

Preparation of Insoluble Cationic Starches and Their Use in Heavy Metal Anion Removal

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Synopsis

A series of water-insoluble anion exchange starches were prepared by the reaction of various cationic monomers with highly crosslinked starches. These starch products contain tertiary amine and quaternary ammonium functionalities which are effective in removing chromate, dichromate, ferrocyanide, ferricyanide, molybdate, permanganate, and other heavy metal anions from industrial waste effluents. The binding capacity of these anion exchange starches is similar to that of commercial macroreticular resins.

INTRODUCTION

Commercial anion exchange resins containing tertiary amine and quaternary ammonium groups are very useful in industrial wastewater treatment to remove heavy metal anions.^{1,2} Initial cost to install these exchange resin systems has limited the industrial application of this antipollution technique. The main reason for the high cost is that these resins are petrochemically based. Because of the present petrochemical shortages, these products will likely increase the cost and may even be limited in supply.

This cost problem might be solved by using a naturally occurring, annually renewable, low-cost polymer such as starch. Starch can be highly crosslinked with epichlorohydrin or other agents to be made water insoluble. Chemical modification of the crosslinked starch (CLS) with various reactive cationic monomers yields products which show efficacy for the removal of heavy metal anions from wastewater.

The preparation and use of water-soluble cationic starches is well known.³ Cationic cellulose or crosslinked dextrans⁴⁻⁸ are water insoluble and in a highly purified form have been useful in chromatography. These products usually have only moderate capacity (<1.0 meq/g) and are expensive.

Very little information has been published about crosslinked starch⁹ as a water-insoluble matrix for cationic monomers.¹⁰⁻¹³ Insoluble starch products containing tertiary amine (TA-CLS) and quaternary ammonium (QA-CLS) ethers of different degrees of substitution and capacity (2.13-2.75 meq/g) were prepared and evaluated as heavy metal anion scavengers. Previously, it was shown that insoluble starch xanthate (ISX) effectively removed heavy metal cations from wastewater.¹⁴⁻¹⁶

TABLE I
Quaternary Ammonium Crosslinked Starch (QA-CLS)

Experiment no.	Crosslinked starch, ^a g	NaOH, g	Active monomer, ^b g	Conditions	Product, g	%N	%Cl	%H ₂ O	D.S. ^c	Capacity, ^d meq/g
1	50	13	40	e	59.0	1.52	3.83	11.68	0.20	1.03
2	50	10	50	e	48.4	0.05	0.13	10.26	0.01	0.06
3	50	15	50	e	77.0	3.31	8.31	15.21	0.59	2.34
4	50	20	50	e	74.5	2.87	7.67	15.05	0.48	2.04
5	50	30	50	e	60.5	2.12	5.46	11.92	0.31	1.48
6	50	40	50	f	59.0	1.67	4.32	14.30	0.23	1.17
7	250	100	250	g,h	396.0	2.99	8.29	15.71	0.51	2.13
8	50	20	25	e	57.0	1.68	4.08	12.28	0.23	1.17
9	50	20	75	e	48.0	0.30	0.65	8.53	0.03	0.18
10	50	30	75	e	75.1	3.04	8.52	13.28	0.52	2.15
11	50	20	50	h	73.4	2.93	7.64	15.33	0.49	2.07
12	50	20	50	i	55.0	1.60	3.96	11.76	0.22	1.13
13	50	20	50 ^j	h	64.0	2.12	5.52	11.76	0.31	1.49
14	50	20	75 ^j	h	71.0	2.74	7.28	12.90	0.44	1.93

^a Commercial or experimental crosslinked starch.

^b 3-Chloro-2-hydroxypropyltrimethylammonium chloride (~50% solution), Story Chemical Corporation, Muskegon, Michigan 49445.

^c D.S. (degree of substitution) calculation: %N/100 = 14D.S./(162 - D.S. + 152D.S.) (use 148D.S. instead of 152D.S. for experiments 13 and 14).

^d Capacity calculation: meq/g = 1000D.S./(162 + 152D.S.) (use 148D.S. instead of 152D.S. for experiments 13 and 14).

^e Crosslinked starch in 170 ml water with NaOH in 50 ml water is stirred 30 min. Monomer is added and stirred at 65°C for 2 hr. Product is filtered, washed with water, neutralized to pH 6.5 with 2% HCl, and rewashed with water, acetone, and ether. The product is then air dried.

