

Metal Ion Removal Properties of Crosslinked Poly(acrylamide-co-2-acrylamide-2-methyl-1-propane sulfonic acid)

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ABSTRACT: Poly(acrylamide-co-2-acrylamide-2-methyl-1-propane sulfonic acid) P(AAm-co-APSA) copolymers have been prepared to be used in the extraction of Pb(II), Hg(II), Cd(II), Zn(II), Al(III), and Cr(III) metal ions from aqueous solution by a batch and column equilibration procedures. The adsorption capacity was increased with pH for all metal ions

studied. The contact time and the temperature did not affect the retention significantly. The resin did not show a preference in a mixture of Pb(II), Cd(II), Zn(II), and Cr(III). © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 586–591, 2011

Key words: radical polymerization; resins; ion exchangers

INTRODUCTION

Heavy metals, which find many useful applications in our life, are very harmful if they are discharged into natural water resources. For example, lead, mercury, and cadmium are examples of heavy metals that have been classified as priority pollutants. The amount of lead used in many products has been reduced due to potentially harmful health effects. The symptoms of Hg(II) intoxication depends on the type of compound and the mode of contact. Cadmium is another heavy metal ion that is highly corrosion-resistant and is used as a protective coating for iron, steel, and copper, but it is an irritant to the respiratory tract, and prolonged exposure to this metal can cause anosmia and yellow stains that gradually appears on the necks of the teeth.¹

Solvent extraction and solid phase extraction are the most common methods for the preconcentration and separation of trace elements from various matrices. Solvent extraction has some disadvantages because of the use of excess of solvent, which not only makes the method costly but is also contrary to the idea of green chemistry. During the past two decades, the use of chelating resins for metal ion preconcentration and separation has been considerably increased.²

Chelating polymers have attracted more interest, due to their applications in waste water treatment, metal recovery from diluted solution, as protective coating on metal surfaces or as a priming layer, coating on paper, fiber and fabrics, selective binding of enzymes.³ The selective removal and recovery of metal ions has a potentially vast range of applications in conservation of the environment and use of resources.⁴

The design of tailored chelating agents represents one of the basic challenges in the field of synthetic coordination chemistry. Tailored chelating reagents can be used to govern the stability of a complex or to modulate the electronic properties of a metal cation. Chelate-forming polymeric ligands characterized by reactive functional groups containing O, N, P, S, and donor atoms capable of coordinating different metal ions have been extensively studied.^{5–18}

For practical uses, strong and selective binding of the target metal ion, rapid interaction between the active site and the metal ion, and recovery of the resin are necessary. Moreover, minimal loss of the metal ion retention capability after many cycles of applications is needed.

The aim of this article is the synthesis of a resin-containing amide and sulfonic acid moieties with the ability to remove environmentally impacting metal ions.

EXPERIMENTAL PART

Materials

Acrylamide (AAm, 99%, Aldrich) and 2-acrylamide-2-methyl-1-propanesulfonic acid (APSA, 99%, Merck) was utilized as obtained. *N,N'*-methylenebisacrylamide (MBA, 99%, Aldrich) and ammonium

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peroxide disulfate (AP, Fluka) were used as obtained as crosslinking and initiator reagents, respectively.

For adsorption studies, the metal salts used were $\text{Cd}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3$, $\text{Hg}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, and $\text{Zn}(\text{NO}_3)_2$. Metal salts were purchased from Merck. The analytical grade HNO_3 , HClO_4 , and HCl were purchased from Fisher.

Synthesis of the resin

The resin poly(acrylamide-co-2-acrylamide-2-methyl-1-propanesulfonic acid) P(AAm-co-APSA) was performed in a polymerization flask as follows: the system was kept under N_2 at 70°C for 4 h. Then, the resin was filtered and washed with distilled water and dried up to constant weight at 40°C . The resin was screened, and a particle size fraction in the range of 180–250 μm was chosen for all experiments.

