethylenetriamine functionalized, nanosized magnetite ion exchanger for, amongst others, PGM extraction. Since PGM extraction using (poly)amines generally takes place under acidic conditions (13) and as magnetite particles are soluble in aqueous solutions (25) at pHs less than approximately 4, it was necessary to provide the magnetite with a protective silica coating. We have investigated the extraction efficiency, selectivity, and resistance to various aqueous solution matrices and longer term performance of the functionalized magnetite ion exchanger compared to that of bare magnetite and silica coated magnetite through the extraction of Cu(II) and Pd(II) from a Cu(II), Pd(II) and a mixed Cu(II)/Pd(II) solution.

EXPERIMENTAL

Reagents and Analytical Methods

All reagents and solvents were purchased from commercial sources and were used without further purification. $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, and 25% NH_4OH (Merck) were used for the precipitation of magnetite. Tetraethoxysilane (TEOS), tetramethyl ammonium hydroxide (TMA), N′-(3-trimethoxysilylpropyl)diethylenetriamine (DETA) (Aldrich), and citric acid (Merck) were used for the coating and functionalising of the magnetite particles. Ultrapure Milli-Q water (MQ $>18\ M\Omega$) was used for the preparation of aqueous solutions.

Transmission electron microscopy (TEM) micrographs were obtained using a LEO EM912 electron microscope. Particle size was determined using the TEM micrographs and ImageJ, a public domain image processing program (26). Fourier Transform Infrared (FTIR) spectra were recorded on a Nexus Nicolet Fourier Transform Infrared Spectrometer using dried powder dispersed in a KBr matrix. Thermogravimetric analysis (TGA) was performed on a 7 mg FeSi sample heated at 20°C per minute from 45°C to 920°C in a Perkin Elmer TGA 7 unit. The chamber was purged with nitrogen at 20 ml/min. Magnetic measurements were obtained on a SQUID magnetometer. Elemental analyses (Fe, C, H, and N) were carried out by the Microanalytical Laboratory of the University College Dublin. Two replicates were obtained per sample.

Ion Exchanger Synthesis

Nanosized magnetite (Fe_3O_4) particles were prepared by the method of Massart (27) as follows: for a typical preparation of approximately 0.9 g Fe_3O_4, 2.1 g $FeCl_3 \cdot 6H_2O$ and 1.1 g $FeSO_4 \cdot 7H_2O$ were added to 50 ml water. The resultant solution was heated to 35°C. 10 ml 25% NH_4OH was added to the iron solution with rapid agitation. The resultant Fe_3O_4 precipitate was stirred for 10 minutes and washed via magnetic decantation four times with 200 ml water.

The magnetite particles were then coated with silica by the sol-gel method (28) modified as follows: after washing the precipitate, the magnetite was diluted to 5.6 g l^{-1} Fe_3O_4 (80 ml total volume). 1.1 g citric acid was dissolved in 320 ml water and added to the magnetite precipitate whilst stirring. The initial pH of ~2.8 was raised to ~7 by the addition of TMA to redisperse the precipitate. The final volume of 400 ml had a magnetite concentration of ca. 1.1 g l^{-1}. 150 ml of this magnetite suspension (approximately 0.17 g magnetite) was added to 2.025 l ethanol, 540 ml water and 135 ml ammonia solution (25%) and stirred. 2.7 ml TEOS was added to the mixture and after approximately 24 h, a further volume of 5.4 ml TEOS was added to the suspension. The silica coated magnetite will be referred to as FeSi. The FeSi was washed with an 80 % ethanol in water solution and excess liquid removed by magnetic decantation. The FeSi was dried by evaporation of the solvent at room temperature.

For immobilization of diethylenetriamine (DETA) onto the silica surface, 60 mg FeSi particles were resuspended in 600 μl ethanol (5–10 ml solvent/g FeSi) before 15 μl DETA were added to the FeSi particles (approximately 1.7 mmol DETA/g FeSi) (29, 30). After 2 days the samples were washed with an 80% ethanol in water solution by magnetic decantation and dried by evaporation of the solvent at room temperature. The functionalized silica coated magnetite will be referred to as FeSiDETA.

