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Metal ion sorption and swelling studies of psyllium and acrylic acid based hydrogels

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Abstract

In order to utilize the psyllium husk a natural polysaccharide for developing new green polymeric materials for specialty applications, we have prepared psyllium and acrylic acid based polymeric networks by using *N*,*N*′-methylenebisacrylamide (*N*,*N*-MBAAm) as crosslinker. The polymeric networks thus formed have been characterized with scanning electron micrography (SEM), FTIR and Thermogravimetric Analysis (TGA) techniques to study various structural aspects of the networks. This paper discusses the swelling response of the polymeric networks as a function of time, temperature, pH and [NaCl]. Equilibrium swelling has been observed to depend on both structural aspects of the polymers and environmental factors. The swelling response indicates that these materials are potential candidates for use in colon specific drug delivery. Metal ion sorption shows that these polymeric networks can be used for removal, separation, and enrichment of hazardous metal ions from aqueous solutions and can play an important role for environmental remediation of municipal and industrial wastewater.

Keywords: Psyllium; Hydrogels; Metal ion sorption; Swelling behavior

1. Introduction

Psyllium is the common name used for several members of the plant genus *Plantago* whose seeds are used commercially for the production of mucilage. The mucilage obtained from the seed coat by mechanical milling/grinding of the outer layer of the seed and yield amounts to approximately 25% of the total seed yield. Mucilage is a white fibrous material that is of hydrophilic nature and forms the clear colorless mucilaginous gel by absorbing water. Gel-forming fraction of the alkali-extractable polysaccharides is composed of arabinose, xylose and traces of other sugars (Fischer et al., 2004).

Modification of carbohydrates is reported by graft copolymerization. The graft copolymerization of reactive pre-gelled starch with methacrylonitrile has been reported. The resultant copolymers when applied to cotton textile imparted it higher tensile strength and abrasion resistance than that was sized with original pre-gelled starch (Mostafa & Morsy, 2004). Flow behavior of sago starch-*g*-poly(AAc) prepared by the UV irradiation has been reported to be dependent on the extent of the UV treatment, degree of grafting and type of gelatinizing solvent, whereby the volume fraction of the granules varies in accordance with the swelling capacities (Lee, Kumar, Rozman, & Lee et al., 2004).

Crosslinking has been the common practice to improve the functional properties of the biopolymers to obtain functional three-dimensional polymeric networks those have different property profile than the native backbone. A novel biopolymer-based semi interpenetrating polymer network (IPN) of carboxymethyl cellulose (Bajpai et al., 2004) and kappa-carrageenan (Pourjavadi et al., 2004) with crosslinked poly-acrylic acid [poly(AAc)] has been prepared and its water-sorption capacity has been evaluated as a function of chemical architecture of the IPN, pH, and temperature of the swelling medium. The water uptake potential of the IPNs has also been investigated in inorganic salt containing aqueous solutions. Maximum water absorbency of the IPN was found to be 789 g/g and overall activation energy of the graft polymerization reaction was found to be 293 kJ/mol (Bajpai & Mishra, 2004; Pourjavadi, Harzandi, & Hosseinzadeh, 2004).

Modified polymers of renewable origin are environment friendly and offer highly cost effective technologies to enrich or separate metal ions from water system by binding, through adsorption, chelation and ion-exchange processes. Chemical modification of crosslinked starch with various reactive monomers yield ionomers those have been used to remove heavy metal ions from wastewater. The metal-ion

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complexation behavior and catalytic activity of 4 mol% (*N*,*N*-MBAAm) crosslinked poly(AAc) were investigated. The polymeric ligand was prepared by solution polymerization. The metal-ion complexation was studied with Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions. The metal uptake followed the order: $Cu^{+2} > Cr^{+3} > Mn^{+2} > Co^{+2} > Fe^{+3} > Zn^{+2} > Ni^{+2}$. The catalytic activity of the metal complexes was investigated toward the hydrolysis of *p*-nitrophenyl acetate. The Co^{+2} complexes exhibited high catalytic activity. The kinetics of catalysis was first order (John, Jose, & Mathew, 2004). Adsorption behavior of Zn^{2+} and Cu^{2+} on crosslinked amphoteric starches with quaternary ammonium and carboxymethyl groups in aqueous solutions was investigated. It was observed that adsorption capacity increase with the increase in the degree of substitution of the carboxymethyl groups. The adsorption followed a Freundlich adsorption isotherm (Cao et al., 2004; Xu et al., 2004). Two chemically modified starch derivatives; crosslinked amino starch and dithiocarbamates modified starch, were prepared and used for the removal of Cu^{2+} from aqueous solutions. Crosslinked amino starch was found to be effective for the adsorption of Cu^{2+}, which tended to form a stable amine complex (Li et al., 2004).

