Journal of Environmental Chemical Engineering 6 (2018) 2137–2147

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Grafting polymerization of acrylic acid onto chitosan-cellulose hybrid and application of the graft as highly efficient ligand for elimination of water hardness: Adsorption isotherms, kinetic modeling and regeneration

Xiaojian Zhou[a], Hisham A. Essawy[b,*], Magdy F. Mohamed[c], Hanan S. Ibrahim[d], Nabila S. Ammar[d]

[a] *Yunnan Provincial Key Laboratory of Wood Adhesives and Glued Products, Southwest Forestry University, Kunming, China*
[b] *Department of Polymers and Pigments, National Research Centre, Dokki 12622, Cairo, Egypt*
[c] *Delta Agrochemicals Company, Giza, Egypt*
[d] *Department of Water Pollution, National Research Centre, Dokki 12622, Cairo, Egypt*

ARTICLE INFO

Keywords:
Chitosan-cellulose
Acrylic acid grafting
Water hardness
Removal

ABSTRACT

Grafting copolymerization of acrylic acid from chitosan-cellulose hybrid ((CTS/Cell)-g-PAA) was conducted and the grafting efficiency and crosslinking level were optimized at 86.5% and 2.5%, respectively. Investigation using scanning electron microscopy (SEM) indicated a mechanically robust material with a porous surface which allows diffusion. This property along with the high water absorption under wide range of pH values qualified the material for application as adsorbent/ligand to metal ions from aqueous solutions. This was additionally signified using fourier transform infrared (FTIR) spectra collected for the graft before and after chelation to metal ions that cause water hardness, which confirmed that the oxygenated and nitrogenated groups are the main sites for binding metal ions in high capacity with removal efficiency above 90% in most cases. Application of Langmuir and Freundlich adsorption isotherm models for the metal ions on the graft copolymer indicated that the adsorption data are better fitted by Freundlich model for all metal ions while a chemisorption nature of adsorption was deduced by a kinetic modeling study. Further, the adsorption was highly favoured in case of Ca(II) and Mg(II) while to a much lesser extent in case of Na(I). The polymeric ligand showed also outstanding performance during competitive removal of a mixture of metal ions from aqueous solution with a selectivity order Ca(II) > Mg(II) > > Na(I), such selective removal activity of the ligand was almost not influenced after induced desorption and reuse for additional four succeeding cycles.

1. Introduction

Polymeric superabsorbents are characterized by high absorption levels of water in short time [1,2]. This makes them largely liable for utilization in various fields [3–5]. Graft polymerization is considered as one of the most important methods devoted for preparation of superabsorbents by polymerizing vinyl monomers onto natural bio-based materials such as starch [6,7], chitosan [8–11], sodium alginate [12], carrageenan [13], and cellulose [14,15]. This gives rise to unique characteristics including low toxicity, antibacterial, enhanced chemical activity and reduced cost [16–21].

Chitosan is a natural polysaccharide containing free amino and hydroxyl groups which entitles it for crosslinking and chelation reactions. Chitosan was utilized as backbone for grafting polymerization of acrylic acid and yielded materials that exhibited superabsorbency [22], while cellulose is another material belonging to natural linear carbohydrate polymers and considered as the most abundant biopolymer, present mostly in wood, cotton and other sources [23]. Superabsorbents made from chitosan lonely exhibit weak mechanical strength therefore limited possibility of reusability is encountered. This induced other researchers for blending it with cellulose or other reinforcing materials such as attapulgite, hydroxypropyl cellulose, muscovite or pillared clay, before grafting [24–29]. However, this route was associated by a drop in water absorption and mass transfer. In addition, the chemical activity was not that high as for superabsorbents constructed from chitosan and its blends with analogous structures.

The need for fresh water in some areas of the world exceeded the natural capacity in particular that the fast population growth and growing spending of per capita caused further limitations of the world's resources of fresh water which imposes an extreme need in few years to get fresh water from conversion of sea water via desalination. However, this will be far too expensive and impractical for wide use. Thus, it is

* Corresponding author.
E-mail address: ha.el-fatah@nrc.sci.eg (H.A. Essawy).

https://doi.org/10.1016/j.jece.2018.03.022
Received 25 November 2017; Received in revised form 9 March 2018; Accepted 10 March 2018
Available online 11 March 2018
2213-3437/

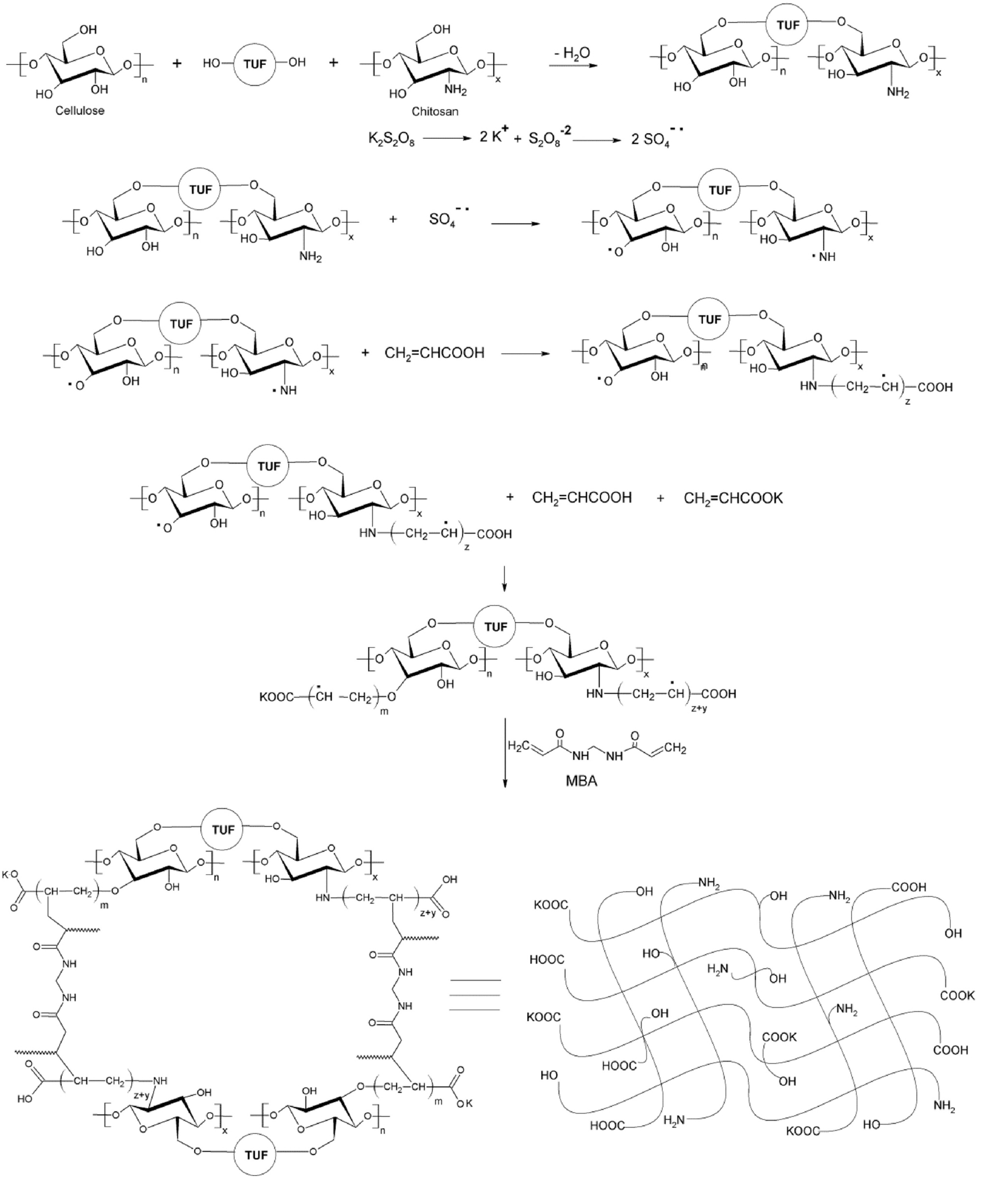

Fig. 1. A simplified scheme for cellulose–chitosan combination via chemical crosslinking using thiourea formaldehyde and use of their hybrid as precursor for preparation of a polymeric ligand ((CTS/Cell)-g-PAA) via graft copolymerization of acrylic acid in presence of MBA as a crosslinker.

necessary to make maximum avail of the present resources of natural water. Unfortunately, dissolved salts of different concentrations are usually included in natural waters. Additionally, industry produces water contaminated with salts, which renders it unsuitable for drinking. Consequently, reducing salts content in water is an essential issue to avoid serious health problems associated with their accumulation in human organs, e.g., disorder of the nervous system, high blood pressure, anemia, weakness in fingers and wrists, etc.

Various techniques have been broadly employed for softening of water from existing divalent ions such as Ca(II) and Mg(II) [30–40]. Two major methods are typically applied to remove hardness form water, namely using lime soda and ion exchange. The main disadvantages of the lime soda method are the production of a high sludge volume which requires post-treatment, too much use of chemicals and