



Chitosan hydrogel beads impregnated with hexadecylamine for improved reactive blue 4 adsorption

Mohammadtaghi Vakili^a, Mohd Rafatullah^{a,*}, Mahamad Hakimi Ibrahim^a, Ahmad Zuhairi Abdullah^b, Babak Salamatinia^c, Zahra Gholami^d

^a School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia

^b School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

^c School of Engineering, Monash University Malaysia, Jalan Lagoon Selatan, 46150 Bandar Sunway, Selangor, Malaysia

^d Centralized Analytical Laboratory, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak Darul Ridzuan, Malaysia

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ABSTRACT

Adsorption performance of chitosan (CS) hydrogel beads was investigated after impregnation of CS with hexadecylamine (HDA) as a cationic surfactant, for the elimination of reactive blue 4 (RB4) from wastewater. The CS/HDA beads formed with 3.8% HDA were the most effective adsorbent. The adsorption capacity was increased by 1.43 times from 317 mg/g (CS) to 454 mg/g (CS/HDA). The RB4 removal increased with decrease in the pH of dye solution from 4 to 9. The isotherm data obtained from RB4 adsorption on CS and CS/HDA are adequately described by Freundlich model ($R^2 = 0.946$ and 0.934 , $\chi^2 = 22.414$ and 64.761). The kinetic study revealed that the pseudo-second-order rate model ($R^2 = 0.996$ and 0.997) was in better agreement with the experimental data. The negative values of ΔG° (-2.28 and -6.30 kJ/mol) and ΔH° (-172.18 and -101.62 kJ/mol) for CS beads and HDA modified CS beads, respectively; suggested a spontaneous and exothermic process for RB4 adsorption.

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1. Introduction

Dyes have been widely used for a long time in different aspects of human life such as textile, paint, pigment and many other industries. It is of extreme necessity to remove dyes from wastewater effectively to ensure safe discharge of treated liquid effluent into water bodies (Tan et al., 2015). Reactive dyes are important available textile dyes that are known to be highly water-soluble polyaromatic molecules that are non-degradable and cannot be absorbed well by biological solids (Geethakarthis & Phanikumar, 2011). Among many water treatment technologies, adsorption is considered the best one due to its capacity to remove dyes from colored aqueous solutions, ease of operation, inexpensiveness, universal nature, effectiveness, rapid action and convenience, yields nontoxic by-products, and produces high-quality discharged effluents (Ali, 2010, 2012, 2013; Ali, Asim, & Khan, 2012; Ali & Gupta, 2007; Vakili et al., 2014a).

Organic materials obtained from living or dead creatures are known as biomass and are reported to be used as low-cost sorbents

for removal of pollutions (Salamatinia, Kamaruddin, & Abdullah, 2007). Chitosan (CS) as a naturally abundant biopolymer has attracted considerable attention as an appropriate adsorbent for dye elimination due to its favorable properties (mainly cationicity and macromolecular structure) (Crini & Badot, 2008; Muzzarelli et al., 2012). The amino groups in CS backbone could be in the form of neutral or protonated one depending on the pH. In acidic environment, due to protonation of the amino groups, CS will have a strong positive charge. Thus, it has gained a generous amount of interest to act as a cationic adsorbent in adsorption processes (Milhome et al., 2009). The adsorption capacity of CS could be enhanced by different physical and chemical modifications (Acharyulu, Gomathi, & Sudha, 2013). Physical modifications are such as the conversion of raw CS flakes or powders into beads (Mello, Bedendo, Nome, Fiedler, & Laranjeira, 2006), while chemical modifications include cross-linking, impregnation and grafting (Vakili et al., 2014b). Impregnation of CS with cationic surfactants is an appropriate strategy leading to an increase in the positive charge density of CS.

The use of CTAB as a cationic surfactant to increase the adsorption capacity of chitosan beads has been reported to successfully adsorb the congo red (Chatterjee, Lee, Lee, & Woo, 2009). In spite of good adsorption performance of CTAB modified chitosan bead, leaching of CTAB in the aqueous environment due to solubility of

* Corresponding author.

E-mail addresses: mohd.rafatullah@yahoo.co.in, mrafatullah@usm.my (M. Rafatullah).

CTAB in water is a main drawback. Some environmental concerns are raised because of this problem. CTAB as the only cationic surfactant used so far for chitosan beads and adsorption capacity of chitosan beads has shown 1.94 times increase (Chatterjee et al., 2009). This finding suggests the importance of studying other alternative cationic surfactants which are more stable and do not suffer from leaching problems. The present study aims at improving the adsorption performance of CS beads using a cationic surfactant. Hexadecylamine (HDA) is a cationic surfactant with a hydrophilic head (NH_2) and it has been chosen to impregnate CS beads. Therefore the originality of this study is seen with regards to the use of HDA to increase the cationicity of CS beads for reactive dye removal from aqueous solution. In addition the tendency for surfactant leaching into the water could be avoided due to the insolubility of HDA in water. To the knowledge of the authors so far there has been no report on studying the combination of Chitosan and HAD to be used for dye removal. Therefore, there is a necessity in understanding the behavior of this combination as a low cost adsorbent for improved dye removal. A comparison between the adsorption capacities of HDA modified CS beads and unmodified CS beads for reactive blue 4 (RB4) dye removal in batch operation has also been studied. Effects of pH and HDA concentration on RB4 adsorption have also been demonstrated. Equilibrium isotherm, kinetic and thermodynamic studies have been performed to express the adsorption mechanism of RB4 onto the prepared adsorbents. The CS and CS/HDA beads were also characterized to elucidate the adsorption behavior.

2. Experimental

2.1. Materials

Medium molecular weight CS (75–85% deacetylated), HDA, acetic acid, sodium hydroxide (NaOH), and the commercial Reactive Blue 4 (RB4) as an anionic dyestuff (Procion Blue MX-R, Color index number 61205, CAS number 13324–20–4, dye purity 35%, chemical formula $\text{C}_{23}\text{H}_{14}\text{Cl}_2\text{N}_6\text{O}_8\text{S}_2$) were all purchased from Sigma–Aldrich, Malaysia. All the chemicals used were of analytical grade. The chemicals were used directly without further purification.

2.2. Adsorbents preparation

The CS beads were prepared by dissolving 2 g of chitosan flakes in 100 mL of 1% (v/v) acetic acid solution. The mixture was then stirred using a magnetic stirrer for 5 h at room temperature. The obtained solution was then added drop-wise into a 2 M NaOH solution to form beads. The beads inside the solution were left overnight under stirring for neutralization of the acetic acid in the CS gel. The beads were then collected by filtration and washed to remove NaOH until neutral pH. The beads were then oven-dried at 50 °C for 24 h to eliminate any moisture that remained in the pore structure of the adsorbent.

To prepare the CS/HDA beads, the desired amount of HDA (0–5%) was added into the CS solution (2 wt.% CS and 1% (v/v) acetic acid). This solution was stirred for 6 h at 50 °C and then added drop-wise into the NaOH solution. The CS/HDA beads were then filtered, thoroughly and washed until neutral pH. The beads were then dried at 50 °C for 24 h.

2.3. Characterization

The adsorbents were characterized using a scanning electron microscope (SEM) (Quanta FEG450) and Fourier transform infrared spectrometer (FT-IR) (Thermo Scientific, Nicolet IS10, USA) in the range of 500–4000 cm^{-1} . In addition, surface charge of the adsorbents was assessed by zeta potential measurements using a

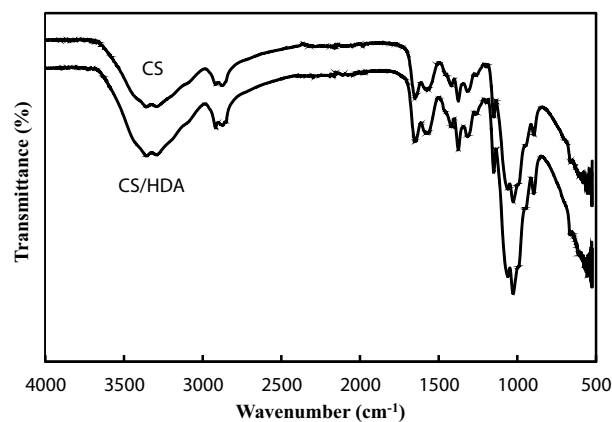


Fig. 1. The FT-IR spectra of CS and CS/HDA beads.

zetasizer (Malvern, UK). To determine the zeta potential, about a 0.1 g of the adsorbents was ground into powder and poured into 100 mL of deionized water, followed by sonication and then stirring for 4 h and 24 h, respectively, and allowed to settle overnight. After this step, the samples were drawn out and introduced into vials. The pH was adjusted to pH 5 using 0.1 M HCl or 0.1 M NaOH solution.

2.4. Adsorption experiments

Adsorption experiments were conducted at room temperature (30 ± 2 °C) in a batch process. A 250 mL Erlenmeyer flask containing 200 mL of RB4 solution was first placed in contact with 0.20 g of the adsorbents under stirring at 200 rpm. During the adsorption process, 5 mL of the solution was drawn out at certain time intervals. The concentration of RB4 in solution was measured using a Cary 60 UV-Vis Spectrophotometer–Agilent Technologies at 599 nm. The amount of RB4 adsorbed (q_e , mg/g) was measured based on the change in the RB4 concentration before and after the adsorption process using equation (Eq. (1)) as given below:

$$q_e = \frac{(C_0 - C_{eq}) \times V}{W} \quad (1)$$

where q_e is the dye adsorption capacity (mg/g); C_0 , represents the initial RB4 concentration (mg/L) in the solution; C_{eq} , represents the equilibrium RB4 concentration (mg/L) in the solution; V , is the volume of the RB4 solution (L); and W , is the dry weight of adsorbents (g). All the experiments in this study were conducted in triplicate to assure the accuracy of the results.

3. Results and discussion

3.1. Characterization

The prepared CS and CS/HDA beads were characterized using FT-IR spectrophotometer to reveal any modifications in the vibration modes of the main groups. As presented in Fig. 1, for CS beads, the characteristic bands are around 3289 cm^{-1} due to the stretching vibrations of the –OH and –NH groups (Yan, Dai, Yang, Yang, & Cheng, 2011). The peak at 2917 cm^{-1} could be attributed to the existence of –CH groups (Igberase, Osifo, & Ofomaja, 2014). Other important characteristic bands are such as the peak at 1645 cm^{-1} and 1574 cm^{-1} and 1418 cm^{-1} that are assigned to amide I, –NH₂ bending vibration and aliphatic C–H bending vibration, respectively (Cao et al., 2014). A band at 1374 cm^{-1} could be ascribed to the –CH₃ symmetrical deformation mode (El Harmoudi et al., 2014). The peaks at 1197 cm^{-1} and 1149 cm^{-1} are attributed to the –CN stretching vibrations (Zhang, Zhang, & Helleur, 2015). In

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