

Heavy Metal Ion Scavengers from Cyanuric Chloride

KYOJI KAERIYAMA, TADANORI ROKUSHA, and KEIKO NAOMI,
*Research Institute for Polymers and Textiles, Kanagawa-ku, Yokohama
221, Japan*

Synopsis

Cyanuric chloride was reacted with polyamines and thiourea, and subsequent hydrolysis of the isothiuronium salt yielded amine polymers with divalent sulfur. The polymers scavenge cupric, cadmium, lead, and mercuric ions from considerably concentrated hydrogen chloride solutions, and they were compared with polystyrene-sulfonic acid resin. Zinc, cobaltous, and nickel ions are adsorbed only at relatively high pH (4.8–6.8). Removal of cupric, cadmium, and mercuric ions is not affected by the addition of sodium chloride.

INTRODUCTION

The pollution of the environment is increasing with increase in industrial activities. Pollution with heavy metals causes serious diseases. It is therefore important to prepare polymeric materials that can remove heavy metal ions from water, such as mercuric, lead, cadmium, and cupric ions.

Thiourea reacts with active chlorides to form isothiuronium salts. Hydrolysis with base yields the mercaptan in good yields. Cyanuric chloride reacts with thiourea.^{1,2} Cyanuric chloride reacts also with polyamines to yield network polymers. In the present paper, polycondensation of cyanuric chloride with polyamines was carried out in the presence of thiourea. Hydrolysis of isothiuronium salt gives polymers with mercaptan fixed in the matrix amine. The polymers scavenge mercuric, cadmium, and cupric ions from aqueous solution. Thus, heavy metal ion scavengers are obtained from cheap raw materials.

EXPERIMENTAL

Commercial cyanuric chloride was twice purified by vacuum sublimation. Solvents were distilled in nitrogen atmosphere just before use. Polymers were prepared by (1) interfacial polycondensation, where cyanuric chloride in water-immiscible solvents was reacted with polyamines and thiourea in water under vigorous agitation; (2) solution polycondensation, where cyanuric chloride and polyamines were reacted in organic solvents, and the resulting polymers were then reacted with thiourea in water; and (3) suspension polycondensation, where polyethylenimine and thiourea in aqueous solution were reacted with cyanuric chloride in water-miscible solvents. After the mixture of all other reactants, sodium hydroxide was added dropwise to accept hydrogen chloride and to decompose the isothiuronium salts. The polymers were washed with acetone, water, dimethylformamide, and alcohol to remove unreacted reactants and low molecular weight by-products. Recipes are summarized in Table I, where polymers are denoted by the amine component. The $\text{NaN}_3\text{-I}_2$ test revealed the presence of divalent sulfur in these polymers.³ The polymers are insoluble in all common solvents.

TABLE I
 Preparation of Polymers

Notation	Cyanuric chloride		Amine		Amount, Thiourea, Yield,	
	Wt, g	Solvent	Type	g	g	g
DEDA	3.69	2-methylcyclohexanone	diethylenediamine	1.72	1.52	2.59
EDA	9.22	4-methylcyclohexanone	ethylenediamine	3.91	3.81	3.61
Trien	1.84	chlorobenzene	triethylenetetramine	0.73	0.76	1.64
Tetraen	3.69	toluene	tetraethylenepentamine ^a	2.00	5.00	—
PEI-1	3.69	chlorobenzene	polyethylenimine ^b	7.66	7.60	3.69
PEI-2	3.69	tetrahydrofuran	polyethylenimine ^b	7.00	7.60	
PEI-3	3.69	dioxane	polyethylenimine ^b	7.00	7.60	5.02
(DEDA)	2.46	2-methylcyclohexanone	diethylenediamine	1.72	0	2.64
(Trien)	1.97	chlorobenzene	triethylenetetramine	1.20	0	1.76
(PEI)	1.97	chlorobenzene	polyethylenimine ^b	6.13	0	2.20

^a In toluene.

^b 30% aqueous solution.

The ability of the polymers to scavenge heavy metal ions was evaluated using heavy metal ion concentrations after 20 ml aqueous solution was shaken with 100 mg of the polymer overnight. Metallic salts used were divalent chlorides of cadmium, copper, nickel, cobalt, and mercury; nitrates of zinc and lead; and potassium dichromate. Hydrogen chloride and sodium hydroxide were applied to adjust the pH. Heavy metal ion concentrations were measured by means of atomic absorption.

RESULTS AND DISCUSSION

Heavy metal ions were scavenged from mixed solutions of five kinds of divalent heavy metal ions by polymers. Results are shown in Table II. At relatively low pH (2.0–4.0), the polymers scavenged cupric and cadmium ions well, but did not adsorb zinc, cobaltous, and nickel ions efficiently. At higher pH (4.8–6.8), PEI-1, PEI-2, and PEI-3 removed all five metal ions. After the scavenging experiments, the polymers were collected on a glass filter, dried, and decomposed at 170°C with sulfuric acid. The same amounts of cupric and cadmium ions were found in the acid as those removed from the aqueous solutions. It is apparent that the polymers adsorbed heavy metal ions from aqueous solutions.