^f As in (e), but base in 75 ml H₂O.

^g Quantities of H₂O were increased five times over those in (e).

^h As in (e), only 1 hr at 68°C.

ⁱ As in (e), but no heat.

^j 4-Chloro-2-butenyltrimethylammonium chloride, Miles Laboratories, Elkhart, Indiana.

TABLE II
Tertiary Amine Crosslinked Starch (TA-CLS)

Experiment no.	Crosslinked-starch, ^a g	NaOH, g	Active monomer, ^b g	Conditions	Product, g	%N	%Cl	%H ₂ O	D.S. ^c	Capacity, ^d meq/g
1	50	20	50	e	71.0	3.86	6.27	10.47	0.71	2.75
2	250	100	250	f	365.0	3.82	6.64	1.10	0.70	2.72
3	500	200	500	g	727.0	3.83	7.04	9.01	0.70	2.73

^a Commercial or experimental crosslinked starch.

^b 2-Chlorotriethylamine hydrochloride, Eastman Organic Chemicals, Rochester, New York.

^c D.S. (degree of substitution) calculation: $\%N/100 = 14D.S./(162 - D.S. + 136D.S.)$

^d Capacity calculation: $\text{meq/g} = 1000D.S./(162 + 136D.S.)$

^e (e) in Table I.

^f Quantities of water were increased five times over those in (e).

^g Same monomer but practical grade and quantities of water were increased ten times over those in (e).

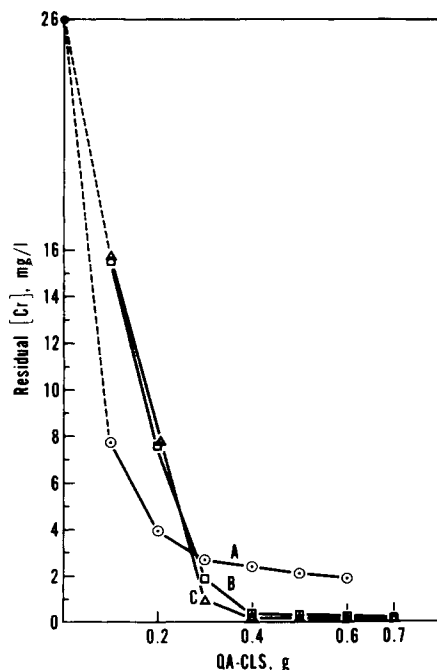


Fig. 1. Chromate (CrO_4^{2-}) solutions (500 ml, 26 mg/l. as Cr^{6+}) at pH 4 (curve A), 7 (curve B), and 9 (curve C) were treated with increasing amounts of quaternary ammonium crosslinked starch (QA-CLS) (capacity = 2.13 meq/g). Aliquots (10 ml) of the supernatant were removed for chromium analysis 10 min after each addition. Theoretical weight required is 0.23 g.

EXPERIMENTAL

Crosslinked Starches

Commercial crosslinked starches [Vulca 90, National Starch and Chemical Corp., Bridgewater, N.J. (10.9% H_2O), and HPD-53-91E, The Hubinger Company, Keokuk, IO (9.1% H_2O)] were used as received. Experimental samples of crosslinked starch were prepared as follows:

Commercial corn starch (100 g, 10% H_2O) was slurried in water (150 ml) containing sodium chloride (1.5 g) and epichlorohydrin (7 ml). To this slurry was added potassium hydroxide (6 g) in water (40 ml) slowly over 15 min, and the mixture was stirred 16 hr. The product was isolated by filtration or reacted as is with cationic monomer after the addition of water (150 ml).

Quaternary Ammonium Crosslinked Starch (QA-CLS)

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. Then, 3-chloro-2-hydroxypropyltrimethylammonium chloride (100 ml, 50% active) was added, and the mixture was stirred at 65°C for 1 hr. The slurry was cooled, filtered, and washed with water. The cake was reslurried in water and the pH was adjusted to 6.5 with hydrochloric acid (2%). The slurry was filtered, washed with water, acetone, and ether, and air dried. Weights and volumes of reactants and analyses of final product for several preparations are found in Table I.

