Carbohydrate Polymers 153 (2016) 34–46

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Development of a sodium alginate-based organic/inorganic superabsorbent composite hydrogel for adsorption of methylene blue

Sourbh Thakur[a], Sadanand Pandey[a], Omotayo A. Arotiba[a,b,*]

[a] Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa
[b] Centre for Nanomaterials Science Research, University of Johannesburg, South Africa

ARTICLE INFO

Article history:
Received 15 March 2016
Received in revised form 26 June 2016
Accepted 27 June 2016
Available online 29 June 2016

Keywords:
O/I hydrogel nanocomposite
Sodium alginate
Methylene blue
Acrylic acid
Adsorption
Water pollution

ABSTRACT

Batch adsorption experiments were carried out for the removal of methylene blue (MB) cationic dye from aqueous solution using organic/inorganic hydrogel nanocomposite of titania incorporated sodium alginate crosslinked polyacrylic acid (SA-cl-poly(AA)-TiO_2). The hydrogel was prepared by graft copolymerization of acrylic acid (AA) onto sodium alginate (SA) biopolymer in the presence of a crosslinking agent, a free radical initiator and TiO_2 nanoparticles. The hydrogel exhibited a high swelling capacity of 412.98 g/g. The factors influencing adsorption capacity of the absorbents such as pH of the dye solutions, initial concentration of the dye, amount of absorbents, and temperature were investigated and used to propose a possible mechanism of adsorption. The adsorption process concurs with a pseudo-second-order kinetics and with Langmuir isotherm equation. A very high adsorption capacity (Q_{max} = 2257.36 (mg/g)) and a correlation coefficient of 0.998 calculated from isotherm equations show the high efficiency of the absorbent and thus expected to be a good candidate as an absorbent for water treatment.

1. Introduction

Dyes cause worldwide concern because of their toxicity towards human and aquatic life (Suteu, Zaharia, Muresan, Muresan, & Popescu, 2009). Dyes spread undesirable colour to water and reduce the penetration of sunlight. Their breakdown products in the water may be toxic, carcinogenic or mutagenic to life forms (Suteu et al., 2009). Methylene blue (MB) is a cationic dye with broad applications such as colorants for paper, hair and cotton; and strainers for medicinal surgery (Levin et al., 2004; Patel, 2006). MB has been shown to cause retching, stun, cyanosis, jaundice, and tissue necrosis in human (Kumar, Ramamurthi, & Sivanesan, 2005; Vadivelan & Kumar, 2005). Consequently, there is a need for the removal of these types of dyes from wastewater or industrial effluents for a more secured environment. Among the various wastewater treatment methods, adsorption method has been effectively utilized for lowering the concentration of dissolve dyes and metal ions in effluents (Pandey & Mishra, 2011; Pandey & Tiwari, 2015; Shi, Xue, Wang, & Wang, 2013; Singh, Pandey, Singh, & Sanghi, 2007, 2008). Different types of materials such as polymers, carbon, filaments and so on are being utilized as absorbents in water purification. These materials can be functionalized and are combined in diverse ways to enhance their adsorption capacities and specificities.

In order to achieve the improvement of adsorption capacity of absorbents, the synthesis and the characterization of diverse functional groups hydrogels have become an interesting area of research globally (Alla, Sen, & El-Naggara, 2012; Buchholz & Graham, 1997; Wang & Wang, 2010). Superabsorbent hydrogel are characterized as hydrophilic, three-dimensional (3-D) systems with ability to absorb large values of water, saline solution, or physiological fluids (Li, Wu, Wang, & Duan, 2006). They are extensively used in diverse applications like wastewater treatment, health, drug conveyance, beauty care products, and farming. The use of hydrogels for wastewater treatment is of interest owing to their high adsorption limits, recovery capacities and reuse for nonstop procedures (Shi et al., 2013). To enhance the adsorption limit of hydrogels, there are some report where hybrids, blends, and composites based on polyacrylamide (PAM) hydrogels have been broadly created by including some functional components such as loess (Feng, Ma, Wu, Wang, & Lei, 2014), medicinal stone (Wang, Wang, Kang, & Wang, 2011), diatomite (Mukerabigwi et al., 2015), rectorite (Yang, Ma, & Guo, 2011), muscovite (Wang, Yuru Kang, & Wang, 2010), montmorillonite (MMT) (Islam, Rahaman, & Yeum, 2015), silica (Yang & Ni, 2012), laponite clay (Yi & Zhang, 2008), poly(2-acrylamido-2-methylpropanesulfonic acid) (Atta, Ismail, &

---

* Corresponding author at: Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa.
E-mail addresses: oarotiba@uj.ac.za, omotayoarotiba@gmail.com (O.A. Arotiba).

http://dx.doi.org/10.1016/j.carbpol.2016.06.104
0144-8617/

Elsaaed, 2012) methylcellulose (Aouada, Pan, Orts, & Mattoso, 2009) and chitosan (Dragan, Perju et al., 2012).

Recently, organic/inorganic (O/I) hydrogels nanocomposite are been considered because of their enhanced mechanical/thermal stability and swelling properties when contrasted with the pure hydrogels (Kaur et al., 2013; Pandey & Nanda, 2016; Pandey, Goswami, & Nanda, 2013a, 2013b). To further enhance the properties of hydrogels, preparation of hydrogel composites and nanocomposites through in situ polymerization of monomers utilizing micronized inorganic materials, such as montmorillonite (MMT) (Lee & Yang, 2004), kaolin (Wan, Wang, Yuan, & He, 2006), attapulgite (Chen & Wang, 2009) mica (Lin, Wu, Yang, & Pu, 2001), secite (Wu et al., 2000), bentonite (Tao, Xiaoqing, Yi, & Wenqiong, 2006) and titania have been researched. Pourjavadi et al. (Pourjavadi, Doulabi, & Doroudian, 2014) reported the incorporation of TiO_2 nanoparticles (NPs) into polymer hydrogels to improve their water absorbencies. However, only a few works on the adsorption performance of hydrogels with TiO_2 can be found in literature so far (Pourjavadi et al., 2014). The fundamental goals of our paper are: (i) to build up a new strategy for high return synthesis of sodium alginate-crosslinked-poly(acrylic acid)/TiO_2 (SA-cl-poly(AA)-TiO_2) O/I-hydrogels (ii) to investigate the possibility of using SA-cl-poly(AA)-TiO_2 O/I- hydrogels nanocomposite as an absorbent for the removal of a methylene blue dye, (iii) to study the different parameters effecting the sorption, for example,TiO_2 content, initial pH values of solution, contact time and initial MB concentration were investigated. (iv) to determine kinetic and thermodynamic parameters for the adsorption process and finally (v) attempt to understand the adsorption mechanism of MB onto SA-cl-poly(AA)-TiO_2.

2. Experimental

2.1. Materials

Sodium alginate (SA) biopolymer with a molecular weight, molecular formula and viscosity of 216.12 g/mol, $C_6H_9NaO_7$ and 15–20 cP respectively was obtained from sigma (UK). The acrylic acid (AA, 99%,) monomer was obtained from Aldrich (Netherlands) and were used without further purification. Potassium persulfate (KPS), 99% (Merck, Germany), the crosslinker –N, N-methylenebisacrylamide (MBA), 99% (Aldrich, UK), titanium dioxide (TiO_2) nanopowder, ≥25 nm particle size with the molecular weight of 79.87 g/mol, CAS Number: 1317-70-0, 99.97% trace metals basis; and, methylene blue (MB) cationic dye, were obtained from Aldrich (UK) and used without further purification. All other reagents used were of analytical grade. Distilled water was used to prepare all the dye solutions.