Polymers prepared in the absence of thiourea (designated by parentheses) did not remove metal ions at all, except for cupric ion removed by (PEI). The sulfur atom is suggested to play an important role in binding heavy metal ions to polymers. When cyanuric chloride is reacted with thiourea in excess of the former, only trithiocyanuric acid is obtained.¹ It cannot be built into the polymeric skeleton. Therefore, the molar ratio of reactants and solvents and the reaction conditions should be chosen carefully to obtain amine polymers with divalent sulfur which can scavenge heavy metal ions.

Lead, chromic, and mercuric ions were removed from separate solutions. The results are shown in Table III. Lead ion is removed from aqueous solutions considerably well. Adsorption of chromic ion is unsatisfactory. Mercuric ion

TABLE II
Scavenging of Heavy Metal Ions

Polymer	pH	Scavenging, % ^a				
		Cu(II)	Cd(II)	Zn(II)	Co(II)	Ni(II)
DEDA	4.2	99	99	27	0	0
EDA	—	99	100	40	8	23
Trien	4.0	100	84	0	0	0
Tetraen	3.0	100	100	100	0	0
PEI-1	6.8	100	100	100	100	100
PEI-1	2.1	100	87	3	12	1
PEI-2	5.4	98	99	98	94	97
PEI-2	3.8	99	100	5	15	40
PEI-3	4.8	94	99	96	83	98
PEI-3	3.6	98	99	4	7	4
(DEDA)	2.9	0	0	0	0	0
(Trien)	3.0	0	0	0	0	0
(PEI)	3.4	70	0	0	0	0

^a Scavenging from mixture of 10 ppm metallic ions.

TABLE III
Scavenging of Heavy Metal Ions

Polymer	Scavenging, % ^a		
	Pb(II)	Cr(VI)	Hg(II)
DEDA	100	71	100
Trien	70	71	97
Tetraen	97	18	100
PEI-1	100	10	100
PEI-2	100	93	100 ^b
PEI-3	96	96	100 ^b

^a Scavenging from 10 ppm solutions. pH range: Pb, 2-4; Cr, 3-5; Hg, 1-2.

^b Undetected <0.1 ppb.

is scavenged completely. With PEI-2 and PEI-3, mercuric ion could not be detected in the solution at all. This means that the concentration of mercuric ion was lowered from 10 ppm to below 0.1 ppb. The result fulfills our legal environmental standards.

Figure 1 shows the dependence of scavenging on cupric ion concentration. The polymers remove cupric ion well. They adsorb about 1 meq Cu/g polymer at 1000 ppm. All adsorption sites would be saturated at this value.

Figure 2 explains the dependence of scavenging on hydrogen chloride con-

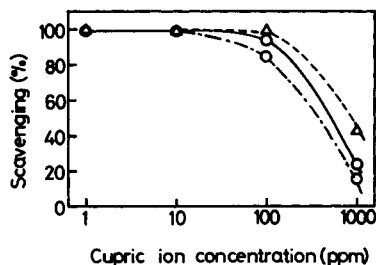


Fig. 1. Dependence of scavenging on cupric ion concentration: (---) EDA, pH 3; (—) DEAD, pH 3; (---) DEDA, pH 1.

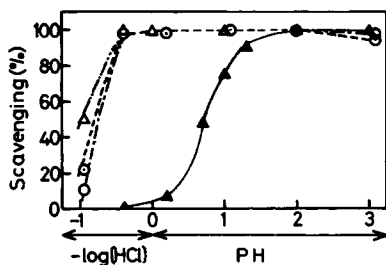


Fig. 2. Dependence of scavenging on hydrogen chloride concentration; cupric ion 10 ppm: (---) DEDA; (- · - ·) PEI; (· · ·) TETA; (—) poly(styrenesulfonic acid).

centration. The results are compared with those by polystyrene sulfonic acid, which is one of the strongest acids among commercially available cation exchangers. Whereas the scavenging by the sulfonic acid resin starts to fall at pH 1.3, the present polymers remove cupric ion satisfactorily even at 3*N* hydrogen chloride solution. This shows one of the excellent properties of the polymers.

In order to examine the effect of coexisting salts, sodium chloride was added to cupric ion solution. Results are shown in Figure 3. While scavenging starts to descend at a salt concentration of 0.1 g/100 ml for poly(styrenesulfonic acid) resin, DEDA completely removes cupric ion even at a salt concentration of 10 g/100 ml. This salt concentration is three times as high as that of sea water. Thus, it is clear that sodium chloride does not affect scavenging by DEDA.

