

Use of Novel Hydrogels Based on Modified Cellulosics and Methacrylamide for Separation of Metal Ions from Water Systems

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ABSTRACT: Interpenetrating networks (IPNs) based on extracted cellulose and its derivatives such as hydroxypropyl cellulose (HPC), cyanoethylcellulose, hydroxyethylcellulose, hydrazinodeoxycellulose, cellulosephosphate with methacrylamide (MAAm), and *N,N*-methylene bisacrylamide were synthesized at reaction conditions evaluated for optimum network yield as a function of irradiation dose, concentrations of monomer and crosslinker, and amount of water. These networks were used in sorption of Fe^{2+} , Cu^{2+} , and Cr^{6+} ions. The networks were further functionalized by

means of partial hydrolysis with 0.5N NaOH and metal ion sorption studies were carried out. Appreciable amount of all the three ions was sorbed and partial functionalization of the hydrogels results in selectivity in ion sorption with enhanced affinity for Fe^{2+} ions and total rejection of Cr^{6+} ions. These results are of interest for the development of low-cost technologies based on smart hydrogels. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 667–671, 2002

Key words: crosslinking; hydrogels; irradiation; networks

INTRODUCTION

Removal of metal ions from sewage and industrial waste is a big problem, and new materials are being developed to correct imbalances of water systems caused by effluents. Conventional precipitation processes do not work up to satisfactory levels and synthetic ion-exchange resins are quite expensive. So new materials like smart hydrogels are finding increased use in separation and enrichment technologies—especially those based on natural polymers like cellulose, starch, dextran, and chitosan, which are being constantly searched for remediation of metal ions from water bodies. These polymers are of renewable origin, are environment friendly, and offer highly cost-effective technologies and enrich or separate metal ions by binding, through adsorption, chelation and ion-exchange processes.

Membranes formed by blending of alginic acid with cellulose cuoxam are reported as ion-exchange membranes in the water-swollen state.¹ Ionomers used to remove heavy metal ions from wastewater have been prepared by chemical modification of crosslinked starch with various reactive monomers.² Starch xanthate,^{3,4} chitosan,^{5,6} and even amino resins are widely

used as complexing agents for collection of metal ions from aqueous solutions.⁷ Dextran has been used for concentration and separation of metal ion from aqueous solution of Cu^{2+} , Ni^{2+} , and Fe^{3+} .⁸

Among the biopolymers, cellulose is of special interest due to easy availability and applicability both in natural as well as modified form. Chemical modification of cellulosics can be used to obtain functionalized hydrogel beads for ion-exchange and affinity chromatography.⁹ Hydrazinodeoxy cellulose and carboxylalkyl hydrazinodeoxy cellulose show adsorption behavior toward heavy metal ions.¹⁰ We have earlier reported use of the structure–property relationship in the case of cost-effective cellulose-based materials for the sorption of Cu^{2+} ion. Functionalization of cellulose or cellulosics by simple processes like grafting improves its membrane workability in a marked manner. In the present article we report the sorption of some common water effluents like Cu^{2+} , Fe^{2+} , and Cr^{6+} ions by the equilibration method onto hydrogels of cellulose and some of its derivatives with methacrylamide (MAAm) synthesized in the presence of *N,N*-MBAAm.

EXPERIMENTAL

Materials and methods

Extraction of cellulose, and synthesis of HPC and other cellulosics, has been carried by earlier reported methods.¹² Their networks with methacrylamide (MAAm) in the presence of *N,N*-MBAAm have been synthesized by the simultaneous radiation-induced

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method using the same set of reaction conditions.¹³ Partial saponification of the hydrogels was effected by immersion of the same in 0.5N NaOH for 48 h at 25°C. Copper sulfate, ferrous sulfate, and chromium oxide (analytical grade, CDH, India) were used as received. All weights were taken on a Denver TR-203 Balance having minimum readability of 1.0 mg.

Sorption studies

Each hydrogel of known weight was immersed for 24 h in 50.00 mL metal ion solution of known strength. The hydrogels were washed with distilled water to remove any physically adsorbed ions. Filtrates of the solutions were analyzed for concentration of rejected ions on a DR 2010 spectrophotometer (Hach Co., U.S.A.) by using its standard pillow reagents. On this instrument, the maximum limit of ion strength that can be studied is 5.0, 3.0, and 0.6 mg/L of solution, respectively, for Cu^{2+} , Fe^{2+} , and Cr^{6+} ions. Thus, the residual filtrate was diluted to reach this range. Results of analysis have been presented in the tables. The different relationships used to express sorption behavior are as follows¹⁴:

Percent uptake (P_u)

$$= \frac{\text{Amount of metal ion in the polymer}}{\text{amount of metal ion in the feed}} \times 100$$

Partition coefficient (K_d)

$$= \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion left in the solution}} \times \frac{\text{Volume of solution (mL)}}{\text{Weight of dry polymer (g)}}$$

Retention capacity (Q)

$$= \frac{\text{Amount of metal ion in the polymer (m Eq)}}{\text{Weight of dry polymer (g)}}$$

RESULTS AND DISCUSSION

Cellulose has the capacity to complex with metal ions at its glycolic groups, and substitution by attachment of active groups on its anhydroglucose units leads to improvement of membrane workability and also induces selectivity. Thus, derivatized cellulose like hydrazinodeoxy cellulose that has a metal-active hydrazino group is expected to have a high degree of adsorption of metal ions. In the present study such structural differentiation of polymers, apart from the pore size and structure differences, as function of heterogeneity and homogeneity nature of synthetic reactions of the hydrogels should affect metal ion sorption

behavior. Thus, it is expected that apart from the nature of the metal ion in aqueous solution, structural differences in hydrogels should lead to selectivity in metal ion sorption.

Structural aspects of hydrogels and sorption behavior of Fe^{2+} ions

Results of sorption of Fe^{2+} ions is presented in (Table I). Metal ions are partitioned between hydrogels and liquid phase, and it is reflected in high values of partition coefficients (K_d). The structure and nature of polymeric backbone with respect to the metal binding groups on the hydrogels like hydrazino groups have no effect on ion uptake—neither does any relationship between the network yield with respect to incorporation of poly(MAAm) and metal ion uptake (P_u), as a higher amount of poly(MAAm) does not necessarily leads to higher Fe^{2+} uptake. Both these observations have been exemplified by hydrazinodeoxy cellulose and cellulose phosphate as both have active functionalities and high network yield, respectively, 230.0 and 234.8. But these hydrogels have low P_u values of 26.0 and 49.8, respectively, as compared to cellulose based hydrogels that has comparable $P_{\text{add-on}}$ of 225.9 and has appreciably high P_u of 88.20 (Table I). Thus, it can be stated that Fe^{2+} uptake is more a sorption process. The order for Fe^{2+} ions uptake can be formulated as hydroxyethylcellulose-*cl*-poly(MAAm) > hydroxypropylcellulose-*cl*-poly(MAAm) > cellulose-*cl*-poly(MAAm) > cyanoethylcellulose-*cl*-poly(MAAm) cellulosephosphate-*cl*-poly(MAAm) \gg hydrazinodeoxycellulose-*cl*-poly(MAAm).

Effect of hydrolysis on Fe^{2+} ion sorption

Affinity of partially hydrolyzed hydrogels has been observed for Fe^{2+} ions, and it is witnessed in higher Q_r and K_d . This enhanced uptake by functionized hydrogels has been so encouraging that these hydrogels were subjected to three feeds of higher amount of metal ions. All these were almost fully sorbed by the hydrogels (Table I). This tremendous increase in the Fe^{2+} ion uptake has been observed in all the hydrogels. Hydrolysis of all the hydrogels affects metal ion uptake by activation of functional groups of poly(MAAm) chains by opening up the hydrogel network and activating amide functional groups into more active groups like the carboxylate groups, which have a stronger tendency to chelate and exchange ions. It is important that partial hydrolysis increase water uptake of hydrogels many times and it is this tendency of these functionized hydrogels that leads to enhanced metal ions sorption.

TABLE I

Fe ²⁺ sorption behavior of poly(MAAm) based hydrogels ^a								
Sr. no.	Hydrogel	$P_{\text{add-on}}$	Percent swelling (P_s)	Amount of Fe ²⁺ sorbed (mg)	Amount of Fe ²⁺ rejected (mg)	P_u	Partition coefficient (K_d) (g/g)	Retention capacity (meq/g)
1	HPC	185.6	420.0	9.50	0.50	95.0	1520.00	0.680
2	Cellulose	225.9	456.0	8.82	1.18	88.20	597.96	0.632
3	Hydrazinodeoxycellulose	230.0	370.0	2.60	7.40	26.0	28.10	0.186
4	Cellulose Phosphate	234.8	485.0	4.98	5.02	49.8	79.36	0.356
5	HEC	185.5	473.0	9.92	0.08	99.2	9920.00	0.71
6	Cyanoethyl cellulose	229.4	352.0	7.96	2.04	79.6	312.15	0.57