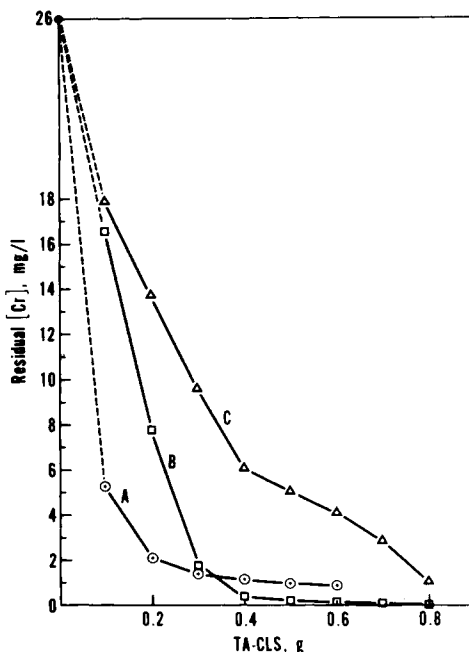


Fig. 2. Chromate (CrO_4^{2-}) solutions (500 ml, 26 mg/l. as Cr^{6+}) at pH 4 (curve A), 7 (curve B), and 9 (curve C) were treated with increasing amounts of tertiary amine crosslinked starch (TA-CLS) (capacity = 2.75 meq/g). Aliquots (10 ml) of the supernatant were removed for chromium analysis 10 min after each addition. Theoretical weight required is 0.18 g.

Tertiary Amine Crosslinked Starch (TA-CLS)

These products were prepared as previously described for the quaternary ammonium crosslinked starch but with 2-chlorotriethylamine hydrochloride. Analysis of the tertiary amine products are found in Table II.

Heavy Metal Anion Removal

The QA-CLS and TA-CLS were evaluated as heavy metal anion scavengers. Their optimum pH range, capacity, and salt effect were determined by adding small amounts of the starch-based products to solutions of the metal anions.

RESULTS AND DISCUSSION

Optimum conditions for the reaction of crosslinked starch (CLS) and reactive cationic monomers were evaluated in the preparation of the 2-hydroxypropyl-trimethylammonium chloride ether of CLS. Table I shows the conditions and analyses of the products prepared in this study. Maximum efficiency of monomer incorporation was obtained using a CLS:NaOH:monomer molar ratio of 0.3:0.5:0.27. Changing the ratio of the base or monomer significantly sometimes led to no ether formation and, with larger ratios of base, only hydrolysis of the monomer. The conditions presented here should allow the preparation of most crosslinked starch ethers from appropriate monomers. Heavy metal anion capacities of the QA-CLS were usually 2.0–2.1 meq metal anion/g.

Tertiary amine ethers of CLS (TA-CLS) were also synthesized (Table II) under the optimum conditions established for the QA-CLS. The heavy metal anion

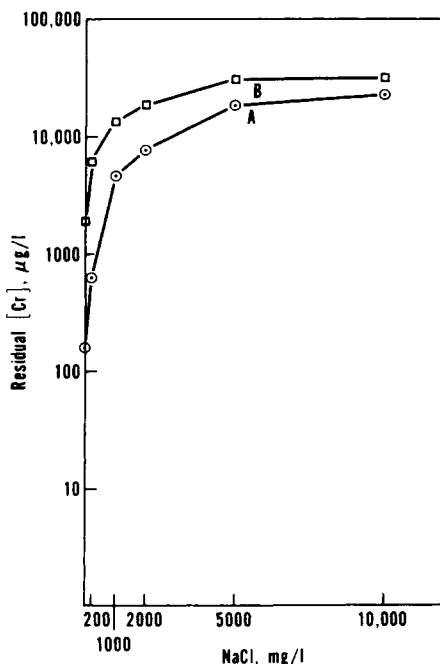


Fig. 3. (a) Chromate solutions (50 ml, Cr^{6+} concn. = 26 mg/l.) containing various amounts of sodium chloride were treated at pH 6 with QA-CLS (0.1 g, 2.13 meq/g). (b) Dichromate solutions (50 ml, Cr^{6+} = 49.7 mg/l.) containing various amounts of sodium chloride were treated at pH 4 with TA-CLS (0.05 g, 2.75 meq/g).

binding capacity for these TA-CLS products was 2.72–2.75 meq metal anion/g.