Extraction Using FeSiDETA Particles

To determine extraction potentials, 50 mg of Fe_3O_4, FeSi and FeSiDETA particles were added to 20 ml of the following solutions (prepared using 1000 mg l^{-1} Cu(II) and Pd(II) solution standards in 4% HNO_3 and 10% HCl respectively):

- 20 mg l^{-1} Cu(II) solution in a 0.6 M NaOAc/HOAc buffer matrix (pH 4 and pH 6) (solution I),
- 7.5 mg l^{-1} Pd(II) in a 0.5, 1, 2 and 3 M HCl and 0.6 M NaOAc/HOAc buffer solution (pH 2–6) (solution II) and
- 7.5 mg l^{-1} Pd(II)/7.5 mg l^{-1} Cu(II) solution in a 0.5, 1, 2 and 3 M HCl and 0.6 M NaOAc/HOAc buffer solution (pH 2–6) (solution III).

The effect of pH (solution matrix type) on the extraction efficiency, the selectivity and the Fe dissolution during extraction and from materials handling were investigated. Samples were agitated in sealed polytops at 110 rpm on a Labcon horizontal shaker for approximately 24 hours to attain equilibrium. Samples were then placed on a ferrite magnet for approximately 2 minutes to allow for magnetic sedimentation. 5 ml of the supernatant was added to 5 ml 1.8 M H_2SO_4 solution and analysed for Cu(II), Pd(II) and Fe using an Inductively Coupled Plasma-Atomic Emission Spectrometer (Varian Liberty II ICP-AES) and a linear calibration method. Calibration standards were prepared in 0.9 M H_2SO_4.

Successive Recovery Extraction Studies

All FeSiDETA samples from the extraction studies were used for successive extraction and desorption studies for solutions I to III (excluding the 2 and 3 M HCl solutions). Four successive extraction studies were performed with the conditions and analyses as described above with the exception of a shorter contact time of one hour for extraction. Samples were desorbed using a 2 M HCl solution (5 ml) by agitation on the horizontal shaker for one hour. Supernatant samples were used for metal analysis by ICP-AES as described previously.

The percentage extraction and desorption of metal ions was calculated from the initial and final concentrations of metal ions in the supernatants. The percentage iron dissolution from the magnetite (bare or coated) was calculated as a percentage of the Fe in the supernatant compared to the initial Fe mass present using values obtained from ICP-AES analysis. Final samples were weighed to obtain an overall Fe mass balance.

RESULTS AND DISCUSSION

FeSi and FeSiDETA Synthesis and Characterization

Figure 1 shows a TEM micrograph of FeSi particles with an average particle diameter of 63 ± 13 nm. The number of magnetite particles (each approximately 10 nm diameter) in the magnetite core varies such that the mean FeSi core diameter is 28 ± 10 nm while the silica shell is 35 ± 3 nm thick.

FTIR (data not shown) and TGA data (Fig. 2) confirmed the silica coating on the magnetite core. FTIR data showed the characteristic Si-O-Si asymmetric stretch (31–34) appearing at $\sim$1083 cm^{-1} while the decreases in mass as observed from TGA data can be explained as follows (35): up to 200°C, there is a removal of hydrogen bonded and absorbed water; up to 500°C, all vicinal silanol groups (Si-OH) are completely condensed and above 600°C, isolated Si-OH groups are removed and the silica surface is fully dehydrated.

The magnetization curve (Fig. 3, with insert showing the magnetic moment as a function of field between -0.006 and 0.006 T) indicates that the FeSi is superparamagnetic (5): as the field is increased from 0 T to maximum field ($\sim$3 T), the magnetic moment increases until saturation magnetization ($\sim$16 emu g^{-1}) is reached. No further magnetization takes place with an increase in field. As field is decreased, the magnetisation

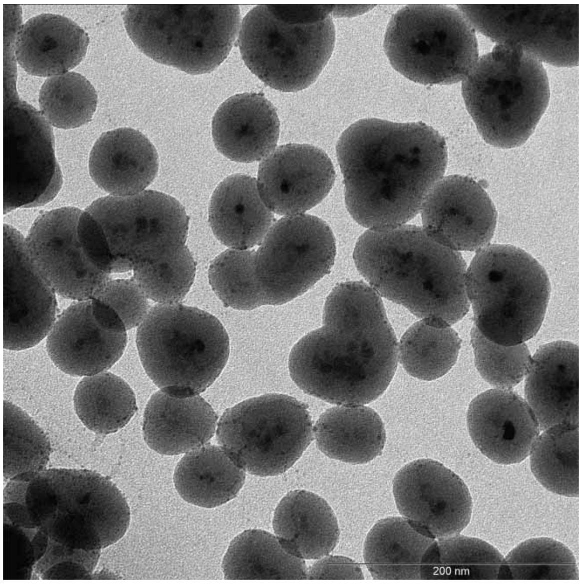


Figure 1. TEM micrograph of nanosized FeSi particles.

decreases and at zero applied field, the remanent magnetisation is very small, ~0.5 emu g^{-1} i.e. the material will exhibit almost no magnetization when the external applied field is removed. This is indicative of a superparamagnetic material.

