

Imprinted polymers for the removal of heavy metal ions from water

Syed Ashraf, Angela Cluley, Ckarlos Mercado and Anja Mueller

ABSTRACT

In wastewater treatment, the removal of heavy metals is difficult due to the limited affinity of heavy metal ions to ion exchange resins. Here imprinting polymerization is used to develop resins with high capacity and selectivity for heavy metal ions for water treatment. A random copolymer of methacrylate and methacrylamide was found to be most effective for the removal of hydrophilic metal complexes, like CdCl_2 , ZnCl_2 , and the metalloid NaH_2AsO_4 , particularly when the porosity of these resins is increased. For hydrophobic complexes imprinting emulsion polymerization was developed and data for the effective removal of mercury dithizonate will be described. Complete removal for up to 80 ppm of cadmium and mercury with only 200 mg of imprinted resin was obtained; competition and co-imprinting experiments are described as well.

Key words | capacity, emulsion polymerization, heavy metal ions, imprinting polymerization, remediation

Syed Ashraf
Angela Cluley
Ckarlos Mercado
Anja Mueller (corresponding author)
Department of Chemistry,
Central Michigan University,
Mt. Pleasant,
MI 48859,
USA
E-mail: muell1a@cmich.edu

INTRODUCTION

Heavy metal ions are toxic and persistent contaminants that are relatively accessible and accumulate along the food chain (Wittmann 1983; Wright 2005). The source of heavy metal contamination is commonly industrial activity. Examples are mining and ore processing facilities around the great Lakes that release cadmium, mercury, lead, and the toxic metalloid arsenic (EPA 2006).

Heavy metal ions are difficult to remove in wastewater treatment processes such as flocculation or use of aerobic bacteria (Eilbeck 1987; Canizares *et al.* 2000; Tchobanoglous *et al.* 2003c). Industrial wastewater is progressively more heavily regulated with heavy metal ions being an important target. Industry commonly employs onsite treatment, including precipitation, ion-exchange, and/or filtration (Tchobanoglous *et al.* 2003b).

Lime precipitation is a common method for heavy metal remediation. Lime treatment was developed for the removal of turbidity and phosphorus from domestic sewage (Culp & Culp 1971). It was then extended to remediation of heavy metal-contaminated industrial wastewater (Patterson 1975), groundwater (Lee *et al.* 2007), surface water (Daniels *et al.* 2006), and soil (Hamon *et al.* 2002; Polettini *et al.* 2004). It was found that for each heavy metal the most effective precipitation conditions were different. For arsenic and nickel, for example, ferric chloride was more effective than lime

(Patterson 1975; Tchobanoglous *et al.* 2003a). Maximum cadmium remediation required an additional filtration step, and mercury remediation sulfide precipitation followed by vacuum filtration. Additionally, each method requires a different pH for maximum heavy metal removal (Patterson 1975; Tchobanoglous *et al.* 2003a). In this research, a more general method for heavy metals is being developed by using polymeric resins.

Soluble polymers have been used in wastewater mostly as flocculants (Bolto 1995). Recently, though, soluble polymers have been used in an ultrafiltration set-up, also called liquid-phase polymer-based retention technique (Rivas *et al.* 2003; Pizarro *et al.* 2007; Schulte & Schuster 2008; Rivas *et al.* 2009). These techniques can remove a variety of heavy metal and metalloid ions, but they still require specialized polymer syntheses.

Insoluble polymers have been employed in the removal of these toxic metal ions using methods such as membrane filtration (especially reverse osmosis) and ion exchange (Manahan 1984; Koltuniewicz & Drioli 2008). Generally, these methods are unspecific and bind heavy metal and arsenic ions only weakly (Malachowski *et al.* 2004). To increase selectivity and metal and metalloid ion capacity, different approaches have been developed; for example, Holcombes's group immobilized peptides on solid supports

(Malachowski *et al.* 2004), Güçlü's group copolymerized starch with acrylic acid as a resin for nickel(II), cobalt(II), and zinc(II) ions, specifically (Guclu *et al.* 2007), Wane-kaya's group developed cysteine-modified polymer nanowires for As^{3+} , Cd^{2+} , Pb^{2+} , and Cu^{2+} ions (Tolani *et al.* 2010), and lead can be remediated by Xu's zwitterionic hybrid polymer (Liu *et al.* 2010). All of these techniques are effective, but all require a special synthesis and each of the techniques can only remove a few types of heavy metals and metalloid ions.

Recently, the goals to recover the metal and to reuse the material that performs the separation of the metal have become more important. One example uses a combination of zeolites as metal adsorbent and membranes to remove the metal-loaded zeolites (Bloecher *et al.* 2003). The zeolites could then be regenerated and reused. Here, molecularly-imprinted resins made from polyacrylates and polyacrylamides, cheap resins commonly used in wastewater treatment (Mangravite *et al.* 1985; Morahashi *et al.* 1996; Li *et al.* 1999), are described. They can be implemented as ion exchange resins or membranes. The resin can be regenerated, concentrating the heavy metal ions in the process. Molecular imprinting is a general method that can be used for all heavy metal ions as well as other impurities such as polyaromatic hydrocarbons.

Imprinting polymerization involves the preparation of a crosslinked polymer in the presence of an imprinting molecule, in this case a heavy metal ion complex (see Figure 1). The crosslinking makes the polymer insoluble; it also stabilizes the shape of the polymer and thus the imprint in the polymer resin. When the imprinting molecule is removed, a specific void fitting that molecule remains in the polymer. The imprinted polymer will now allow more efficient binding of its metal complex.

Imprinting polymerization based on non-covalent forces is usually done in organic solvents, because weak forces between molecules (for example hydrogen bonding) are

stronger in organic solvents (Yan & Ramstroem 2005). In water, hydrogen bonding from the water molecules competes with the polar bonding between molecules. In this research project imprinting polymerization is performed in water to avoid swelling; although the specificity will not be as high as in organic solvents, it will still be sufficient for ion exchange resins and membranes, which also require additional non-specific binding.

Molecular imprinting polymerization is a new and flexible approach for wastewater treatment. It has been used effectively in enantiomer separation, where imprinted polymers are tested primarily for selectivity (Yan & Ramstroem 2005). In wastewater treatment, capacity is the primary requirement. High selectivity is usually not necessary, since compounds of a similar chemical structure are often equally unwanted in purified water. This has been demonstrated in Mattiason and Guieysse's work (Le *et al.* 2006); their estrogen-imprinted polymers remained effective also for estrogen-mimicking compounds of similar structure, a possible cause for a variety of health problems.

Here polymers that are imprinted with various heavy metal and metalloid ion complexes in water are reported. These resins are designed for maximum capacity. The capacity of the imprinted ion exchange resins is increased significantly above the capacity of simple ion exchange resins. For hydrophobic heavy metal ion complexes, an imprinting emulsion polymerization was developed.

METHODS

Materials

Methacrylate (99%), methacrylamide (98%), phenyl methacrylate (98%), 2,2-azobis(2-methylpropionamide) dihydrochloride (AAPD, 97%), ethylene glycol diacrylate (EDMA, 90%), 1,6-hexanediol diacrylate (80%), potassium

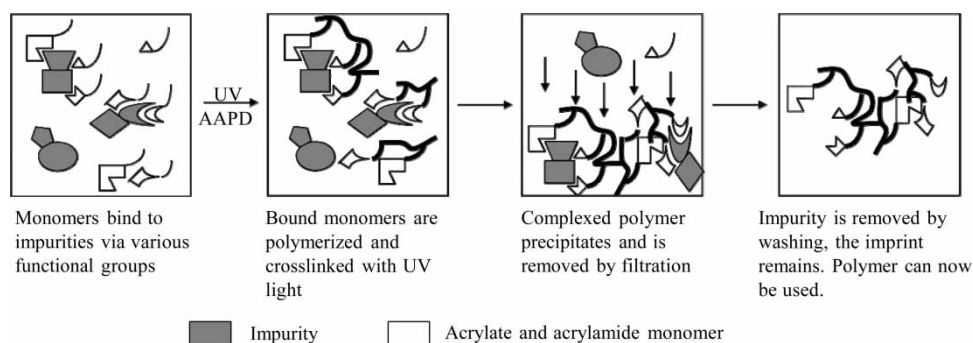


Figure 1 | Imprinting polymerization.

persulfate, Brij-56, and mercury(II) dithizonate were obtained from Aldrich. Methyl methacrylate (99%) was purchased from Acros Organics, cadmium chloride (99.8%) and zinc chloride (98%) from Fisher, and sodium arsenate from Sigma. Water was purified through Barnstead E-pure filter system and collected at 18 MOhm (DIUF water). Snake skin pleated dialysis tubing, molecular weight cut-off 3,500, was obtained from Pierce.