2.2. Characterization

Dynamic mechanical analysis (DMA) single cantilever test was conducted on Perkin Elmer DMA 8000 (USA). The reconstituted SA-g-PAA/TiO_2 hydrogel nanocomposite discs (dimension 12.44 × 7.48 × 1.41 mm) were tested using parallel plate (20 mm) with a gap 53 μm and covered by a thin layer of silicon oil to serve the purpose of avoiding evaporation of water during frequency sweep test. Storage modulus(G'), loss modulus(G''), real complex viscosity(η'), imaginary complex viscosity(η'') were recorded. All the rheological tests were performed in triplicate. FTIR spectra of samples were taken in KBr pellets using a Perkin–Elmer PE 1600 FTIR spectrophotometer (USA) in the range of 4000–400 cm^{-1}. X-ray diffraction (XRD) patterns were collected on Rigaku Ultima IV by employing Cu Ka radiation of the wavelength of 1.5406 Å with visible slights at 45 kV/40 mA (Japan). The surface morphology of the O/I-hydrogel was examined by a scanning electron microscopy, (TESCAN VEGA, Czech Republic) under a 20 kV electron acceleration voltage by carbon coating of samples. The presence of TiO_2 NP within the polymer network of SA-g-PAA O/I-hydrogel was confirmed using JEOL JEM–2100 F field emission electron transmission microscope (TEM) with an accelerating voltage of 90 kV (Japan). The concentration of the dye was measured with a Schimadzu UV-1208 model UV–vis spectrophotometer (Japan). The pH measurements were made with OHAUS starter 2100 (USA). Powdering of hydrogel nanocomposite were perform by Ball milling model Fritsch analysette 3 spartan starter 2100 (Germany), Shaking water bath labcon, magnetic stirrer model MSH 300 N Boeco (Germany). Sonication of TiO_2 nanoparticle was performed by using Ultra sonic manufacturing company (Pvt) Ltd. UMC 10 (South Africa).

2.3. Synthesis of SA-cl-poly(AA)-TiO_2 O/I- hydrogels nanocomposite and SA-cl-poly(AA) hydrogel

A polymer matrix composed of SA-cl-poly(AA) was prepared by using MBA as crosslinker and kPS as initiator in hot air oven. The grafting of acrylic acid monomer onto SA in the presence of TiO_2 NPs and MBA cross linker by free radical co-polymerization technique is presented in Scheme 1. On the basis of the SA-cl-poly(AA) superabsorbent, a SA-cl-poly(AA)-TiO_2 O/I hydrogel nanocomposite was prepared according to the following procedure: In the O/I-hydrogels synthesis various amount of TiO_2 (0.05, 0.1, 0.2 g) NPs was dispersed in 34 mL at pH 9 of deionized water and stirred for 12 h (speed of stirrer was 200 rpm). Then, the TiO_2 NPs solution was sonicated for 4 h. An amount of 1 g SA was poured in TiO_2 NPs solution and was stirred at 25 °C temperature for 2 h. Different concentrations of AA monomer (0.6 mol/L, 0.8 mol/L, 1.0 mol/L and 1.2 mol/L) were used one at a time, and 0.05 g of MBA (dissolved in 2 mL of distilled water) were added into solution containing SA and dissolve completely. Finally, KPS initiator (0.05 g in 2 mL water) was transferred into solution containing SA. The reaction mixtures were kept at 70 °C for 3 h. After the reaction, the synthesized SA-g-PAA/TiO_2 O/I-hydrogels were subjected to precipitations with acetone to completely remove the uncross-linked polymer from the copolymers. The synthesized nanocomposites hydrogels were cut into small pieces of ~10 mm in length and were dried in an oven at 60 °C to constant weight.

The method for the synthesis of SA-cl-poly(AA) hydrogel was identical to that SA-cl-poly(AA)-TiO_2 O/I-hydrogels nanocomposite. But in this case synthesis was performed in absence of TiO_2 nanoparticles. All the other steps are similar. During the precipitation process unreacted SA, AA and KPS are separated from the hydrogel. The confirmation of hydrogel can be brought forward by the texture of form hydrogel (Fig. 1a).

2.4. Determination of percent swelling and percent grafting

The swelling (g/g) of the O/I-hydrogels was performed by pouring the pre-weighted O/I-hydrogels in excessive DI water and was permitted to soak at room temperature for 960 min. After that, the soaked O/I-hydrogels nanocomposite was taken out from water, dried with filter paper and weighed. The swelling (S) (g/g) (g water/g dried O/I-hydrogels nanocomposite) was calculated using Eq. (1):

$$S\,(g/g) = \frac{w_s - w_d}{w_s} \tag{1}$$

where W_s is the weight s of the samples swollen in water and W_d are the weights of the samples in dry state.