

# Carboxyl-Containing Starch Graft Polymer: Preparation and Use in Heavy Metal Removal

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## Synopsis

Water-insoluble carboxyl-containing starches were prepared by grafting acrylonitrile onto a highly crosslinked starch followed by base saponification to convert nitrile groups into a mixture of carboxamide and carboxylate groups. Ceric ammonium nitrate or ferrous sulfate-hydrogen peroxide was used to initiate graft polymerization of acrylonitrile. The isolated products were evaluated for the removal of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$  from aqueous solution.

## INTRODUCTION

Over the past few years much attention has been given to the quality of water discharged to our nation's waterways. Although existing treatment methods,<sup>1-3</sup> i.e., chemical precipitation, ion exchange, reverse osmosis, evaporative recovery, and electrochemical treatment, have been proved effective for most wastewaters, some limitations (prohibitive cost and inability to reach discharge limits) have prevented their overall acceptance. Stricter limitations have recently been placed on the toxic heavy metal ion concentrations of discharged industrial effluents; therefore, new treatment methods had to be developed to meet these limitations.

Several heavy metal treatment methods<sup>4-13</sup> developed at our Center have been proven effective in lowering heavy metal concentrations to below present discharge levels. Carboxyl-containing polymers and their ability to bind heavy metals have been documented.<sup>14-19</sup> Several investigators have reacted chloroacetic acid with crosslinked starch,<sup>20-22</sup> and the product's capability for heavy metal removal has been mentioned but no metal removal data have been reported. Jellinek and Sangal<sup>23</sup> reported that a carboxyl-containing natural polysaccharide complexed considerable amounts of several metals; however, residual metal concentrations remained well above acceptable limits. In our continuing research we have prepared water-insoluble crosslinked starch, grafted with acrylonitrile and saponified, to yield carboxyl-containing starch-based products.

The saponified crosslinked starch-polyacrylonitrile graft copolymer described in this report is capable of reducing the concentration of heavy metal ions in water to low residual values. Data are presented for the removal of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$ . The insoluble starch product can be regenerated for reuse.

## EXPERIMENTAL

### Grafting with Ceric Ammonium Nitrate Initiation

A highly crosslinked starch (50 g, 10.9% H<sub>2</sub>O) was slurried in water (170 ml) and was purged for 15 min with nitrogen to remove oxygen. Ceric ammonium nitrate (1.1 g) in water (20 ml) was added, and the mixture was stirred 10 min. Acrylonitrile (50 ml) was added, and after 15 min an exothermic reaction resulted (temperature increased from 23 to 55°C). After 60 min, sodium hydroxide (25 g) in water (250 ml) was added to the thickened slurry, and the temperature was adjusted to 75°C on a hot plate. The slurry was stirred 2 hr, with the color changing from white to maroon to pale yellow. Ammonia was given off during the saponification step. The slurry was allowed to cool and was neutralized to pH 6.5 with 2% hydrochloric acid. The slurry was filtered on Whatman No. 54 filter paper on a Büchner funnel, and the product was washed with water (500 ml). The product (25% solids) was dewatered with acetone (500 ml) and then washed with ether (100 ml). After drying 2 hr under vacuum the product was analyzed. Yield: 120 g; H<sub>2</sub>O, 18.39%; N, 3.84%; ash, 17.16%; capacity,<sup>24</sup> 3.92 meq metal ion/g.

Weights and volumes of reactants and analysis of the final products for several preparations are found in Table I.

### Grafting with Ferrous Sulfate Initiation

A highly crosslinked starch (50 g, 10.9% H<sub>2</sub>O) was slurried in water (160 ml), and the mixture was purged for 15 min with a slow stream of nitrogen to remove oxygen. Ferrous sulfate (0.3 g) in water (20 ml) was added, and the mixture was stirred for 10 min. Acrylonitrile (50 ml) was added; and after stirring for 10 min, hydrogen peroxide (30%, 2 ml) in water (28 ml) was added slowly. During this time the reaction mixture thickened; so additional water (50 ml) was added, and the slurry was allowed to stir 1 hr. The previous saponification and work-up procedure was employed. Yield: 84 g; H<sub>2</sub>O, 11.30%; N, 3.24%; ash, 3.48%; capacity,<sup>24</sup> 2.29 meq metal ion/g.

