



Synthesis of co-polymer-grafted gum karaya and silica hybrid organic–inorganic hydrogel nanocomposite for the highly effective removal of methylene blue



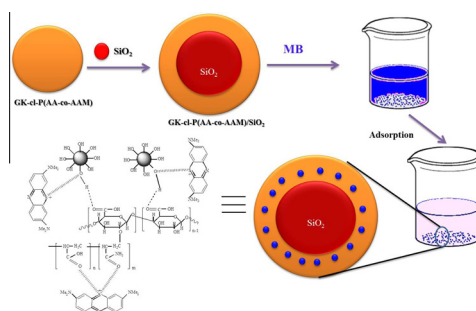
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HIGHLIGHTS

- GK-cl-P(AA-cl-AAM)/SiO₂ nanocomposite (HNC) was synthesized using grafting method.
- Cross-linked hydrogel nanocomposite was used for the removal of methylene blue.
- A superior maximum adsorption capacity was found to be 1408.67 mg g⁻¹.
- Adsorption process was spontaneous and endothermic in nature.
- The HNC was used successfully for three cycles of adsorption–desorption.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work was to study the adsorption behavior of the nanosilica-containing hydrogel nanocomposite of gum karaya grafted with poly(acrylic acid–acrylamide) (GK-cl-P(AA-co-AAM)) in the adsorption of methylene blue (MB) from aqueous solutions. The hydrogel nanocomposite was synthesized by the base-catalyzed hydrolysis and water condensation reactions of tetraethylorthosilicate in an aqueous medium containing a dispersion of GK-cl-P(AA-co-AAM). Structural and morphological characterizations using Fourier transform infrared spectroscopy, X-ray diffraction, and transmission and scanning electron microscopies supported the formation of the grafted hydrogel polymer of GK and the SiO₂-containing nanocomposite. The Brunauer–Emmett–Teller adsorption studies showed that the surface area and porosity of the hydrogel polymer significantly increased after nanocomposite formation with SiO₂. The hydrogel nanocomposite was employed for the removal of MB from an aqueous solution: 96% of the MB was removed with a hydrogel nanocomposite dose of 0.2 g L⁻¹. The adsorption process was found to follow pseudo-second-order kinetics, and the adsorption isotherm was best fitted with the Langmuir monolayer isotherm model with a maximum adsorption capacity of 1408.67 mg g⁻¹, which was much higher than that of the hydrogel polymer. Different adsorption thermodynamic parameters supported the endothermic nature as well as the spontaneity of the adsorption process. The hydrogel nanocomposite showed excellent regeneration capacity in the acidic medium and was successfully used over three adsorption–desorption cycles. Therefore, the GK-cl-P(AA-co-AAM)/SiO₂ hydrogel nanocomposite has shown potential as an efficient adsorbent for the highly effective removal of cationic dyes from aqueous solution.

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1. Introduction

In recent years, because of burgeoning population and industrial growth, the demand for water has increased tremendously; however, the total available water that can be used for human activity has remained the same. Improper water management at the industrial level has also contributed to the problem of safe water supplies. For example, industries such as the cosmetics, petroleum, dyeing, and textile industries use synthetic dyes on a large scale and generate huge amounts of toxic and/or colored effluents. The contamination of our water resources through the discharge of these toxic effluents without proper treatment [1,2] has become one of the world's major environmental challenges from the toxicological point of view. Most synthetic dyes are carcinogenic and adversely affect the human health, even at very low concentrations [3]. The treatment of dye-contaminated water is very difficult because dyes are highly soluble and stable in water. Moreover, they are non-degradable and cannot be decomposed in municipal water treatment plants [4]. Their presence can affect biological activities as well as photosynthesis [5]. Therefore, they must be effectively removed from industrial effluents before being discharged into the environment.

Techniques such as oxidation–reduction [6], coagulation–flocculation [7], electrochemical treatment [8], photocatalysis [9], solvent extraction [10], reverse osmosis [11], membrane separation [12], and adsorption [13] have been used to remove synthetic dyes from contaminated water. Most of these techniques have associated drawbacks such as high operational cost, generation of toxic residues causing secondary pollution, or incomplete removal of pollutants [14]. Recently, adsorption techniques have attracted a great deal of attention because they are cost-effective and easily performed; they are also able to remove even very low concentrations of synthetic dyes from contaminated water [15].