Elemental analysis performed on two separate sets of FeSi and FeSiDETA samples indicated a ligand concentration of 0.05–0.07 mmol g^{-1} ion exchanger (Table 1). FeSi and FeSiDETA from Set 2 were used for the extraction studies.

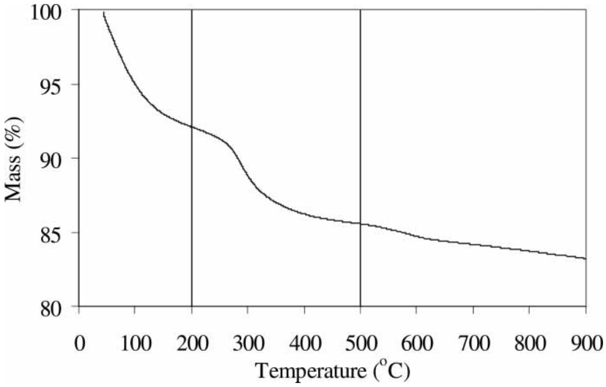


Figure 2. TGA plot for FeSi sample.

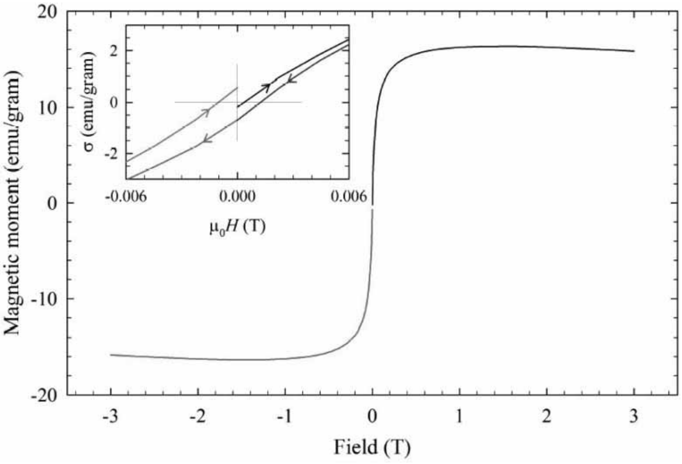


Figure 3. Magnetisation curve of FeSi sample.

Single Stage Extraction from the Cu(II), Pd(II) and Mixed Metal Ion Solutions

The percentage Cu(II) extraction for Fe_3O_4, FeSi, and FeSiDETA from the Cu(II) solution is illustrated in Fig. 4. Since a 0.5 ligand:Cu(II) ion molar ratio was used for the extraction experiments, a maximum extraction of only 50% of the Cu(II) initially present in solution can be attained, assuming maximum binding of one metal ion per ligand molecule.

The magnetite surface charge is established by the dissociation or ionization of surface hydroxyl groups corresponding to the adsorption or desorption of protons depending on the pH of the solution (36). The point of zero charge (PZC) for magnetite (36–40) has been reported to be in the range of 6 to 8.2. At a pH less than the PZC, the $FeOH_2^+$ groups predominate. At a pH greater

Table 1. Elemental analysis for two FeSi and FeSiDETA samples

		Fe (%)	C (%)	H (%)	N (%)	Ligand concentration (mmol g^{-1})[a]
Set 1	FeSi	12.6–12.8	4.1	1.4	0.7–0.8[b]	
	FeSiDETA	12.3	5.8–5.9	1.7–1.8	1.0	0.07
Set 2	FeSi	16.5–17.0	3.6	1.4	0.9[b]	
	FeSiDETA	16.4–16.5	3.7–3.8	1.4–1.5	1.0–1.1	0.05

[a] Based on the difference in nitrogen percentage between the FeSi and FeSiDETA.

[b] N present in the FeSi is believed to originate from the ammonia solution used in the FeSi synthesis.

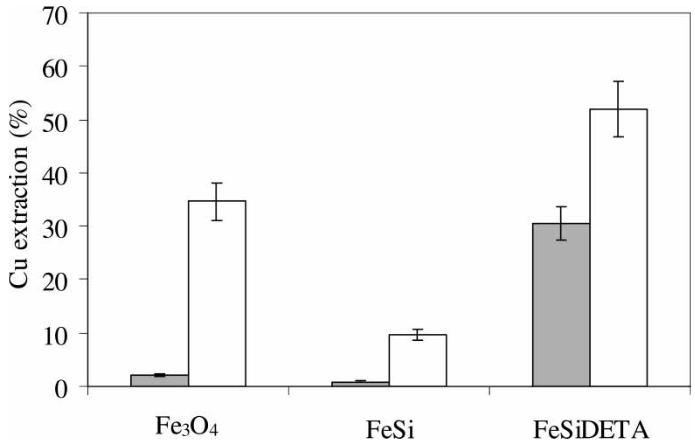


Figure 4. Percentage Cu(II) extraction by Fe_3O_4, FeSi and FeSiDETA from buffered solution I at pH 4 (in grey ■) and pH 6 (no colour □). A ligand: Cu(II) metal ion mole ratio of 1:2 was used.

than the PZC, the FeO^- groups predominate. When the pH equals the PZC, the number of $FeOH_2^+$ groups equals the number of FeO^- groups (36).

It is most likely (13, 41, 42) that the blue-green cationic aqua ion $[Cu(H_2O)_6]^{2+}$ (or neutral $[CuCl_2(H_2O)_2]$) would be present in solution and the percentage Cu(II) extraction by the magnetite most likely increases with an increase of pH from 4 to 6 as illustrated in Fig. 4 as more FeO^- groups become available on the unmodified magnetite surface for cation extraction.

The FeSi particles show a lower percentage Cu(II) extraction at both pH 4 and 6 than the bare magnetite and FeSiDETA as a result of their silica surface covering. It is unlikely that the silica coating provides complete shielding of the iron oxide from the Cu(II) solution and the higher percentage extraction occurring at pH 6 as compared to that at pH 4 for the FeSi particles is probably as a result of ion pairing with exposed or uncoated FeO^- groups. Alternatively, Sjöberg reports that at a pH higher than the PZC of silica ($\sim$pH 2), cation adsorption by an electrostatic interaction with negatively charged SiO^- may take place (43) with Cu(II) adsorption increasing significantly above pH 6. The increased extraction of Cu(II) by the FeSi at pH 6 could therefore possibly also be as a result of the electrostatic interaction of the Cu(II) ions with the surface SiO^-.

The FeSiDETA shows the highest overall extraction compared to the bare magnetite and FeSi particles at these pHs. Extraction of Cu(II) is believed to occur through a complexation (chelating) ion mechanism in which coordination to the cationic Cu(II) readily takes place to the amine groups (44) rather than through an anion exchange mechanism. Depending on solution pH and the Cu(II) speciation in solution, extraction therefore increases with an increase in pH due to competitive coordination of the Cu(II) by the amine moiety.

For the magnetite, FeSi and FeSiDETA, it is also possible that, at higher pH, $Cu(OH)_2$ precipitates form thereby reducing the dissolved Cu(II) in solution and subsequent percentage metal ion analysed by ICP-AES.

The percentage Pd(II) extraction from the Pd(II) solution is illustrated in Fig. 5. Theoretically, the 1.7 ligand:Pd(II) ion molar ratio should allow for complete extraction of the Pd(II) ions by the DETA-containing extractant.

Pd(II) readily forms $[PdCl_4]^{2-}$ anionic complexes in acidic chloride media (10). In the acidic solutions, it is believed that the positively charged amine groups of the FeSiDETA extract anions from solution via an anion exchange mechanism between the Pd(II) chlorocomplex and the chloride or acetate counterion. In the 2 and 3 M HCl solutions, no extraction occurs as the chlorides compete with the $[PdCl_4]^{2-}$ for binding to the ion exchanger (42, 44, 45). However almost quantitative Pd(II) removal could be achieved at pH 2 and 3. The percentage extraction decreases somewhat at higher pH, where it is possible that the increasing anionic acetate ions may compete for extraction or extraction may occur increasingly through a chelating ion exchange mechanism: coordination to cationic Pd(II) ions takes place via the lone pairs of the amine groups (44).

The percentage Pd(II) and Cu(II) extraction from the mixed metal ion solution III is illustrated in Figs. 6 (a) and (b) respectively. (Data for the Cu(II) extraction at pH 2 is excluded from Fig. 6 (b) owing to inconsistent results in the ICP-AES measurements.)