The same experiments were carried out for cadmium ion as for cupric ion. Similar tendencies are observed for both of ions, but removal of cadmium ion is not as complete as that of cupric ion.

We attempted to remove lead ion from hydrogen chloride solution at various concentrations. The results are shown in Figure 4. The polymers adsorb lead ion from hydrogen chloride solutions considerably better than poly(styrenesulfonic acid) resin, but the removal of the ion is not complete. The trend is more similar to cadmium ion than to cupric ion, removal of which is complete up to 3*N*, then drops sharply.

Figure 5 shows the dependence of scavenging of mercuric ion on hydrogen chloride concentration. Mercuric ion is removed very effectively from hydrogen chloride solutions. PEI-1 removed mercuric ion from 7*N* hydrogen chloride solution. DEDA adsorbed the ion even from 12*N* solution.

The effect of sodium chloride on the scavenging of lead and mercuric ions is shown in Fig. 6. Tetraen adsorbs lead ion better than poly(styrenesulfonic acid) resin, but removal decreases with increase in sodium chloride concentration.

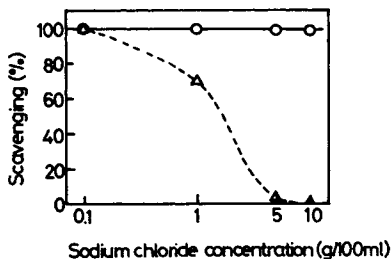


Fig. 3. Effect of sodium chloride on scavenging; cupric ion 10 ppm: (—) DEDA, pH 1; (- - -) poly(styrenesulfonic acid), pH 3.

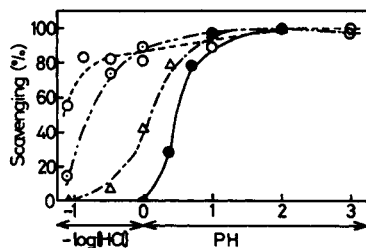


Fig. 4. Dependence of scavenging on hydrogen chloride concentration; lead ion 10 ppm: (---○---) PEI-1; (- - ○ - - -) Tetraen; (---△---) DEDA; (—●—) poly(styrenesulfonic acid).

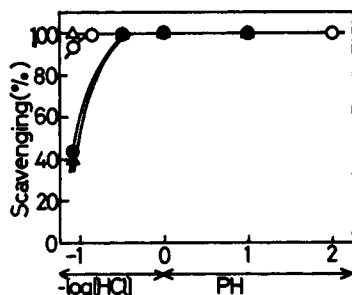


Fig. 5. Dependence of scavenging on hydrogen chloride concentration; mercuric ion 10 ppm: (—△—) DEDA; (—○—) PEI-1; (—▲—) Trien; (—●—) Tetraen.

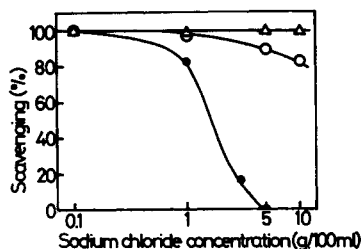


Fig. 6. Dependence of scavenging on sodium chloride concentration: (—△—) mercuric ion 10 ppm, PEI-1 pH 1.1; (—○—) lead ion 10 ppm, Tetraen pH 2.1; (—●—) lead ion 10 ppm, poly(styrenesulfonic acid) pH 2.1.

Adsorption of mercuric ion is not affected at all by the addition of the salt. It is apparent that the present polymers have high selectivity for such metallic ions as cupric, cadmium, and mercuric ions.

It is one of the remarkable characteristics of these polymers to remove heavy metal ions from acidic solutions. To find out why, a dye test was performed. Rhodamine B changes color from pink to orange between pH 1.2 and 0.1. Polymer was placed in hydrogen chloride solution containing rhodamine B. After equilibrium was attained, the polymer was separated from the solution by filtration and the color was examined. While the color of the solution is orange at pH 0.34, the polymer changed color to orange at 4*N*. It is suggested that the pH in the polymer is higher than that of the solution which is in equilibrium with the polymer. This effect would enable the polymer to scavenge heavy metal ion in more acidic solution.

The polymers obtained here have preferable chemical properties. At the present stage, the polymers are not produced in the form of beads like commercial

ion exchange resin, but in the form of powder or flakes. It is necessary for the polymers to be reformed in a more usable shape.

The authors are grateful to Drs. M. Suzuki, M. Hasegawa, and Y. Shimura for their interest and encouragement during this work.

References

1. A. Pollak, S. Stanovik, and M. Tisler, *Can. J. Chem.*, **44**, 899(1966).
2. S. R. Sandler and W. Karo, *Organic Functional Group Preparations*, Academic Press, New York, 1968, p. 481.
3. F. Feigl, *Spot Test*, Vol. 2, Elsevier-Maruzen, Amsterdam, 1961, pp. 242-247.

Received April 29, 1977

Revised July 19, 1977