Reactive & Functional Polymers 91-92 (2015) 43–50

Contents lists available at ScienceDirect

Reactive & Functional Polymers

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

Removal of Reactive Blue 21 onto magnetic chitosan microparticles functionalized with polyamidoamine dendrimers

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ARTICLE INFO

Article history:
Received 28 September 2014
Received in revised form 28 March 2015
Accepted 24 April 2015
Available online 27 April 2015

Keywords:
Chitosan
Magnetic particles
PAMAM dendrimers
Anionic dye
Adsorption model

ABSTRACT

Chitosan/poly(amidoamine) (MCS/PAMAM) microparticles were prepared as magnetic adsorbents for removal of Reactive Blue 21 (RB 21) dye from aqueous solution. Characterization of these particles was carried out using scanning electron microscopy, Fourier transform-infrared spectroscopy, X-ray diffractometry and vibrating sample magnetometry. The results indicate that the magnetic chitosan microparticles (MCS) were functionalized with PAMAM dendrimers and maintained its intrinsic magnetic properties. The effects of initial pH, adsorbent dose, initial concentration, contact time and temperature on adsorption were investigated. Kinetic studies showed that the dye adsorption process followed a pseudo-second-order kinetic model but that the adsorption rate was also influenced by intraparticle diffusion. Equilibrium adsorption isotherm data indicated a good fit to the Langmuir isotherm. The maximum adsorption capacities obtained from the Langmuir model were 555.56, 588.24, 625.00 and 666.67 mg g^{-1} at 303, 313, 323 and 333 K, respectively. The thermodynamic parameters revealed the feasibility, spontaneity and endothermic nature of the adsorption. Recycling experiments confirmed the relative reusability of the adsorbent.

1. Introduction

Synthetic dyes are used widely in various industrial fields, such as in textiles, dyeing, paper, tanneries and printing [1]. It is estimated that more than 100,000 commercially available dyes exist and that over 7×10^5 tonnes of dyestuff is produced annually [2–4]. Many dyes are stable and are difficult to biodegrade because of their synthetic origin and complex aromatic molecular structure. Dye-bearing wastewater, if released into the environment, can damage aquatic life and human beings because it is toxic, mutagenic and carcinogenic [5–7]. It is therefore important to treat colored effluents for the removal of dyes. In recent years, various techniques have been used to decolorize dye effluents, including coagulation [8], flocculation and membrane filtration [9]. These processes all display limitations.

Adsorption is one of the prominent methods used in wastewater treatment for dye removal, because of its universal nature, affordability and ease of operation [10]. Commercial activated carbon is an effective adsorbent, but its high cost limits its large-scale application. For these reasons, the search for alternative adsorbents has intensified in recent years. Various renewable materials have been utilized to remove dyes from wastewater, including rice husk [11], sawdust [12], banana peel [13], wheat shell [14] and peanut hull [15]. However, most of these materials have low adsorption capacities in their as-received form. Therefore, new biosorbents that are more effective, eco-friendly and cost-effective are highly desired.

Chitosan is produced by the partial deacetylation of chitin, which is the second most abundant natural biopolymer after cellulose [16,17]. It is found mostly in the shells of prawns, crabs, fungi, insects and other crustaceans. Chitosan has attracted particular attention as a functional material because of its biocompatibility, biodegradability, non-toxicity and adsorption properties [18]. Various biomaterials based on chitosan have already been explored as excellent adsorbents for the removal of various dyes from aqueous solutions since amino and hydroxy functional groups on chitosan chains can serve as electrostatic interaction and coordination bonds, respectively [19]. However, to improve its adsorption capacity and to enhance separation rates, the design and synthesis of novel adsorbents is critical [20].

Dendrimers are attractive molecules owing to their highly branched three-dimensional shape, large number of end (reactive) terminal groups, space availability within their interior and

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http://dx.doi.org/10.1016/j.reactfunctpolym.2015.04.007
1381-5148/

uniform molecular weight structures [21]. Poly(amidoamine) (PAMAM) dendrimers are among the most widely studied dendrimers, because of their early discovery and commercial availability. Recently, PAMAM dendrimers have received considerable attention in many fields, such as in engineering, materials science, chemistry and biological sciences [22,23]. The use of PAMAM dendrimers in environmental applications has been reported for the removal of heavy metals and dyes from aqueous solution [24–27].

Magnetic separation has been considered to be an effective method for solid–liquid phase separation and has been applied to wastewater treatment and in environmental pollution control. In recent years, many studies have reported on dye and metal ion removal using magnetic chitosan (MCS) composite adsorbents. However, only limited research has been conducted on MCS functionalized with PAMAM and it application in dye removal from aqueous solution.

