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Preparation of Chitosan Beads for the Adsorption of Reactive Blue 4 from Aqueous Solutions

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ABSTRACT

In the present study, chitosan beads were prepared at different preparation conditions and then applied for adsorption of Reactive Blue 4 (RB4) in a batch adsorption process. Effect of beading parameters such as chitosan concentration, acetic acid concentration and temperature in the removal of RB4 from aqueous solution was investigated. It is found that increasing the concentration of chitosan, acetic acid, and temperature decreased dye removal. The chitosan beads prepared with 2% chitosan and 1% acetic acid concentration at room temperature (30 ± 2 °C) were more suitable for RB4 removal. The beading parameters were found to be effective on the adsorption properties of the prepared adsorbents. Thus, the preparation of chitosan beads at appropriate conditions is a suitable method to improve the anionic dyes adsorption from aqueous solutions.

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INTRODUCTION

In recent years, rapid expansion of the textile industry has led to an increase in colored effluents. This is considered as one of the main environmental and water pollution sources due to their high visibility, resistance and toxic impact [1]. The release of dyes to the environment through untreated wastewater poses serious threats to the environment. Hence, an effective method for treatment of dyes wastewater is necessary to control water pollution. Adsorption is one of the superior methods for dye removal because it is rapid, convenient and able to screen out toxic contaminants. This method also has low initial costs, simple design and operation [2, 3].

Chitosan is one of the world's most plentiful biopolymers produced from chitin using fungal species and exoskeleton of sea creatures such as crayfish, lobster, prawn, crab and shrimp. Use of chitosan as an ideal absorbent for dye removal has received much attention by researchers because of its relatively low cost and extraordinary absorption capability for dye removal [4, 5]. Chitosan is a heterogeneous, linear, cationic and polysaccharide biopolymer with a high molecular weight [6]. The applications of chitosan as an adsorbent in form of flakes are limited by their high crystallinity, low surface area, nonporosity, resistance to mass transfer and low adsorption capacity [7].

To overcome these disadvantages, chitosan could be physically modified via conversion to a conditioned form on the consideration of the favorable properties and applications of the derivatives. Chitosan flakes are usually subjected to physical modification by converting into gel beads, membrane and film. All these modifications lead to increase porosity, expand chitosan polymer chains, increase surface area, decrease crystallinity and improve access to internal sorption sites and consequently enhanced adsorption capacity [1]. Conversion of chitosan flake to beads has been performed by many researchers by dropping acid dissolved chitosan into an alkali solutions such as

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NaOH or methanol-NaOH, followed by drying [8]. Chitosan, in the form of membrane and films, has been reported by a few researchers as an adsorbent for dye removal from aqueous solutions. However, a matured understanding is yet to be achieved. Chitosan membrane and film can be made by casting the chitosan solution mixed with alkali into a flat surface to evaporate the solvent [9].

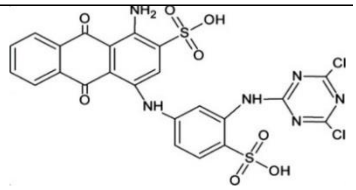
In general, the adsorption properties of chitosan beads depends on several parameters such as chitosan concentration, acid concentration and temperature during beads preparation. The current study aims at discovering the optimal conditions for preparing chitosan beads as a suitable adsorbent in the adsorption of the dye Reactive Blue 4 (RB4). The beads were prepared at different conditions by varying chitosan concentration, acetic acid concentration and temperature.

MATERIALS AND METHODS

Materials

The chitosan flakes (medium molecular weight, 75 to 85% deacetylated), acetic acid, sodium hydroxide (NaOH), and RB4 were obtained from Sigma-Aldrich, Malaysia. The significant properties of RB4 are listed in Table 1. These chemicals were used directly without further purification, and distilled water was used for all dilution and solution preparations purposes throughout this work.