Fe ²⁺ ion sorption behavior of hydrolyzed poly(MAAm)-based hydrogels ^a							
Sr. no.	Hydrogel	P_s	Amount of Fe ²⁺ sorbed (mg)	Amount of Fe ²⁺ rejected (mg)	Partition coefficient (K_d) (g/g)	Retention capacity (meq/g)	
First feed (Fe ²⁺ ions) = 10 mg/L							
1	HPC	7117.0	10.00	0.00	∞	0.716	
2	Cellulose	1868.0	10.00	0.00	∞	0.716	
3	Hydrazinodeoxycellulose	1567.0	10.00	0.00	∞	0.716	
4	Cellulosephosphate	1505.0	10.00	0.00	∞	0.716	
5	HEC	1769.0	10.00	0.00	∞	0.716	
6	Cyanoethylcellulose	3390.0	10.00	0.00	∞	0.716	
Second feed = Fe ²⁺ ions = 20 mg/L							
1	HPC	7117.0	20.00	0.00	∞	1.43	
2	Cellulose	1868.0	20.00	0.00	∞	1.43	
3	Hydrazinodeoxycellulose	1567.0	20.00	0.00	∞	1.43	
4	Cellulose phosphate	1505.0	20.00	0.00	∞	1.43	
5	HEC	1769.0	20.00	0.00	∞	1.43	
6	Cyanoethylcellulose	3390.0	20.00	0.00	∞	1.43	
Third feed (Fe ²⁺ ions) = 20 mg/L							
1	HPC		20.00	0.00	∞	1.43	
2	Cellulose		19.94	0.06	33233.33	1.43	
3	Hydrazinodeoxycellulose		19.96	0.04	49900.00	1.43	
4	Cellulose phosphate		19.86	0.14	14185.71	1.43	
5	HEC		19.96	0.04	49900.00	1.43	
6	Cyanoethylcellulose		20.00	0.00	∞	1.43	

^a Weight of dry hydrogel = 0.5 g; P_s = percent swelling at 25°C and 24 h without metal ions.

Structural aspects of hydrogels and sorption behavior of Cu²⁺ ions

It is evident from Table II that sorption of Cu²⁺ ions is not as appreciable as was observed in case of Fe²⁺ ions. Low P_u values have been obtained for all the hydrogels, and it is only in the case of cellulose- and cellulosephosphate-based hydrogels that highest value of 18.40 and 19.30 respectively have been observed. Thus, functionalization of cellulose by fixation of different groups has not resulted in improvement of Cu²⁺ uptake. Instead, *N,N*-MBAAm crosslinked poly(MAAm) network leads to comparatively very uptake of Cu²⁺ ions. However, results obtained for hydrogels based on cellulose do not reflect any relationship

between metal ion uptake and $P_{\text{add-on}}$ i.e., amount of poly(MAAm) incorporated. These results are again independent of the amount of poly(MAAm) incorporated on different cellulose.

Effect of hydrolysis on Cu²⁺ ion sorption

On partial hydrolysis, sorption behavior of hydrogels toward Cu²⁺ ions also changes in similar manner as was observed for sorption of Fe²⁺ ions. A manifold increase in P_u even close to 100 was observed (Table II) though increase in ion uptake is not of the same magnitude as was witnessed in case of Fe²⁺ ions. So further feeds were not tried in this case.

TABLE II

Cu ²⁺ sorption behavior of poly(MAAM)-based hydrogels ²								
Sr. no.	Hydrogel	$P_{\text{add-on}}$	Percent swelling (P)	Amount of Cu ²⁺ sorbed (mg)	Amount of Cu ²⁺ rejected (mg)	P_u	Partition coefficient (K_d)(g/g)	Retention capacity (meq/g)
1.	HPC	185.6	420.0	1.30	11.40	10.20	85.52	0.40
2.	Cellulose	225.9	456.0	2.34	10.36	18.40	169.40	0.73
3.	Hydrazinodeoxycellulose	230.0	370.0	0.06	12.64	0.47	3.56	0.02
4.	Cellulose phosphate	234.8	485.0	2.46	10.24	19.30	180.17	0.77
5.	HEC	185.5	473.0	0.86	11.84	6.77	54.47	0.27
6.	Cyanoethyl cellulose	229.4	352.0	1.98	10.72	15.50	138.52	0.62

Cu ²⁺ sorption behavior of hydrolyzed poly(MAAM)-based hydrogels ^a							
Sr. no.	Hydrogel	P_s	Amount of Cu ²⁺ sorbed (mg)	Amount of Cu ²⁺ rejected	P_u	Partition coefficient (K_d) (g/g)	Retention capacity (meq/g)
1.	HPC	7117.0	12.4	0.28	97.63	33214.28	3.90
2.	Cellulose	1868.0	5.9	6.80	46.45	650.53	1.85
3.	Hydrazinodeoxycellulose	1567.0	12.3	0.44	96.85	20965.90	3.87
4.	Cellulosephosphate	1505.0	10.2	2.48	80.30	3084.67	3.21
5.	HEC	1769.0	9.6	3.10	75.50	2322.58	3.02
6.	Cyanoethylcellulose	3390.0	11.2	1.46	88.18	5753.42	3.52

^a Weight of dry hydrogel = 0.1 g, * P_s = percent swelling at 25°C and 24 h without metal ions.