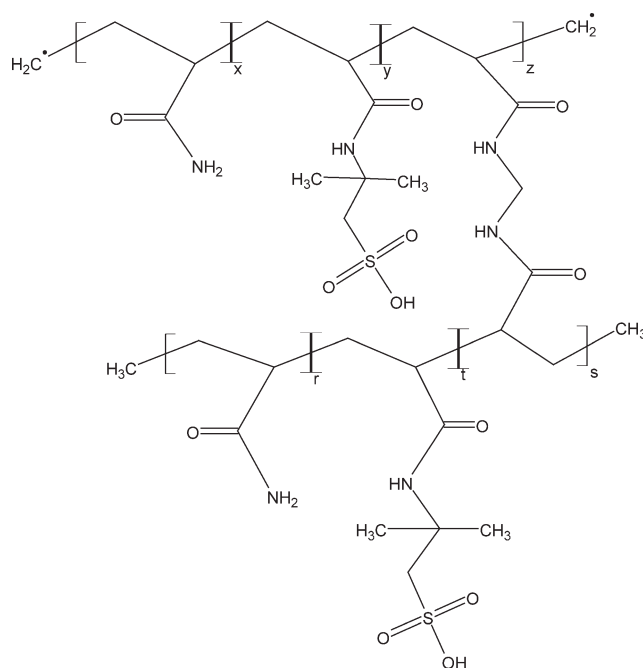
Metal ion removal

A batch equilibrium procedure was applied to determine the metal ion binding ability of the synthesized adsorbents. All experiments were performed in a flask mounted on a shaker. The adsorption equilibrium experiments were carried out to study the effects of pH, metal ion concentration, contact time, and temperature. Additionally, the retention ability for divalent and trivalent cations $\text{Cd}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Hg}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Cr}(\text{III})$, and $\text{Al}(\text{III})$ under competitive conditions was studied.

Then, 0.05 g of dried resin and 5 mL of metal ion solution were shaken for 1 h at 20°C . After shaking, the resin samples were filtered and washed with water at the same pH. The metal ion concentrations in the filtrate were determined by atomic absorption spectroscopy (AAS). Batch metal uptake experiments under competitive conditions were performed with the following divalent metal ion mixtures: Cd-Zn-Pb-Cr at pH 5. For this test, 0.20 g of resin and 20 mL of metal ion solution were used. The resin-metal ion ratio in the mixture (in mol) was 20 : 1. After shaking for 1 h, the resin samples were further handled as described for the noncompetitive experiments.

In the regeneration experiments, HNO_3 , HCl , and HClO_4 at two concentrations were studied as potential stripping reagents by using the batch method. A total of 0.05 g of resin-loaded with $\text{Cd}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Cr}(\text{III})$, and $\text{Pb}(\text{II})$ ions were eluted with 5 mL of eluent for 1 h.

For the column experiments, 0.1 g of resin was placed into a column with 15 cm length and 1 cm diameter. In all runs, a 10 mL metal salt solution passed through the column. The fractions were collected and analyzed for the metal ion concentration by AAS.



Scheme 1 General structure of the resin.

Measurements

A Julabo air-batch shaker was used for shaking the solution at a desired temperature. The pH was measured with a digital pH meter. AAS (H. Jürgens, A Unicam Solar M series) was used for the determination metal ions. The FTIR spectra of the samples were recorded with a Magna Nicolet 550 spectrophotometer. The thermograms of the loaded and unloaded resins were recorded on an STA-625 thermoanalyzer. Approximately 5 mg of the dry sample was heated at a heating rate of $20^\circ\text{C}/\text{min}$ under a dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

Water-insoluble resins containing sulfonate and amido groups were obtained by copolymerization of an equimol ratio of the comonomers 2-acrylamide-2-methyl-1-propane sulfonic acid and acrylamide, and AP was used as an initiator and MBA as a crosslinking reagent (see Scheme 1). The yield for this resin was 98%. The resin shows a high thermal stability up to 200°C with a weight loss lower than 11%; then, the weight loss increased until reaching 78.1% at 500°C . Among the most characteristic absorption bands shown in the FTIR spectrum of P(AAm-co-APSA) are the following (in cm^{-1}): 3429.41(N-H), 1667.42 (C=O), 1040 and $\sim 1200 \text{ cm}^{-1}$ (S-O).

