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Removal of congo red and methyl violet from water using nano clay filled composite hydrogels of poly acrylic acid and polyethylene glycol

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HIGHLIGHTS

- Composite hydrogels were made from acrylic acid, PEG and nano clay.
- Nano clay fillers were incorporated in situ during polymerization.
- The gels were characterized by FTIR, SEM, DTA–TGA and XRD.
- Swelling, diffusion and dye adsorption of the gels were evaluated.
- Composite hydrogels showed high dye adsorption and removal%.

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ABSTRACT

Superabsorbent hydrogels were synthesized from polyethylene glycol (PEG) and crosslinked polyacrylic acid. Nano clay filled composite hydrogels were also synthesized by incorporating 0.5, 1.0 and 1.5 wt% nano size bentonite filler in the hydrogels. These hydrogels were characterized by FTIR, SEM, XRD, DTA–TGA, swelling and diffusion characteristics. The filled composite hydrogels showing the best result in swelling was further used for adsorption of congo red (CR) and methyl violet (MV) dye from water. The composite hydrogel showed high adsorption and removal% for these dyes for both low (2.5–50 mg/L) and high range (100–600 mg/L) of feed dye concentration. The dye adsorption data were fitted to different kinetics and adsorption isotherm models. The external mass transfer coefficient, diffusion coefficient and thermodynamic parameters of dye adsorption were also determined.

1. Introduction

Chemical industries such as textile, plastic, paper, printing, pharmaceutical and food industries use more than 10,000 different dyestuffs and pigments for coloring its products. However, around 15 wt% of dyestuffs remains as pollutants in waste water [1]. Most of these dyes are synthetic aromatic compounds. Various treatment processes such as coagulation/flocculation, membrane treatment, ion exchange, oxidation, degradation by biological, photochemical or electrochemical method and adsorption are used for removal of these non-biodegradable dyes from water. Amongst the various processes adsorption is extensively used because of its easy operation, low cost and high efficiency. The hydrogels based on crosslinked functional polymers such as poly ethylene glycol (PEG) are very effective for selective adsorption of synthetic dyes from water.

Polyethylene glycol (PEG) is non-toxic and non-immunogenic. PEG is also biocompatible and soluble in water. This low cost polymer is extensively used in pharmaceutical preparation, tissue culture and also as an adsorbent [2]. PEG derivatives can be free radically polymerized to introduce several functional groups in its structures [3]. In an earlier study Kesenci and Erhan produced hydrogel beads carrying the amide functional groups based on ethylene glycol dimethacrylate and acryl amide via suspension polymerization [4]. PEG derivatives are most commonly functionalized with vinyl groups at the chain-ends such as poly ethylene glycol diacrylate (PEGDA). These active vinyl groups may be crosslinked to form PEG based superabsorbent hydrogel [5]. The hydrogels based on PEG have been used as an effective adsorbent. Accordingly, Kwak et al. [5] prepared sodium methallyl sulfonate-co-poly(ethylene glycol) diacrylate (SMS-co-PEGDA) microspheres by suspension polymerization. These microsphere beads showed

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high sorption for Co(II). Karadag et al. reported synthesis of a novel ternary semi IPN by copolymerization of acrylamide and sodium acrylate in the presence of PEG. This PEG based semi IPN hydrogel showed high swelling in water and also high adsorption of Janus Green B dye from water [6]. In another work acrylic acid was partially neutralized with potassium hydroxide in water and the resulting acrylate and unreacted acrylic acid monomers were polymerized free radically with crosslinker methylene bis acrylamide (MBA) in aqueous solution of PEG. The semi IPN hydrogels prepared by this method were reported to show high adsorption for methyl orange dye [7]. Semi IPN hydrogels were also synthesized by crosslink copolymerization of acrylamide, methyl succinic (itaconic) acid and MBA in aqueous solution of PEG. The resulting superabsorbent hydrogels were observed to show high swelling characteristics and sorption of basic blue 12 dye from water [8]. Composite hydrogels were synthesized by intercalation of PEG and silica in bentonite by ultrasonic sol–gel technique. These organic–inorganic hybrid hydrogels were found to be an effective adsorbent for volatile organics like phenol and dyes like malachite green and methyl blue [9].

From the above discussion it is evident that apart from biological applications, PEG based hydrogels have also been extensively used as adsorbents for removal of metal ions and organic pollutants. Thus, in the present work composite superabsorbent hydrogels were prepared from acrylic polymers, PEG and also an inorganic adsorbent, viz. bentonite.