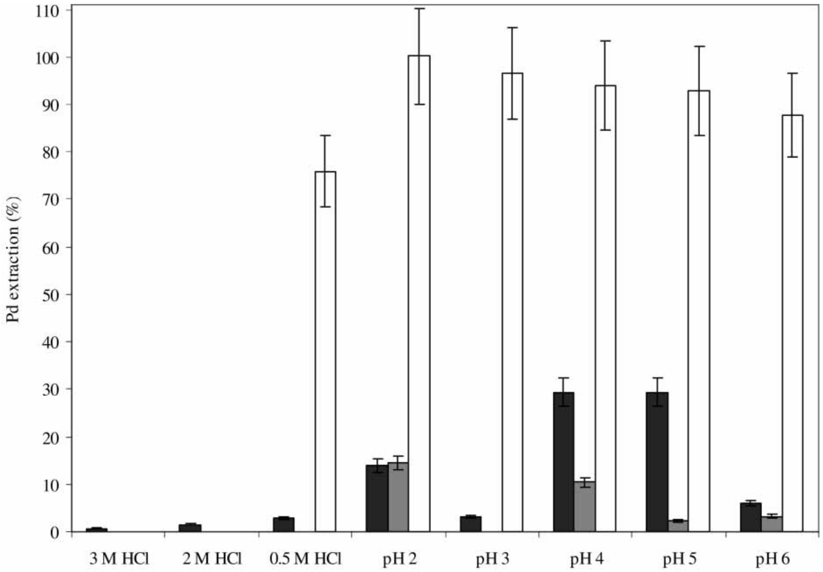


Figure 5. Percentage Pd(II) extraction by magnetite (in black ■), FeSi (in grey ▨) and FeSiDETA (no color ☐) from solution II.

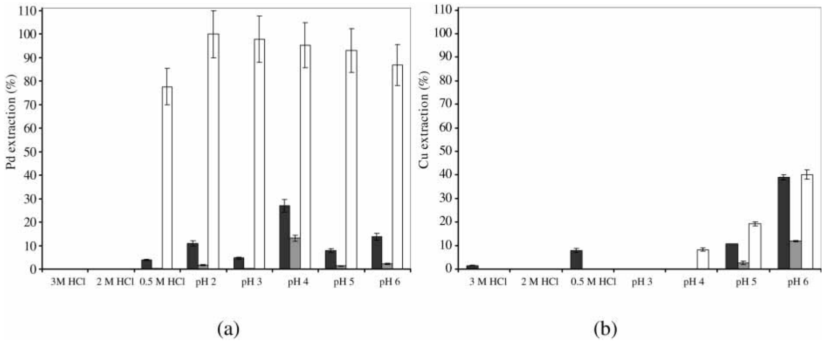


Figure 6. pH dependent competitive (a) Pd(II) and (b) Cu(II) extraction from mixed solution III for magnetite (in black ■), FeSi (in grey ▨) and FeSiDETA (no color ☐).

A 0.6 ligand:total metal ion (Cu(II) + Pd(II)) mole ratio was used and some degree of selectivity of the DETA towards one of the metal ions might be expected. It was found that the FeSiDETA preferentially extracts Pd(II) with the higher binding constant (10) under these conditions as compared to Cu(II) from solution III. With increasing pH and decreasing protonation of the amino groups, there is increased Cu(II) extraction, probably due to amine coordination (44). The Pd(II) to Cu(II) selectivity is greatest in acidic media where the DETA is sufficiently protonated to form ion pairs with the anionic Pd(II) chlorocomplex whilst Cu(II) tends to form cationic species which are not extractable by our materials under these conditions. The observations are consistent with the extraction patterns observed for the single metal solutions I and II.

In general, the FeSi shows low Pd(II) extraction (<15%) with some Cu(II) extraction at pH 5 and 6. As in the case of the magnetite, extraction probably takes place via electrostatic interaction with uncoated magnetite at the FeSi centre ($FeOH_2^+$ or FeO^- depending on the pH) or via electrostatic adsorption by negatively charged SiO^- at higher pH (43).

The bare magnetite shows some extraction of Pd(II) in most solutions (<30%) except from the 2 and 3 M HCl solutions. Depending on the magnetite surface charge, Pd(II) would be extracted as either anionic $[PdCl_4]^{2-}$ or cationic Pd^{2+} (aquated) species. Increased cationic Cu(II) extraction (36) by the increasing magnetite surface FeO^- groups is observed above pH 4.

