Imprinted Polymers for Water Purification

Manny Randhawa,[1] Isabelle Gartner,[2] Cassandra Becker,[3] James Student,[4] Minghui Chai,[1] Anja Mueller[1]

[1]*Department of Chemistry, Central Michigan University, Mt. Pleasant, Michigan 48859*
[2]*Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*
[3]*Department of Chemistry, Clarkson University, Potsdam, New York 13699*
[4]*Department of Geology, Central Michigan University, Mt. Pleasant, Michigan 48859*

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ABSTRACT: Imprinting polymerization is used to make resins with a high capacity for cadmium ions for wastewater treatment. A random copolymer of methacrylate and methacrylamide was found to be most effective, especially when the porosity of the resin is increased. Complete removal for up to 80 ppm of cadmium with only 50 mg of resin was demonstrated with the imprinted resins, but not the nonimprinted reference samples. This shows that imprinting polymerization improves the capacity of the resin in the uptake of cadmium ions. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3321–3326, 2007

Key words: molecular imprinting; resins; adsorption; waste

INTRODUCTION

Industrial and residential wastewater containing heavy metals, such as cadmium, chromium, copper, lead, and mercury, is polluting lakes, rivers, and seas. It causes health problems in both animals and humans. Moreover, heavy metals are toxic to the sludge bacteria that are currently used in water purification.[1,2] Also, the resulting activated sludge is then unsuitable for application to agricultural land.[2] Therefore, removal of heavy metal ions from water would play a significant role in reducing health problems and accelerating the biodegradation process in sludge.

Common flocculants have been proven inefficient in removal of heavy metal ions from wastewater.[3,4] Much research has been done to find alternative materials, such as waste materials like hazelnut shell,[5] lignin,[6] and starch.[7] Specialized resins have been synthesized and tested as well: diallyldimethylammonium chloride was grafted onto polyacrylamide for a flocculent specialized for titanium dioxide.[8] Five milligram of polymer can remove 1 g of TiO_2 within 20 min, but as increasing amounts of polymer were used, longer times were required for flocculation to occur. A chelating polymer was prepared from glycidyl methacrylate and iminodiacetic acid.[9] From pH 2–6 the adsorption capacity for Cr^{3+} and Cu^{2+} was found to be 2.7 and 1.8 mmol/g, respectively. The adsorption of Cd^{2+} and Pb^{2+} increases with the pH, but was lower than Cu^{2+}. An adsorbent containing carboxylate groups was prepared by grafting hydrous tin(IV) oxide gel onto polyacrylamide.[10] This adsorbent was shown to have a greater selectivity for Pb^{2+} than for Hg^{2+} and Cd^{2+}. Two hundred fifty to 300 mg of adsorbent was able to remove 2 mg of Pb^{2+}.

In this project a resin is made specific, not by synthesizing a new resin but by imprinting a resin similar to the ones used in wastewater treatment with a specific heavy metal ion. In addition to the specific adsorption of the heavy metal ion, random adhesion of other impurities in wastewater to the improved coagulant can still occur. Thus this resin would be sufficient for clarification of water as well as the removal of heavy metal ions.

Imprinting polymerization involves the preparation of the polymer in the presence of an imprinting molecule, in this case cadmium chloride (Fig. 1). 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 cadmium ions during water purification. The effect of surface area on metal ion retention is also described.

MATERIALS AND METHODS

Materials

Methacrylic acid (99%), methacrylamide (98%), acrylamide (99%), 2,2-azobis(2-methylpropionamidine)

Correspondence to: A. Mueller (muell1a@cmich.edu).
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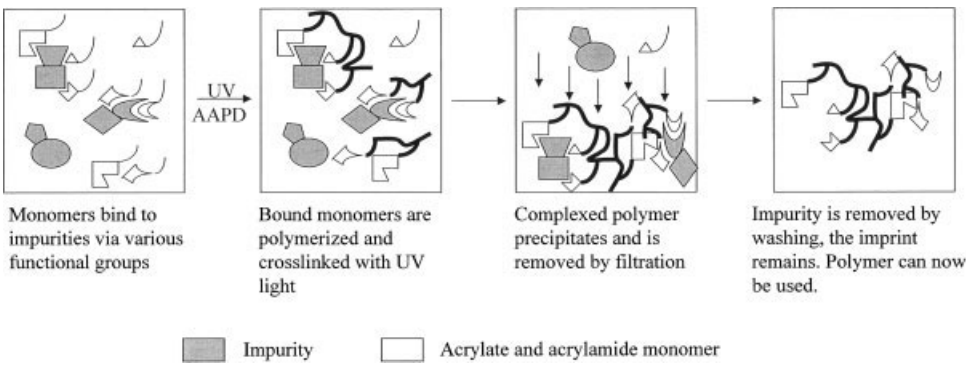

