Chemical Engineering Journal 229 (2013) 276–284

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Unusual dye adsorption behavior of κ-carrageenan coated superparamagnetic nanoparticles

Ana M. Salgueiro, Ana L. Daniel-da-Silva *, Ana V. Girão, Paula C. Pinheiro, Tito Trindade

Department of Chemistry, CICECO, Aveiro Institute of Nanotechnology, University of Aveiro, 3810-193 Aveiro, Portugal

HIGHLIGHTS

- Synthesis of superparamagnetic κ-carrageenan coated Fe_3O_4 nanoparticles.
- κ-Carrageenan coated Fe_3O_4 nanoparticles for removal of methylene blue from water.
- The nanoparticles display fast MB removal (5 min) and high MB adsorption capacity.
- The MB adsorption follows a Z-type adsorption isotherm.

ARTICLE INFO

Article history:
Received 26 April 2013
Received in revised form 6 June 2013
Accepted 9 June 2013
Available online 17 June 2013

Keywords:
Magnetic nanoparticles
Polysaccharide
κ-Carrageenan
Dye removal
Cationic dye
Methylene blue

ABSTRACT

κ-Carrageenan coated magnetic iron oxide nanoparticles (NPs) were synthesized and tested as adsorbents for the magnetically assisted removal of methylene blue (MB) from aqueous solutions, a cationic dye commonly present in wastes from the textile industry. The resulting composite NPs were superparamagnetic and contained *ca.* 12 wt% carrageenan. The MB uptake ability was found to vary with the pH solution and was larger in alkaline conditions. Both pseudo-first-order and pseudo-second-order equations predicted well the kinetics with the maximum adsorption achieved very fast, within 5 min. The MB adsorption has shown an unusual Z-type isotherm which suggests the generation of new adsorbing sites with increasing MB initial concentration. Under the experimental conditions used (23 °C, pH 9) the materials presented here displayed MB adsorption capacity (185.3 mg/g) higher than other magnetic sorbents previously reported. Thus κ-carrageenan coated magnetic NPs are very promising eco-friendly materials for removing MB from wastewater using magnetic separation.

1. Introduction

Dyes are present in the effluents of a number of industries, including textile, paper, plastic, cosmetic, leather and rubber. The discharge of dyes in water supplies is a matter of concern due their harmful impact on the environment. Most of these compounds cause depletion of water's oxygen that may result in death of the aquatic life. In addition several dyes and their degradation products exhibit toxicity and potential mutagenic and carcinogenic effects [1]. Methylene blue (Fig. 1a) is commonly used for dying textiles and wood [2] and although MB is less hazardous as compared to other dyes, it has also various harmful effects namely because acute exposure causes nausea and chest pain [3].

The methods used for the removal of methylene blue and other cationic dyes from industrial effluents include chemical precipitation [4], photochemical degradation [5] and adsorption [2,6]. Among these purification techniques, adsorption is by far the most commonly used due to its simplicity, low cost and effectiveness. A number of materials have been explored as dye adsorbents, such as inorganic materials, activated carbon and inexpensive waste materials [2,7]. The research for environmentally friendly and low-cost dye adsorbents has raised the attention to biopolymers obtained from renewable resources, such as polysaccharides. Polysaccharides have specific functional groups in their structure which explains their affinity towards a wide diversity of molecules and ions. The list of low cost polysaccharides tested as dye adsorbents is extensive [8] and include alginate [9], chitosan [10–12], cyclodextrins [13] and starch [14].

Carrageenan comprises a family of linear water-soluble sulfated polysaccharides extracted from red seaweeds. Due to their biocompatibility and ability to form hydrogels, carrageenan has been extensively used as gelling agent in food and pharmaceutical industries [15]. κ-Carrageenan (Fig. 1b) bears one sulfonate group per disaccharide unit, that corresponds to *ca.* 20 wt% sulfate content. It forms hydrogels stabilized by alkali-metal cations, such as potassium ions and presents the best gelation properties within the carrageenan family, thus being selected as adsorbent for this

---

* Corresponding author. Tel.: +351 234 370 368; fax: +351 234 370 084.
E-mail address: ana.luisa@ua.pt (A.L. Daniel-da-Silva).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.06.015

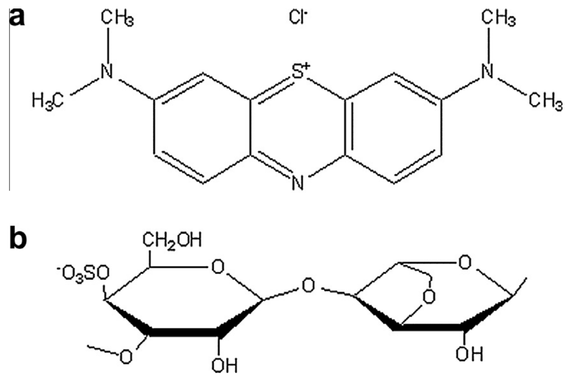

Fig. 1. Chemical structure of (a) methylene blue and (b) disaccharide repeated unit of κ-carrageenan.

study. The sulfonate anions of carrageenan are the groups primarily responsible for the interaction with cationic dyes [16]. Taken together, the ability of carrageenan to form complexes with cationic dyes [16] and their gelling properties, make these biopolymers interesting candidates for dye adsorbents in wastewater treatment.