Metal ion removal properties

It is well known that metal ions have free orbitals, which are available to receive electrons originate of

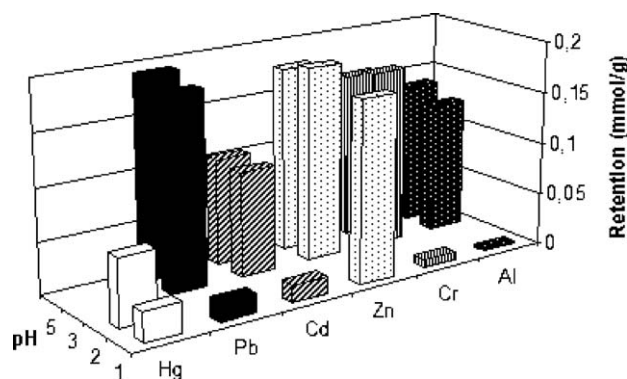


Figure 1 Effect of the pH on the metal ion retention.

atoms as O, N, S, and P formed a complex. In this case, the synthesized resin P(AAm-co-APSA) contains this kind of atoms. The affinity between the resin's active site and metal ions is studied by batch and column equilibrium procedure, using a resin particle size of 180–250 μm and resin–metal ion relationship in mol between functional group on the resin and metal ion, 20 : 1. This ratio ensures the metal ion's access to ligand sites.

Effect of pH on the removal

The uptake of Cd(II), Cr(III), Zn(II), Al(III), Pb(II), and Hg(II) ions as a function of pH by batch method was examined over pH range of 1–5. The pH studied depends on metal ion solubility. The resin showed a high dependence on pH, as the metal ion form and the ligand groups change with the pH; the metal ion absorption is favored at higher pH because the ligand groups are deprotonated and the groups are free to exchange or complex the metal ion. The Figure 1 shows experimental results obtained at pH 1 and 5 by batch equilibrium procedure.

The highest retention capacities for the resin were obtained at pH 5: Cd(II), 99.9%, (8.27 mg/g), Zn(II) 99%, (11.5 mg/g), Pb(II) 100% (40.4 mg/g), Cr(III) 99%, (8.27 mg/g), and Al(III) 84%, (3.71 mg/g). The optimal retention value for all metal ions was pH 5. Therefore, these pH values were chosen for the following runs.

TABLE I
Maximum Retention Capacity for the Resin P(AAm-co-APSA) at the Optimum pH

Metal ion	MRC (mmol/g dry resin; by batch procedure)	MRC (mmol/g dry resin; by column procedure)
Pb ²⁺	0.71	0.74
Cd ²⁺	0.70	1.32
Zn ²⁺	1.27	1.25
Cr ³⁺	1.89	1.45

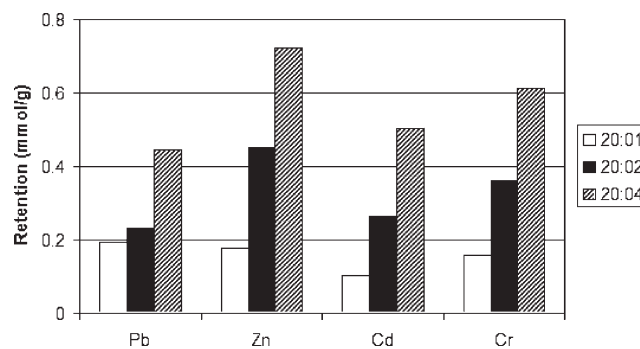


Figure 2 Effect of the concentration on the metal ion retention.

To explore the applications of the resin, the maximum adsorption capacity (MAC) needs to be known. Based on the retention ability results at different pH, the maximum retention capacity (MRC) in batch and column equilibrium procedures was determined for Cd(II), Cr(III), Zn(II), and Pb(II). These values are shown in Table I.

For Pb(II), Zn(II), and Cr(III) ions, the results are very close for both equilibrium procedures, but not for Cd(II).

Effect of the metal ion concentration

Maintaining retention capacity, even when the concentration of the different species in the wastewater changes, it is essential for practical use. The effect on the metal uptake under metal ion concentration was studied for each metal ion. This concentration was varied between resins : metal ion ratio 20 : 1 and 20 : 4. For all resins, the metal ion retention was maintained with the increase in the ratio resin : metal ion. This result indicates that the resin still has active sites to retain the metal ions (see Fig. 2).

Effect of contact time

The interaction between the metal ion and the active site of the resin can take a determined time, being in

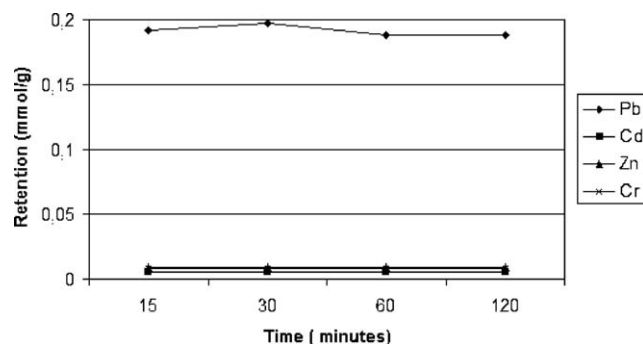


Figure 3 Effect of the contact time on the metal ion retention.

TABLE II
Effect of the Temperature on the Retention Behavior of the Resin P(AAM-co-APSA) by Batch Equilibrium Procedure

Temperature (°C)	Retention (mmol/g resin)			
	Pb(II)	Cd(II)	Zn(II)	Cr(III)
20	0.175	0.102	0.177	0.185
25	0.170	0.156	0.152	0.185
30	0.173	0.156	0.151	0.188
35	0.173	0.154	0.155	0.190
45	0.173	0.177	0.183	0.190
60	0.173	0.178	0.183	0.190

some cases longer than another. To the resin P(AAm-co-APSA), the equilibrium polymer functional group-metal ion is achieved during the first 15 min of the contact time, after that did not change the retention behavior (see Fig. 3).

Effect of temperature

In same case of retention, the temperature could affect the metal ion retention, depending of kind of retention, chemical or physical. To this resin, the changes in the temperature did not produce significant effect on the metal ion retention for Pb(II), Zn(II), and Cr(III). However, the difference in metal retention for Cd(II) ion depending on temperature is highest (0.102 at 20°C and 0.178 mmol/g at 60°C). The results are shown in the Table II.

Selectivity behavior

Inside a mixture of several metal ions, the interaction on preference of the resin could vary. To determine metal ion retention under competitive conditions, a test was performed. At first, 200 mg of dry resin was contacted at pH 5 during 1 h with 20 mL of an aqueous solution containing the same concentration of each metal ion Cd(II), Cr(III), Zn(II), and Pb(II). Second, 200 mg of dry resin was contacted at pH 2 during 1 h with 20 mL of an aqueous solution containing the same concentration of each metal ion

TABLE III
Selectivity of the Resin P(AAm-co-APSA) from a Quaternary Metal Ion Mixture at pH 5 by Batch Equilibrium Procedure

Metal ion mixture	Retention (%) ^a	Retention (mmol/dry resin) ^b
Pb ²⁺	10	0.0423
Zn ²⁺	26	0.1100
Cd ²⁺	27	0.1044
Cr ³⁺	37	0.1460

^a Respect to the total of mol retained.
^b Respect to each metal ion.

TABLE IV
Selectivity of the Resin P(AAm-co-APSA) from a Quaternary Metal Ion Mixture at pH 2 by Batch Equilibrium Procedure

Metal ion mixture	Retention (%) ^a	Retention (mmol/g dry resin) ^b
Pb ²⁺	18	0.126
Zn ²⁺	30	0.141
Cd ²⁺	25	0.115
Hg ²⁺	27	0.154

^a Respect to the total of mol retained.
^b Respect to each metal ion.

Cd(II), Hg(II), Zn(II), and Pb(II). The resin showed in the contact at pH 5 almost the same retention (around the 20%) for Cd(II), Cr(III), Zn(II), and Pb(II). The resin showed a small difference in retention for the metal ion in the mixture. Cr(III) showed the highest value of retention, but this value is not useful to separate this metal inside a mixture. The Cr(III) has highest charge, presenting a highest electrical interaction with the SO₃⁻ groups. In the contact at pH 2, Zn(II) presented the best retention; however, this retention is not significantly different to the other and is impossible to affirm a preference for this metal ion. This pH was selected to avoid the precipitation of mercury ions: Moreover, at this pH the mixture ions contain only divalent ions. Thus, it can be concluded that the predominant interaction is an electrostatic interaction between the active group and the metal ions (see Tables III and IV).