The main purpose for preparing these products was to evaluate their heavy metal anion removal capabilities for industrial wastewaters. The examples which follow will exploit these capabilities. The QA-CLS used was product 7 of Table I, and the TA-CLS was product 1 of Table II. Owing to the small particle size of these products, they were only evaluated in batch-type experiments and not in columns. However, they could be pelletized for use in pressurized columns with acceptable flow rates, or could be used as a precoat on filters.¹⁷

These products can be added directly as solids to the polluted wastewater stream containing heavy metal anions. Examples which show the effectiveness of the starch-based products include the removal of chromate, dichromate, ferricyanide, ferrocyanide, permanganate, and molybdate ions. Generally, the starch-based products are of similar capacity and are regenerable like the petroleum-based ion exchange resins.

Chromate (CrO_4^{2-}) and Dichromate ($\text{Cr}_2\text{O}_7^{2-}$) Removal

The use of chromates and dichromates in plating and as corrosion control agents in cooling water systems is quite extensive. Chromium(VI) is very toxic and must be removed from industrial wastewaters before discharge. The chromium(VI) level allowed in waste effluents, which are discharged to natural waterways, has been established at a maximum concentration of 0.05 mg/l.¹⁸ Rinse waters of plating operations may vary in composition, but they usually

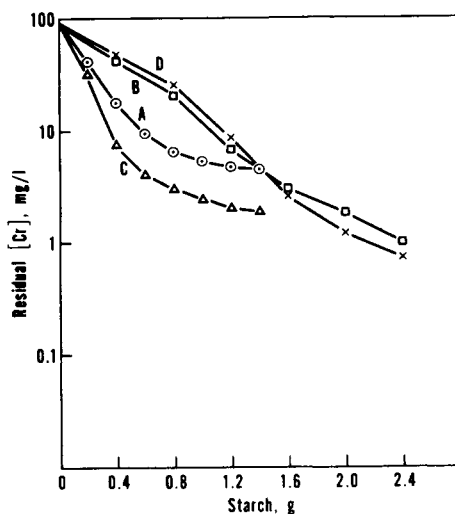


Fig. 4. Solutions (500 ml, 92 mg/l. Cr) at pH 4 and 7 were treated with increasing amounts of QA-CLS (capacity = 2.13 meq/g; curve A, pH 4; curve B, pH 7) and TA-CLS (capacity = 2.75 meq/g; curve C, pH 4; curve D, pH 7). Aliquots (10 ml) of the supernatant were removed for chromium analysis 10 min after each addition. Theoretical weight required is 0.83 and 0.64 g, respectively.

contain 20–100 mg/l. Cr^{6+} and have a pH of 2–3. These rinses are treated for three reasons: (1) pollution control, (2) water reuse, and (3) Cr^{6+} recovery.

Treatment for Cr^{6+} usually involves chemical reduction to Cr^{3+} with sulfur dioxide, sodium bisulfite, sodium metabisulfite, or ferrous salts^{18–22} at pH 2–3. The Cr^{3+} is then precipitated at alkaline pH as the hydroxide with caustic or lime. Nonreductive treatments of Cr^{6+} include anion exchange^{23–28} and activated carbon.²⁹

The effectiveness of anion exchange resins prompted our evaluation of the starch-based cationic products for removing Cr^{6+} from solution. The TA-CLS and the QA-CLS were initially evaluated to determine their optimum pH range and capacity for removing Cr^{6+} as chromate. Figures 1 and 2 show the optimum pH for removal of chromate at higher concentrations of Cr^{6+} to be around 4. However, as the Cr^{6+} concentration decreases to 3–4 mg/l, a pH near 7 is optimum to reach levels near the discharge limit of 0.05 mg/l. The capacity of QA-CLS and TA-CLS for chromate is also shown in these figures with 80–90% of the Cr^{6+} removed when the theoretical amount of the starch product is used at pH 4. The capacity of the products and optimum pH for dichromate removal are very similar to those for chromate.

These starch-based products are effective in both the chloride and hydroxide forms, and in most cases no pretreatment would be necessary as with typical ion exchange columns. To reach discharge limit levels, an excess of product over that theoretically required is necessary. The oxidative nature of chromate and dichromate ions does not appear to affect these starch-based products. The chromate or dichromate is released from these products by washing with sodium hydroxide (1*N*), hydrochloric acid (2%), or sodium chloride (5%). The regenerated product is still effective (~90%) in Cr^{6+} removal. Since sodium chloride is effective in removing Cr^{6+} from the products, these starch-based products would not be expected to tolerate high salt concentrations in the treatment of industrial effluents.

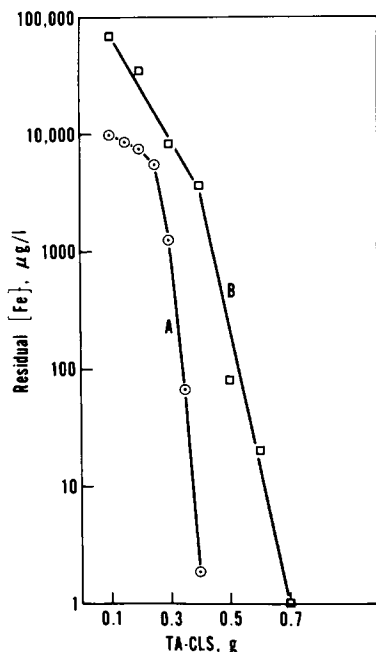


Fig. 5. Solutions (500 ml) at pH 5 were treated with increasing amounts of TA-CLS (capacity = 2.75 meq/g). Aliquots (10 ml) of the supernatant were removed for iron analysis after each addition. Curve A: Ferricyanide concn. = 25.5 mg/l. as Fe, initial; theoretical weight TA-CLS required is 0.25 g. Curve B: Ferrocyanide concn. = 25.9 mg/l. as Fe, initial; theoretical weight TA-CLS required is 0.34 g.

The salt effect is shown in Figure 3. When sulfate ion is used in the system, the Cr^{6+} removal is slightly lower. If salt concentrations are too high (>100 mg/l.), the effluent would have to be diluted with other process waters to lower the salt concentration in order to have effective Cr^{6+} removal with these starch-based cationic polymers. The products could possibly be pelletized for use in pressurized columns having acceptable flow rates to overcome this salt effect to some extent.

Figure 4 shows the use of the starch-based products for a chromic acid industrial effluent. The results previously described are also evident in these curves. Small amounts of Cr^{3+} (1 mg/l.) is present which prevents total chromium removal below 1 mg/l. This particular effluent does contain several other heavy metal cations that were not removed by these products.

Ferricyanide (FeCN_6^{3-}) and Ferrocyanide (FeCN_6^{4-}) Removal

Aqueous cyanide pollution in industrial wastes causes widespread problems. Several methods of cyanide removal are used today. These include alkaline chlorination, electrolytic oxidation, ozonation, ion exchange, Kastone (H_2O_2 -formaldehyde), and activated carbon.³⁰⁻³⁵ Recently, a process was developed to convert free cyanides into the very stable ferrocyanide complex and then to remove the complex on a weakly basic ion exchange resin.^{36,37}

The tertiary amine-crosslinked and quaternary ammonium-crosslinked starches were evaluated for ferricyanide and ferrocyanide removal. The most effective pH range for ferricyanide and ferrocyanide removal is pH 4-5. Figures

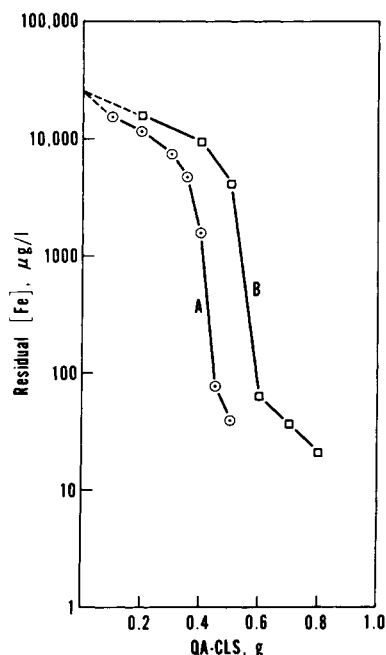


Fig. 6. Solutions (500 ml) at pH 5 were treated with increasing amounts of QA-CLS (capacity = 2.13 meq/g). Aliquots (10 ml) of the supernatant were removed for iron analysis 10 min after each addition. Curve A: Ferricyanide concn. = 25.5 mg/l. as Fe, initial; theoretical weight QA-CLS required is 0.32 g. Curve B: Ferrocyanide concn. = 25.9 mg/l. as Fe, initial; theoretical weight QA-CLS required is 0.44 g.