Based on the favorable adsorption properties of chitosan and the unique properties of PAMAM, in this study, the possibility of using MCS/PAMAM as biosorbents was explored. The MCS microparticles functionalized with dendrimer-like PAMAM polymers were synthesized, and then characterized by scanning electron microscopy (SEM), X-ray diffractometry (XRD), Fourier transform-infrared spectroscopy (FT-IR) and vibrating sample magnetometry (VSM). Reactive Blue 21 (RB 21), an anionic dye, was used as a model dye for bath adsorption experiments to investigate the adsorption properties of the MCS/PAMAM. The effects of solution pH and initial dye concentration on RB 21 adsorption were investigated. The Lagergren pseudo-first-order and pseudo-second-order models were evaluated to describe the adsorption kinetics. Equilibrium isotherms and thermodynamic parameters were also determined and will be discussed. These results will be useful for further applications involving dye removal from aqueous solutions.

2. Materials and methods

2.1. Materials

Chitosan (deacetylation degree: 85%, molecular weight: 3.0×10^5 g mol^{-1}) was supplied by Sinopharm Chemical Reagent Co., Ltd., China. The $FeCl_3{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$, methyl acrylate (MA), ethylenediamine (EDA) and glutaraldehyde compounds used were of analytical grade and were purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China. A stock solution of RB 21 (1000 mg L^{-1}) was prepared in double-distilled water. Desired RB 21 solution concentrations were obtained by successive dilution of the stock solution.

2.2. Preparation of MCS/PAMAM

MCS microparticles were prepared by a one-step co-precipitation method according to our previous work [28]. Chitosan was dissolved in 2% (v/v) acetic acid solution. $FeCl_3{\cdot}6H_2O$ and $FeSO_4{\cdot}7H_2O$ were mixed in the solution and dripped into NaOH solution to form Fe_3O_4 magnetic particles under a N_2 atmosphere. After 6 h, the black products were washed several times and dispersed in a glutaraldehyde solution for crosslinking. Three hours later, the products obtained were separated and washed several times with distilled water and then dried in a vacuum.

The modification of MCS with amino-terminated PAMAM polymers was carried out according to Ma et al. [24] (Fig. 1). Formation of PAMAM dendrimers on the MCS surface was achieved by repeating two processes: Michael addition and amidation of terminal ester groups with EDA. Each Michael addition reaction produces a half generation of PAMAM dendrimers and the amidation reaction creates a full generation.

Michael addition was carried out as follows. Methanol (150 mL) containing 6 g MCS was placed in a round-bottom flask with a condenser. MA (15 mL) was added and stirred for 24 h at 50 °C under N_2. The resultant product was separated and washed repeatedly with methanol.

Amidation of the terminal ester group was carried out as follows. Methanol (150 mL) and 30 mL of EDA were added into a 250 mL flask that contained the MCS after Michael addition of MA. The mixed solution was stirred at 50 °C under N_2. After 24 h, the particles were separated and washed repeatedly with methanol. The two steps were repeated for a different number of cycles until the specified generation of dendrimers was obtained.

2.3. Characterization of MCS/PAMAM

The morphologies and microstructures of the samples were observed by SEM with an accelerating voltage of 15 kV. FT-IR spectra were measured at room temperature on an FT-IR spectrometer (Nicolet 560) to study the microparticle functional groups. The microparticle crystal structures were determined by XRD (Rigaku D/max-2200 diffractometer) using Cu Kα radiation at 40 kV and 30 mA. Magnetic hysteresis loops were obtained at 300 K by VSM. Zeta potentials and sizes of particles were measured using Malvern Zetasizer Nano 90.

The point of zero charge (pH_{zpc}) of MCS/PAMAM was determined by the pH drift method. The pH was adjusted to a value between 2 and 11 using 0.5 M HCl or 0.5 M NaOH. 20 mg of MCS/PAMAM was added into 50 mL of the pH-adjusted solution in a conical flask and equilibrated for 720 min. The final pH was measured by pH meter and plotted against the initial pH. The pH at which the curve crosses the $pH_{initial} = pH_{final}$ line is taken as pH_{zpc}.

2.4. Adsorption experiments

Batch adsorption experiments were conducted by adding the adsorbent samples to 50 mL of different RB 21 test solutions in a 250 mL conical flask on a thermostatic rotary shaker at 120 rpm. After adsorption, the adsorbent was removed from the solution using an adscititious magnet. The concentration of residual RB 21 was analyzed using an ultraviolet–visible spectrophotometer at $\lambda_{max} = 626$ nm. The amount of RB 21 adsorbed on the biosorbent, q_t (mg g^{-1}), was calculated from:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where C_0 and C_t are the initial and instantaneous RB 21 concentrations (mg L^{-1}), respectively; V is the volume of the dye solution (L) and W is the adsorbent mass (g).

3. Results and discussion

3.1. Material characterization

3.1.1. SEM analysis and size measurement

The surface morphology of MCS/PAMAM was investigated by SEM. Honeycomb-like porous structures can be seen in Fig. 2(a). The shapes of the particles are irregular and their surfaces are relative rough because of aggregation. Malvern Zetasizer Nano 90 instrument was used to measure particle size and size distribution of MCS/PAMAM. The results are shown in Fig. 2(b) and indicate that the distribution curve is single-peak distribution with a maximal size evaluated at 1.476 μm. The measurement was conducted