



Sorption of Pb(II), Cu(II), Fe(II) and Cr(VI) metal ions onto cross-linked graft copolymers of chitosan with binary vinyl monomer mixtures



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ABSTRACT

Novel adsorbents for sorption of Pb(II), Cu(II), Fe(II) and Cr(VI) metal ions from waste water were synthesized by simultaneous cross-linking and graft copolymerization of chitosan (Ch) with N-isopropyl acrylamide (NIPAM) and its binary comonomers acrylic acid, acrylamide and acrylonitrile in presence of azo-bis(isobutyronitrile) (AIBN) as free radical initiator and *N,N'*-methylene bisacrylamide (MBA) cross-linker. FTIR, XRD, SEM and TGA/DTA techniques were used to describe the structural aspects of cross-linked graft copolymers. The improvement in swelling properties of the synthesized hydrogels was utilized to explore their potential for sorption of toxic metal ions from aqueous solutions. Metal ion sorption by synthesized cross-linked adsorbents was studied as a function of the change in contact time, pH, temperature and concentration of metal ions from a solution of individual metal ions. Selective sorption of metal ions was performed by immersing polymeric samples in a solution containing four metal ions in the same concentration. Candidate polymers showed preferential sorption of metal ions in order of Cu(II) > Pb(II) > Fe(II) > Cr(VI) ions. Cross-Ch-g-poly(NIPAM-co-AAc), Cross-Ch-g-poly(NIPAM-co-AAm) and Cross-Ch-g-poly(NIPAM), showed best results for sorption of all ions from single and four component solutions.

1. Introduction

Graft copolymerization [1] and cross-linking [2] of the synthetic monomer with desired functional groups onto natural polymers is of immense interest because of their application to industry and environment [3]. The modifications of biopolymers result into improvement in their properties like solubility, swelling, thermal stability etc. [4]. Chitosan is such a one of well-known biopolymer as it attracts enormous attention in recent times [5]. It is a hydrophilic biopolymer derived from chitin by its *N*-deacetylation in the presence of hot NaOH [6]. It is a copolymer of β -(1,4) linked glucosamine and *N*-glucosamine units [7]. The solubility of chitin is limited [8], but chitosan is soluble in acidic solution and behaves as cationic polymer due to the protonation of amino groups [9]. Chitosan has much imperative recompense as compared to other biopolymers including non-toxicity, biodegradability, biocompatibility etc. [10–11]. Also due to its bifunctionality (–OH and –NH₂), chitosan is known as an outstanding adsorbent for metal ions [12–13], it is chiefly competent for the uptake of transition metal ions like Cr(VI) [14], Fe(II) [15], Cu(II) [16], Pb(II) [17], Ni(II) [18], Zn(II) [19] etc. The retention capacity of chitosan is credited to

the ability of chelation or complex formation by amino groups of chitosan with the metal ions [20–22]. However, the properties of chitosan like strength, thermal stability, solubility etc. can be improved through graft copolymerization or cross-linking and result into the betterment of properties like swelling, metal ion uptake, flocculation etc. [23–25]. A number of researchers reported removal of hexavalent chromium through cross-linked chitosan [26–28]. Cross-linked chitosan-g-poly(butyl acrylate) biosorbent was synthesized for the removal of Cr(VI) from wastewater [29]. Chitosan-g-n-butyl acrylate [30], cross-linked-Ch-g-polyaniline [31], chitosan-cross-linked-poly(alginic acid) nano-hydrogel [32] were also reported for adsorption of Cr(VI) ions from the water bodies. Cross-linked chitosan beads [33], amino acid protected cross-linked chitosan [34] and epichlorohydrin cross-linked chitosan [35] were used for adsorption of copper(II) ions. Chitosan cross-linked with glutaraldehyde, epichlorohydrin and ethylene glycol diglycidyl ether were investigated for comparative adsorption behavior of Fe(II) and Fe(III) ions in aqueous solution [36] and cross-linked chitosan beads found to have enhanced retention capacity as compared to chitosan itself. The chitosan-based hydrogel was prepared by grafting of polyacrylic [37] and then used as the adsorbent to recover Ni(II)

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Table 1
Effect of N, N'-MBA on grafting of NIPAM onto chitosan^a.

Sr. no.	Amount of solvent		Conc. of AIBN moles/L $\times 10^{-2}$	Conc. of N,N'-MBA moles/L $\times 10^{-2}$	Conc. of Monomer [NIPAM] moles/L $\times 10^{-2}$	Time (h)	Temp. (°C)	P _g	%GE
	H ₂ O (ml)	Acetone (ml)							
1	15.0	5.0	2.5	0.00	110.463	1.5	80	376.06	150.424
2	15.0	5.0	2.5	0.312	110.463	1.5	80	266.67	106.668
3	15.0	5.0	2.5	0.625	110.463	1.5	80	310.11	124.044
4	15.0	5.0	2.5	1.25	110.463	1.5	80	443.30	177.320
5	15.0	5.0	2.5	2.50	110.463	1.5	80	518.10	207.240
6	15.0	5.0	2.5	5.00	110.463	1.5	80	450.10	300.040

^a Chitosan = 1 g.

Table 2
Grafting of binary monomer mixtures in presence of N, N'-MBA onto chitosan^a.

Sr. no.	Amount of solvent		Conc. of AIBN moles/L $\times 10^{-2}$	Conc. of N,N'-MBA moles/L $\times 10^{-2}$	Conc. of Monomers in moles/L $\times 10^{-2}$			Time (h)	Temp. (°C)	P _g	%GE
	H ₂ O (ml)	Acetone (ml)			NIPAM	CM	[CM]				
1	15.0	5.0	2.5	2.5	110.463	–	0.00	1.5	80	18.10	207.240
2	15.0	5.0	2.5	2.5	110.463	AAC	276.15	,	,	798.80	123.271
3	15.0	5.0	2.5	2.5	110.463	AAM	276.15	,	,	687.70	107.118
4	15.0	5.0	2.5	2.5	110.463	AN	276.15	,	,	633.21	116.613

^a Chitosan = 1 g.

from coexisting Cu(II) and Pb(II) ions. Comparative studies of removal of Cr(VI), Cu(II) and Ni(II) ions from aqueous solution onto cross-linked chitosan-g-acrylonitrile copolymer is also reported in the literature [38]. Ethylene diamine-grafted chitosan and triethylenetetramine-grafted chitosan copolymers were reported for removal of Fe(III), Cu(II), Cr(VI), Ni(II) and Zn(II) metal ions from water [39]. Chitosan with alginic acid was cross-linked by glutaraldehyde and was used as effective adsorbents for removal of Co(II), Cu(II), and Cd(II) from waste water. The anionic interaction between amino groups of chitosan and carboxyl groups of alginic acid makes the beads strong and durable for the adsorption of Cu(II), Co(II) and Cd(II) ions under acidic conditions [40]. Glutaraldehyde cross-linked chitosan through imine linkage between amine groups of chitosan and aldehyde group was reported for palladium recovery in acidic medium [41]. Chitosan-coated calcium alginate was used as adsorbents for removal of Pb(II) ions from aqueous solutions [42]. Poly(meth acrylamide) grafted cross-linked chitosan was investigated for removal of Pb(II) ion from aqueous solution [43]. Chitosan was cross-linked with epichlorohydrin and was reported for comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution [44]. Barbitol derivative cross-linked chitosan [45], cross-linked magnetic chitosan-phenylthiourea resin [46], magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde, cross-linked chitosan membranes [47] were prepared for removal of Hg(II) from water bodies by batch sorption experiments.

In this paper, chitosan is simultaneously grafted and cross-linked with NIPAM and binary vinyl co-monomers AAC, AAM and AN. The chemical modifications of cross-linked networks were explained by SEM, FTIR, TGA/DTA and XRD. The swelling properties of cross-linked grafted samples were performed at various pH in order to investigate sorption of Cr(VI), Fe(II), Cu(II) and Pb(II) ions from solution containing single and quaternary metal ions.

2. Experimental

2.1. Materials

All the chemicals used in this experimental work were of analytical grade. Chitosan (Ch) with 90% deacetylated and NIPAM (Sisco Research Laboratories Pvt. Ltd., Mumbai, India), AAM (Merck, Germany), AN, AAC and azo-bis(isobutyronitrile) (AIBN), Copper

sulphate, Ferrous sulphate, Potassium dichromate and Lead nitrate (SD Fine, India), N,N'-methylene bisacrylamide (MBA) (Ranbaxy, SAS Nagar, India) were used as received.

2.2. Synthesis of cross-linked graft copolymers

Free radical initiated grafting and cross-linking of NIPAM was performed onto chitosan in presence of AIBN as free radical initiator and MBA cross-linker. The concentration of MBA was varied from 0.00 to 5.00×10^{-2} mol/L for grafting of 110.463×10^{-2} mol/L NIPAM onto 1 g chitosan in H₂O:Acetone (15 mL:05 mL) solvent system, taking 2.50×10^{-2} mol/L of AIBN, for 1.5 h reaction time and at 80 °C reaction temperature (Table 1). Maximum P_g of 818.01 and % GE of 327.204 was obtained at 2.5×10^{-2} mol/L concentration of cross-linker MBA, but in absence of cross-linker 376.06 P_g and 150.464%GE was reported. Using 2.50×10^{-2} mol/L of MBA and 110.463×10^{-2} mol/L of NIPAM, a Binary monomer mixture of NIPAM with comonomers AAC, AAM and AN were grafted in molar ratio 1.0:2.5 with NIPAM. The remarkable increase in P_g and %GE was noticed for binary monomer mixtures, this may be because of the addition of cross-linker with binary monomers during graft copolymerization results into inter-linking of all the polymeric chains forming a massive network of the chains intertwined together. The P_g and %GE of Cross-Ch-g-poly(NIPAM-co-AAC) were 1098.8 and 169.568, in the case of Cross-Ch-g-poly(NIPAM-co-AAM) was 887.7 and 138.271 and in the case of Cross-Ch-g-poly(NIPAM-co-AN) was reported 833.21 and 153.446 respectively (Table 2). The proposed structure of grafted chitosan and cross-linked graft copolymer of chitosan is represented in Fig. 1. As the reaction product consists of a mixture of homopolymers and cross-linked graft copolymer, solvent extraction technique was utilized to separate cross-linked graft copolymer from the homopolymers by stirring the product with the solvent in which homopolymers were soluble. The product after stirring is dried at low temperature and this method of extraction of the homopolymer is repeated till constant weight of the product was obtained. The homopolymer poly(NIPAM) was removed by stirring the synthesized products in water. Homopolymers of NIPAM and comonomers were separated by using different solvent systems such as H₂O for poly(NIPAM-co-AAM) and poly(AAM); H₂O-methanol for poly(NIPAM-co-AAC) and poly(AAC). Whereas H₂O-DMF solvents were used one after the other for

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