70:30 Methacrylate:methacrylamide random copolymers ('hydrophilic resin')

For the 70:30 methacrylate:methacrylamide copolymer non-imprinted control, 0.70 and 0.30 mol of methacrylate and methacrylamide along with 0.001 mol AAPD, 0.0005 mol EDMA, and 150 mL of DIUF water were reacted under nitrogen and UV light (Rayonet photochemical reactor). For imprinting polymerization, 0.001 mol of cadmium chloride, zinc chloride, or NaH_2AsO_4 was added to the mixture and polymerized in the same manner; for the cadmium- and zinc-imprinted resin, 0.0005 mol of each CdCl_2 and ZnCl_2 was used. To synthesize the porous samples, N_2 is purged through the reaction during polymerization; all other procedures remain the same. After polymerization, the solvent was removed and purified by dialysis in water. IR: non-porous control: 3600–3000, 2950, 1701, 1458, 1255, 1174, 925, 700, 600, 510 cm^{-1} ; imprinted, non-porous (Cd): 3600–3000, 2950, 1701, 1458, 1255, 1161, 925, 700, 600, 510 cm^{-1} ; porous control: 3600–3000, 2950, 1701, 1474, 1388, 1249, 1176, 925, 920, 700, 600, 510 cm^{-1} ; imprinted, porous (Cd): 3600–3000, 2950, 1701, 1482, 1388, 1260, 1178, 925, 920, 782, 510 cm^{-1} .

50:50 Methyl methacrylate:phenyl methacrylate random copolymers ('hydrophobic resin')

A random copolymer of phenyl methacrylate and methyl methacrylate (50%:50%) was prepared by adding 3.85 mL of phenyl methacrylate (0.025 mol), 2.34 mL of methyl methacrylate (0.0217 mol), and 0.240 g (8.86×10^{-4} mol) potassium persulfate initiator to 3.03 g (0.0044 mol) of Brij-56 surfactant under nitrogen and exclusion of light. 1.12 mL (0.005 mol) of 1,6-hexanediol diacrylate was added prior the addition of 200 mL of deionized H_2O . The reaction was stirred at 70 °C for three hours. For imprinting, 0.217 g of mercury(II) dithizonate (3.03×10^{-4} mol) was added last to the reaction. For porous samples, nitrogen was purged through the reaction mixture. After completion, the reaction was cooled to room temperature and 200 mL of

water was added to precipitate the polymer. Precipitation was completed at 4 °C and the polymer was obtained via gravity filtration. Yield: non-porous control 2.40 g (38.4%), non-porous imprinted 2.25 g (36.5%), porous control 4.36 g (71.0%), and porous imprinted 4.65 g (75.7%). IR: non-porous control: 3600–3000, 2993, 2950, 2845, 1734, 1443, 1246, 1141, 987, 860, 790, 510 cm^{-1} ; imprinted, non-porous (Hg): 3600–3000, 2940, 2848, 1725, 1600, 1520, 1460, 1200–1090, 790, 710 cm^{-1} ; porous control: 3600–3000, 2950, 1726, 1440, 1326, 1249, 1164, 925, 920, 700 cm^{-1} ; imprinted, porous (Hg): 3600–3000, 2931, 1734, 1463, 1388, 1260, 1165, 1021 cm^{-1} .

Metal ion retention

Unless otherwise stated, 200 mg of polymer sample were used as the solid phase in a small chromatography column (I. D. = 0.9 cm). 10 mL of a known concentration of CdCl_2 , CsCl, sodium arsenate, or ZnCl_2 in water, or mercury(II) dithizonate in 80% acetonitrile in water, were loaded onto the column and the elute was collected. For the Cd/Zn co-imprinted resin, 100 mg of resin was used; first, 10 mL of Zn solution was passed through the column, then 10 mL of Cd solution, to a total of 80 ppm of metal ions. Each retention experiment was performed in triplicate.

Infrared (IR) spectroscopy

Polymer samples were analyzed with a Nicolet Magna-IR 560 Spectrometer via a KBr pellet.

Differential scanning calorimetry (DSC)

Samples of 2–5 mg were measured from 10 °C to 80 °C, (5 °C/min) using a TA Instruments model 2100 system with a model 2910 DSC cell under dry nitrogen atmosphere (50 mL/min).

Thermogravimetric analysis (TGA)

Samples of 3–6 mg were measured using a TA Instruments model 2950 TGA unit interfaced with the Thermal analyst model 2100 control unit (heating rate 10 °C/min, Pt sample pan) under nitrogen atmosphere (50 mL/min).

BET surface area

Surface area and porosity of resins were analyzed using Micrometrics ASAP 2020 analyzer. 2.0 g of sample were

degassed for 4 h, then N₂ gas adsorption was measured in duplicates using a temperature ramp of 1 °C/min.

Atomic absorption (AA) spectroscopy

Cadmium, cesium, and zinc amounts were measured using flame Perkin Elmer Atomic Absorption Spectrometer 3100. Mercury samples were measured via furnace Perkin Elmer Zeeman Atomic Absorption Spectrometer 4100ZL. Arsenic was not directly measured by AA due to safety reasons. Instead, it was first precipitated as magnesium ammonium arsenate (MgNH₄AsO₄·6H₂O) by reacting it with known amounts of magnesium ammonium chloride and ammonia (Vogel 1961). The precipitate was filtered out and the remaining magnesium was measured by using the flame AA.