Limitations associated to the separation of dispersed polymer based adsorbents from the treated effluents have restrained their use mostly in fixed-bed systems or packed in sorption columns [8]. Hence, magnetic adsorbents appear as advantageous alternatives that allows the easy magnetically assisted separation of the adsorbents from the treated effluents [17,18]. Magnetic nanoparticles (MNPs) such as iron oxide nanoparticles, besides bearing a large surface area favorable for adsorption processes, possess magnetic features which enables them to be separated within a short time by employing an external magnetic field [18–20]. Moreover iron oxide nanoparticles (*e.g.* magnetite – Fe_3O_4 and maghemite-γ-Fe_2O_3) show no severe toxicity hence these materials are attractive for the development of water purification systems. Polymer coated MNPs have received much attention since the polymer shell may prevent the aggregation of the magnetic cores and improve the dispersion stability of the nanoparticles in aqueous medium. The combination of MNPs with polysaccharides for dye adsorption from wastewater was investigated in the past for cyclodextrins [13], alginate [9] and chitosan [12,21,22]. Magnetic κ-carrageenan hydrogels have been explored for biomedical purposes [23–25] but to the best of our knowledge, the use of this polysaccharide for coating magnetic nanoparticles for the removal of cationic dyes from aqueous solutions is an unexplored strategy, despite its affinity to cationic dyes being known for several years [16].

In this work we report the preparation of κ-carrageenan coated magnetite (Fe_3O_4) nanoparticles and their applications for the removal of methylene blue from aqueous solutions. The removal capability was evaluated in a batch mode process and the kinetics and equilibrium of the adsorption were investigated, as well as the reusability of the sorbents. The system reported here combines the possibility of easy and fast magnetic separation with the advantages of low cost biodegradable materials, resulting in efficient eco-friendly materials for wastewater treatment.

2. Materials and methods

2.1. Materials

κ-Carrageenan (300.000 g/mol, Fluka Chemie), potassium chloride (KCl) (>99%, Sigma–aldrich), ammonia (NH_4OH) (25% NH_3, Riedel-de-Häen), iron (III) chloride hexahydrated ($FeCl_3{\cdot}6H_2O$, >99%, Sigma–aldrich), iron (II) chloride tetrahydrated ($FeCl_2{\cdot}4H_2O$, >99%, Sigma–aldrich), methylene blue ($C_{16}H_{18}ClN_3S$, Riedel-de Häen), nitric acid (HNO_3 25%, Panreac) and hydrochloric acid (HCl 37%, Fluka) were used as received.

2.2. Preparation of κ-carrageenan coated magnetic nanoparticles

Magnetic iron oxide nanoparticles (NPs) were first synthesized using the co-precipitation method, as follows. Typically 4.43 g $FeCl_3{\cdot}6H_2O$ and 1.625 g of $FeCl_2{\cdot}4H_2O$ were dissolved in 190 mL of distilled water at room temperature, under nitrogen atmosphere and mechanical stirring. Afterwards, 10 mL of ammonia were added to the solution and stirred for 10 min. The final suspension displayed a black coloration which, together with the observed magnetic properties, suggests the presence of magnetite (Fe_3O_4). The NPs were magnetically separated, washed five times with distilled water and freeze-dried.

κ-Carrageenan coated MNPs were prepared starting from (i) bare MNPs prepared as described above and (ii) acid treated MNPs. In the later, before the coating procedure, the NPs were washed twice with an aqueous solution of HNO_3 2 M, magnetically separated, washed with distilled water and the pH was set around 4. The acidic treatment aimed to convert the surface charge of the MNPs from negative to positive in order to increase the amount of the anionic polysaccharide κ-carrageenan adsorbed onto the surface of the MNPs.

For the κ-carrageenan coating, 200 mg of MNPs were dispersed in distilled water under ultrasounds bath. Then 77.3 mg of κ-carrageenan was dissolved in distilled water and added to the MNPs solution, performing a total volume of 40 mL. The suspension was kept under mechanical stirring (400 rpm) at 60 °C till a homogenous solution was obtained. This was followed by the addition of KCl aqueous solution (4 mL, 1 M) as gelling agent and stirring for 30 min. Afterwards the suspension was sonicated for 15 min and mechanically stirred for 60 min to ensure complete homogenization. After these steps, the suspension was cool down until room temperature in order to promote the gelation of κ-carrageenan onto NPs surface. The coated NPs were centrifuged at 6000 rpm for 30 min, washed with water for the removal of polymer in excess and the sample was freeze dried.

2.3. Characterization of nanoparticles

2.3.1. Chemical and structural properties

Fourier transform infrared (FTIR) spectra of the lyophilized bare and carrageenan coated MNPs were collected using a spectrometer Bruker optics tensor 27 coupled to a horizontal attenuated total reflectance (ATR) cell, using 256 scans at a resolution of 4 cm^{-1}. The crystallite phase of the MNPs was identified by X-ray diffraction (XRD). The X-ray powder diffraction patterns of the lyophilized samples were recorded using a X-ray diffractometer Philips X'Pert equipped with a Cu Kα monochromatic radiation source. The carrageenan content in the coated MNPs was calculated by thermogravimetric analysis (TGA) using a TGA 50 from a Shimadzu instrument. Samples were heated from 25 °C to 900 °C at 10 °C min^{-1}, under nitrogen atmosphere. The morphology and size of bare and coated NPs was investigated by transmission electron microscopy (TEM) using a transmission electron microscope Hitachi 9000 operating at an accelerating voltage of 300 kV. Samples for TEM analysis were prepared by evaporating dilute suspensions of the nanoparticles on a copper grid coated with an amorphous carbon film. The surface charge of the bare and carrageenan coated MNPs were assessed by zeta potential measurements, using a Zetasizer Nanoseries instrument from Malvern Instruments. The zeta potential measurements were performed in aqueous solutions prepared with distilled water.