Figure 1 Schematic of imprinting polymerization.

dihydrochloride (AAPD) (97%), and ethylene glycol diacrylate (EDMA; 90%) were obtained from Aldrich Chemical Company (St. Louis, MO). Cadmium chloride (99.8%) and concentrated nitric acid (70%) were obtained from Fisher Chemical Company (Pittsburg, PA). Water used in the experiments is purified through Barnstead (Dubuque, IA) E-pure filter system and collected at 18 MΩ. Snake skin pleated dialysis tubing, molecular cutoff 3500, is obtained from Pierce.

Polymer synthesis and characterization

50 : 50 methacrylate : methacrylamide random copolymer

For the 50 : 50 methacrylate : methacrylamide copolymer, 0.50 mol each of methacrylate and methacrylamide, along with 0.001 mol AAPD, 0.0005 mol EDMA, and 150 mL of deionized water are placed in a round-bottom flask inside a glove box under inert atmosphere. The mixture is then placed inside a Rayonet (Branford, CN) photochemical reactor and stirred for 8 h. The polymer obtained is the nonimprinted polymer control. For imprinting polymerization, 0.001 mol of cadmium chloride is added to the mixture described earlier and polymerized in the same manner. After polymerization, both polymers are dried by rotary evaporation. Impurities, unreacted monomer, and cadmium were removed in batches from the imprinted polymers by dialysis in water to result in the washed, imprinted samples.

70 : 30 methacrylate : methacrylamide random copolymer

For the 70 : 30 methacrylate : methacrylamide copolymer, 0.70 and 0.30 mol of methacrylate and methacrylamide, respectively, along with 0.001 mol AAPD, 0.0005 mol EDMA, and 150 mL of deionized water are placed in a round-bottom flask under inert atmosphere. The mixture is then placed inside a Rayonet photochemical reactor and stirred for 8 h. The polymer obtained is the nonimprinted polymer control. For imprinting polymerization, 0.001 mol of cadmium chloride is added to the mixture described earlier and polymerized in the same manner. To synthesize the porous, imprinted polymer and porous, nonimprinted control, N_2 is purged additionally through the reaction mixture during polymerization; all other conditions and procedures remain the same. After polymerization, all polymers are dried by rotary evaporation. Impurities, unreacted monomer, and cadmium were removed in batches from the imprinted polymers by dialysis in water to result in the washed, imprinted samples. The final yield after dialysis is still being determined.

Nonimprinted, nonporous IR: 3600–3000, 2950, 1701, 1458, 1255, 1174, 925, 700, 600, 510 cm^{-1}; imprinted, nonporous IR: 3600–3000, 2950, 1701, 1458, 1255, 1161, 925, 700, 600, 510 cm^{-1}; Nonimprinted, porous IR: 3600–3000, 2950, 1701, 1474, 1388, 1249, 1176, 925, 920, 700, 600, 510 cm^{-1}; imprinted, porous IR: 3600–3000, 2950, 1701, 1482, 1388, 1260, 1178, 925, 920, 782, 510 cm^{-1}.

IR spectroscopy

Polymer samples were analyzed with a Nicolet (Thermo Scientific, Waltham, MA) Magna-IR 560 Spectrometer via KBr pellet.

Differential scanning calorimetry

The differential scanning calorimetry (DSC) samples were measured from 10°C to 80°C, at a rate of 5°C/min, with sample weights ranging from 2.00 to 5.00 mg using a TA Instruments (New Castle, DE) model 2100 thermal analysis system equipped with a model 2910 DSC cell. The sample compartment was exposed to a constant purge of dry nitrogen at 50 mL/min.