The experiment was repeated using acrylonitrile (75 ml) and ferrous sulfate (0.2 g). Yield: 73 g; H<sub>2</sub>O, 15.51%; N, 3.28%; ash, 3.74%; capacity,<sup>24</sup> 2.43 meq metal ion/g.

### Sequential Crosslinking and Grafting

Commercial corn starch (100 g, 10% H<sub>2</sub>O) was slurried in water (150 ml) containing sodium chloride (1.5 g) and epichlorohydrin (8 ml). To this slurry was added potassium hydroxide (6 g) in water (40 ml) slowly over 30 min. The mixture was stirred for 16 hr at room temperature. The slurry, now containing a highly crosslinked starch, was adjusted to pH 6.5 with 2% hydrochloric acid. The mixture was purged with nitrogen, and ceric ammonium nitrate (2.2 g) in water (100 ml) was added. The mixture was allowed to stir 10 min, and acrylonitrile (100 ml) was added. After stirring 1 hr, sodium hydroxide (50 g) in water (250 ml) was added and the temperature was adjusted to 75°C for 2 hr. The mixture was allowed to cool and then adjusted to pH 6.5 with 2% hydrochloric acid. The product was filtered and washed with water (1000 ml), acetone (500

TABLE I  
Preparation of Carboxyl-Containing Starch Graft Polymers

Experiment No.	Crosslinked starch, <sup>a</sup> g	Ceric ammonium nitrate, g	Acrylonitrile, ml	NaOH, <sup>b</sup> g	Product, g	% H <sub>2</sub> O	% N	% Ash	Capacity, <sup>c</sup> meq/g
1	50	1.0	25	20	77.0	12.91	3.04	15.05	1.94
2	50	1.0	50	20	100.5	13.80	5.93	15.36	2.22
3	50	1.0	75	20	142.0	19.35	7.47	14.42	2.65
4	50	1.0	100	20	160.0	18.35	8.97	15.00	2.43
5	50	1.1	50	25	120.0	18.39	3.84	17.16	3.92
6	50	1.5	50	30	105.0	17.64	4.28	19.12	3.36
7	50	1.5	75	20	139.0	14.78	6.49	20.44	2.92
8	50	1.5	75	30	136.0	14.06	5.38	24.98	3.09
9	50	1.5	75	40	146.0	13.48	5.26	23.52	3.58
10	250	7.5	375	150	710.0	15.55	6.42	18.95	3.41

<sup>a</sup> HPD-53-91E (The Hubinger Company, Keokuk, Iowa).

<sup>b</sup> All saponifications were run at 75°C for 2 hr.

<sup>c</sup> Reference 25.

ml), and ether (100 ml). After drying 2 hr under vacuum, the product was analyzed. Yield: 163 g; H<sub>2</sub>O, 12.71%; N, 2.22%; ash, 14.09%; capacity, 1.85 meq metal ion/g.

### Carboxymethyl-Crosslinked Starch

A highly crosslinked starch (50 g) was slurried in water (170 ml), sodium hydroxide (20 g) in water (50 ml) was added, and the mixture was stirred 30 min at room temperature. Monochloroacetic acid (50 g) in water (25 ml) was neutralized to pH 6 with 7.1N NaOH (75 ml) and was added. The mixture was stirred at 65°C for 1 hr. The slurry was cooled, filtered, and washed with water (500 ml). The cake was reslurried in water, and pH was adjusted to 6.5 with hydrochloric acid (2%). The slurry was refiltered, washed with water, acetone, and ether, and air dried. Yield: 56.3 g; H<sub>2</sub>O, 12.18%; ash, 6.12%; capacity,<sup>24</sup> 1.43 meq metal ion/g.

