International Journal of Biological Macromolecules xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Effective removal of cationic dyes from aqueous solution using gum ghatti-based biodegradable hydrogel

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ARTICLE INFO

Article history:
Received 10 February 2015
Received in revised form 27 March 2015
Accepted 8 April 2015
Available online xxx

Keywords:
Gum ghatti
Adsorption
Isotherms
Kinetics
Methylene blue
Methyl violet
Biodegradation

ABSTRACT

Biodegradable hydrogels of gum ghatti (Gg) with a co-polymer mixture of acrylamide (AAm) and methacrylic acid (MAA) (termed as Gg-cl-P(AAm-*co*-MAA)) were synthesised by microwave-assisted free radical graft co-polymerisation technique. The hydrogel polymer was characterized by FTIR, SEM, and Brunauer–Emmett–Teller. The Gg-cl-P(AAm-*co*-MAA) was studied as an adsorbent for the removal of methylene blue (MB) and methyl violet (MV) from aqueous solutions. Both the dyes followed pseudo-second-order kinetics and Langmuir adsorption isotherm models. The hydrogel polymer adsorbed 98% of MB and 95% of MV from aqueous solution. The Gg-cl-P(AAm-*co*-MAA) maintained its original sorption capacity for three cycles of adsorption-desorption. Furthermore, the hydrogel polymer degraded fully within 50 days in soil compost. In summary, the Gg-cl-P(AAm-*co*-MAA) hydrogel could be a potential adsorbent for the remediation of dyes from industrial wastewater.

1. Introduction

Water pollution by various pollutants, such as synthetic dyes, heavy metal ions, and other organic contaminants, is a serious environmental threat to the eco-system [1]. The contamination of water by synthetic dyes affects the microbial activities of aquatic organisms and reduces photosynthetic activity by decreasing the transparency of water [2]. Moreover, some synthetic dyes are carcinogenic and mutagenic, so they have adverse effects on human health. Synthetic dyes are visible pollutants because minute amounts can be observed in water. Many industries, such as the textile, leather, plastic, cosmetics, food, and pharmaceutical industries, use synthetic dyes on a large scale and generate a large amount of colored effluents. The discharge of this effluent without proper treatment contaminates different water bodies. Treatment of dye-contaminated water is very difficult because dyes have high solubility and stability in water. Most synthetic dyes are non-biodegradable and cannot be degraded in municipal treatment plants [3].

Methylene blue (MB) and methyl violet (MV) are toxic cationic dyes. MB has many industrial applications include coloring paper and dyeing clothes and wool, as a hair colorant, as a photosensitizer, and redox indicator in analytical chemistry. MB is not highly hazardous; however, high concentrations of MV can cause many harmful effects, such as hypertension, precordial pain, fever, mental confusion, staining of skin, decoloration of urine, cyanosis, and anaemia [4]. MV has been used in large quantities in the textile and paper dyeing industries and as a pH indicator. Compounds related to MV are considered to be highly carcinogenic, mutagenic, and mitotic poisons. Some forms of MV also inhibit the growth of many gram-positive bacteria and have the tendency to bind to DNA; sometimes the binding causes replication errors in living tissue and results in mutation and cancer [5]. Therefore, to avoid the adverse effects of MB and MV on human health and even on the eco-system, it is very important to remove the dyes from the contaminated wastewater.

Previously, dye-polluted water was treated using various methods, such as adsorption, coagulation/flocculation, photocatalysis, chemical oxidation, and microbiological or enzymatic degradation [6,7], but most of these methods are ineffective for the complete removal of dyes from aqueous solutions. Moreover, these methods have been associated with some challenges, such as high operational costs, low selectivity, and the generation of secondary waste. Among water treatment technologies, adsorption is the best method studied to date for the removal of synthetic dyes from wastewater [8]. Different adsorbents including kaolinite [9], reduced graphene oxide-based hydrogels [10], sand from

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http://dx.doi.org/10.1016/j.ijbiomac.2015.04.045
0141-8130/

the Sahara desert [11], porous silicon [12], and metal hydroxide sludge [13] have been used for the removal of cationic dyes from aqueous solutions. However, most of these adsorbents have drawbacks, such as being non-biodegradable nature, expensive, low in adsorption capacity and slower kinetics. To overcome these drawbacks, biopolymers-based polymers have been used as adsorbents [14–17]. Unmodified biopolymers have very poor mechanical properties, so they cannot be used repeatedly as adsorbents. Therefore, the biopolymers have been modified with synthetic monomers, such as acrylic acid and acrylamide, through graft co-polymerisation to improve their properties. Graft co-polymers of biopolymers with some synthetic monomers have shown potential as adsorbents [18]. The main advantage of these graft co-polymers is that they combine the properties of both the biopolymers and the synthetic monomers. Ghorai et al. [19] successfully utilised the xanthan gum and nanosilica-based hydrogel nanocomposites for the effective removal of Congo red (CR) dye from aqueous solution. In another study, a guar gum and cerium (IV) tungstate-based hydrogel nanocomposite was employed for the adsorption of MB from aqueous solution and an adsorption capacity of 120.68 mg g^{-1} [20].

Gum ghatti (Gg) is an anionic gum polysaccharide and is composed of the sugars L-arabinose, D-galactose, D-mannose, D-xylose, and D-glucoronic acid in the molar ratios of 48:29:10:5:10. The main chain of Gg contains alternating 4-O-subsituted and 2-O-subsituted α-D-mannopyranose units and chains of 1 → 6 linked β-D-galactopyranose units; the side chains are most frequently single L-arabinofuranose residues [21]. Because of the abundance of anionic functionalities in the structure of Gg, Gg has potential applications in the adsorption of cationic impurities from aqueous solution. The synthesis of graft co-polymers using conventional methods was observed to be time consuming and the synthesised products have a high cross-linking density and fewer adsorption sites. In contrast, graft co-polymers synthesised using microwave-assisted graft co-polymerisation have a lower cross-link density and more adsorption sites because of the much shorter exposure time [22]. Furthermore, graft co-polymers with binary monomer mixtures were observed to have much longer grafted polymer chains and exhibit much better swelling capacity than graft co-polymers with single monomers [23–25].

Previously, gum polysaccharides based hydrogel polymers were used as adsorbents for the removal of different pollutants from the aqueous solution but most of them were either found to be non-biodegradable in nature or they showed very low adsorption efficiency [26,27]. The hydrogel polymer of gum arabic with glycidyl methacrylate, polyacrylate, and PAAm showed very less adsorption capacity (48 mg L^{-1}) for the adsorption MB [26]. In another study, the non-biodegradable hydrogel polymer of alginate having the magnetic nanoparticles and the activated carbon showed only 290 mg L^{-1} adsorption capacity for the adsorption of MB [27]. Therefore, in order to get better adsorption efficiency, here we have reported on the synthesis of fully biodegradable hydrogel polymer of Gg and the co-polymer mixture of the acrylamide (AAm) and methacrylic acid (MAA) via microwave-assisted graft co-polymerization technique and the synthesized hydrogel polymer was used for the highly effective removal of MB and MV from aqueous solution.

2. Experimental

2.1. Materials and methods

Gg, AAm, MAA, N,N′-methylene-bis-acrylamide (MBA), potassium persulphate (KPS), ascorbic acid (ABC), MB, and MV were purchased from Merck (South Africa) and were used as received. All other chemicals were of analytical grade and were used without further purification. Stock solutions of MB (1000 mg L^{-1}) and MV (1000 mg L^{-1}) were prepared by dissolving appropriate amounts of MB and MV, respectively, in distilled water. The solutions at different working concentrations were prepared by further diluting the stock solutions with distilled water.

2.2. Synthesis of the Gg-cl-P(AAm-co-MAA) hydrogel

The cross-linked hydrogel of Gg with the co-polymer mixture of P(AAm-*co*-MAA) was synthesized using KPS-ABC as a redox initiator and MBA as a cross-linking agent through microwave assisted graft polymerisation. For the synthesis of the Gg-cl-P(AAm-*co*-MAA) hydrogel, AAm was used as the principal monomer and MAA was used as the secondary monomer, and the graft co-polymerisation was conducted under different optimised reaction parameters to synthesise hydrogel of Gg with PAAm, as described in our previous publication [24,28]. Briefly, the reaction conditions were used as follows: time = 90 s, distilled water = 10 mL, pH = 7.0, initiator molar ratio (KPS:ABC) = 1:0.5, MWP = 80%, [AAm] = 0.9859 mg L^{-1}, and [MBA] = 0.0974 mg L^{-1}. First, 1.0 g of Gg was dissolved in 30 mL of deionised water in a 100 mL beaker and was undisturbed for 24 h. Afterwards, 30 mg of KPS and 20 mg of ABC were added to the reaction mixture, the mixture was stirred continuously, and AAm and MAA were added. The concentration of AAm (0.9859 mg L^{-1}) was kept constant whereas the concentration of MAA was varied from 3.51 to 8.201 mg L^{-1}. In the last step, 0.0974 mg L^{-1} of MBA was added with continuous stirring, and the reaction vessel was placed in the microwave reactor. After 90 s, the reaction vessel was removed from the microwave oven and was allowed to cool at room temperature. The unreacted monomers and homopolymers were separated by Soxhlet extraction with acetone. Finally, the synthesised graft co-polymer i.e. Gg-cl-P(AAm-*co*-MAA) was dried at 50 °C in a hot air oven until a constant weight was achieved.

2.3. Characterization

The Gg and the Gg-cl-P(AAM-*co*-MAA) hydrogel polymer were characterized by means of FTIR and SEM. The successful graft co-polymerisation and the formation of a cross-linked network between Gg and the co-polymer mixture of P(AAm-*co*-MAA) were demonstrated by FTIR spectroscopy. The FTIR spectra of the Gg and the Gg-cl-P(AAm-*co*-MAA) hydrogel were recorded on a Perkin Elmer Spectra 100 spectrophotometer (USA) using KBr pellets. All the samples were dried in a vacuum oven prior to the FTIR measurement. To prepare KBr pellets, 10 mg of sample was mixed with 250 mg of KBr and was pressed under 10 K kg cm^{-1} for 5 min. All the spectra were recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. The changes on the surface of the Gg after the graft co-polymerisation were studied by means of SEM (LEO, 435VF, LEO Electron Microscopy Ltd, Japan). All the samples were non-conducting, so they were coated with a thin gold layer. The change in the surface area of the Gg after the graft co-polymerisation was studied with a Micromeritics ASAP 2020 gas adsorption apparatus (USA) using the low temperature N_2 gas adsorption–desorption technique. Changes in the thermal behavior of Gg after graft co-polymerization and cross-linking with P(AAm-*co*-MAA) and MBA were studied using the TGA (TG/DTA 6300, SII EXSTAR 6000, SII Nanotechnology Incorporation, Japan) in air at a heating rate of 10 °C min^{-1}. The point of zero charge (pzc) of the Gg-cl-P(AAm-*co*-MAA) hydrogel was determined by following the procedure reported by Moreno-Castilla et al. [29]. Briefly, in 50 mL plastic bottles, 0.2 g of the hydrogel polymer was added to solutions with different pH values from 2.0 to 11.0. The solutions were shaken periodically until the pH had stabilised. The final pH of the solution

Please cite this article in press as: H. Mittal, et al., Int. J. Biol. Macromol. (2015), http://dx.doi.org/10.1016/j.ijbiomac.2015.04.045