Retention by column procedure

It is important to the resin that maintains its retention behavior in a continuously operated process in comparison with a discontinuously operated process. A column (15 cm in length and 1 cm in diameter) was prepared. The resin was packed at the pH of the retention experiment. The experience was realized at 20°C with a resin : metal ion ratio of 20 : 1 and at flux rate of 20 mL/h.

TABLE V
Regeneration Capacity of the Resin P(AAm-co-APSA) by Batch Equilibrium Procedure

Stripping reagent	Concentration (mol/L)	Elution (%)			
		Pb(II)	Cd(II)	Zn(II)	Cr(III)
HCl	1	63	100	75	13
	4	93	100	84	16
HNO ₃	1	79	100	71	16
	4	88	100	83	25
HClO ₄	1	75	100	74	12
	4	88	100	81	13

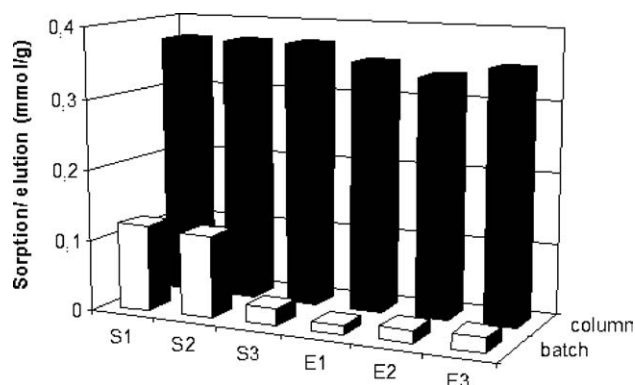


Figure 4 Sorption–elution cycles for the resin charged with Pb(II) and 4M HCl as eluent.

Resin reusability

To use this resin in a continuously operated process, the resin's metal ion capacity should be maintained after the treatment with an eluent reagent, and the metal ion adsorbent by the resin should be easily released under appropriate conditions. The batch desorption studies were carried out first by separately loading resin samples. The three stripping reagents studied (HCl, HClO₄, and HNO₃) in two different concentrations were selected because they should be able to displace the metal ions. The results are summarized in Table V. For all the metal ion-loaded resin, the elution was increased by increasing the eluent concentration. All the divalent cations were removed at above 60%, and only Cd(II) was completely eluted with the three stripping reagents. The three eluents at both concentrations showed a lower ability to remove Cr(III) ions.

Therefore, for resin reusability, the sorption–desorption cycle was repeated three times with the same sorbent in batch and column processes. The results are presented in Figures 4–6. Figure 4 shows that the resin was loaded with Pb(II), and the desorption was performed with 4M HCl, and it was

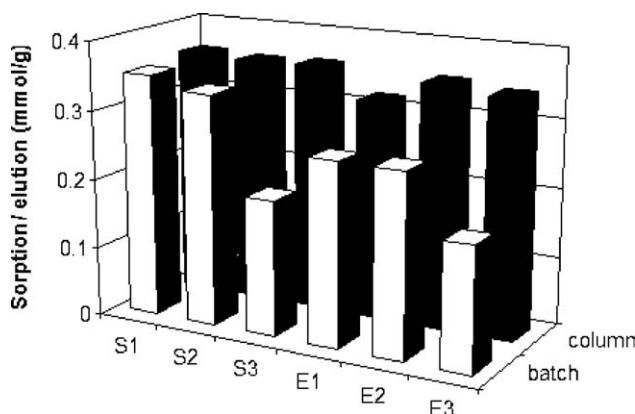


Figure 5 Sorption–elution cycles for the resin charged with Cd(II) and 1M HNO₃ as eluent.