TABLE 1. Structure and properties of Reactive Blue 4

Properties	Info
Molecular structure	
Molecular formula	$C_{23}H_{14}Cl_2N_6O_8S_2$
Molecular Weight	620.4
λ max (nm)	599
Appearance	Deep blue powder
CAS number	13324-20-4
Color index number	61205
Ionization	Reactive
Purity (%)	35

Preparation of adsorbents

The chitosan solution was prepared under magnetic stirring for 5 h by dissolving different concentrations of chitosan flakes (1, 2, 3, 4, and 5 wt.%) in 100 mL of acetic acid solution with different acid concentrations (0.5, 1, 2, 3, 4, 5 and 7%) at different temperatures (30, 50 and 70°C) until complete dissolution. The obtained solution was then added drop-wise into a 2 M NaOH solution to form beads and the mixture was then continuously stirred overnight. The beads were then washed using distilled water until neutrality. Finally, the beads were oven-dried.

RESULTS AND DISCUSSION

Chitosan beads preparation

When chitosan was dispersed in acetic acid solution, a dissolution phenomenon caused by the chemical reaction of acetic acid and NH_2 groups in chitosan molecular structure, resulted in the protonation of the amino groups, rendering it soluble. Drop-wising the prepared chitosan gel into the NaOH solution lead to occurrence of liquid–liquid phase separation between the acetic acid and NaOH [10]. Meanwhile, NaOH concentration (2 M) was higher than that of acetic acid concentration (0.17 M) at the boundary of the two phases so that NaOH reacted with the acetic acid protonated amino groups.

Thus, chitosan gel coagulated to form porous, spherical and uniform chitosan beads. Thereafter, the chitosan beads were dried and it shrank because of the evaporation of large amount of water present in chitosan beads. According to Zhao and Yu [11], water content and diameter of the chitosan beads could be affected significantly by the NaOH concentration. Increasing the concentration of the NaOH solution decreases the diameter and weight of the prepared beads, which means that the chitosan beads could shrink considerably. Therefore, the porosity decreased.

Effect of chitosan concentration

The RB4 adsorption behaviors of the chitosan beads prepared from different concentrations of chitosan (1 to 5 wt.%) were studied and the results are shown in Figure 1. Acetic acid concentration and temperature were 1% and 30°C, respectively. When the chitosan concentration increased, the size of beads increased due to the presence of higher amount of chitosan in the dropped beads [12].

At concentrations lower than 2 wt.%, the injected chitosan solution could not solidify to form beads in the NaOH solution. On the other hand, the chitosan solution with 5 wt.% chitosan concentration was extremely viscous and not injectable.

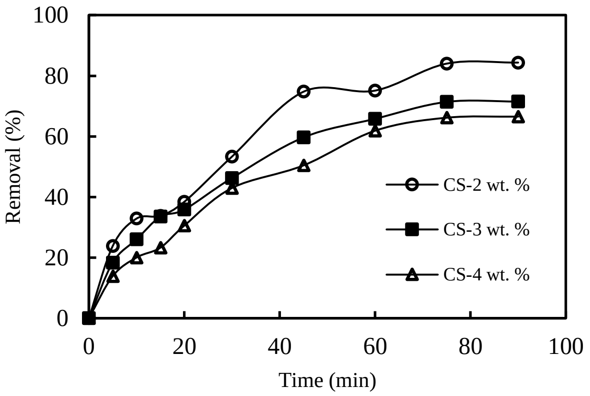


Figure 1. Effect of chitosan concentration on RB4 adsorption; initial RB4 concentration, 10 mg/L

When the chitosan concentration increased from 2 to 4 wt.% the dye removal decreases from 84.3 to 66.5%. This reduction could be due to the increased intermolecular entanglement of chitosan chains at higher chitosan concentration (>2 wt.%). Thus, the freedom of movement of the individual chains became restricted because of the increased extent of entanglement, which resulted in a significant change in the porous network and decrease in the number of available functional groups and consequently reduced adsorption capacity [13]. Thus, the dye removal gradually decreased with increasing chitosan concentration. Dye molecules, which penetrated into the pores of beads, were adsorbed on functional groups located on the external surface and the formation of adsorbed dye clusters was constricted or completely blocked the pores. This hindrance could increase with increasing chitosan concentration, which consequently decreased the accessibility of dyes to available active sites [14].