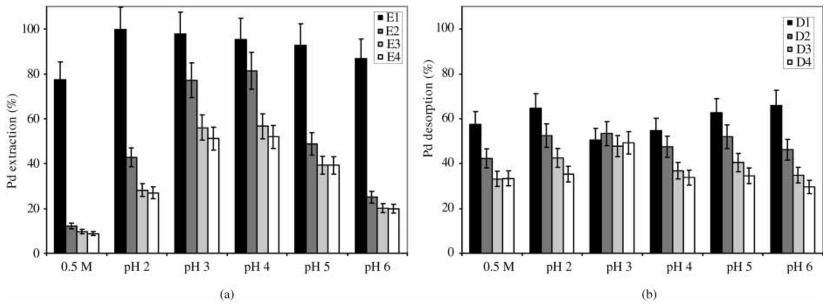
Because an almost quantitative percentage of Pd(II) is extracted using the 50 mg sample, no significant additional Pd(II) is extracted when the FeSiDETA mass is increased to 100 mg at pH 4 for solution III. Instead, the additional DETA allows for an increased Cu(II) extraction of 24% with a corresponding decrease in selectivity, $k_{Pd/Cu}$, from 7.4 to 2.1 ($k_{Pd/Cu} = [Pd]_{IX}[Cu]_{sol}/[Pd]_{sol}[Cu]_{IX}$ with ion-exchanger concentrations, [metal ion]$_{IX}$, in mmol g^{-1} and solution phase concentrations, [metal ion]$_{sol}$, in mg l^{-1} (46)). In the case of the magnetite and FeSi, the percentage Pd(II) extraction increases by approximately 15% probably as a result of the additional magnetite surface available for extraction. There is no further uptake of Cu(II) by the magnetite or FeSi because at pH 4 and with the $FeOH_2^+$ predominating, the anionic $[PdCl_4]^{2-}$ will most likely be extracted in preference to the cationic $[Cu(H_2O)_6]_2^+$.

Extraction from the Cu(II), Pd(II), and Mixed Metal Ion Solutions during Successive Recovery Studies

The successive percentages of extraction (cycles E1 to E4) and desorption (cycles D1 to D4) of Pd(II) from solution III in four successive recovery cycles are illustrated in Figs. 7 (a) and (b).

The percentage successive Pd(II) and Cu(II) extraction and desorption from solutions I and II were also determined. Although the data is not presented here, these results indicated similar trends as for the mixed metal ion solution.

A high (>75%) to quantitative extraction of Pd(II) is achieved in extraction cycle E1 (Fig. 7(a)), with the percentage extraction decreasing over successive cycles. The possible reasons for this decrease in extraction are threefold. The desorption takes place using 2 M HCl which provides large quantities of competing Cl^- anions to strip the Pd(II) (42). However, dissolution of the Fe in the FeSiDETA may occur, resulting in a deterioration of the FeSiDETA over an extended period of time. DETA functionalized silica no longer possessing a magnetic core may be lost in the magnetic decantation washing process resulting in a decreased extraction potential in successive cycles. A second possible reason for the decrease in extraction with successive cycles is that the ion exchanger may become saturated with extracted Pd(II). As can be seen from the first desorption cycle D1 and for all solution matrices, less than ~70% of the extracted Pd(II) is desorbed from the material. There are therefore, not as many available "sites" on the ion exchanger in the



(a)

(b)

Figure 7. pH dependent successive percentage (a) Pd(II) extraction and (b) Pd(II) desorption by FeSiDETA from solution III with ligand:total metal ion ratio of 0.6.

subsequent extraction cycle E2, for Pd(II) extraction. Finally, the decrease in Pd(II) extraction at higher pH may occur as a result of competition from Cu(II) for binding sites. In fact, this decrease in Pd(II) extraction above pH 5 drops off less rapidly for extraction cycles E2 and onwards in solution II (containing only Pd(II) and no Cu(II), data not presented here) as compared to solution III (containing both Pd(II) and Cu(II)). For example, the extractions for solution II, pH 6 and cycles E1, E2, E3, and E4 are 87, 59, 45, and 45% respectively as compared to the 87, 25, 20, and 20% found for solution III. This is very likely owing to the lack of competing Cu(II) ions. The percentage Cu(II) extraction is low for most extraction cycles with Pd(II) being selectively extracted from the solution over Cu(II) with a decrease in pH (data not shown).

The initial percentage Pd(II) desorption (D1) is less than $\sim$70% for most cases with the desorption decreasing over time (Fig. 7 (b)). The percentage desorption in D2 is calculated as a function of the amount of Pd(II) extracted in the previous cycle E2 plus any Pd(II) remaining on the extractant after desorption in cycle D1. It is possible that the ability to desorb Pd(II) from the extractant surface decreases with time as a result of a build-up of Pd(II) on the extractant surface owing to irreversible binding. An additional possibility is that FeSiDETA loaded with Pd(II) is lost during materials handling as up to 10% Fe is lost from materials handling and/or degradation of the extractant. Although this Pd(II) (attached to the FeSiDETA) has now been removed from the system, it is still included and may result in an under-reported desorption percentage in the desorption calculations. Alternatively, Pd coordination changes on the polymer may occur with time leading to more stable (possibly chelated) complexes which are difficult to desorb.