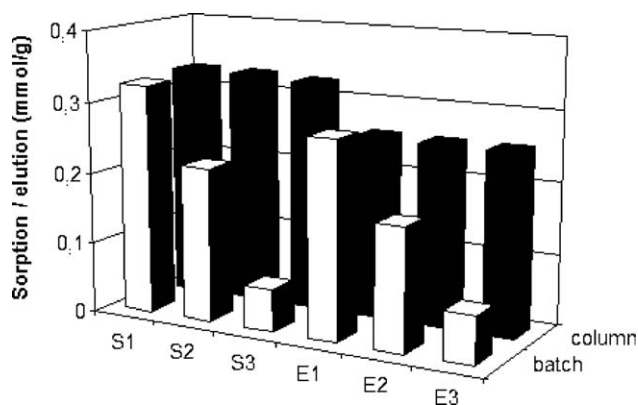


Figure 6 Sorption–elution cycles for the resin charged with Zn(II) and 4M HCl as eluent.

able to maintain the retention capacity in the three cycles, and a high percentage of elution was produced in the three cycles in the batch and column processes. The Figure 5 shows that the resin loaded with Cd(II), here the desorption was performed with 1M HNO₃, and the resin was able to maintain the retention and the elution over 60% in batch and column processes, but by comparison, the behavior in column procedure is better than that batch technique. The Figure 6 shows where the resin was loaded with Zn(II), and the desorption was performed with 4M HCl; the resin in batch technique loss gradually the retention and elution capacity. In the column process, the resin maintains the capacity of retention over 98% during the three cycles and can be eluted over the 50%. Considering this resin's behavior in a continuously operated process, it can be used to remove undesirable metal ions.

CONCLUSIONS

Using radical solution polymerization, the cross-linked P(AAm-co-APSA) was synthesized. The resin showed a high retention for Cd(II), Cr(III), Zn(II), and Pb(II) at pH 5. The most common equilibrium procedures, batch and column, were tested, finding no important differences in the results at the optimum pH. Consecutive sorption and elution showed the feasibility of using and reusing this resin to remove Cd(II), Pb(II), and Zn(II).

References

1. Kesenci, K.; Say, R.; Denizli, A. *Eur Polym J* 2002, 38, 1443.
2. Dutta, S.; Das, A. K. *J Appl Polym Sci* 2007, 103, 2281.
3. Joshi, J. D.; Patel, S. D.; Patel, G. P. *J Macromol Sci Part A* 2007, 44, 65.
4. Rivas, B. L.; Maturana, H. A.; Luna, M. *J Appl Polym Sci* 1999, 74, 1557.
5. Biswas, M.; Mukherjee, A. *Adv Polym Sci* 1994, 115, 89.
6. Kantipuly, C.; Karagadda, S.; Chow, A.; Gesser, H. D. *Talanta* 1990, 37, 491.

7. Rivas, B. L.; Pooley, S. A.; Maturana, H. A.; Villegas, S. *Macromol Chem Phys* 2001, 202, 491.
8. Rivas, B. L.; Pereira, E. D. *Bol Soc Chil Quim* 2000, 45, 165.
9. Rivas, B. L.; Pereira, E. D.; Gallegos, P. *Bol Soc Chil Quim* 2002, 47, 253.
10. Rivas, B. L.; Pooley, S. A.; Maturana, H. A.; Villegas, S. *J Appl Polym Sci* 2001, 80, 2120.
11. Liu, R.; Zhang, B.; Tang, H. *J Appl Polym Sci* 1998, 70, 7
12. Rivas, B. L.; Moreno-Villoslada, I. *Chem Lett* 2000, 166.
13. Wang, B.; Liu, W.; Huang, L. *J Appl Polym Sci* 2008, 107, 501.
14. Yang, Y.; Ma, N.; Zhang, Q.; Chen S. *J Appl Polym Sci* 2009, 113, 3638.
15. Alexandratos, S. D. *Ind Eng Chem Res* 2009, 48, 388.
16. Rivas, B. L.; Pereira, E. D.; Gallegos, P.; Geckeler, K. E. *Polym Adv Technol* 2002, 13, 1000.
17. Kabay, N.; Sarper, S.; Yuksel, M.; Arar, Ö.; Bryjak, M. *React Funct Polym* 2007, 67, 1643.
18. Guibal, E.; Milot, C.; Tobin, J. M. *Ind Eng Chem Res* 1998, 37, 1454.