Bentonite is a low cost inorganic adsorbent. It carries a permanent negative charge because of isomorphous substitution of Si^{+4} in tetrahedral layers by Al^{+3} and in octahedral layers by Mg^{+2} [10]. This rich clay material has been widely used alone or as one of the constituents of a composite adsorbent for removal of synthetic dyes and metal ions from water [10–14]. In the present work composite hydrogels were prepared by crosslink copolymerization of acrylic acid and MBA in the presence of PEG and bentonite in water. The wt ratios of acrylic polymer and PEG were varied to produce several hydrogels. The hydrogel showing the highest swelling in water was identified (designated as F0) and it was further filled with 0.5, 1 and 1.5 wt% (of total polymer) nano size bentonite fillers by in situ mixing during polymerization. These filled hydrogels were designated as F0.5, F1 and F1.5, respectively. The effect of various parameters, viz., wt% of PEG and filler, type and concentration of various salts and solution pH on swelling and diffusion of these composite superabsorbents were studied. The filled or composite F1 gel showing the optimum swelling characteristic and the unfilled F0 gel was then used for removal of the varied concentrations of two industrial dyes, i.e. congo red (CR) and methyl violet (MV) from water.

2. Experimental

2.1. Materials

Poly ethylene glycol (PEG) of molecular weight 4000 was procured from Merck and used as obtained. The redox pair of initiators, i.e., ammonium persulfate and sodium metabisulfide were obtained from Merck and used as obtained. The monomers, viz., acrylic acid and N′N′ methylene bis acrylamide (MBA) were of analytical grades and used as obtained. These monomers were also procured from Merck. Sodium montmorilonite rich nano size (30–90 nm, aspect ratio 300–500, mineral's thickness 1 nm, cation exchange capacity 120 meq/100 g) bentonite filler was gifted as free samples by Amrfeo Pte. Ltd., Kolkata. Congo red (CR) and methyl violet (MV) dyes used in adsorption studies were purchased from SRL Chemical, India. Distilled water was used for polymerization, swelling and sorption experiments.

2.2. Methods

2.2.1. Synthesis and characterization of the hydrogels

Semi IPN type hydrogels of PEG and polyacrylic acid were synthesized by solution polymerization in a three-necked reactor at ambient temperature (30 °C) for 3 h. At first 5 wt% aqueous solution of PEG was prepared by gradual addition and stirring of the required amount of PEG in distilled water in a 250 mL glass beaker. Polymerization of acrylic acid monomer and MBA crosslinker was allowed in this solution in the presence of the redox pair of initiator, i.e., ammonium persulfate and sodium meta bisulfite. For synthesizing filled composite hydrogel, bentonite nano filler was taken in the polymerization mixtures and the acrylic acid monomer was allowed to polymerize in situ in this aqueous dispersion.

2.2.2. Characterization of the hydrogels

The various functional groups present in the hydrogels were characterized by Fourier transform infrared (FTIR) spectra. FTIR of the polymer samples were recorded on a FTIR spectrometer (Perkin Elmer, model-Spectrum-2, Singapore) using KBr pellet. KBr pellet was prepared in a mold by mixing dry KBr powder with fine powder of the hydrogel samples (10:1 wt ratio of KBr to polymer). The morphology of the composite gels were characterized by scanning electron microscopy (SEM) at a magnification of 1 K (Scanning Electron Microscope, Model No. S3400N, VP SEM, Type-II, made by Hitachi, Japan) and accelerating voltage set to 10 kV. The crystallinity of the hydrogel samples was characterized by its wide angle X-ray diffraction (XRD) profile in a diffractometer (Model: X'Pert PRO, made by PANalytical B.V., The Netherlands) using Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) and a scanning rate of 0.005 degree (2θ)/s) over 2–72° angle of diffraction. Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) of the hydrogel samples were carried out in nitrogen atmosphere in the temperature range of 60–600 °C at the scanning rate of 10 °C per minute in a Perkin Elmer instrument.

2.2.3. Study of swelling

The swelling of the hydrogels in water was studied by gravimetric method. Small amount of accurately weighed hydrogel samples (W_i) was immersed in distilled water at ambient temperature. The gel samples were withdrawn from water at different time intervals (t) and weighed (W_t) after removing the excess surface water carefully by using a filter paper without pressing the sample. Each sample was weighed three times to minimize error and the average values of these three measurements were taken. Swelling experiments were continued till the hydrogels reach its equilibrium swelling value (W_e).

The swelling ratio (S_t) and equilibrium swelling ratio (S_e) of the hydrogel samples were determined from the following Eqs. (1) and (1a), respectively:

$$S_t(g/g) = \frac{W_t - W_i}{W_i} \tag{1}$$

$$S_e(g/g) = \frac{W_e - W_i}{W_i} \tag{1a}$$

The swelling experiments were also carried out at different pH (3.9–9.7) by immersing the hydrogels in buffer solutions. The buffer solutions of varied pH were prepared by dissolving phosphoric acid, potassium phosphate (KH_2PO_4), potassium hydrogen phosphate (K_2HPO_4), sodium chloride and sodium hydroxide in distilled water.

2.2.4. Study of dye removal capacity of the hydrogels

100 mg (w) of the hydrogel sample was brought in contact with dye by immersing the gel sample in 100 mL (V) distilled water