RESULTS AND DISCUSSION

Cadmium, cesium, zinc, mercury, and arsenic were chosen because they have been problems in the Great Lakes region (EPA 2006). The actual heavy metal and metalloids compounds were chosen for their relative non-toxicity, to increase safety in the laboratory. When implemented, imprinted ion-exchange resins and filters could either be used in combination or a concentrate of the specific industrial wastewater stream could be used as the source of imprinting solution. We are aware that, as soon as metal ions dissolve in water, other complexes such as metal hydroxides will form as well. Since those complexes are part of the imprinting solution, this will not change the amount of metal ions removed from water. For simplicity the original metal complex is used for the description of the solution.

Polymer chains are inherently flexible and need to be crosslinked in order to keep the structural integrity of the imprint after the removal of the imprinting molecule. At the same time, the crosslinking density has to be low enough to allow for complete removal of the imprinting

molecule before use. The most promising material for hydrophilic heavy metal ion removal has been a crosslinked 70:30 methacrylate:methacrylamide random copolymer (called 'hydrophilic resin' from now on). The monomers, methacrylate and methacrylamide, are toxic due to their reactivity, but the resulting polymer is non-toxic. In fact, these polymers are approved for water remediation (Mangravite et al. 1985; Tchobanoglous et al. 2003c) and even biomedical applications, e.g. (Lipatowa 1986). IR spectra demonstrated that the heavy metal ions did not inhibit the radical polymerization (see Experimental). Thermo-gravimetric analysis (TGA) data show that the imprinted samples are thermally stable up to 200 °C (Table 1). Differential scanning calorimetry (DSC) gave glass transition temperatures (Tg's) for all samples within 1 °C of 40 °C, indicating that the molecular weight distribution of all samples was similar (Table 2). The broadened transition indicated an increased molecular weight distribution, but the transition was repeatable across all samples (Ashraf et al. 2007).

The hydrophilic resin is charged; therefore it will act as an ion exchange resin. Imprinting results in sites within this ion exchange resin that will additionally allow for metal-ligand bonds to the heavy metals Cd(II), Hg(II), and Zn(II). Carboxylic-type and acrylamide-type complexes are the expected result (Rivas et al. 2003). The ion-exchange sites are non-specific, but the imprinted sites are specific to the heavy metal. We are using imprinting for the metalloid As (V) as well. Arsenate is a large, trivalent ion; its hydroxyl groups are strongly bound and are not likely to exchange

Table 2 | Glass transition temperatures (Tg's) from differential scanning calorimetry (DSC) for Cs- and Cd- im-printed hydrophilic resins

Resin	CsCl-imprinted resin (Tg, °C)	CdCl ₂ -imprinted resin (Tg, °C)
Non-porous control	42	39
Non-porous imprinted	45	39
Porous control	43	41
Porous imprinted	41	40

Table 1 | Thermo-gravimetric analysis (TGA) weight-loss steps for Cs- and Cd-imprinted resins

Resin	CsCl-imprinted resin	CdCl ₂ -imprinted resin
Non-porous control	221 °C (12%), 439 °C (88%)	202 °C (11%), 451 °C (89%)
Non-porous imprinted	222 °C (9%), 414 °C (90%)	196 °C (16%), 428 °C (84%)
Porous control	229 °C (8%), 428 °C (90%)	201 °C (10%), 429 °C (88%)
Porous imprinted	224 °C (5%), 416 °C (90%)	198 °C (8%), 428 °C (90%)

unless thiols are used (Rey et al. 2004). Even so, the resin only offers monovalent groups; therefore, when imprinted with the trivalent arsenate, sites will form that perfectly arrange around the charges of the arsenate and thus form a specific cavity.

Four different samples were prepared for retention measurements: two of normal porosity ('non-porous') and two of increased porosity ('porous'). For each one sample was imprinted with the heavy metal ion complex, one sample was not (called 'imprinted' and 'non-imprinted', respectively). With these four samples it was possible to study both the effect of imprinting and porosity on heavy metal ion retention. Porosity was determined by measuring the BET surface area with a porosimeter. The highest surface area was found in the porous cadmium-imprinted sample ($0.54 \text{ m}^2/\text{g}$) (Table 3).

Metal retention was measured using the different polymer samples as the solid phase in a chromatography column. This is a quick measurement indicating minimum, not total, capacity. Solutions of known concentration of metal ions in water were passed through these columns and the amounts of metal ions in the eluent were measured by AA. In all cases, the imprinted polymers are compared with the non-imprinted controls to determine the effect of imprinting on cadmium retention. All data are an average of three replicates. Since all of the hydrophilic resins are negatively charged at neutral pH, all will retain metal cations due to electrostatic forces. In this project it was determined that imprinting increases retention due to the creation of additional specific binding pockets for heavy metal ions. Table 4 shows the retention of cadmium ions for all four samples.

In both porous and non-porous hydrophilic resins the imprinted polymer demonstrates increased retention in comparison to the non-imprinted controls. All of these polymers were tested at higher concentration than what is found in the environment (20, 40, and 80 ppm) to show the large capacity of the resins. The non-porous, imprinted polymer showed complete retention for 20, 40, and 80 ppm CdCl_2 – no cadmium was found in the eluent. These samples, though, experienced excessive swelling in the column so

Table 3 | BET surface area of cadmium imprinted hydrophilic resins

CdCl_2 resin	Non-porous control	Non-porous imprinted	Porous control	Porous imprinted ^a
BET surface area (m^2/g)	0.27	0.30	0.34	0.54

^aSample only measured once. All other samples measured in triplicate.

Table 4 | Retention of CdCl_2 by Cd-imprinted hydrophilic resins

ppm CdCl_2	Retention calculated from eluted CdCl_2 by polymers of given mass			
	Non-porous control (200 mg) (%)	Non-porous imprinted (50 mg) ^a (%)	Porous control (200 mg) (%)	Porous imprinted (200 mg) (%)
20	100 ± 0.03	100 ± 0.16	98 ± 0.04	100 ± 0.01
40	95 ± 0.01	100 ± 0.00	98 ± 0.03	100 ± 0.00
80	92 ± 0.72	100 ± 0.00	87 ± 0.43	100 ± 0.00

^aAmount of polymer reduced due to excessive swelling of the resin in the column.

that the CdCl_2 solution had to be forced through with pressure. When the amount of resin in the column was reduced to 50 mg, no pressure was needed. The porous, imprinted samples demonstrated clear improvement over the control samples and showed complete retention as well, albeit with 200 mg of resin.

The hydrophilic resin was also imprinted with cesium chloride and retention was measured as above. For CsCl retention, no difference between the imprinted and the non-imprinted resin was found (Table 5). Also, when sodium ions were added to the solution, cesium ion retention was reduced. Cesium ions bind mostly via ionic forces, cadmium via ionic and metal-ligand forces. Therefore this data indicates that metal-ligand forces are necessary for improvement in capacity with imprinting.

Competition experiments with cadmium and sodium ions were performed as well (Table 6). Cadmium ion retention on the porous imprinted resin was reduced to 92% in the presence of three times more sodium than cadmium (keeping the total ion concentration constant at 80 ppm). However, only 50 mg of resin was used, 1/4 of the amount

Table 5 | Retention of CsCl by Cs-imprinted hydrophilic resins

ppm CsCl	Retention calculated from eluted CsCl (200 mg of resin)			
	Non-porous control (%)	Non-porous imprinted (%)	Porous control (%)	Porous imprinted (%)
20	93 ± 0.03	88 ± 0.01	93 ± 0.03	95 ± 0.00
40	91 ± 0.13	97 ± 0.02	95 ± 0.00	97 ± 0.00
80	87 ± 0.23	88 ± 0.10	98 ± 0.00	98 ± 0.03
120 + 60 ppm NaCl	31 ± 0.00	31 ± 0.01	31 ± 0.02	29 ± 0.13
140 + 40 ppm NaCl	41 ± 0.43	41 ± 0.00	32 ± 0.13	41 ± 0.20
160 + 20 ppm NaCl	53 ± 0.00	54 ± 0.43	47 ± 0.04	51 ± 0.01

Table 6 | Retention of CdCl₂ of Cd-imprinted hydrophilic resins in the presence of sodium ions

ppm CdCl ₂ and NaCl	Retention calculated from eluted CdCl ₂			
	Non-porous control (200 mg) (%)	Non-porous imprinted (100 mg) (%)	Porous control (200 mg) (%)	Porous imprinted (50 mg) (%)
60 + 20	100 ± 0.00	100 ± 0.00	100 ± 0.40	100 ± 0.00
40 + 40	75 ± 0.00	75 ± 0.02	87 ± 0.12	100 ± 0.01
20 + 60	70 ± 0.10	79 ± 0.01	83 ± 0.43	92 ± 0.02

used earlier (Table 5), to show the large capacity of the resins and to avoid swelling. Total capacity measurements are currently in progress as well.

