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Research article

Novel carboxymethyl cellulose based nanocomposite membrane: Synthesis, characterization and application in water treatment

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ABSTRACT

Significant efforts have been made to develop composite membranes with high adsorption efficiencies for water treatment. In this study, a carboxymethyl cellulose-graft-poly(acrylic acid) membrane was synthesized in the presence of silica gel, which was used as an inorganic support. Then, different amounts of bentonite were introduced to the carboxymethyl cellulose (CMC) grafted networks as a multifunctional crosslinker, and nanocomposite membranes were prepared. The nanocomposite membranes were characterized using Fourier transform infrared spectroscopy, and scanning electron microscopy, which revealed their compositions and surface morphologies. The novel synthesized nanocomposite membranes were utilized as adsorbents for the removal of crystal violet (CV) and cadmium (Cd (II)) ions, which were selected as representatives of a dye and a heavy metal, respectively. We explored the effects of various parameters, such as time, pH, temperature, initial concentration of adsorbate solution and amount of adsorbent, on membrane adsorption capacity. Furthermore, the kinetic, adsorption isotherm models and thermodynamic were employed for the description of adsorption processes. The maximum adsorption capacities of membranes for CV and Cd (II) ions were found to be 546 and 781 mg g^{-1}, respectively. The adsorption of adsorbate ions by all types of nanocomposite membranes followed pseudo-second-order kinetic model and was best fit with the Freundlich adsorption isotherm. The results indicated that the synthesized nanocomposite membrane is an efficient adsorbent for the removal of cationic dye and metal contaminants from aqueous solution during water treatment.

1. Introduction

Environmental pollution has become increasingly important, due to world population growth and industrial development (Shah et al., 2013). The majority of water pollution, which includes contaminants such as toxic heavy metals and dyes, comes from industrial production activities (e.g., dye, cosmetic, leather, paper, plastics, food, textile, planting, and mining) (Saber-Samandari et al., 2014b). These contaminants even at low concentrations are harmful to the environment and human (Mahdavinia and Zhalebaghy, 2012). Therefore, the considerable amount of pollutants contained in industrial wastewaters, which can potentially endanger public health and the environment, should be discharged with adequate treatment. Their degradation products are toxic and carcinogenic, and some cannot be degraded or destroyed at all (Mahajan and Bali, 2012). Among many available treatment techniques, including reduction, ion exchange, reverse osmosis, chemical precipitation and adsorption, the process of adsorption onto a solid substrate is considered optimal (Saber-Samandari and Gazi, 2013). Adsorption method is cheap, efficient, energy economical, simple, and does not produce waste by-products (Ardejani et al., 2008; Saber-Samandari and Gazi, 2015). To minimize processing costs, several recent investigations have focused on the use of low cost adsorbents, such as agricultural by-products

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(Pellera et al., 2012), waste materials (Zyoud et al., 2015), biosorbents (Mahmoud, 2015), slag and clay materials (e.g., montmorillonite, sepiolite, talc, kaolinite and bentonite) (Musso et al., 2014; Potgieter et al., 2006).

Bentonite, low-cost and abundant clay that is primarily composed of montmorillonite (Mt), is a type of aluminum phyllosilicate mineral with exchangeable cations in its framework channels and reactive–OH groups on its surface. Until now, bentonite embedded in several different polymers has been applied in the uptake process of non-ionic or anionic dyes (Li et al., 2010) and several metals, such as Zn (Mellah and Chegrouche, 1997), Pb (Ayari et al., 2007), Cd (Bentouami and Ouali, 2006), Cu (Karapinar and Donat, 2009), Ag (Hefne et al., 2010), As (Al-Jlil, 2010) and Cr (Al-Jlil, 2010), from aqueous solution. This can be attributed to the action of bentonite as a multifunctional crosslinker, with a large effective functionality in polymer networks. This functionality includes increasing ion exchange, as well as strength and stiffness properties (Can et al., 2007).

In this study, we synthesize a carboxymethyl cellulose-graft-poly(acrylic acid) membrane in the presence of silica gel, which acts as an inorganic support. The membrane is thermally and mechanically stable, non-toxic and highly resistant to microbial attacks (Reshmi et al., 2006). Carboxymethyl cellulose (CMC) is a derivative of cellulose, with carboxymethyl groups ($-CH_2COOH$) bound to some of the hydroxyl groups on the cellulose backbone (Liu et al., 2010). Carboxymethyl cellulose is broadly applied as an adsorbent, due to the presence of polar carboxyl groups, which make the polymer soluble in water and increase chemical reactivity and chelate ability. Then, bentonite, a physical crosslinker, was introduced to the polymer network to modify the mechanical properties and increase the ion exchange capability of the membrane. The synthesized membranes were characterized using FTIR and SEM. Finally, they were applied for the adsorption of crystal violet (CV) ions, as representative of dye, and cadmium (Cd (II)) ions, as representative of heavy metals, from aqueous solution.