Over the last few years, gum polysaccharide-based biodegradable adsorbents have become of particular interest because of their ready availability, low cost, and environmentally friendly natures. Moreover, their surfaces can be easily tailored to meet functional requirements [13,16,17]. Despite all these advantages, the use of gum polysaccharide-based adsorbents has been limited by their poor specific surface areas, poor mechanical properties, and comparatively low hydrodynamic volumes [18]. An ideal adsorbent should have the ability to adsorb very high amounts of a pollutant with a minimum mass of the adsorbent and, at the same time, be efficiently regenerated for repeated recycling [19,20]. Recently, a number of efforts have been undertaken to develop modified gum polysaccharide-based adsorbents with these desired properties. In this direction, a number of gum polysaccharide-based nanocomposites have been synthesized with higher surface areas, increased numbers of adsorption sites, enhanced thermal stability, and higher hydrodynamic volume [13,17,20,21]. Monodisperse silica nanoparticle-based polymer nanocomposites have also attracted special attention because of their low cost and flexibility in surface modification [22,23]. Moreover, graft co-polymers of gum polysaccharides have been reported to act as self-templates for the *in situ* generation of silica (SiO₂) particles and their growth through interactions between the hydroxyl groups present on the surface of the gum polysaccharides and SiO₂. The incorporated SiO₂ nanoparticles enhanced the surface area of the polymer matrix as well as provided additional binding sites for the more efficient adsorption of pollutants [20,21].

Gum karaya (GK) is a branched acidic polysaccharide obtained from *Sterculia urens* of the Sterculiaceae family. The solubility of GK in water is very low, although it swells to many times its original weight to form dispersion in aqueous media [24,25]. It is a highly branched complex polysaccharide consisting of D-galacturonic acid,

D-galactose, L-rhamnose, and D-glucuronic acid. The carbohydrate structure has a rhamnogalacturonan main chain consisting of α -(1 → 4)-linked D-galacturonic acid and α -(1 → 2)-linked-L-rhamnosyl residues. The side chain is made up of (1 → 3)-linked β -D-glucuronic acid, or (1 → 2)-linked β -D-galactose on the galacturonic acid unit where half of the rhamnose is substituted by (1 → 4)-linked β -D-galactose (Fig. S1, supporting information) [24,25].

Recently, gum xanthan- and SiO₂-based hybrid nanocomposites have been used as adsorbents for the removal of dyes and heavy metal ions from aqueous solutions. The graft co-polymer of poly(acrylamide) and gum xanthan was used for the *in situ* generation of SiO₂, and a modified xanthan gum/silica hybrid nanocomposite was used for the successful removal of Congo red from aqueous solution [26]. In another study, modified carboxymethyl tamarind/SiO₂-based nanocomposites were used for the adsorption of methylene blue (MB) from aqueous solution, but a significantly lower adsorption capacity was observed ($q_m = 43.85 \text{ mg g}^{-1}$) [1]. Therefore, considering the structural diversity of GK and the presence of abundant anionic functionalities in its structure, we here report the *in situ* generation of SiO₂ inside the graft co-polymer of GK and the co-polymer mixture of acrylamide (AAM) and acrylic acid (AA). The synthesized hydrogel nanocomposite (HNC), GK-cl-P(AA-co-AAM)/SiO₂, was examined in the adsorption of MB from aqueous solution. The hybrid material had a high surface area and exhibited an enhanced electrostatic attraction to MB. The exceptionally high adsorption capacity of the HNC in the uptake of MB ($q_m = 1408.67 \text{ mg g}^{-1}$) was explained on the basis of different structural and morphological characterization results.

2. Experimental section

2.1. Chemicals

GK, AA, AAM, potassium persulfate (KPS), ascorbic acid (ABC), N,N'-methylenebisacrylamide (MBA), tetraethylorthosilicate (TEOS, 98%), ammonium hydroxide (30%, NH₄OH), ethanol, MB, rhodamine B (RhB), brilliant green (BG), and Congo red (CR) were purchased from Merck, South Africa. All chemicals were of analytical grade and used without further purification. All samples were prepared in double-distilled water. A stock solution of MB (1000 mg L⁻¹) was prepared by dissolving the calculated amount of dye in 1000 mL double-distilled water; the working solution of MB was prepared by diluting the stock solution to a desired concentration.

2.2. Synthesis of the GK-cl-P(AA-co-AAM) hydrogel polymer

The GK-cl-P(AA-co-AAM) hydrogel polymer was synthesized via the free radical graft co-polymerization technique using a mixture of KPS and ABC as the redox initiator and MBA as a crosslinking agent. Grafting parameters such as grafting time, temperature, amount of double-distilled water, initiator ratio, amount of crosslinker, and amounts of the monomers were optimized on the basis of percentage swelling (P_s) to obtain a hydrogel polymer with a maximum swelling capacity. Initially, GK (1 g) was dispersed in double-distilled water (20 mL) in a 100 mL glass beaker and left undisturbed for 24 h. After complete dispersion with water, a fixed KPS:ABC ratio (1:1) of the redox initiator was added to the reaction mixture and stirred vigorously. The details regarding optimized reaction conditions can be found in Table S1 (supporting information). In the second step, the calculated amount of MBA was added to the reaction mixture with continuous stirring. In the last step, varying amounts of the monomers were added to the reaction

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