5–8 show the capacity of the products and their effectiveness in the presence of 1%–4% sodium chloride. The products have a strong binding capacity as is shown in Figures 5 and 6, as there was no detectable amount of complex, as evidenced by atomic absorption analyses, in some of the treated solutions. The presence of salt does not limit $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ removal as much (Figs. 7 and 8) as shown with chromate. A 1% sodium hydroxide treatment effectively regenerates the products.

Molybdate (MoO_4^{2-}) Removal

The QA-CLS and TA-CLS were evaluated for the removal of Mo^{6+} as molybdate. Optimum molybdate removal occurs at pH 4, with theoretical amounts of the products removing MoO_4^{2-} close to its nondetectable limit (0.1 mg/l.).

Permanganate Removal

QA-CLS and TA-CLS are very effective in lowering manganese(VII) levels from solutions of permanganate. Optimum removal occurs at pH 7, and the QA-CLS is slightly more effective than the TA-CLS at theoretical capacity. Even though these products lower the manganese(VII) level well below established discharge limits, they turn brown-purple due to oxidation and become nonregenerable. Since the product is very efficient in permanganate removal, an excess of product is not required.

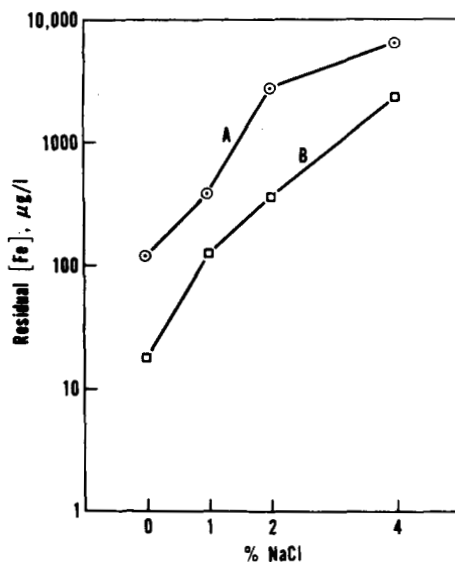


Fig. 7. Solutions (50 ml) of ferrocyanide (25.9 mg/l. as iron) containing various amounts of sodium chloride were treated at pH 4. Curve A: QA-CLS (capacity = 2.12 meq/g, 0.065 g). Curve B: TA-CLS (capacity = 2.75 meq/g, 0.055 g).

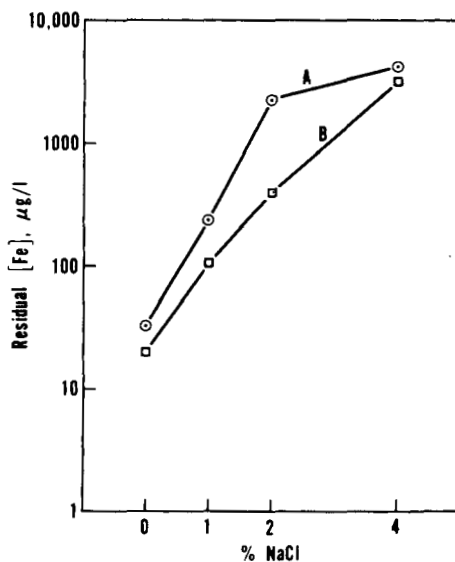


Fig. 8. Solutions (50 ml) of ferricyanide (25.5 mg/l. as iron) containing various amounts of sodium chloride were treated at pH 4. Curve A: QA-CLS (capacity = 2.12 meq/g, 0.05 g). Curve B: TA-CLS (capacity = 2.75 meq/g, 0.04 g).

Other Heavy Metal Anion Removal

Heavy metal anions such as HgCl_4^{2-} , AuCl_4^- , and $\text{P}_2\text{O}_7^{4-}$ should also be removable by these starch-based products.

SUMMARY

Several starch-based products have been prepared containing tertiary amine and quaternary ammonium groups. These products having capacities of 2.1–2.75 meq/g were evaluated as heavy metal anion scavengers. The products are regenerable for reuse.