BET surface area

Two grams of each polymer was measured in the ASAP 2020 analyzer (Micrometrics, Grasford, New South Wales, Australia). The samples were weighed, degassed for 4 h, and then reweighed to ensure

that all water was removed. The temperature ramp during BET surface measurements was 1°C/min, and N_2 was the gas that was adsorbed. The sample was then reweighed and another measurement was taken.

Cadmium retention measurements

Column chromatography

Two hundred milligram of polymer sample was used as the solid phase in a small chromatography column (ID = 0.9 cm) with the exception of the imprinted, nonporous polymers, where 50 mg was used. Ten milliliter of $CdCl_2$ solution in water with the concentrations of 20, 40, and 80 ppm was loaded onto the column and the elute was collected.

Atomic absorption spectroscopy

For atomic absorption (AA) measurements, the elute of the columns was diluted 100-fold. The samples were measured by a Perkin–Elmer Flame AA instrument.

Inductively coupled plasma mass spectroscopy

For inductively coupled plasma mass spectroscopy (ICP-MS) measurements the elute was diluted to parts per billion. Nitric acid was added to result in a 2% nitric acid solution. These samples were measured by a VG-Plasmaquad (PQ-1) ICP-MS (upgraded to PQ-2 in 2002).

NMR relaxation time measurements of water inside the polymer resins

Sixty milligrams of each polymer sample were weighed out and soaked with 0.75 mL of water. All of the polymers are insoluble. ^1H T_1 relaxation measurements were done on a 500 MHz Varian Inova spectrometer using the ultra linear gradient indirect detection $^1H/X$ (X is tunable from ^{15}N to ^{31}P) probe. The ^1H 90° pulse used was 5.6 μs, and all nuclear magnetic resonance (NMR) data were processed using Varian VNMR 6.1C software on a SUN 2000 Blade workstation.

RESULTS AND DISCUSSION

In this project, a coagulant is being developed that is specific for heavy metal ions. The coagulant is made from materials similar to the ones already being used in wastewater treatment. These resins have a large capacity for cadmium ions, in fact much larger than the common concentrations of cadmium ions in wastewater. However, they still function as unspecific coagulants, which will block the majority of the cadmium ion binding sites, thus a large access of binding sites is needed.

Imprinting polymerization based on noncovalent forces is usually done in organic solvents due to the higher polar forces and thus higher specificity compared to water.[11] Although the specificity will not be as high, it will still be sufficient for coagulants, and so in this study, the imprinting polymerization is done in water. Imprinted polymers for use in wastewater should be made in water; if it is made in organic solvent and then transferred, the imprint would swell along with the polymer, making it no longer specific for the imprinting molecule.

The first imprinting molecule chosen in this study was cadmium chloride, because of its high toxicity and frequent occurrence in wastewater.[12] It is emitted from industries such as mining and steel manufacturing. The first polymer chosen was polyacrylamide, which is a common resin for flocculants.[11]

Polymer chains are inherently flexible and need to be crosslinked 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. In our experiments with crosslinked polyacrylamide, it was not possible to remove more than 90–95% of the cadmium at any crosslinking density studied.[13] Therefore, a different resin was needed.

A 50 : 50 methacrylate-methacrylamide random copolymer was then studied. As with all of the copolymers, a noncrosslinked sample was prepared first to study its chemical structure with NMR. In this case, the copolymer precipitated in D_2O could not be redissolved; thus no NMR spectrum could be obtained. Initial cadmium retention data were collected with this copolymer and were promising (Table II). However, because of the difficulty of studying its structure, no further experiments were performed with this copolymer.

The most promising material for cadmium removal so far has instead shown to be a 70 : 30 methacrylate : methacrylamide random copolymer. The resins are synthesized by radical polymerization initiated by UV light. AAPD and EDMA are the water-soluble radical initiator and crosslinker, respectively. To increase the porosity of the resin, nitrogen gas was bubbled through the polymerization reactions.

