



# Grafting polymerization of acrylic acid onto chitosan-cellulose hybrid and application of the graft as highly efficient ligand for elimination of water hardness: Validation of high selectivity in presence of interfering ions

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## ABSTRACT

Graft Copolymer resulting from polymerization of acrylic acid from chitosan is non-coherent, brittle and exhibit modest swelling in water, which limits its application. Chitosan-cellulose hybrid was initially prepared and novel polymeric ligand ((CTS/Cell)-g-PAA) derived from grafting polymerization of acrylic acid from this hybrid was fabricated and investigated using fourier transform infrared (FTIR) and Scanning electron microscopy (SEM). Also, the graft copolymer exhibited high mass transfer under a wide range of pH values due to its elevated hydrophilicity in addition to a good mechanical strength with respect to the comparable graft derived from chitosan as sole backbone for the grafting. The high content of different oxygen and nitrogen-containing groups in a crowded chemical atmosphere along with the high swelling qualified the graft to act as very efficient polymeric ligand with high capacity of removal of metal ions from water under broad conditions. The polymeric ligand performed outstandingly and competitively in the removal of water hardness even in presence of other interfering ions.

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## 1. Introduction

Polymeric hydrogels are defined as hydrophilic networks with three dimensional structures [1,2]. They can absorb water amounts up to many several times of their weight as a result of their huge number of hydrophilic function groups [3–9].

Grafting polymerization is a very important method among the devoted methods for preparation of hydrogels. It proceeds by initial linking of vinyl monomer onto the surface of a backbone such as chitosan [8–13] or cellulose [14,15] followed by its polymerization from the surface [16–22].

Chitosan is a partially deacetylated chitin, which contains both amino and hydroxyl groups. This renders it entitled for a variety of complicated reactions. Also, cellulose belongs to natural linear carbohydrate polymers and is considered as the most abundant biopolymer in nature [23].

Chitosan-based hydrogels reveal poor mechanical strength which provoked many authors attempt to augment its strength and handling [24–29]. Most of these trials focused on blending chitosan with cellulose or one of its derivatives as reinforcing matter. However, the strength

was found not to be satisfactorily improved if the miscibility between components is not sufficient in the sense of developed hydrogen bonding.

The current work aims to treat the poor mechanical properties of chitosan-based graft copolymers through linking chitosan and cellulose using an amino resin, thiourea-formaldehyde resin (TUFR). The crosslinking using the amino resin contributes to obtaining of a more robust hybrid. The new hybrid can serve as excellent backbone for grafting polymerization of acrylic to be initiated from its surface in presence of a crosslinker.

Many techniques [30–40] were elaborated for softening of water from ions like  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ . However, extensive use of chemicals and addition of acids for pH adjustment make the operation costs using such techniques too high [41,42]. On the other hand, adsorption is regarded as the most promising existing purification technique for water considering practicality, cost effectiveness and simplicity.

As hydrogels can be utilized as adsorbent for metal ions from aqueous solutions due to presence of groups known for their high potential to bind metal ions ( $-\text{COOH}$ ,  $-\text{NH}_2$  and  $\text{OH}$ ) [43]. The unique features present in the developed graft copolymer of the current study are proposed to enrich the field of water purification from toxic ions through high adsorption capacity either on competitive or non-competitive basis. The successive crosslinking reactions encountered during preparation are expected to

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result a multitude of active function groups in this compact structure, which is expected to impart selectivity during competitive adsorption. In particular, the selectivity in company with ease of preparation, cost effectiveness, improved strength and reusability, make such graft copolymer hydrogel farther advantageous with respect to other similar developed materials so far [18,36–38,43].

## 2. Experimental

### 2.1. Materials

Acrylic acid (AA) and ammonium persulfate (APS) were purchased from Sigma-Aldrich, USA. Chitosan (CTS, with deacetylation above 85%) was purchased from Euromedex, France. Cellulose pure powder (Cell) and potassium hydroxide were supplied from S.d. fine Chem., India. *N,N'*-methylenebisacrylamide (*N,N'*-MBA) was ordered from Merck, Germany. Calcium chloride ( $\text{CaCl}_2$ ), magnesium sulfate ( $\text{MgSO}_4$ ) and sodium chloride (NaCl) of analytical grade from Merck, were used in the preparation of stock standard solutions (1000 mg/L). Various concentrations of metal ion in aqueous media were prepared by dilution from stock standard solutions. Unless specified, other chemicals were analytical grade.

### 2.2. Hybridization of chitosan and cellulose

Huang et al. [44] applied an easy process to chemically link both chitosan and cellulose, which can be summarized as follows: 1.2 g of chitosan was dissolved in 100 mL of 2 wt% aqueous solution of acetic acid. Another cellulose suspension was prepared by dispersing 1.2 g of its powder in 100 mL distilled water under vigorous stirring at ambient temperature. The chitosan solution was filtered and the solutions were mixed and stirred together at room temperature for one day. The resulting suspension was poured into a glass plate and dried at room temperature for several days until a film was removed out from the plate. Crosslinking of the film was achieved by immersion in a homogeneous solution combining 2.5 wt% thiourea, 2.2 g formaldehyde solution (37%), and 2.5 wt% sulfuric acid solution dissolved in 100 mL of ethanol-water (1:1) mixture at room temperature for 2 h. About four washing cycles were employed to the film using distilled water before drying at room temperature for 48 h. The film was mechanically disintegrated and sieved into pieces of 75  $\mu\text{m}$  size or less of (CTS/Cell) hybrid.

### 2.3. Graft copolymerization onto (CTS/cell) hybrid

The graft copolymer was fabricated according to a well-established procedure [45–48]. In a three-neck flask equipped with reflux condenser, funnel, and nitrogen line, the crosslinked CTS/Cell hybrid (1 g) was dispersed in about 30 mL of distilled water while keeping vigorous stirring. Then, nitrogen was flushed in the system for 30 min. Afterward, the initiator APS (0.1 g) was inserted to generate free radicals on the surface of the hybrid. 15 min later, a mixture including 3.60 g acrylic acid and 0.1 g *N,N'*-MBA as crosslinker was charged to the solution. The agitation continued for 3 h while the temperature was maintained at 70 °C to ensure almost full polymerization of the monomers. Later, cooling down to room temperature was undertaken and 1 mol L<sup>-1</sup> KOH solution was used to adjust the pH to neutrality. Washing with a large amount of distilled water was performed to get rid of any lasting species and drying was undergone at 70 °C. The produced graft ((CTS/Cell)-g-PAA) was milled to a size of 400–840  $\mu\text{m}$ .

### 2.4. Evaluation of the grafting polymerization

FTIR spectrophotometer (Jasco, Model 6100, Japan) was employed to record the related IR spectra of the samples at a resolution of 4 cm<sup>-1</sup>. The samples were dried and mixed with KBr then shaped into

discs using a press before the acquisition. The surface morphology of the graft copolymers was investigated using SEM-EDS (JSM-5500LV, JEOL, Ltd.) operated in a vacuum mode after gold coating of the samples using a sputter Coater (SPI-Module). Zeta potential measurements of the samples were achieved using NICOMP 380 ZLS dynamic light scattering (DLS) (Santa Barbara, CA, USA) with 632 nm line of HeNe laser as the incident light, angle 90° and zeta potential of external angle 18.9°. The dispersions were diluted with distilled water adjusted to different pH values and the measurements of zeta potential were recorded and presented as average value of three readings.

### 2.5. Evaluation of the graft copolymer for potential use in metal ions removal

The graft copolymer was added as a ligand to solutions containing the different metal ions either separately or combined while a mechanical shaker was operated continuously at 120 rpm to make sure of homogeneity and ultimate contact between the solutions and the graft. Contact time, graft dose, metal ions concentrations, temperature and pH were set as system variables. Levels of the metal ions were then determined in solutions after filtration with Whatman® filter papers (No. 44) using inductive coupled plasma optical emission spectrometry (Agilent ICP-OES 5100, Australia) according to a well-established procedure for examination of water [49]. The removal processes were undergone in triplicates and the efficacy of metal ions uptake (%) by the polymeric ligand was evaluated according to a simple formula:

$$R, \% = \frac{C_o - C_f}{C_o}$$

where  $C_o$  and  $C_f$  (mg/L) are the initial and final concentrations of metal ions in solution, respectively.

## 3. Results and discussion

### 3.1. Investigation of the grafting process

Polymeric grafts containing chitosan units are promising because of their high water absorption, which permits fast diffusion. Furthermore, such materials have high ability to go through succeeding regenerations [50,51]. However, the expansion of their use is not that high as a result of the insufficient mechanical strength and weak resistance at acidic pH values [52]. Many efforts were undergone to surmount such drawbacks. Chemical combination of chitosan with cellulose was among the available options. Cellulose was mainly suggested because it is a cheap naturally abundant material. The mechanical strength and similarity of its chemical composition afford principally a good way for obtaining a homogeneous hybrid with high strength and chemical activity, which permit prominent regeneration ability for the grafts based on this hybrid [53].

Crosslinking of chitosan and cellulose can be undergone chemically with a variety of reagents such as glutaraldehyde, ethylene glycol diglycidyl ether or epichlorohydrine [54]. The current work uses thiourea formaldehyde (TUF) as a type of amino resin crosslinker. Amino resins are known to bind cellulosic matter with polyhydroxy compounds [16]. The crosslinking process can be well controlled by regulation of pH and time of polycondensation. A straightforward grafting polymerization of acrylic acid was then undertaken from the produced hybrid. It is expected that the grafted macromolecular chains with COOH end groups on the resulting crosslinked backbone can additionally bind the cellulose and chitosan through condensation reactions, radical terminations as well as hydrogen bonds, which improve the strength and handling.

Fig. 1 reveals the chitosan can be connected to cellulose by employing thiourea formaldehyde (TUF) resin as binder [50]. The produced hybrid is liable to serve as a base from which acrylic acid can be

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