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References

1. T. R. Higgins, *Environ. Sci. Technol.*, **7**, 1110 (1973).
2. R. Kunin, *Prod. Finish. (Cincinnati)*, **33**, 71 (1969).
3. E. F. Paschall, in *Starch: Chemistry and Technology*, Vol. II, R. L. Whistler and E. F. Paschall, Eds., Academic Press, New York, 1967, pp. 403–422.
4. R. R. Benerito, B. B. Woodward, and J. D. Guthrie, *Anal. Chem.*, **37**, 1693 (1965).
5. L. Kuniak, Czech. Pat. 152,781 (April 15, 1974).
6. Brown Company, Berlin-Gorham Div., Berlin, N.H., *Selectacel Data Sheets*, December 1974.
7. C. S. Knight, W&R Balston, Ltd., Brit. Pat. 1,001,481 (August 18, 1965).
8. Aktiebolaget Pharmacia, Brit. Pat. 1,013,585 (December 15, 1965).
9. C. H. Hullinger, *Starch: Chemistry and Technology*, Vol. II, R. L. Whistler and E. F. Paschall, Eds., Academic Press, New York, 1967, pp. 445–450.
10. L. Kuniak and R. Marchessault, Canad. Pat. 960,652 (January 7, 1975).
11. Aktiebolaget Pharmacia, Brit. Pat. 936,039 (September 4, 1963).
12. A. L. Bullock and J. D. Guthrie, USDA, U.S. Pat. 3,065,222 (November 20, 1962).
13. A. L. Bullock and J. D. Guthrie, USDA, U.S. Pat. 2,992,215 (July 11, 1961).
14. R. E. Wing, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **19**, 847 (1975).
15. R. E. Wing, *Ind. Wastes (Chicago)*, **21**(1), 26 (1975).
16. R. E. Wing and W. M. Doane, USDA, U.S. Pat. 3,979,286 (September 7, 1976).
17. J. F. Zievers, Industrial Filter and Pump Mfg. Corp., Cicero, Ill., personal communication.
18. K. C. Leimkuehler, *Ind. Wastes (Chicago)*, **21**(5), 38 (1975).
19. G. B. Hill, *Plating (East Orange, N.J.)*, **56**, 172 (1969).
20. J. F. Zievers and C. J. Novotny, Industrial Filter and Pump Co., U.S. Pat. 3,681,210 (August 1, 1972).
21. J. A. Landy, *J. Water Pollut. Control Fed.*, **43**, 2242 (1971).
22. E. I. Onstott, W. S. Gregory, and E. F. Thode, *Environ. Sci. Technol.*, **7**, 333 (1973).
23. S. Rothstein, *Plating (East Orange, N.J.)*, **45**, 835 (1958).
24. T. V. Arden and M. Giddings, *J. Appl. Chem.*, **11**, 229 (1961).
25. A. W. Oberhofer, Nalco Chemical Co., U.S. Pat. 3,414,510 (December 3, 1968); U.S. Pat. 3,223,620 (December 14, 1965).
26. A. J. Saraceno, R. H. Walters, D. B. Jones, and W. E. Wiehle, U.S.A.-Atomic Energy Comm., U.S. Pat. 3,664,950 (May 23, 1972).
27. L. Sloan and N. J. Nitti, Crane Co., U.S. Pat. 3,306,859 (February 28, 1967).
28. J. F. Zievers, C. W. Riley, and R. W. Crain, Industrial Filter and Pump Co., U.S. Pat. 3,658,470 (April 25, 1972).
29. K. D. Linstedt, C. P. Houck, and J. T. O'Connor, *J. Water Pollut. Control Fed.*, **43**, 1507 (1971).
30. J. F. Zievers, R. W. Crain, and F. G. Barclay, *Plating (East Orange, N.J.)*, **57**, 56 (1970).
31. M. Beevers, *Met. Finish. J.*, **18**, 232 (1972).
32. V. V. R. Sastry and S. Mahapatra, *Indian Chem. J.*, **12**(9), 27 (1974).
33. A. N. Sulfaro and A. H. Stein, Oxy Metal Finishing Corp., U.S. Pat. 3,715,308 (February 6, 1973).

34. Q. D. Mehrkam, *Met. Progr.*, **108**(4), 103 (1975).
35. Anon., *Environ. Sci. Technol.*, **5**, 496 (1971).
36. W. Fries, Rohm and Haas Co., U.S. Pat. 3,788,983 (January 29, 1975).
37. N. L. Avery and W. Fries, *Ind. Eng. Chem., Prod. Res. Dev.*, **14**, 102 (1975).

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