### Heavy Metal Removal

Solutions (1000 ml) containing metal ions were treated with the water-insoluble carboxyl-containing starches (added as solid). After a 30-min contact time, aliquots (10 ml) were filtered through Whatman No. 54 filter paper, and the residual metal concentrations in the filtrates were measured by atomic absorption spectrometry.

## RESULTS AND DISCUSSION

It has been demonstrated by Wing et al.<sup>7-10</sup> that placing reactive functional groups on the backbone of highly crosslinked starches yields products that are effective in removing heavy metal ions from industrial wastewaters. We now report that acrylonitrile grafted onto crosslinked starch can be saponified to yield a carboxylated water-insoluble product that effectively removes heavy metal ions from water. Several reaction variables were evaluated, i.e., free-radical initiation, amount of acrylonitrile, and amount of sodium hydroxide, to determine grafting level and degree of saponification necessary to yield a high-capacity cation exchange starch. The number-average molecular weight ( $M_n = 240,000$ ) of the grafted side chains was determined by the method of Onyon.<sup>24</sup> Table I shows that the grafting efficiency with ceric initiation is high (< 0.1% homopolymer), based on the weights of saponified product obtained. Similar results were also obtained using the ferrous-peroxide initiator system. Using 1.1 g ceric ammonium nitrate with 0.3 mole (50 g) crosslinked starch and 0.75 mole (50 ml) acrylonitrile gave after saponification what was considered an optimum-capacity product.

Increasing the concentration of base during saponification appears to give products that had higher capacity (Table I). Increasing the temperature from 75 to 90°C during saponification shortened the saponification time from 2 hr to 45 min (as shown by the faster color change). After saponification the product is neutralized to pH 6.5 with hydrochloric acid. If the product was adjusted to pH 3 and then washed with water before filtering, the rate of filtration was increased considerably and the product was easier to dry. Most samples were

solvent dried; however, drum-, spray-, or flash-drying could be used commercially.

The theoretical capacity of the carboxylated products was determined by the method of Reinhardt et al.<sup>25</sup> When the actual capacities were evaluated for several metals at pH values below where hydroxide precipitation would occur, using concentrated or dilute metal solutions, the determined capacity values were very accurate.

Figures 1 and 2 show copper and cadmium removal using increasing amounts of the carboxyl-containing starch graft copolymer (curve A). For comparison, a carboxymethylated crosslinked starch (curve B) was also evaluated. The slight excess of starch product required is due to the fact that the percent moisture was not taken into account when the theoretical amounts of products were calculated.

To determine the effectiveness of the products for heavy metal removal, we evaluated the products in several ways. First, we evaluated the product with several metals to determine if there was an optimum pH to obtain maximum removal. Figures 3 and 4 show a comparison over the pH range of 4 to 9 with cadmium and lead. The same metals were also precipitated as their hydroxides with caustic for comparison. Optimum removal for these metals and the others evaluated ( $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Cr^{3+}$ ,  $Mn^{2+}$ , and  $Ni^{2+}$ ) is at pH 6 or above. The carboxylated starches were added to the metal-containing solutions in solid form, and near maximum removal was always obtained within 30 min (Fig. 5). Longer contact times usually decreased residual concentrations further.

The effect of dissolved solids (salts) on the effectiveness of these ion exchange

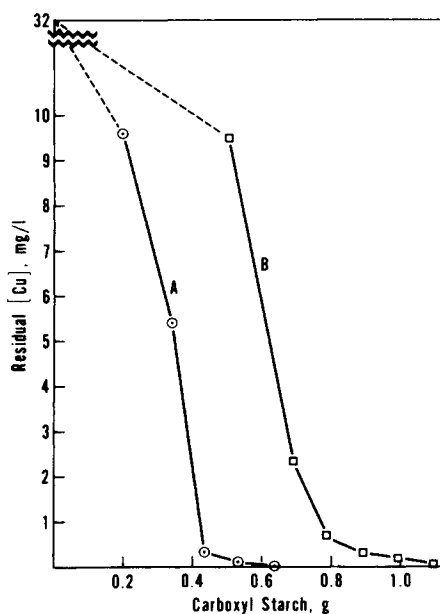


Fig. 1. Copper removal with carboxyl-containing starch graft polymer. Copper solutions (1000 ml, 31.8 mg  $Cu^{2+}$ /l) were treated at pH 5 with increasing amounts of carboxyl-containing starch graft polymer (2.92 meq metal ion/g, curve A; theoretical wt. required 0.34 g) and carboxymethyl-cross-linked starch (1.43 meq metal ion/g, curve B; theoretical wt. required 0.69 g). Aliquots (10 ml) of the supernatant were removed for residual copper analysis.

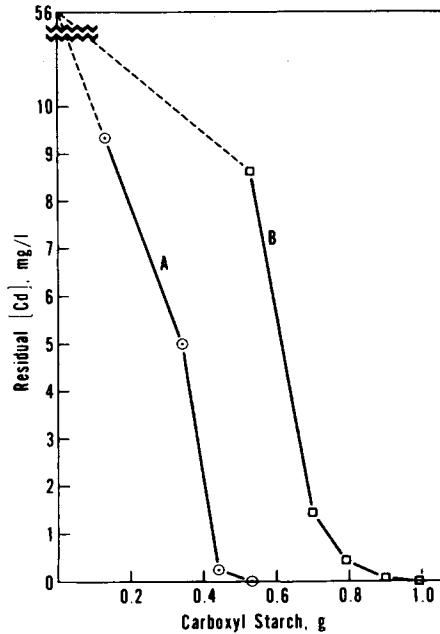


Fig. 2. Cadmium removal with carboxyl-containing starch graft polymer. Cadmium solutions (1000 ml, 56.2 mg  $\text{Cd}^{2+}/\text{l}$ ) were treated at pH 7 with increasing amounts of carboxyl-containing starch graft polymer (2.92 meq metal ion/g, curve A; theoretical wt. required 0.34 g) and carboxymethyl-crosslinked starch (1.43 meq metal ion/g, curve B; theoretical wt. required 0.69 g). Aliquots (10 ml) of the supernatant were removed for residual cadmium analysis.

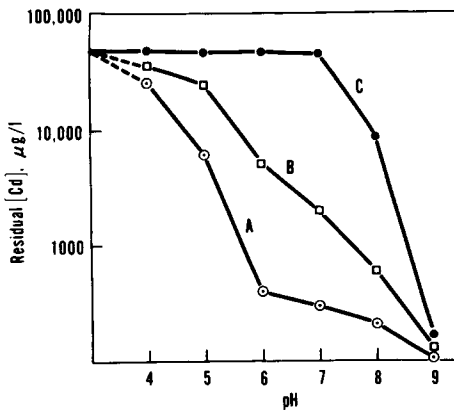


Fig. 3. Effect of pH on cadmium removal with carboxyl-containing starch graft polymer. Cadmium solutions (1000 ml, 50 mg  $\text{Cd}^{2+}/\text{l}$ ) were treated with carboxyl-containing starch graft polymer (3.92 meq metal ion/g, 0.5 g for curve A and 0.23 g for curve B) at the indicated pH for 30 min. Curve C represents the addition of 0.1N NaOH only. Samples were removed, filtered, and analyzed for residual cadmium.

starches is shown for lead removal in Figure 6. The presence of high concentrations of sodium or other alkali metal ions seems to have a definite detrimental effect on the capacity of the products for heavy metals.

The reusability of the carboxyl-containing starch graft polymer (25 g, 3.41 meq

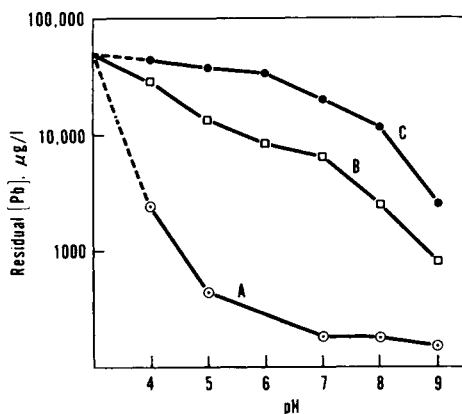


Fig. 4. Effect of pH on lead removal with carboxyl-containing starch graft polymer. Lead solutions (1000 ml, 50 mg Pb<sup>2+</sup>/l) were treated with carboxyl-containing starch graft polymer (3.92 meq metal ion/g, 0.5 g for curve A, and 0.13 g for curve B) at the indicated pH for 30 min. Curve C represents the addition of 0.1N NaOH only. Samples were removed, filtered, and analyzed for residual lead.

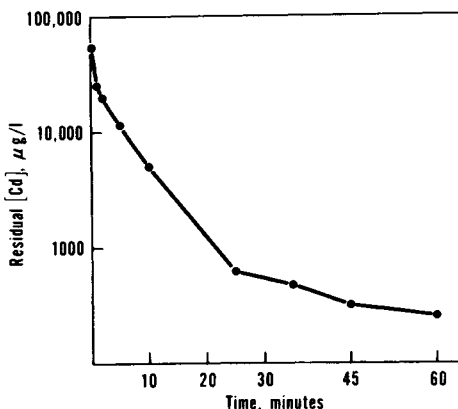


Fig. 5. Rate of cadmium removal with carboxyl-containing starch graft polymer. A cadmium solution (1000 ml, 56.2 mg Cd<sup>2+</sup>/l) was treated at pH 6 with carboxyl-containing starch graft polymer (0.5 g, 3.92 meq metal ion/g). Aliquots were removed at the indicated times, filtered, and analyzed for residual cadmium.

metal ion/g) was evaluated by reusing the product separately on concentrated solutions (2000 ml) of copper (1130 mg/l) and cadmium (2450 mg/l) followed by metal stripping with 2% HCl (500 ml) and water washing (250 ml). The product was oven dried at 125°C for reweighing, and complete product recovery was attained each time after three treatments. Evaluation of the product resulted in 98.6% copper removal and 99.9% cadmium removal from solution. Acid stripping with 2% HCl resulted in 99.6% metal recovery. If the product is going to be reused, it would not be necessary to dry it between treatments.

Evaluation of the carboxyl-containing starch graft polymer on complexed copper solutions (EDTA, Quadrol, citrate, tartrate, and ammonia) gave very little removal unless the pH was lowered sufficiently to dissociate the copper complex.

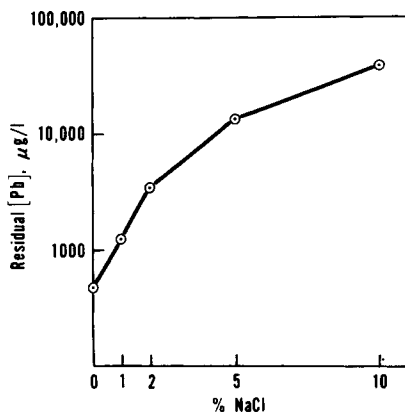


Fig. 6. Effect of salt on lead removal with carboxyl-containing starch graft polymer. Lead solutions (100 ml,  $Pb^{2+}$  concn = 103 mg/l) containing various amounts of sodium chloride were treated at pH 5 with carboxyl-containing starch graft polymer (0.2 g, 3.92 meq metal ion/g). Samples were removed after 30 min for residual lead analysis.

## SUMMARY

Carboxyl-containing starch graft polymers have been prepared by reaction of crosslinked starch with acrylonitrile and ceric ion followed by saponification with caustic. These products have been shown to be effective in heavy metal removal from dilute and concentrated solutions, allowing for metal recovery and product reuse after acid stripping.

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