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Enhancing reactive blue 4 adsorption through chemical modification of chitosan with hexadecylamine and 3-aminopropyl triethoxysilane

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ABSTRACT

The adsorption of dye on chitosan and its derivatives is considered as an alternative and environmentally friendly method. Nevertheless, chemical modification of chitosan can lead to a more suitable adsorbent. In this study, the adsorption performance of chemically modified chitosan beads using a cationic surfactant (hexadecylamine) and an organo-silane (3-aminopropyl triethoxysilane) was studied for removal of reactive blue 4 (RB4) dye from aqueous solution. The chemical structure, surface properties and morphology of modified chitosan beads were analysed using FTIR, SEM and zeta-potential techniques. Results revealed that the adsorption of the RB4 was more favored in acidic conditions (pH 4). After modification adsorption capacity of chitosan beads increased for 1.48 times. The maximum adsorption capacity of chitosan beads increased from 317.1 mg/g to 468.8 mg/g after modification. This increase was attributed to the increase in the positive charge of modified chitosan beads. The experimental data obtained from adsorption of RB4 onto unmodified and modified chitosan confirmed a better fitness to Freundlich isotherm model ($R^2 = 0.946$ and 0.892, $\chi 2 = 22.414$ and 45.62) as compared to Langmuir model ($R^2 = 0.894$ and 0.777, $\chi 2 = 138.301$ and 47.08). It was concluded that chemical modification is a suitable method to improve the anionic dye adsorption efficiency of chitosan beads.

1. Introduction

Reactive dyes are the most popular and extensively used groups of dyes for dyeing purposes in different industries [1]. However, they suffer from some drawbacks such as high salt content of the wastewater, low adsorption ability, non-biodegradability, high water solubility and low degree of fixation on the surfaces which result in the generation of high contaminated wastewater [2]. The presence of reactive dyes in the environmental could threat the ecosystem due to their toxicity effects and sunlight transmission reduction in aquatic environment [3]. These drawbacks will lead to serious environmental issues if the effluents enter the environment without proper dye elimination. Among various techniques used for elimination of dyes, adsorption is reported widely as an effective method due to its low cost, effectiveness, convenience as well as producing high-quality discharged effluents [4,5].

In the recent years, researchers have been tried to produce effective adsorbents with effective adsorption capacity that are cost effective, abundant and environmentally friendly [6–8]. As a low-cost and abundantly natural biopolymer, chitosan possesses desired properties to be used in adsorption process. Chitosan has received significant attention by researchers to act as a cationic sorbent in adsorption processes. In acidic environment, chitosan molecules will be positively charged due to the protonation of the amino groups along the chitosan backbone [9]. Therefore, increasing the amount of functional groups (mainly amino groups) through chemical modification using different types of modification agents will create new chitosan derivatives with improved adsorption properties. In previous research performed the effect of hexadecylamine (HDA) [10] and 3-aminopropyl triethoxysilane (APTES) [11] on chemical modification of chitosan for reactive blue 4 (RB4) removal has been reported. Nevertheless, the effect of simultanious modification of these chemicals has not been reported so far.

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This study aims at obtaining and characterizing the physically and chemically modified chitosan beads for RB4 removal from aqueous solution. To achieve this objective, the physically modified chitosan in form of beads were modified simultaneously by HDA and APTES. HDA is a cationic surfactant with a hydrophilic head (NH_2) and APTES is a cationic amine-terminated organosilane with a hydrophilic group (NH_2). These chemicals have been used with the expectation of increasing the amino groups on the surface of chitosan and the surface charge (cationicity) of the beads to consequently improve the adsorptive performance of chitosan. The prepared modified chitosan beads have been characterized for correlation with the sorption behavior.

2. Materials and methods

2.1. Materials

Chitosan (CS) with deacetylation degree of 75%–85% and medium molecular weight was purchased from Sigma-Aldrich, Malaysia. HDA, APTES, acetic acid, sodium hydroxide (NaOH), and RB4 were all supplied by Sigma-Aldrich, Malaysia. The solvents and materials were of analytical grade and used directly without further purification. Distilled water (prepared in Universiti Sains Malaysia) was used for all dillution purposes and solution preparations.

2.2. Preparation of adsorbents

Preparation of the modified chitosan beads was performed following the conditions as reported by Vakili et al. [10] and Vakili et al. [11]. Briefly, 3.04 mM of HDA was first 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 a 2 M NaOH solution. The CS/HDA beads were then filtered and thoroughly washed with distilled water until constant pH of the washing water. Afterwards, the prepared CS/HDA beads were transferred into an APTES solution at a concentration of 2% (v/v). The obtained solution was stirred for 8 h at 50 °C. Afterward, the resulting modified CS beads (CS/HDA/APTES) were filtered and rinsed with distilled water several times. Finally, the beads were dried in an oven at 50 °C for 24 h.