Structural aspects of hydrogels and sorption behavior of Cr⁶⁺ ions

Results of sorption behavior of Cr⁶⁺ ions by the same group of hydrogels are presented in Table III. It is interesting that apart from sorption of very small percent of Cr⁶⁺ ions by hydrazinodeoxycellulose- and cellulosephosphate-based hydrogels no ion uptake was

observed in case of other hydrogels. Thus, high selectivity guides metal ion sorption behavior of these hydrogels. Noninclusion of Cr⁶⁺ ions in the hydrogel matrices is understandably due to its higher charge density and large size in hydrated state, yet it is perhaps oxidizing nature of Cr⁶⁺ ions that leads to degradation of polymeric matrix itself.

TABLE III

Cr ⁶⁺ sorption behavior of poly(MAAM)-based hydrogels ^a								
Sr. no.	Hydrogel	$P_{\text{add-on}}$	Percent swelling (P_s)	Amount of Cr ⁶⁺ sorbed (mg)	Amount of Cr ⁶⁺ rejected (mg)	P_u	Partition coefficient (K_d) (g/g)	Retention capacity (meq/g)
1.	HPC	185.6	420.0	0.00	130.0	0.00	0.00	0.00
2.	Cellulose	225.9	456.0	0.00	130.0	0.00	0.00	0.00
3.	Hydrazinodeoxycellulose	230.0	370.0	20.00	110.0	15.30	4.54	4.61
4.	Cellulose phosphate	234.8	485.0	12.50	117.5	9.60	10.6	2.88
5.	HEC	185.5	473.0	0.00	130.0	0.00	0.00	0.00
6.	Cyanoethyl cellulose	229.4	352.0	0.00	130.0	0.00	0.00	0.00

Cr ⁶⁺ sorption behavior of hydrolyzed poly(MAAM)-based hydrogels ^a							
Sr. no.	Hydrogel	P_s	Amount of Cr ⁶⁺ sorbed (mg)	Amount of Cr ⁶⁺ rejected	P_u	Partition coefficient (K_d) (g/g)	Retention capacity (meq/g)
1.	HPC	7117.0	0.00	26.0	0.00	0.00	0.00
2.	Cellulose	1868.0	0.00	26.0	0.00	0.00	0.00
3.	Hydrazinodeoxycellulose	1567.0	0.00	26.0	0.00	0.00	0.00
4.	Cellulose phosphate	1505.0	0.00	26.0	0.00	0.00	0.00
5.	HEC	1769.0	0.00	26.0	0.00	0.00	0.00
6.	Cyanoethyl cellulose	3390.0	0.00	26.0	0.00	0.00	0.00

^a Dry weight of hydrogel = 0.5 g, P_s = percent swelling at 25°C and 24 h without metal ions.

Effect of partial hydrolysis on Cr^{6+} ion sorption

It is of interest to note that the selectivity observed in case of rejection of Cr^{6+} ions by these hydrogels gets further increased and sharpened as on partial hydrolysis, no sorption of Cr^{6+} ions was observed (Table III). Apart from the explanation given above, this high selectivity against Cr^{6+} ions is also the result of its solubility in sodium salts that should result in its more seclusion from the polymers.

CONCLUSION

From the foregoing discussion, it can be concluded that these hydrogels have high retention capacity, and partitioning of metal ions is appreciable high between hydrogels and the liquid phase. Absorption of Fe^{2+} ions by these hydrogels is appreciable, which further increases manifold on functionalization of hydrogels by partial hydrolysis, suggesting multiple repeatability and reusability of the hydrogels. Ion uptake is almost independent of amount of methacrylamide incorporated and that of active groups on cellulose, suggesting possible sorption of metals ions in the bulk. Apart from the contribution of the structural aspects of the hydrogels in ion uptake, charge density, hydration energy, and size of hydration sphere of these ions also contribute significantly to the observed results—hence, the sorption order is $\text{Fe}^{2+} > \text{Cu}^{2+} \gg \text{Cr}^{6+}$.

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