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Synthesis and adsorptive characteristics of novel chitosan/graphene oxide nanocomposite for dye uptake

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ABSTRACT

A green approach was utilized to synthesize crosslinked chitosan-based graphene oxide (GO) nanocomposite membrane using tetraethyl orthosilicate (TEOS) as a crosslinking agent. The structural analysis of the membranes was investigated using infrared (IR) spectroscopy. The porosity and morphology of membranes were examined using scanning electron microscopy (SEM) and BET (Brunauer–Emmett–Teller) techniques. The SEM micrographs revealed that GO was uniformly mixed in chitosan matrix. BET results further confirmed that the inclusion of GO led to increase the surface area of the nanocomposite which also improved its adsorptive properties. Congo red (CR) dye was used to study the adsorption efficiency of developed membrane. The effect of time, pH and dose rate on the adsorption behavior of developed membrane was investigated. The maximum loading capacity of CR on CS/GO membrane was 175.9 mg/g. The kinetics and equilibrium isotherms were well described by pseudo-second-order and Langmuir isotherm models respectively. The high adsorption efficacy and green nature of the nanocomposites provide a good alternative to already existing petroleum based (biostable) membranes.

1. Introduction

The most persistent problems facing by the community of this planet are the inadequate accessibility of potable water and sanitation conditions. The rapid industrialization and growing urbanization all over the world have consistently contributed different unwanted anthropogenic pollutants in the ecosystems [1]. The textile dyes are considered one of the major contributors of toxic and carcinogenic contamination in water streams. The largest synthetic organic colorants produced (60–70%) belongs to azo group. It is used for coloration of various substrates, such as: synthetic and natural fibers, plastics, leather, paper, mineral oils, waxes, and even with (selected types) foodstuffs and cosmetics [2,3]. Due to their poor fixation to fabrics, the concentration of these dyes in wastewater is ranging from 5 to 1500 $\mathrm{mg \cdot L^{-1}}$ [4]. The carcinogenicity of azo dyes is well known and has been associated with many health issues such as: bladder cancer in humans, splenic sacromas, hepatocarcinomas and cytoplasm anomalies in experimental animals and chromosomal aberration in mammalian cells [5]. It is prime important to treat all industrial effluents containing dyestuff, colorants and other chemical before their discharge into aquatic streams. In this regard adsorption is recognized as one of the important technique for dye removal from industrial wastewater [6,7].

The fast growth of nano-scale materials and their utilization in science and engineering has generated an avenue to synthesize cheap adsorbents with enhanced surface area and adsorption capacity [8]. Recently, graphene, a two-dimensional nano material having surface area up to 2630 m^2/g has fascinated the researchers due to its unique physicochemical, thermal and electrical properties [9–11]. Wang et al. reported the mechanical properties and failure mechanism of graphene under central load [12]. Graphene is commonly used as graphene oxide (GO) and graphene nanosheets (GNs). Graphene-based composites are also reported in the literature as adsorbent for the removal of water pollutants [9–13]. Conversely, due to its hydrophilic nature, it may readily disperse in aqueous media, so after the adsorption step, separation and recycling of the adsorbent become more difficult, which may raise operational cost and may also cause the treated water to be re-polluted [14,15]. Therefore, it is more appropriate to use GO nanoparticles in polymer [16] to treat wastewater.

For the last few years, chitosan-based composites have been synthesized for the removal of water pollutants especially dyes from wastewater. With these composites, enhanced loading capacity and good resistance against acidic media have been reported in the literature [17,18]. The multifunctional properties of chitosan (CS) and inherent properties of GO are combined together [19]. CS is a linear polysaccharide having randomly distributed β- [1 → 4]-linked D-glucosamine (de-acetylated unit) and *N*-acetyl-D-glucosamine units, which are produced by the deacetylation (DDA) of polysaccharide chitin extracted

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from crustacean shells such as crabs, prawns, fungi etc [20,21]. A large number of oxygen containing groups are present in GO such as carboxyl, epoxy and hydroxyl. These groups have tendency to form chemical bonding with the amino groups of biopolymer (CS) [22]. In this study, we have used a binary polymeric blend integrated with a natural biopolymer (CS) and a synthetic polymer poly (vinyl alcohol), (PVA) to obtain an added advantage of stability, biocompatibility and mechanical strength as well as compared to a single component. Chitosan and their composites were crosslinked in order to give them stability against external environment and temperature. Recently, chitosan/gold/carbon nanotubes nanocomposites were developed and used for catalytic application [23]. This approach offers new possibilities to develop chitosan based nanocomposites using other members of carbon family.

The objective of this work is to prepare CS/GO nanocomposites and explore its application for the removal of CR from aqueous solution using batch process. The effects of various operating parameters on CR adsorption and adsorption mechanism in the light of some well-known isotherm and kinetic models are also studied.

2. Experimental

2.1. Materials and methods

Chitosan (C-3646, degree deacetylation was 75%), PVA (Mw: 146,000–186,000), TEOS, acetic acid, sodium hydroxide, hydrochloric acid, Congo red (CR) and ethanol were purchased from Sigma-Aldrich and used without further purification. Graphene oxide (GO) were synthesized by modified Hummers method [24].

2.2. Preparation of chitosan/graphene oxide membrane

Chitosan/GO membranes (CPG) were synthesized following a modified procedure [25]. Chitosan (1.2 g) was dissolved in 100 mL of acetic acid 2% (*w*/*v*) in a glass reactor. GO (0.10 g) was dispersed in water and sonicated for 1 h then mixed with chitosan solution and sonicated further 2 h. PVA (0.8 g) was dissolved in 10 mL water and then mixed with CS/GO suspension. After half an hour, mixture of hydrolyzed TEOS (152 μL) in ethanol was added to this blend at 40 °C. After an hour, the solution was poured into plastic plates for drying at room temperature in dust free environment. The same procedure was followed to prepare chitosan membrane without GO and represented as CP. After drying membranes were dipped in NaOH 10% solution for 30 min, washed with distilled water until neutralized then dried again.

2.3. Characterization methods

The synthesized samples (CPG & CP) were characterized by using advance instrumentation techniques. The surface morphology of membranes was observed by JEOL EM-10049, 1200EX II electron microscope operating at 10.0 kV. The images were analyzed at different magnifications. For Transmission electron microscope (TEM) studies of GO, 1.0 μL of the aqueous suspension was placed on a carbon-coated Cu-grid, 200 mesh. After drying, the samples were kept in a vacuum desiccator overnight. TEM measurements were carried out on a JEOL JEM 1200 EXII instrument operated at an accelerating voltage of 120.0 kV. The IR spectra of membranes were recorded at room temperature on FTIR spectrophotometer (Nicolet 6700, Thermo Electron Corp, Waltham, Massachusetts, USA) at scanning range of 4000–500 cm^{-1} (116 average scans) at resolution of 6.0 cm^{-1}. BET adsorption desorption experiments were performed by surface area and porosity analyzer (Autosorb-IC, Quantachrome) for determining pore volume, pore size and specific surface area of films. The samples (~50 mg) were degassed at 80 °C for 60 min. All samples were characterized by N_2 adsorption by applying the BET equation to the N_2 adsorption isotherm. Swelling experiments of membranes were performed in water and non-buffer media. A known amount of sample (20 mg) is immersed in vials containing 100 mL swelling solvent at room temperature. After removing the excess surface solution, the swollen weight of sample was determined after given time intervals. The samples were again immersed in solvent until equilibrium swelling is achieved. Swelling was calculated using the following equation [25]:

$$\text{Swelling}\left(\frac{g}{g}\right) = \frac{(W_s - W_d)}{W_s} \tag{1}$$

Here W_d and W_s are the weights of membrane in dry form and swollen form at time 't' respectively.

2.4. Batch adsorption studies

The CR was dissolved in distilled water to prepare the stock solution (1000 mg/L). For isothermal adsorption experiments, a known amount of nanocomposite membrane was placed in a flask containing 10 mL CR solution (10–600 mg/L range) and agitated in a shaker (Orbital shaking incubator, model PA-42/250H) at 250 rpm for 24 h. The concentration of the remaining adsorbate in the filtrated solution was determined using UV–vis spectrophotometer (model UV-1201, Shimadzu) and the adsorbed amount of CR dye (Q) was calculated from the following equation:

$$Q = \frac{(C_o - C_f).V_s}{1000.W_f} \tag{2}$$

Here, C_o and C_f are the initial and final concentrations (mg/L) before and after adsorption in solution, V_s is the volume of experimental solution (L) and W_f is the weight (g) of the membrane.

For kinetic studies, adsorption experiments at 25 °C were carried out by varying contact time (1 to 60 min at initial CR concentration of 5 mg/L). The effect of the adsorbent dose was studied by varying the amount of adsorbent (2.5 to 50 mg) at an initial concentration of $C_0 = 5$ mg/L and a contact time of 60 min. A series of experiments were carried out by taking fixed amount of adsorbent (40 mg) and initial concentration of the adsorbate solution (5 mg/L) for different pH values (from 4 to 9) at room temperature (25 °C).

3. Results and discussions

3.1. Characterization of nanocomposite membranes

The structural morphology of the membrane and dispersion of the nanofiller (GO) in the polymer matrix were studied by SEM. Fig. 1 shows SEM and TEM images of CPG, CPG-after adsorption of CR and GO respectively. The micrograph of CPG membrane is highly porous having well dispersed GO sheets in the polymer matrix [26,27]. The EDX analysis of thread like structure confirmed the presence of silicon which is present in the crosslinking agent. In literature it is reported that the porous network structure is responsible for swelling behavior of membranes [28]. After adsorption of molecules the morphology of the membrane changed and it became more compact and the pore size of the membrane also reduced which may be due to the adsorption of CR molecules. TEM image of GO in Fig. 1E shows the well separated sheets of GO.

FT-IR technique is used to investigate the interaction between polymers and GO. Fig. 2a represents FT-IR spectrum of GO which give information about functional groups present on GO. The presence of following IR peaks of oxygen containing functional groups are observed: COOH at 1706 cm^{-1}, C –OH at 1385 cm^{-1}, C—O—C 1065 cm^{-1}. These oxygen-containing groups improved the miscibility and dispersion of GO in polymer matrix via hydrogen bonding/electrostatic interactions. The peak at 1616 cm^{-1} is correspond to C=C group present in graphene oxide. Han et al. also reported the presence of these groups in GO and their interactions with chitosan [28].