The percentage Cu(II) desorption also decreases with time (data not shown) possibly owing to the build-up of Cu(II) on the extractant surface. The percentage desorption at pH 4 and 6 for the first desorption cycle (D1) is greater than 100%. A potential experimental error may have arisen in these calculations owing to the relatively low mass of Cu(II) extracted in cycles E1 ($< \sim$10% for pH 4). Because low masses of Cu(II) are extracted originally, the liberation of even small quantities of Cu(II) could inflate desorption percentages. In addition, the deterioration of FeSiDETA under the harsh desorption conditions may result in the liberation of extracted Cu(II) into the supernatant which is then reported as being desorbed material.

Similar trends are observed for subsequent extraction and desorption cycles (E3 to E4 and D3 to D4) across all solution matrices.

Fe Dissolution and Losses during Extraction, Desorption, and Materials Handling

For solution III, there is significant Fe dissolution of the Fe_3O_4 at lower pH values (Fig. 8 (a)). The FeSi and FeSiDETA reduce the Fe dissolution for

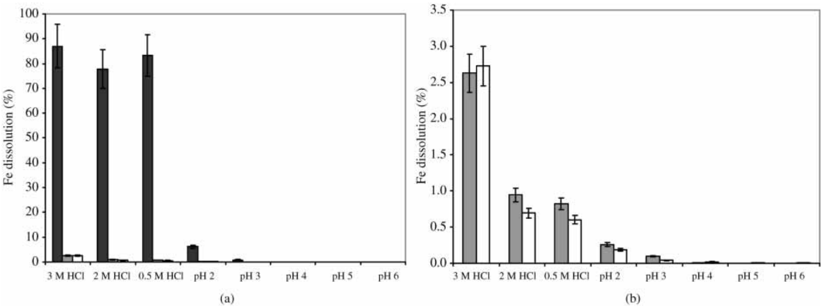


Figure 8. (a) Percentage Fe dissolution during extraction studies for magnetite (in black ■), FeSi (in grey ■) and FeSiDETA (no colour ☐) from solution III with the Fe dissolution below 3% enlarged in (b).

the 0.5, 2, and 3 M HCl solutions from above 75% (up to a maximum of 88%) to below 3% for the silica coated material (see Fig. 8 (b)). This translates to an improvement in resistance to Fe dissolution offered by the silica coating of up to 87%. The fact that some Fe dissolution does take place indicates that the FeSiDETA is slightly porous and magnetite could be leached out from the core depending on the contact time and nature of the contact solution. In this case, the contact time of 24 hours in acidic media resulted in dissolution of the bare magnetite within approximately 1 hour (also noticeable from the solution which became yellowish in colour).

Similar Fe dissolution patterns were observed for solution II while for solution I (pH 4 and 6 buffers), the Fe dissolution from the FeSi and FeSiDETA particles as compared to the bare magnetite is very similar and less than ~1% owing to the low magnetite solubility (25) at and above pH 4.

Table 2 gives the cumulative percentage Fe dissolution from FeSiDETA after successive cycles of extraction at varying pH and with desorption using 2 M HCl for solutions I to III.

In general, the cumulative Fe dissolution after cycle 4 is approximately 40% with the 0.5 M HCl solution matrix showing the greatest Fe dissolution (>60%). The desorption stage contributes mainly to the Fe dissolution as shown by Fig. 9 (Fe dissolution for the FeSiDETA in solution III during the successive recovery studies).

During the extraction cycles (Fig. 9 (a)), the percentage dissolved Fe from the FeSiDETA is low in the higher pH buffers (<0.1%), highest in the 0.5 M HCl and pH 2 and 3 solutions and in general, appears to increase with successive extraction cycles. Although this may indicate a deterioration of the FeSiDETA extractant with time, the maximum overall Fe dissolution is less than 4%.