2.3. Characterization

To analyze the functional groups present on the surface of the adsorbents, FTIR spectra of the CS and CS/HDA/APTES beads were recorded using a FTIR (Thermo Scientific, Nicolet IS10, USA), in the range of 500–4000 cm^{-1}. Scaning electron microscopy (SEM) images of the prepared sorbents were taken using a Hitachi S-3400 N (Japan) SEM to study the surface morphology of the beads. In addition, a zetapotential (Malvern, UK) was applied to study the surface charge of adsorbents.

2.4. Adsorption studies

Batch adsorption experiments were conducted at room temperature (30 ± 2 °C) by adding 0.20 g of the adsorbents in 200 mL of RB4 solution at pH 4 and stirred 200 rpm. Effect of pH, dye concentration and temperature on the adsorption performance of adsorbents were investigated. Afterwards, to evaluate the remaining RB4 concentration at the end of the adsorption process, 5 mL of the solution was drawn out, centrifuged and then analyzed by a spectrophotometer (Cary 60 UV-V) at 599 nm. The adsorption capacities were calculated using equation below:

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

q_e = Dye adsorption capacity (mg/g)
C_0 = Initial RB4 concentration (mg/L)
C_{eq} = Equilibrium RB4 concentration (mg/L)
V = Volume of the RB4 solution (L)
W = Dry weight of adsorbent (g)

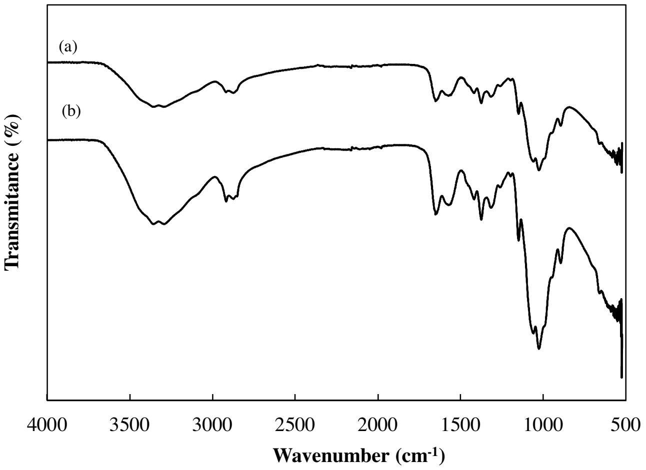

Fig. 1. The FTIR spectra of (a) CS and (b) CS/HDA/APTES beads.

3. Results and discussion

3.1. Characterization

3.1.1. Fourier transform infrared (FTIR) spectroscopy

FTIR analysis was carried out to identify the functional groups available on the surface of the adsorbents to reveal the possible changesin the functional groups which occurred after the modification. The FTIR spectra of prepared adsorbents in the present study (CS and CS/HDA/APTES beads) are presented in Fig. 1. As could be noted in this figure, some changes are observed in the intensity of the peaks following the modification process which could be attributed to the effect of modification and experimental conditions. Fig. 1 illustrates broad bands in the region of 3000–3600 cm^{-1} for both adsorbents attributed to the stretching vibration of both primary amine and OH stretching groups [12]. After modification the intensity of this peak for CS/HDA/APTES beads show an increase as compared to that of unmodified CS beads. This increase is attributed to the presence of both APTES and HDA molecules, leading to accumulation of —OH and —NH_2 groups on the surface of modified beads. The peaks at around 2917 cm^{-1} is attributed to the —C—H stretching in —CH and —CH_2 groups for both adsorbents. However, it can be seen that the peak intensity for modified beads is higher than unmodified beads. The N—H bending vibration at a wavenumber 1574 cm^{-1} and the —CN stretching vibration at 1149 cm^{-1} visibly shift to 1568 cm^{-1} and 1146 cm^{-1}, respectively in CS/HDA/APTES beads. Comparing the spectra of CS and CS/HDA/APTES beads demonstrate an increasing intensity for the peaks at 1021 cm^{-1} and 998 cm^{-1}. There is also a slight shift observed to 1017 cm^{-1}, and 993 cm^{-1}, respectively. These peaks denote the Si—CH_2 stretching, Si—O—Si symmetric stretching and the Si—OH stretching which have occurred in the modified adsorbent using APTES [13]. This result suggests that the HDA and APTES were adsorbed or underwent reaction with chitosan [14]. Moreover, it was observed that after modification of CS, the intensities of these peaks were higher than that of CS beads which could be related to the excessive presence of hydroxyl and amine groups. It could be seen that in all modified and unmodified beads, the peaks are of similar shapes. However, the peaks of the modified bead show higher intensities as compared to those of the CS beads.