Environmental Nanotechnology, Monitoring & Management 6 (2016) 159–163

Contents lists available at ScienceDirect

Environmental Nanotechnology, Monitoring & Management

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

Functionalized hybrid materials assisted organic dyes removal from aqueous solutions

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ARTICLE INFO

Article history:
Received 6 August 2016
Received in revised form 14 October 2016
Accepted 15 October 2016

Keywords:
Carboxymethyl cellulose
Calcium phosphate
Hybrid
Dyes removal

ABSTRACT

Carboxymethyl cellulose grafted polymethacrylic acid (CMC-g-PMAA) was investigated as a template for rod-like hydroxyapatite mineralization. CMC-g-PMAA/hydroxyapatite hybrid material exhibited high removal capacity toward methylene blue (MB), cationic dye model, from aqueous solutions. The adsorption behavior of MB using CMC-g-PMAA/hydroxyapatite hybrid was investigated in detail using batch adsorption technique. The hybrid material exhibited adsorption capacity up to 671 mg/g. Pseudo-second-order and Langmuir isotherm models were found to describe the adsorption mechanism. This new adsorbent material has promising future for waste water purification.

1. Introduction

Removing synthetic dyes from waste effluents has become a challenge area to prevent their environmental hazard in particular for aquatic bio-systems (Ma et al., 2012; Gong et al., 2013). These dyes are biologically non-degredable due to their aromatic structure and their synthetic origin. MB is a typical example of industrial relevant toxic cationic dyes, with known harmful effects on humans (Wang et al., 2011). Adsorption has emerging as an effective and economic technique for decontamination of organic pollutants from waste waters (Salama et al., 2015). The high cost and energy required for producing the adsorbents have inspired the scientists for developing new alternatives low cost adsorbents (Kyzas et al., 2013). Using sustainable and recyclable materials such as polysaccharides presented an ecofriendly and cost effective technologies for dyes removal. Promising studies investigated inorganic materials such as calcium phosphate (El Boujaady et al., 2011) and sodium titanate (Feng et al., 2013) for waste water purification.

Natural polymers, especially polysaccharides, are actually produced in great quantities with low cost and promising alternatives for biomaterials (Salama, 2015). Polysaccharides are an almost sustainable polymeric raw materials with interesting properties for the development of innovative environmentally friendly products (Salama, 2016). Moreover, polysaccharides based materials are more likely to find affordable applications as adsorbents to remove heavy metals and organic pollutants from waste water (Monier et al., 2010). However, the low functionality of polysaccharides hampers their uses as dye adsorbents. To improve the sorption performance of polysaccharides based materials for an efficient use in pollutants sequestration and recovery, polysaccharides have been modified with inorganic materials such as ceramic alumina (Tanhaei et al., 2015), magnetic nanoparticles (Wan Ngah et al., 2011), and silica (Salama, 2016). By these modifications, the advantages of multiple materials are combined into one advanced material. We recently proved the successive mineralization of polysaccharides with calcium phosphate for biomedical applications (Salama and El-Sakhawy, 2014). Recent studies have addressed the interaction between particles and dyes in water-based solution (Meng et al., 2014; Meng and Ugaz, 2015). Moreover, various trails have been carried out to investigate the capability of composite materials as adsorbents for waste water treatment. For example, composite material from hydroxyapatite embedded into chitosan was used as adsorbent for removal of Congo red dye from aqueous solutions. The adsorption results showed that the hydroxyapatite/chitosan composite showed adsorption capacity much higher than pure chitosan and hydroxyapatite (Hou et al., 2012).

In the current study, CMC-g-PMAA/hydroxyapatite, as a sustainable hybrid material, was successfully achieved by calcium phosphate mineralization in the presence of CMC-g-PMAA graft copolymer. CMC-g-PMAA/hydroxyapatite material was introduced as a new adsorbent and its effectiveness for removing MB from aqueous solutions was examined. The effect of variation of pH, time and initial concentration of MB solution on the adsorption process was discussed.

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http://dx.doi.org/10.1016/j.enmm.2016.10.003
2215-1532/

2. Experimental part

2.1. Materials

CMC sodium salt was purchased from Fluka BioChemika. Methacrylic acid, dibasic potassium phosphate, ammonium persulfate were obtained from Sigma Aldrich and used without further purification. The other chemicals were of analytical grade and used as received. Double distilled water was used for adsorption study.

2.2. Preparation of hybrid

Graft copolymerization of methacrylic acid onto CMC was optimized in our previous study (Salama et al., 2016). In brief, 0.2 g CMC was dissolved in 10 mL double distilled water and stirred for 20 min under nitrogen gas with 1250 mM methacrylic acid. Then 7.5 mM ammonium persulphate was added and the reaction mixture was stirred for 2 h at 70 °C. The reaction mixture was poured into acetone for graft copolymer precipitation. The precipitates was washed with methanol and dried under vacuum. Mineralization process was carried out by mixing 50 mL copolymer solution (5 mg/mL) containing 0.48 M $CaCl_2$ with another 50 mL copolymer solution (5 mg/mL) containing 0.24 M K_2HPO_4 at pH 8. After 7 days stirring, the precipitates was centrifuged (5000 rpm, 10 min), washed with THF and dried under vacuum.

