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Research article

Biodegradable and conducting hydrogels based on Guar gum polysaccharide for antibacterial and dye removal applications

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ABSTRACT

Conducting hydrogels possessing antibacterial activity were developed using a two-step free-radical aqueous polymerization method to incorporate polyaniline chains into an adsorbent Guar gum/acrylic acid hydrogel network. The material properties of the synthesized samples were characterized using FTIR spectroscopy, thermal analysis and scanning electron microscopy techniques. Conducting hydrogels were tested for antibacterial activities against gram-positive *Staphylococcus aureus* and gram-negative *Escherichia coli* bacteria and demonstrated antibacterial activity. Synthesized hydrogel samples can be potential adsorbent materials for dye removal applications.

1. Introduction

Hydrogels are polymer networks possessing the ability to absorb water-based fluids, swelling to form a hydrated interlinked network (Shi et al., 2011 Peppas et al., 2000). The water-induced swelling of the network depends on the type of polymer backbone, monomeric composition and extent of cross-linking (Mundargi et al., 2007a, 2007b; Zhang et al., 2005). Modifications of crosslinked hydrogels with conducting polymers (CPs) lead to multifunctional electrically conductive materials that retain the beneficial absorption properties of hydrogels (Fan et al., 2008). Polyaniline (PANI) is an attractive conductive polymer because of its simple methods of synthesis, high stability, variable structure, as well as unique optical, magnetic, electrical, electrochemical and electromechanical properties (Karami et al., 2003; Malhotra et al., 1990; Tiwari et al., 2013; Prokes and Stejskal, 2003; Han et al., 2002). Other useful characteristics include the varied physiochemical properties of different forms of PANI (Feast et al., 1996), as well as the tunable conductivity of PANI, which can be controlled by the protonation of the imine sites present on the main polymer chain (Pron et al., 1988; Syed and Dinesan, 1991; Cortes and Sierra, 2006). Such polymers have potential applications in numerous fields such as the removal of dyes from wastewater (Perju and Dragan, 2010), bioactive electrode coatings (Rylie et al., 2010), electrochemical devices (Zhao et al., 2013) and super capacitors (Ghosh and Inganas, 1999). Such cross-linked polymer networks are gaining importance due to their applications in a variety of different fields including biomedical and environmental engineering, agriculture and water purification (Thakur and Thakur, 2014; Liu et al., 2014).

One of the most environmentally significant applications of hydrogels is in their uses for reducing industrial contamination of natural water sources. Industries such as dye, textile, paper, plastic, plating and mining can release effluents containing toxic pollutants and heavy metals, which may be extremely harmful to people and the environment. Many dyes and pigments are toxic and have carcinogenic and mutagenic effects that influence the environment and human life also. Different adsorbents have been used for removing colored effluents from aqueous solutions. Absorption of pollutants by hydrogel swelling, an inexpensive and simple design, can be used to remove dye contamination from aqueous

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environments. The presence of ionic groups in the superabsorbent hydrogel polymer structure can also increase loading due to larger space for liquid uptake due to ion–ion repulsion (Jiuhui, 2008). Hydrogels are three-dimensional cross-linked polymer networks of flexible chains, which are able to absorb and retain water and solute molecules. The possibility of using hydrogel as a potential adsorbent is due to the presence of ionizable carboxylic and hydroxyl groups in the polymer network.

Şenay et al. (2015) have recently developed a new morphological approach for removing acid dye from leather wastewater. They synthesized p(HEMA–GMA) poly(hydroxyethyl methacrylate-co-glycidyl methacrylate) spherical particulated membranes by UV-photopolymerization. Synthesized membranes were coupled with iminodiacetic acid, chelated with Cr(III) ions as ligand and used for removing acid dye. Adsorption properties of the membranes were investigated under different conditions and results showed that the metal-membranes were effective sorbent systems removing acid dye from leather wastewater.

Several options of decolourisation of textile wastewater by chemical means have been suggested by Verma et al. (2012). The direct discharge of wastewater into environment affects its ecological status by causing various undesirable changes. Researchers and industries are finding novel solutions for developing technologies that can reduce the environmental damage. Color removal from textile wastewater by means of cheaper and environmental friendly technologies is still a major challenge. They have emphasized and encouraged the use of natural materials as the viable alternative because of their eco-friendly nature.

Guar gum polysaccharide is a biodegradable, non-toxic, low cost and renewable raw material and can potentially be used for high performance applications. Research work on the graft copolymerization of vinyl monomers onto Guar gum (Ggum) was reported (Kono et al., 2014; Pandey et al., 2014; Shahid et al., 2013; Yadav et al., 2013; Tiwari, 2007; Tiwari and Singh, 2008), but there is scant information in literature about the synthesis of Ggum-cl-poly(AA/PANI) conducting interpenetrating networks (IPNs). Therefore, Guar gum-acrylic acid (AA) based crosslinked hydrogels were interpenetrated with PANI and evaluated for conductivity, antibacterial properties and dye adsorption application.

2. Materials and methods

2.1. Materials

Guar gum (Ggum) and ammonium persulfate (APS) were purchased from Loba-Chemie Pvt. Ltd. Hexamine and acrylic acids (AA) were purchased from S D Fine-Chem Pvt. Ltd. Aniline,1-methyl-2-pyrrolidone and acetone were procured from Merck India. Methylene blue (MB) dye used for the dye adsorption study was purchased from Sigma–Aldrich. Gram-positive *Staphylococcus aureus* (MTCC 737) and gram-negative *Escherichia coli* (MTCC 739) used for antibacterial investigations were obtained from the Microbial Type Culture Collection and Gene Bank (MTCC).

2.2. Synthesis of Ggum-cl-poly(AA-ipn-aniline) IPN

Guar gum (1 g) was mixed with 17.5 mL of distilled water followed by the addition of a calculated amount of APS (0.262×10^{-1}mol L^{-1}) as an initiator and hexamine (0.356×10^{-1}mol L^{-1}) as cross-linker. Acrylic acid (0.145×10^{-3}mol L^{-1}) was added drop-wise to the solution with continuous stirring to improve homogeneity. The resulting solution was incubated at 60 °C for 3 h and the final product was washed with distilled water in order to remove unreacted homopolymer and then dried in a vacuum oven. Ggum-cl-poly(AA) was used for the preparation of Ggum-cl-poly(AA-ipn-aniline) under neutral (undoped) and acidic (doped) conditions. Different reaction parameters were tested at a range of values to get the maximum percentage swelling in the resultant hydrogel at optimum concentrations. The percentage swelling (P_s) was calculated using the following equation (Kaith et al., 2012),

$$P_s = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

Where, W_s and W_d are the weight of the swelled and dry samples, respectively.

The reaction parameters were varied in following manner; initiator concentration: 0.0131–0.0306 mol L^{-1}, reaction time: 120–240 min, solvent volume: 15–25 mL, monomer concentration: $0.145–0.729 \times 10^{-3}$ mol L^{-1}, pH: 3–7, reaction temperature: 50–90 °C, crosslinker concentration: 0.0214–0.0499 mol $L^{-1}$and aniline concentration: $0.109–0.767 \times 10^{-3}$ mol L^{-1}in case of both neutral (undoped) and acidic (doped) conditions. Doping was carried out in different concentrations of aqueous HCl varying from 0.5 N to 2.5 N.

One gram of Ggum-cl-poly(AA) was added to optimized aniline monomer in aqueous solution for the synthesis of IPNs under neutral (undoped) condition. Optimized amount of APS and hexamine were added with continuous stirring at 80 °C for 150 min. Progress of the reaction was visually assessed by the color change caused by the formation and protonation of PANI chains. The resulting IPN, Ggum-cl-poly-(AA-ipn-aniline), was washed with 1-methyl-2-pyrrolidone to remove the unreacted homopolymer and finally the product was dried in oven at 50 °C. A similar procedure was followed to synthesize Ggum-cl-poly(AA-ipn-aniline) under acidic (doped) conditions (0.5 N aqueous solution of HCl) and summary of these optimized conditions can be found in Table 1.

2.3. Instrumental analysis

The Fourier transform infrared (FTIR) spectrums of the samples were recorded with a Model 8300 Shimadzu IR spectrophotometer. Thermal behavior of samples was assessed using a Shimadzu Simultaneous Thermal Analyzer from 50 to 700 °C in a nitrogen atmosphere with a heating rate of 10 °C/min. Scanning electron microscope (SEM) images were obtained using a Jeol Steroscan 150

Table 1
Optimized process parameters for the synthesis of Semi-IPNs and IPNs.

Sample	Optimized reaction parameters							P_s
	Initiator [APS] $\times 10^{-1}$ mol L^{-1}	Time (min)	Solvent (ml)	Monomer $\times$ mol L^{-1}	pH	Cross-linker [hexamine] $\times 10^{-1}$ mol L^{-1}	Temp. (°C)	
Ggum-cl-poly(AA)	0.262	150	17.5	0.145×10^{-3}	7	0.356	80	2345.06
Ggum-cl-poly(AA-ipn-aniline)-undoped	0.262	150	17.5	0.548×10^{-3}	7	0.356	80	666.60
Ggum-cl-poly(AA-ipn-aniline)-doped	0.262	150	17.5	0.329×10^{-3}	7	0.356	80	306.06