2. Experimental procedures

2.1. Materials

The synthesis of the nanocomposite membrane was achieved using carboxymethyl cellulose (Aldrich), potassium persulfate (BDH) as an initiator and glutaraldehyde solution (25% in H_2O, Aldrich) as a crosslinker of carboxymethyl cellulose. Acrylic acid (Merck) and N,N′-methylene-bis-acrylamide (Aldrich) as monomer and crosslinker, respectively were applied without further purification. Silica gel 60 (0.06–0.2 mm, Merck) and nanoclay, bentonite (300–500 nm from Aldrich), were used. Acetic acid (Aldrich), sulfuric acid (Aldrich), sodium chloride (Merck), hydrochloric acid (Merck), sodium hydroxide (Merck) and methanol (Aldrich) were applied as received. Finally, cadmium chloride (Aldrich), and 1,5 diphenylcarbazide (Merck) and crystal violet (Aldrich) were used for water treatment purposes as received.

2.2. Synthesis of grafted nanocomposite membrane

2.2.1. Synthesis of CMC grafted solution

First, a CMC solution (1.25% W/V) was prepared by dissolving CMC powder (0.5 g) in 40 mL of distilled water in a round-bottom flask, which was close fitting with an argon gas inlet in a water bath at 60 °C and continuously stirred. Then, the initiator, potassium persulfate (0.015 g), was added to the CMC solution. After 10 min, acrylic acid (0.2 mL) and N,N′-methylene-bis-acrylamide (0.008 g) were introduced into the above solution as a monomer and crosslinker, respectively. The mixture was continuously stirred for 1 h. Finally, the graft polymerization and crosslinking was stopped by cooling the solution and removing argon gas flow before reaching the gelation point. The product was named the CMC grafted solution, which was used in the synthesis of the nanocomposite membrane.

2.2.2. Synthesis of grafted nanocomposite membrane

For synthesis of the grafted nanocomposite membrane, silica gel (0.25 g), which was used as an inorganic support, was added to the CMC solution (1.25% W/V). The mixture was stirred for 1 h at room temperature. Then, bentonite, an inorganic filler and multifunctional cross-linker, was introduced to the mixture and vigorously stirred for 2 h. Next, the CMC grafted solution (3 mL), which was prepared previously, was added to the mixture. The main CMC solution and CMC grafted solution were crosslinked by adding 25 wt. % glutaraldehyde solution, which was prepared by mixing methanol, sulfuric and acetic acid with volume ratios of glutaraldehyde/methanol/acetic acid/sulfuric acid at 1:1:1.5:0.5. The mixture was stirred and mixed for 8 h. Finally, the grafted nanocomposite membrane was prepared using a solution casting and solvent evaporation technique Scheme 1. Before casting the solution in a clean glass plate, the solution was sonicated for 20 min. The bubble free solution was dried on a glass plate in an oven at 50 °C for 14 h. The thickness of the obtained membrane was approximately 200 μm. By employing this method, different nanocomposite grafted membranes (M0, M2, M6 and M10), which contained different amounts of bentonite (0, 0.02, 0.06 and 0.1 g), were synthesized.

2.3. Characterization of grafted nanocomposite membrane

The synthesis of grafted nanocomposite membranes was verified by FTIR spectra, which were taken using Fourier transform infrared spectrophotometer (PerkinElmer Japan FTIR-140 8700) in the range of 500–4000 cm^{-1}. The morphology of the membranes was characterized using scanning electron microscopy (Stereoscan S-360 Cambridge) operated at an accelerating voltage of 25 kV.

In addition, the pH at point of zero charge (pHzpc) was determined using a standard technique. pH_{ZPC} indicates the pH at which the acidic or basic functional groups no longer contributes to the pH of the solution (Saber-Samandari and Gazi, 2013). To find the pH_{ZPC}, 50 mL of NaCl solution (0.01 mol L^{-1}) was placed in a 100-mL flask and the pH of the solutions was adjusted from 2 to 10 by adding either sodium hydroxide or hydrochloric acid solutions (0.1 mol L^{-1}). Subsequently, 0.1 g of the prepared nanocomposite membrane was immersed in solutions at 20 °C and allowed to stir for 24 h. Then, the membranes were removed from the solutions and their final pH values were measured using an ion pH meter. The final pH of the solutions has been plotted as a function of the initial Ph. Finally, the pH_{ZPC} was calculated from the point, where final pH equals to initial pH (Sartape et al., 2013).

2.4. Adsorption experiments

2.4.1. Adsorption of crystal violet

The crystal violet (CV) adsorption capacity of the grafted nanocomposite membranes was examined using a batch equilibrium procedure. First, dried samples (0.1 g) placed in a beaker with an aqueous dye solution (100 mg L^{-1}), and shaken for a night at room temperature (~20 °C). Then, the dye-adsorbed membrane was removed, and the remaining residual dye concentration in the filtrate was determined using UV–vis spectroscopy at 598 nm. Finally, the dye adsorption capacity of the membrane ($mg.g^{-1}$) was calculated via the following Equation: