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Simulated visible light photocatalytic degradation of Congo red by TiO_2 coated magnetic polyacrylamide grafted carboxymethylated chitosan

N.A. Abdelwahab*, F.M. Helaly

Department of Polymers and Pigments, National Research Centre, 33 El Bohouth St., Dokki, Giza, P.O. 12622, Egypt

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ABSTRACT

Carboxymethyl chitosan was prepared, grafted with polyacrylamide in the presence of synthesized Fe_3O_4 nanoparticles and coated with TiO_2 (TMPAM-g-CMC). Synthesized materials were characterized using FT-IR spectra, XRD, EDX, SEM, TEM, BET surface area, UV–vis/DRS and PL spectra. MPAM-g-CMC and TMPAM-g-CMC were comparatively investigated for decolorization of Congo red dye solution under visible light irradiation. The effect of various experimental parameters on the decolorization rate was investigated. MPAM-g-CMC and TMPAM-g-CMC showed decolorization rate, 55.4% and 99.2% after 90 and 180 min, respectively. Photocatalytic decolorization follows pseudo-first-order according to Langmuir–Hinshelwood (L–H) model. The decolorization rate by TMPAM-g-CMC attained 92.4% after eight repetitive cycles that confirmed its stability.

Introduction

Soluble organic dyes in different water resources arised from discharging the wastes of textile dyeing, plastic and paper factories [1]. Generally, organic dyestuffs have high degree of toxicity and cancer causing effects [2]. So, it is necessary to treat these coloured effluents before their ejecting into water resources.

The principal techniques for removal of these hazardous dyes from coloured effluents include chemical oxidation, electrochemical treatment, membrane separation, adsorption, photocatalysis, bioremediation, microbiological decomposition, etc [3]. Among them, the most common and potent method is photocatalytic degradation which showed excellent treatment for wastewater contaminated with organic pollutants [4]. Visible light irradiation induced photocatalysis indicated high efficiency and rapid degradation without any secondary contamination [5].

Once upon a time, semiconducting photocatalysts played potential role for degradation and mineralization of organic dyes [6]. Different inorganic semi-conducting photocatalysts include TiO_2, SiO_2, ZnO, CdS, Fe_3O_4, etc were used, TiO_2 is considered as the most potent one where complete degradation of organic pollutants achieved [7]. It has high photo-stability, non-toxicity and low cost [8]. Inspite of these adventages, TiO_2 showed difficulty to be recovered [9]. Importantly, TiO_2 combination with other metal oxides not only facilitate its recovery but also increased its photocatalytic performance. The combination between TiO_2 and Fe_3O_4 in hybride nanocomposite leads to improved recyclability by magnetic separation under external magnetic field [10]. Additionally, increased surface area and enhanced photodegradation rate of the photocatalyst were obtained [11].

Chitosan (CS) is common, plentiful and naturally occurring biopolymer which bearing amino and hydroxyl groups as active sites [12]. Chemical modification of chitosan is an important issue to increase its functionality, carboxymethyl chitosan (CMC) resulted from carboxymethylation of chitosan, it is water soluble, non-toxic, biocompatible and film forming agent [13]. CMC can not be stored for long period, so, grafting of CMC with appropriate vinyl monomer prolongs its stability and also increases its adsorption and photocatalytic efficiency. Polyacrylamide is hopeful and has long history in water purification field and grafting of CMC with polyacrylamide achieved good stabilization of the photocatalyst and prevent its agglomeration. When a photocatalyst is hosted into polymer matrix, this will generate bifunctional material, i.e., adsorbent and photocatalyst [14]. In a previous work, chitosan/TiO_2/Fe_3O_4 composite was synthesized with high adsorption and photocatalytic properties [15]. Also, about 99.4% of Rhodamine B was photodegraded by TiO_2/Fe_2O_3/chitosan thin film composite that prepared by solution casting method [16]. Another study illustrated that Cu_2O/chitosan/Fe_3O_4 had efficient degradation of reactive brilliant red X-3B under visible light irradiation [17].

* Corresponding author.
E-mail address: nor_5020@yahoo.com (N.A. Abdelwahab).

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Moreover, Fe_3O_4/chitosan/TiO_2 nanocomposite served as suitable, effective, and recyclable photocatalyst for degradation of 93% of methylene blue [18].

However, no work was directed towards preparation of TiO_2 coated magnetic polyacrylamide grafted carboxymethyl chitosan (TMPAM-g-CMC) and its application for photocatalytic degradation of Congo red. The main goal of this research is to prepare magnetic polyacrylamide grafted carboxymethylated chitosan nanocomposite (MPAM-g-CMC) through synthesis of Fe_3O_4 nanoparticles, carboxymethylation of chitosan and insitu grafting of carboxymethylated chitosan in the presence of Fe_3O_4 nanoparticles, followed by coating with TiO_2 using low temperature solvothermal method. The synthesized materials were characterized by FT-IR spectra, XRD patterns, scanning electron microscopy (SEM), energy dispersive X-ray (EDX), transmission electron microscopy (TEM), BET surface area, UV–vis diffused reflectance spectroscopy (UV–vis/DRS) and Photoluminescence (PL) spectra. The synthesized material was evaluated as photocatalyst for photodegradation of Congo red.

Materials and experimental methods

Materials

High molecular weight chitosan (average M.wt.,10,104) and *N*, *N*′, methylene diacrylamide were obtained from Sigma-Aldrich, USA. Acrylamide was used as a product of Alpha Chemika, mombai, India. Isopropanol, sodium hydroxide, hydrochloric acid, iron(III) chloride hexahydrate, ethylene glycol, sodium citrate, sodium acetate were purchased from sd fine-CHEM limited Mombai, India. Monochloroacetic acid, titanium tetraisopropoxide (TTIP), Congo red and Potassium persulphate (KPS) were given by LobaL Chemie for laboratory reagents and fine chemicals, Mumbai, India.

Dye solution was prepared by dissolving definite weight of Congo red in double distilled water.

Congo red is an anionic azo dye, its IUPAC name is 1-napthalenesulfonic acid, 3,3-(4,4-biphenylenebis(azo))bis(4-aminodisodium) and its chemical structure is represented in Scheme 1.

Preparation of Fe_3O_4 nanospheres

As described previously [19], Fe_3O_4 nanoparticles were prepared by solvothermal method. In this method, 3.0 g $FeCl_3{\cdot}6H_2O$, 1.3 g sodium citrate and 5.0 g sodium acetate were dissolved in 85 mL ethylene glycol. The mixture was stirred vigorously for 30 min to achieve complete homogenization. The reactants were transferred to autoclave and heated at 200 °C for 10 h. The black precipitated Fe_3O_4 was filtered, washed with distilled water and ethanol and dried at 80 °C for 12 h.

Preparation of magnetic polyacrylamide grafted carboxymethylated chitosan composite (MPAM-CMC)

CMC was prepared as follows [20]: About 3.0 g of chitosan was suspended in 70 mL isopropanol with magnetic stirring for 30 min, 8.16 g of NaOH were dissolved in predetermined amount of deionized water to reach 40%, and then added to chitosan suspension with stirring for 1 h at (25 ± 2) °C. Then, 14.4 g of monochloroacetic acid/isopropanol solution (1:1 in mass) were added to the suspension for 4 h under stirring at (25 ± 2) °C and the reaction terminated by the addition of 100 mL methanol. The CMC was filtered, washed with ethanol/water mixture of (9:1 ratio in mass). 10 mL HCl was added to the solid product with stirring for 30 min for neutralization followed by filtration, washing with ethanol and drying under vacuum. The degree of substitution of CMC was determined by potentiometric titration [21], in which definite weight of CMC (m) was dissolved in specific volume of distilled water, then pH was adjusted to <2.0 by 0.1 M hydrochloric acid. The solution was titrated against 0.1 M NaOH. The substitution degree was calculated according to Eq. (1):

$$\text{Degree of substitution} = \frac{(161 \times V \times C)}{(m - 58 \times V \times C)} \quad (1)$$

where C and V are concentration and volume of NaOH respectively, 58 and 161 are molecular weights of carboxymethyl group and glucoseamine unit of chitosan.

In the beginning of the experiment, 100 mg of Fe_3O_4 nanoparticles was dispersed in 50 mL double distilled water and ultrasonicated for 30 min. Carboxymethylated chitosan was dissolved in appropriate amount of double distilled water, then added gradually to Fe_3O_4 dispersion with stirring for 1 h, the contents were purged with nitrogen gas for 30 min. Predetermined amount of KPS was dissolved in adequate amount of distilled water and introduced to the mixture at 70 °C to create radicals on CMC and to supress homopolymer formation. 0.71 gm of acrylamide and 0.005 gm of MBA mixed aqueous solution was charged to the reaction mixture with mechanical stirring for 4 h. At the end of the reaction the Fe_3O_4/PAM-g-CMC nanocomposite (MPAM-g-CMC) was precipitated by addition of acetone, followed by filtration and rinsing with ethanol. The yield was dried in an oven at 60 °C until the weight remained constant.

Preparation of TiO_2 coated MPAM-g-CMC (TMPAM-g-CMC)

Definite amount of TTIP was dissolved in 80 mL of isopropanol, the pH of the mixture was adjusted to 2.0. Then, 0.1 g of the as-synthesized MPAM-g-CMC was added to this mixture with stirring. Predetermined amount of urea and polyethylene glycol were added to the previous mixture with stirring for 1 h. Then, the mixture was heated at 80 °C for 4 h. The resulted TiO_2 coated MPAM-CMC was washed several times with ethanol and distilled water and dried under vacuum at 60 °C for 6 h.

Characterization

X-ray diffraction (XRD)

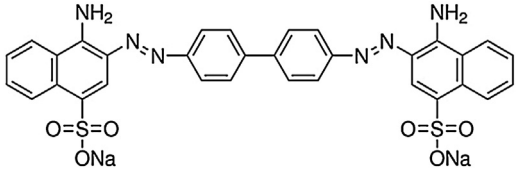
The XRD patterns were detected using BRUKUR D_8 ADVANCE diffractometer in the range of $2\Theta = 10–80°$. The instrument operates at 40 kV and 40 mA with Cu Kα monochromator ($\lambda = 1.5405$ A°) radiation.

FT-IR spectra

The FT-IR spectra were recorded by JASCO FT-IR-6100 Spectrometer, in the range of 4000–400 cm^{-1}. This was performed by mixing traces of powdered samples with definite weight of KBr and pressing them into pellets.

Scanning electron microscopy (SEM)

The surface morphology was recorded by JEOL JXA-840A Electron Probe Microanalyzer. The acceleration of the electron beam was at 10 kV.



Scheme 1. Chemical structure of Congo red.

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