The chemical modification of mucilage of *Plantago psyllium* (Psy), a polysaccharide, is not much reported. Some work on the use of Psy grafted with polyacrylamide [poly(AAm)] (Agarwal et al., 2002) and polyacrylonitrile [poly(AN)] (Mishra et al., 2003) on Psy has been reported for use as flocculent. The flocculation efficiency of Psy-*g*-poly(AN) was tested against tannery effluents. The maximum extent of the suspended solid (SS) and total dissolved solids (TDS) removal was, respectively, reported to be 89% (pH 7.0) and 27% (pH 9.2), when treated with polymer dose of 1.2 mg/L for 3 h. Whereas water-soluble Psy-*g*-Poly(AAm) was reported to be more effective flocculant, capable of removing more than 93% of SS (in alkaline pH after 5 h) and 72% of TDS and 15.24% of color (in neutral pH treated after 3 h) from the textile wastewater using 1.6 mg/L of polymer (Agarwal, Srinivasan, & Mishra, 2002; Mishra et al., 2002; Mishra et al., 2004Mishra et al., 2004; Mishra, Yadav, Agarwal, & Rajani, 2004).

The present paper discusses the synthesis of Psy and AAc based hydrogels by using *N*,*N*-MBAAm as crosslinker and ammonium persulfate (APS) as initiator. The polymeric networks [Psy-*cl*-poly(AAc)], thus formed were characterized by SEM, FTIR, TGA, and swelling response of the hydrogels as a function of time, temperature, pH and [NaCl]. The hydrogels, thus prepared and well characterized have been used as metal ion sorbents.

2. Experimental

2.1. Materials and method

Plantago psyllium mucilage (Sidpur Sat Isabgol Factory, Gujarat, India), acrylic acid (Merck-Schuchardt, Germany), ammonium persulphate and *N*,*N*′-methylenebisacrylamide (S.D. Fine Mumbai, India) were used as received.

Table 1
Optimum reaction parameters for the synthesis of Psy-*cl*-poly(AAc)

Sr. No.	APS (mol/L)×10^2	Amt of water (ml)	Time (min)	Temperature (°C)	Max. P_s (after 24 h)
1	0.0	15	120	65	X
2	1.46	15	120	65	1518.0
3	2.92	15	120	65	1502.0
4	4.38	15	120	65	X
5	5.84	15	120	65	X
6	7.30	15	120	65	X
7	2.19	10	120	65	345.0
8	1.46	15	120	65	605.0
9	1.09	20	120	65	976.0
10	0.876	25	120	65	979.0
11	0.625	35	120	65	X
12	0.486	45	120	65	X
13	0.876	25	30	65	510.0
14	0.876	25	60	65	780.0
15	0.876	25	90	65	810.0
16	0.876	25	120	65	950.0
17	0.876	25	150	65	920.0
18	0.876	25	180	65	610.0
19	0.876	25	120	25	X
20	0.876	25	120	35	X
21	0.876	25	120	45	X
22	0.876	25	120	55	883.0
23	0.876	25	120	65	976.0
24	0.876	25	120	75	936.0

Psyllium = 1 g, where X indicates uncrosslinked polymer.

2.2. Synthesis of Psy-cl-poly(AAc)

The optimum reaction parameters were evaluated for the synthesis of Psy-*cl*-poly(AAc) by variation of ammonium persulfate (APS), reaction time, reaction temperature and amount of the solvent from the morphology and swelling behavior of the polymeric networks (Table 1). Reaction was carried out with 1 g of psyllium husk, 1.095×10^{-2} moles/L of APS, known concentration of monomer and crosslinker in the aqueous reaction system at 65 °C temperature for 2 h. Polymer thus former was stirred for 2 h in distilled water and for 2 h in ethanol to remove the soluble fraction and then was dried in air oven at 40 °C. Different polymeric networks were synthesized by varying [AAc] (from 1.45×10^{-1} to 7.25×10^{-1} moles/L) and by varying [MBAAm] (from 6.45×10^{-3} to 32.40×10^{-3} moles/L) to study the effect of monomer and crosslinker variation on the structure of three dimensional network and thereafter on the percent swelling of these polymeric networks.

2.3. Characterization

Psyllium and Psy-*cl*-poly(AAc) polymer were characterized by the following techniques.

2.3.1. Scanning electron micrography (SEM)

To investigate and compare surface morphology of psyllium and Psy-*cl*-poly(AAc), SEMs of these polymer were taken on Jeol Steroscan 150 Microscope.