2.3. Batch adsorption study

CMC-g-PMAA/hydroxyapatite hybrid material was investigated as adsorbent for MB removal from waste water. Batch adsorption experiments were conducted in 50 mL glass bottles with 50 mg dried hybrid. After adsorption for a desired condition, the solution was separated from the adsorbents with a syringe filter (PTFE, hydrophobic, 0.5 μm) and the dye concentration was measured at maximum absorbance (670 nm) using spectrophotometer UNICO UV-2000. Data are representative of at least three experiments, and standard deviations are less than 8.0%.

2.4. Characterization

FTIR spectra of CMC-g-PMAA/hydroxyapatite was recorded, in KBr disc, using Brücker IFS FTIR spectrometer. XRD was performed using X-ray diffractometer (PANalytical, Netherlands) with a monochromatic CuKα radiation source (λ = 0.154 nm) in step-scan mode with a 2θ angle 5 to 70° with 0.04 step. The surface morphology of CMC-g-PMAA/hydroxyapatite was investigated by SEM using the non-destructive energy dispersive X-ray analysis (EDX) in a Jeol JSM 6400 equipment with a silicon drift detector. Transmission electron microscope (TEM) images were taken with a JEOL JEM-2100 electron microscopy at 100kx magnification, with an acceleration voltage of 120kV. The particle size was mesured using VASCO2 (from Cordouan Technologies, France)

3. Results and discussion

3.1. CMC-g-PMAA/hydroxyapatite hybrid characterization

The current hybrid material was synthesized through hydroxyapatite mineralization in the presence of water-soluble graft copolymer CMC-g-PMAA. The hybrid material was evaluated as new sustainable and cost effective adsorbent for organic dyes removal from waste water.

FT-IR spectra of CMC-g-PMAA/hydroxyapatite was presented in Fig. 1(A). CMC-g-PMAA/hydroxyapatite showed characteristic

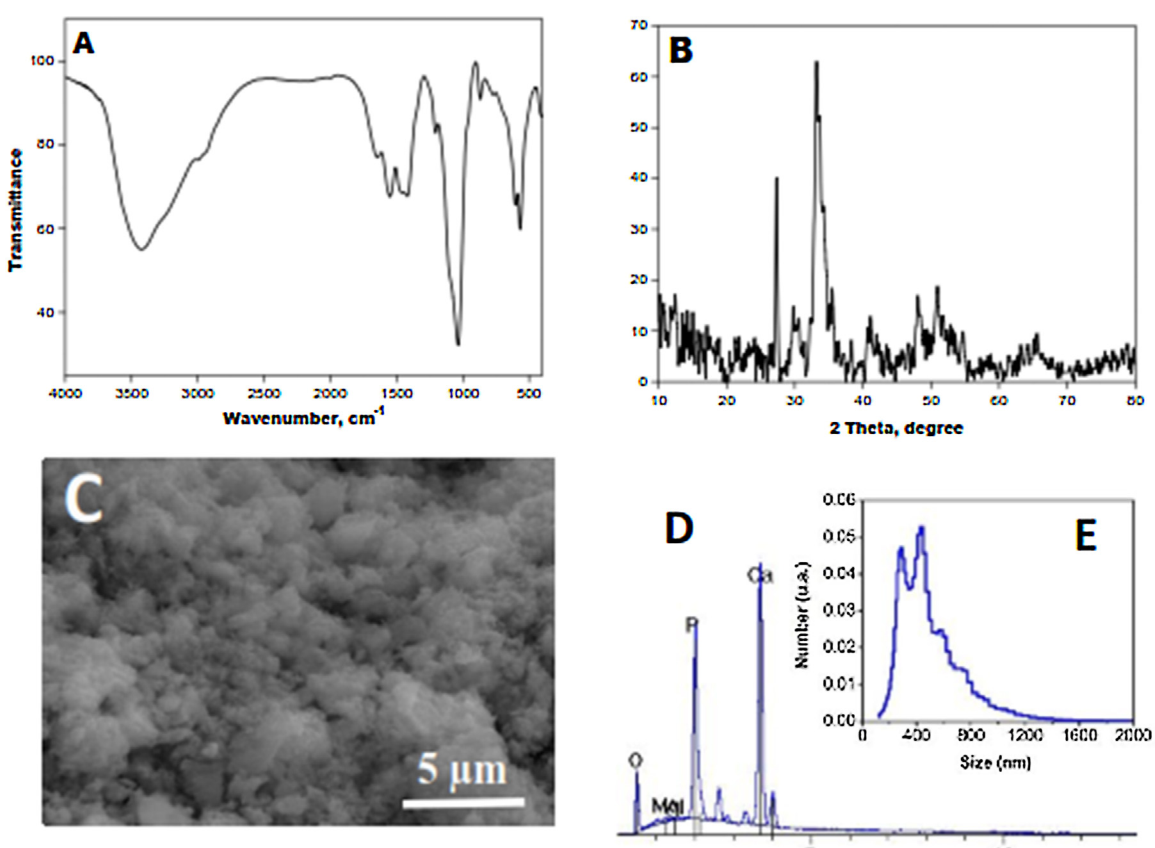

Fig. 1. FTIR spectra (A), XRD (B), SEM (C), EDX (D) and size distribution histogram (E) of CMC-g-PMAA/hydroxyapatite hybrid.