Four different samples were prepared: two of normal porosity (''nonporous'') and two of increased porosity (''porous''). To be able to determine the effect of imprinting on cadmium retention, polymerizations with and without the imprinting molecule (called ''imprinted'' and ''nonimprinted,'' respectively) were performed for both the nonporous and porous samples. With these four samples it is possible

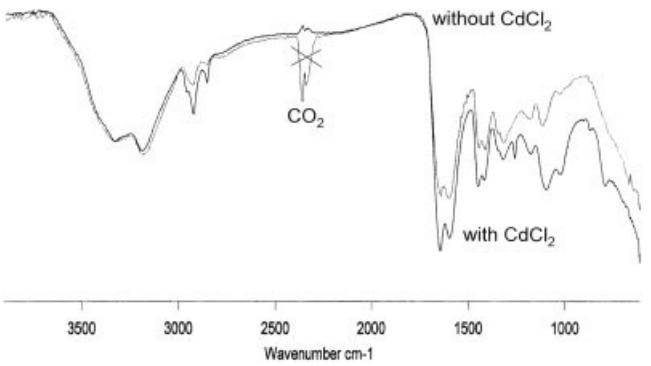

Figure 2 IR spectra of imprinted 70 : 30 polyacrylate–polyacrylamide copolymer and nonimprinted control.

to study both the effect of imprinting and the effect of porosity on cadmium retention.

Polymer characterization

To prove that the polymerization occurs in the presence of cadmium ions, IR spectroscopy was performed. IR spectra of the imprinted and the nonimprinted 70 : 30 methacrylate : methacrylamide copolymer are identical (Fig. 2), proving that cadmium does not inhibit the radical polymerization.

Since the crosslinked polymers are insoluble, it is not possible to determine the molecular weight of the samples by gel permeation chromatography or NMR end-group analysis. DSC can be used to compare the glass transition temperatures (T_g). Because T_g is dependent on the molecular weight and molecular weight distribution in the low-molecular-weight range, this can be used as a rough comparison of sample molecular weights, even though crosslinking broadens the T_g transitions. All T_g were close to 40°C (± 1°), indicating that the molecular weight distributions of all samples are similar.

In both the porous and nonporous samples, the imprinted polymer (which still contained cadmium) proved denser and less porous than the respective nonimprinted polymer. Since porosity changes the surface area of the sample and thus possible metal uptake, it is important to measure the porosity of each sample. Relative porosity of the polymers was investigated by measuring the ^{1}H NMR T_1 relaxation time of water. T_1 values obtained from the ^{1}H NMR study show an average motion of freely moving water molecules outside and inside the polymer resins. The water molecules outside the polymer matrix are free to move, leading to a high T_1 value; while the water molecules trapped inside the polymer (i.e., interacting with the polymer tightly) have their motion greatly restricted by the polymer matrix, resulting in a lower T_1 value. For the nonporous samples a big difference in T_1 values was seen between the imprinted and nonimprinted polymers. For the imprinted sample, the high T_1 value of water indicated that water moved quickly and freely in the system, indicating that there was little interaction of water with that polymer (Table I). The T_1 values of water in both porous polymer gels were close to each other, indicating the similar interactions of water with both polymers.

Porosity was also determined by measuring the BET surface area with a porosimeter. The highest surface area was found in the porous imprinted sample. This seems to contradict the T_1 relaxation time data; however, these measurements show porosity under different conditions and therefore are not directly comparable. The T_1 relaxation data is measured in the presence of D_2O and thus takes swelling of the polymers in water into account. The polymer that exhibits the most swelling is the nonporous, imprinted sample; in fact it seems to swell enough that even the water inside the polymer sample can freely move, indicated by the high T_1 relaxation time. BET surface area, on the other hand, is measured in the absence of water, thus swelling is not taken into account. Under these conditions the highest porosity is found in the porous, imprinted polymer.

Cadmium retention

Cadmium retention was measured by using different polymer samples as the solid phase of a chromatography column. Known concentrations of cadmium chloride in water were passed through these columns and the amounts of cadmium in the elute and solid phase were measured. In all cases, the imprinted polymers are compared with the nonimprinted controls to determine the effect of imprinting on cadmium retention. Since all of the studied resins are negatively charged at neutral pH, all will retain

TABLE I
Differences in Porosity between Porous and Nonporous Polymers Measured by ^{1}H NMR Relaxation Time and Porosimeter

	Nonporous		Porous	
Polymer sample	Nonimprinted	Imprinted	Nonimprinted	Imprinted
^{1}H T_1 relaxation time of water (s)	8.18 (± 0.50)	12.14 (± 0.83)	9.03 (± 0.32)	9.42 (± 0.55)
BET surface area (m^2/g)	0.27	0.30	0.25	3.95

TABLE II
Initial Cadmium Retention Data for 50 : 50 Methacrylate : Methacrylamide Copolymer

Cadmium chloride added to ~ 50 mg of polymer (ppm)	ppm retained in polymer	
	Nonimprinted control	Imprinted polymer
10	10.01 (100.1)[a]	15.70 (157.0)[b]
50	14.81 (29.6)	46.81 (93.6)
100	25.43 (25.4)	50.85 (50.8)
200	35.95 (18.0)	39.80 (20.0)

[a] Within error of the instrument. Values in parentheses indicate percentages.
[b] Appromimately 1% if the imprinting cadmium chloride had remained in the polymer, distributed inhomogeneously.

cadmium due to electrostatic forces. In this project it is determined whether imprinting increases retention because of the creation of additional specific binding pockets for cadmium ions.

The first cadmium retention data were obtained with the nonporous 50 : 50 methacrylate : methacrylamide random copolymer (Table II). To prevent precipitation of this polymer, it was used in high dilution. This led in some cases to artifacts, since some of the shorter polymer chains in the sample passed out of the column during the experiment. Also, the polymer was inhomogeneous, and not all of the cadmium could be washed out. Even so, the data shows that the imprinted polymer exhibits higher cadmium than the nonimprinted control.

Because of the difficulties in working with this polymer, no further experiments were conducted with it. The ratio of monomers was changed to 70 : 30 methacrylate : methacrylamide (Table III), resulting in a functional resin that could be handled more easily.

The analysis of cadmium concentrations of elute of the 70 : 30 methacrylate : methacrylamide random copolymer samples was done with an ICP-MS, which has the capability to detect cadmium ions in parts per trillion concentration. Both porous and nonporous samples of the 70 : 30 methacrylate : methacrylamide copolymer were measured with 20, 40, and 80 ppm of $CdCl_2$ (Table III).

In both porous and nonporous samples, the imprinted polymer demonstrates increased retention in comparison to the nonimprinted controls. The nonporous, imprinted polymer showed complete retention for 20, 40, and 80 ppm $CdCl_2$. Unfortunately, these samples experienced more swelling than the porous samples, to such a degree that the $CdCl_2$ solution had to be forced through the chromatography columns with pressure. The porous, imprinted samples showed clear improvement over the control samples but were not as effective as the nonporous, imprinted samples. On the other hand, this polymer was not tested at equally high concentrations. Therefore, it is possible that equally high retention can be reached with the nonporous as with the porous samples. As mentioned earlier, all of these concentrations are above common cadmium ion concentrations found in wastewater. But since these resins will be used in an environment containing particles that will bind unspecifically, an excess of binding sites is needed to remove all cadmium ions present.

The data presented here demonstrate that the imprinted resin is more effective than the control resin in removing cadmium ions from water. Complete removal of 80 ppm of cadmium chloride is removed by only 200 mg of imprinted resin, but not the nonimprinted control. Imprinting polymerization provides a flexible, new approach that can be used for the removal of a variety of water pollutants. Only the imprinting molecule has to be changed to create a different imprinted resin. Experiments with estrogen have already been conducted[14,15] and investigations with cesium chloride are in progress in this laboratory.

It has been shown that the increased surface area provided by a highly porous, imprinted polymer enhances heavy metal ion retention, thus providing a more efficient filtering process. Crosslinking density can easily be adjusted in the polymerization to ensure that the desired density for a functional flocculent resin is obtained.

For hydrophobic contaminants the polymerization can be changed to an emulsion polymerization. Initial experiments with a hydrophobic mercury complex have been performed and the results are promising.

TABLE III
Cadmium Retention Data for 70 : 30 Methacrylate–Methacrylamide Copolymer

$CdCl_2$, ppm added (ppm)	ppm retention calculated from eluted $CdCl_2$ (ppm)			
	Nonporous		Porous	
	Control	Imprinted	Control	Imprinted
20	0.100 ± 0.0003[a]	0.400 ± 0.0001[a]	0.098 ± 0.003	0.100 ± 0.0001[a]
40	0.189 ± 0.005	0.800 ± 0.0002[a]	0.196 ± 0.002	0.200 ± 0.0003[a]
80	0.368 ± 0.026	1.600 ± 0.005[a]	0.349 ± 0.011	0.400 ± 0.001[a]

[a] Complete retention.

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