The hydrophilic resin was also co-imprinted with CdCl₂ and ZnCl₂ simultaneously. The total amount of ions in the imprinting polymerization was the same as before, but half of the imprinted sites were now specific for zinc, half for cadmium ions. For retention measurements, 100 mg of resin was used; first, zinc ion solution was passed through the column, then 10 mL of cadmium ion solution, to a total of 80 ppm of metal ions (Table 7). Even though only half of the specific sites were available for each ion, 94% of all ions were retained from the 60 ppm ZnCl₂/20 ppm CdCl₂ solution. The cadmium retention was lower than zinc retention for the co-imprinted resin; this is possibly due to the weaker metal-ligand bonds for zinc than for cadmium. For zinc ions still 99% of 80 ppm was retained; this suggests that the smaller Zn ions can bind to some of the larger Cd binding sites more easily than the Cd can bind to the Zn binding sites.

Sodium arsenate was used for imprinting, since it is a common arsenic species in the environment. Arsenic is a metalloid, and the hydroxyl groups around the As(V) ion are tightly bound. It is known that they can be replaced by thiols, but replacement is not likely with carboxylic acids and amides (Rey et al. 2004). Imprinting in this case will lead to a specific cavity with perfectly-arranged amides

Table 7 | Retention of ZnCl₂ and CdCl₂ by a co-imprinted hydrophilic resins

ppm ZnCl ₂	Retention calculated from eluted ZnCl ₂ , (100 mg)		ppm CdCl ₂	Retention calculated from eluted CdCl ₂ , (100 mg)	
		Porous imprinted (%)			Porous imprinted (%)
			80		79 ± 0.13
20		99 ± 0.00	60		100 ± 0.00
40		100 ± 0.03	40		95 ± 0.02
60		100 ± 0.02	20		94 ± 0.03
80		99 ± 0.04			

interacting with the hydroxyl groups of the arsenate. Preliminary results found that the imprinted hydrophilic resin removed 50–70% of the arsenic ion. Due to safety reasons, the arsenic was first precipitated as magnesium ammonium arsenate, then the leftover magnesium was quantified by AA. This method, though, is not sufficiently sensitive in the range of arsenic concentrations remaining after removal of arsenic by the hydrophilic resin. We are currently trying to improve this method or find a safe AA method for arsenate. Additionally, we are currently working on a 30:70 methacrylate: methacrylamide crosslinked random copolymer which is expected to increase arsenic retention due to the decrease in negative charges in the polymer.

For retention of hydrophobic contaminants a hydrophobic polymer is needed. Emulsion polymerization has been developed to synthesize hydrophobic polymers in water (Figure 2). Surfactant molecules stabilize hydrophobic monomer droplets in water, and polymerization occurs within these droplets. To our knowledge, imprinting emulsion polymerization has only been reported where a core-shell particle is being imprinted on the surface (Li et al. 2006). In this research, not only the surface but also inside pores are imprinted by metal ion complexes, similar to the imprinting of hydrophilic polymers (Ashraf et al. 2007). The most common mercury complexes in nature are hydrophobic, such as methyl mercury; methyl mercury, though, is too toxic to handle in the laboratory safely. Therefore, mercury dithizonate was chosen as the safest hydrophobic mercury complex for the proof-of-concept of imprinting emulsion polymerizations. Usually surfactants used in emulsion polymerizations are ionic, since charge repulsion further stabilizes the monomer droplets. In this case,

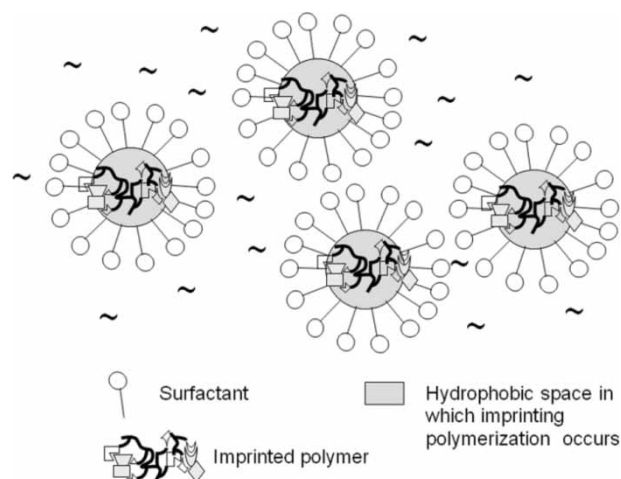
**Figure 2** | Imprinting emulsion polymerization.

Table 8 | Retention of mercury by mercury dithizonate-imprinted hydrophobic resins

ppm Hg ²⁺	Retention calculated from eluted mercury dithizonate			
	Non-porous control (%)	Non-porous imprinted (%)	Porous control (%)	Porous imprinted (%)
20	69	100	62	100
40	82	100	83	100
80	90	95	92	100

though, non-ionic surfactants had to be used, to prevent retention of metal ions on the surface of the surfactants. Thus, a non-ionic alkyl-oligo(ethylene glycol) surfactant was chosen for the polymerization.

Poly(methyl methacrylate) (PMMA) was first imprinted within an emulsion polymerization, but its surface area was very low, due to the high crystallinity of this polymer. Therefore, a random, crosslinked copolymer of 50:50 methyl methacrylate:phenyl methacrylate was synthesized. The resulting hydrophobic resin is not an ion exchange resin, since the polymer is not charged, but it can still be implemented in the same manner. Again, four samples were prepared varying the porosity and metal imprinting. The preliminary data (not yet in triplicate) shows that imprinting increases the capacity for mercury ions (Table 8). Remarkably, it was possible to remove all mercury ions from water with the porous, imprinted resin, even when 80 ppm of mercury ions was added.

Total capacities, kinetic experiments, and continuous break-through curves with low concentrations of heavy metal and metalloid ions are in progress. Metal retention capacities in the presence of more competing ions and source water mimics will be performed as well.

CONCLUSION

In summary, imprinted resins were developed with increased capacity for retention of heavy metal ions and arsenate for water remediation. These resins were made from common, non-toxic materials. For hydrophobic contaminants, this method was expanded by creating a method for imprinting emulsion polymerizations. The imprinted resins can either be implemented as ion exchange resins, filter resins, or membranes. A combination of different imprinted resins can be used as well. Imprinting polymerization is a general method that can be used for a variety of other pollutants as well, such as polyaromatic hydrocarbons (PAH).

REFERENCES

- Ashraf, S. A., Mercado, C., Randhawa, M. & Mueller, A. 2007 Imprinted polymers for the removal of hydrophilic and hydrophobic metal complexes from water. *Proceedings of Engineering and Mathematics*, pp. 265–272.
- Bloecher, C., Dorda, J., Mavrov, V., Chmiel, J., Lazaridis, N. K. & Matis, K. A. 2003 Hybrid flotation-membrane filtration process for the removal of heavy metal ions from wastewater. *Water Research* **37**, 4018–4026.
- Bolto, B. A. 1995 Soluble polymers in water purification. *Progress in Polymer Science* **20**, 978–1041.
- Canizares, V. R. O., Martinez, J. F. & Espinosa, C. F. 2000 Acute toxicity to daphnia magna of effluents containing Cd, Zn, and a mixture of Cd–Zn, after metal removal by *Chlorella vulgaris*. *Environmental Toxicology* **15** (3), 160–164.
- Culp, R. L. & Culp, G. L. 1971 *Advanced Wastewater Treatment*. Van Nostrand Reinhold Company, New York, NY.
- Daniels, J. L., Das, G. P., Hernandez, M. T. S. & Bae, S. 2006 Coastal pollution mitigation with lime and zero valent iron. *Marine Geosciences and Geotechnology* **24** (3), 183–191.
- Eilbeck, W. J. 1987 *Chemical Processes in Waste Water Treatment*. Ellis Horwood Limited, Chichester.
- EPA 2006 Toxic Release Inventory (TRI), EPA (ed.). Available from: http://oaspub.epa.gov/enviro/fii_master.fii_retrieve?city_name=Detroit&state_code=MI&all_programs=YES&program_search=1&report=1&page_no=1&output_sql_switch=TRUE&database_type=TRIS (Accessed May 2006)
- Guclu, G., Guclu, K. & Keles, S. 2007 Competitive removal of nickel(II), cobalt(II), and zinc(II) ions from aqueous solutions by starch-graft-acrylic acid copolymers. *Journal of Applied Polymer Science* **106**, 1800–1805.
- Hamon, R. E., McLaughlin, M. J. & Cozens, G. 2002 Mechanisms of attenuation of metal availability in *in-situ* remediation treatments. *Environmental Science and Technology* **36**, 3991–3996.
- Koltuniewicz, A. B. & Drioli, E. 2008 *Membranes in Clean Technologies*. Wiley-VCH, Weinheim.
- Le, N. M., Guieysse, B. & Mattiasson, B. 2006 Removal of trace contaminants using molecularly imprinted polymers. *Water Science and Technology* **53** (11), 205–212.
- Lee, M., Paik, I. S., Kim, I., Kang, H. & Lee, S. 2007 Remediation of heavy metal contaminated groundwater originated from abandoned mine using lime and calcium carbonate. *Journal of Hazardous Materials* **144**, 208–214.
- Li, D., Zhu, S., Pelton, R. H. & Spafford, M. 1999 Flocculation of dilute titanium dioxide suspensions by graft cationic polyelectrolytes. *Colloid and Polymer Science* **277**, 108–114.
- Li, Y., Fu, Q., Zhang, Q. & He, L. 2006 Preparation and evaluation of uniform-size (–)-ephedrine-imprinted polymeric microspheres by multi-step swelling and suspension polymerization. *Analytical Sciences* **22**, 1355.
- Lipatowa, T. E. 1986 Medical polymer adhesives. *Advances in Polymer Science* **79**, 65–93.
- Liu, J., Ma, Y., Xu, T. & Shao, G. 2010 Preparation of zwitterionic hybrid polymer and its application for the removal of heavy

- metal ions from water. *Journal of Hazardous Materials* **178**, 1021–1029.
- Malachowski, L., Stair, J. L. & Holcombe, J. A. 2004 Immobilized peptides/amino acids on Solid supports for metal remediation. *Pure and Applied Chemistry* **76** (4), 777–787.
- Manahan, S. E. 1984 *Environmental Chemistry*. 4th edition, Brooks/Cole Publishing Company, Monterey, CA.
- Mangravite Jr., F. J., Leitz, C. R. & Galick, P. E. 1985 Organic polymeric flocculants: effect of charge density, molecular weight and particle concentration. In *Paper presented at Flocculation, Sedimentation, and Consolidation*. Engineering Foundation, The Cloister, Sea Island, Georgia, USA.
- Morahashi, S., Takeda, K., Yamamoto, T., Hoshino, K. & Sasakura, T. 1996 Adsorption properties of trivalent metal ions onto hydralyzed polyacrylamide gel. *Journal of Chemical Engineering of Japan* **29** (6), 1060–1063.
- Patterson, J. W. 1975 *Wastewater Treatment Technology*. Ann Arbor Science, Ann Arbor, MI.
- Pizarro, G. D. C., Marambio, O. G., Jeria, O. M., Huerta, M. R., Rodriguez, O. O., Rivas, B. L. & Geckeler, K. E. 2007 Metal ion interaction of water-soluble copolymers containing carboxylic acid groups in aqueous phase by membrane filtration technique. *Journal of Applied Polymer Science* **105**, 2893–2902.
- Polettini, A., Pomi, R. & Valente, M. 2004 Remediation of a heavy metal-contaminated soil by means of agglomeration. *Journal of Environmental Science and Health Part A* **A39** (4), 999–1010.
- Rey, N. A., Howarth, O. W. & Pereira, M. E. C. 2004 Equilibrium characterization of the As(III)-cysteine and the As(III)-glutathione systems in aqueous solution. *Journal of Inorganic Biochemistry* **98**, 1151–1159.
- Rivas, B. L., Pereira, E. & Maureira, A. 2009 Functional water-soluble polymers: polymer-metal ion removal and biocide properties. *Polymer International* **58**, 1093–1114.
- Rivas, B. L., Pereira, E. D. & Morena, V. I. 2003 Water-soluble polymer-metal ion interactions. *Progress in Polymer Science* **28**, 173–208.
- Schulte, B. M. & Schuster, M. 2008 Removal enrichment and recovery of Ni(II), Zn(II) and phosphate from phosphation rinsing waters with liquid-phase polymer-based retention technique. *Separation and Purification Technology* **63**, 172–178.
- Tchobanoglous, G., Burton, F. L. & Stensel, H. D. 2003a Chemical unit processes. In: *Wastewater Engineering, Treatment and Reuse* (M. Eddy, ed.). Tata McGraw-Hill, New Delhi, pp. 475–544.
- Tchobanoglous, G., Burton, F. L. & Stensel, H. D. 2003b Water reuse. In: *Wastewater Engineering, Treatment and Reuse* (M. Eddy, ed.). Tata McGraw-Hill Publishing Company Limited, New Delhi, pp. 1345–1445.
- Tchobanoglous, G., Burton, F. L. & Stensel, H. D. 2003c Wastewater engineering: an overview. In: *Wastewater Engineering, Treatment and Reuse* (M. Eddy, ed.). Tata McGraw Hill Publishing Company Limited, New Delhi, pp. 1–25.
- Tolani, S., Mugweru, A., Craig, M. & Wanekaya, A. K. 2010 Rapid and efficient removal of heavy metal ions from aqueous media using cysteine-modified polymer nanowires. *Journal of Applied Polymer Science* **116**, 308–313.
- Vogel, A. I. 1961 *Quantitative Inorganic Analysis*. Longmans, London, 501 pp.
- Wittmann, G. T. W. 1983 Toxic metals. In: *Metal Pollution in the Aquatic Environment* (U. Foerstner & G. T. W. Wittmann, eds.). Springer-Verlag, Berlin.
- Wright, K. 2005 Our preferred poison. *Discover* **3**, 58–65.
- Yan, M. & Ramstroem, O. 2005 *Molecularly Imprinted Materials, Science and Technology*. Marcel Dekker, New York.

First received 6 April 2010; accepted in revised form 19 August 2010