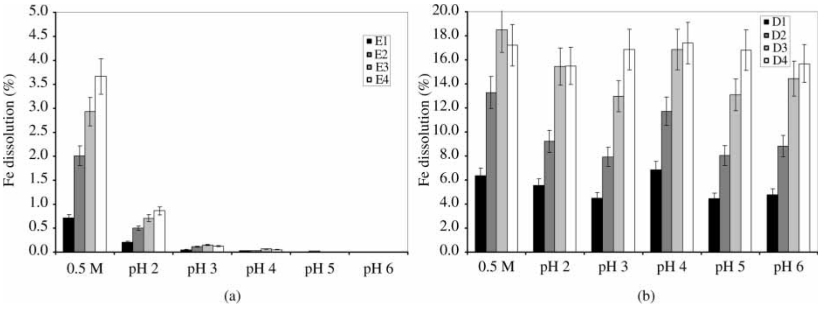
The Fe dissolution shows a steady increase in dissolution per desorption cycle (Fig. 9 (b)) with an overall dissolution per cycle of less than 20% and the percentage desorption per cycle very similar across all conditions (all FeSiDETA samples are exposed to the same conditions during desorption).

Table 2. Cumulative Fe dissolution from FeSiDETA by solutions I to III after each recovery cycle (consisting of one extraction at varying acidity and one desorption cycle using 2 M HCl)

	Cumulative Fe dissolution (%)					
Cycle	0.5 M HCl	pH 2	pH 3	pH 4	pH 5	pH 6
Solution I						
1				4		6
2				8		16
3				14		29
4				25		44
Solution II						
1	7	5	5	5	4	4
2	22	14	14	14	11	13
3	43	28	27	29	21	27
4	63	44	43	48	34	43
Solution III						
1	7	6	5	7	5	5
2	22	16	13	19	13	14
3	44	32	26	36	26	28
4	65	48	43	53	43	44

The increase in dissolution is likely the result of successive attack and entry of the relatively strong acid solution (2 M HCl) into the pores of the FeSiDETA extractant. Increased dissolution of the materials during successive contact with the acid is likely to occur.

Although Fe losses occur from extraction and handling (washing and materials transfer) of the FeSiDETA during the successive recovery studies, Fe losses of up to 50% during desorption are the main contributors. There



(a) (b)

Figure 9. Successive percentage Fe dissolution of FeSiDETA from solution III during (a) extraction and (b) desorption (note different scales on y-axis).

are several options which could be implemented to minimize these losses, something currently being investigated.

To minimize material losses from handling, an alternative embodiment of the technology could be attempted e.g. through the use of stronger rare earth magnets as opposed to ferrite magnets for better retention of magnetic FeSiDETA extractants or the use of a column setup as opposed to batch magnetic decantation of samples.

Commercial resins are also subject to chemical degradation (oxidation, reaction of the resins with organic material present in the process solution or thermal instability) and physical degradation (expansion and contraction by variation in osmotic pressure, attrition during transportation such as in a moving-bed system, precipitation of inorganic solids inside or outside the bead) (9). To obtain additional information as to the longer-term performance of the FeSiDETA, the extent and rate of deterioration of the nanomagnetic resin will be evaluated against that of a commercial resin with both resins under similar operating conditions.

CONCLUSIONS

Nanosized super-paramagnetic DETA-functionalised silica coated magnetite ion exchange particles were synthesized and characterized successfully. These particles show considerable promise for selective metal ion extraction exploiting their magnetic properties. Extraction studies show that more Pd(II) is consistently extracted by the FeSiDETA as compared to the unmodified magnetite and FeSi. In very acidic media (2 and 3 M HCl solutions), no Pd(II) extraction occurs possibly as the chloride ions compete with the anionic $[PdCl_4]^{2-}$ for binding to the anion exchanger, whereas under less acidic conditions quantitative Pd(II) extractions could be achieved selectively over Cu(II), with the greatest selectivity occurring in more acidic media.

In general, for the successive recovery extraction/desorption tests, good (>80%) to quantitative Pd(II) extraction is observed, decreasing with successive cycles. This decrease may occur as a result of deterioration or loss of the FeSiDETA ion exchanger with time thereby decreasing the capacity for successive extraction. The selective extraction of Pd(II) to Cu(II) is again observed in the successive recovery studies. The selectivity is greatest in acidic media in which the DETA is protonated resulting in ion pairing with anionic $[PdCl_4]^{2-}$ complexes, whilst the Cu(II) forms weakly or non-extractable cationic $[Cu(H_2O)_{6-n}Cl_n]^{(2-n)+}$ complexes under these conditions.

Iron dissolution for the silica coated magnetite particles is reduced from up to 88 % to below 3% for a single stage extraction. Fe dissolution during the successive recovery studies is greatest during desorption (maximum of 55%) followed by materials handling (maximum of 18%) and extraction (maximum of 10% in 0.5 M HCl) across all solution matrices. Fe dissolution may pose a problem for continuous or long-term processing in acidic media.

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