Effect of acid concentration

Adsorption performance of the beads prepared with 2 wt.% of chitosan at different acetic acid concentrations (0.5 to 7%) was studied. Results revealed that the RB4 percentage removal enhanced by increasing the concentration of acetic acid from 0.5 to 1%. At a concentration of 1%, dye removal reached its maximum level and then decreased by further increasing the concentration. Figure 2 shows that RB4 removal decreased from 84.3 to 77.1% when the acid concentration was increased from 1 to 3%. This reduction was further intensified by increasing the acid concentration in the chitosan solution. The chitosan bead prepared with 7% acid acetic showed the lowest RB4 removal (72.2%). This reduction could be due to the depolymerization and deformation of macromolecular coils as well as changes in the pore network at high acid concentration, which reduced the adsorption capacity of RB4 [15]. In addition, increasing the acid concentration caused a decrease in polymer viscosity as when the ionic concentration was increased so that long-range electrostatic interactions are screened. These changes caused an increase in the elasticity of polymer chains up to their conformation from long 'sticklike' to coil [16]. Therefore, highest dye removal (84.3%) occurred at 1% acid concentration because at this concentration, chitosan could dissolve and the functional groups were more accessible. The whole macromolecule becomes positively charged at this concentration because of the protonation of amino groups, became chitosan to a cationic polyelectrolyte.

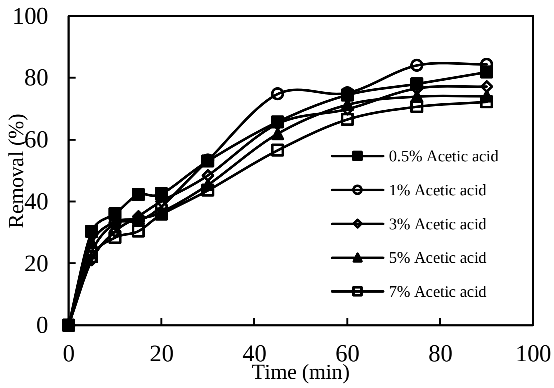


Figure 2. Effect of acetic acid concentration on RB4 adsorption; initial RB4 concentration, 10 mg/L**.**

Effect of temperature

Experimental data shows that increase in temperature during chitosan beads preparation decreases the RB4 removal percentages. When the temperature increased from 30 to 70°C, the dye removal percentage decreased from 84.33 to 62.98% (Figure 3).

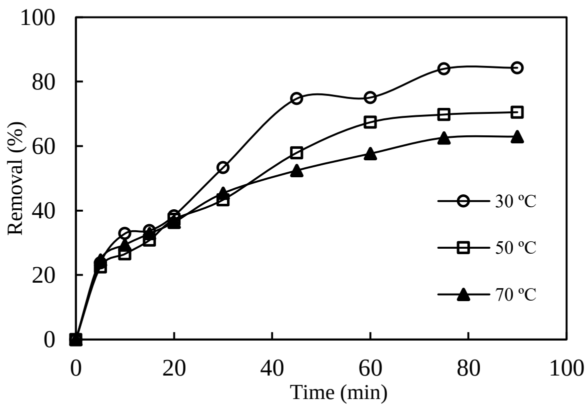


Figure 3. Effect of temperature on RB4 adsorption; initial RB4 concentration, 10 mg/L

This reduction could be due to the chemical change of chitosan to a chitin-like material at high temperatures [17]. Chitosan degrades and rapidly breaks down into polymer chains at high temperatures. As such, the acetylated and deacetylated units of the polymer are dehydrated, depolymerized, and decomposed, thereby decreasing adsorption capacity [16]. In addition, when the chitosan solution is heated, its viscosity decreases, and this decrease is more pronounced at high temperatures. Conversely, high viscosities were observed at low temperatures.

CONCLUSIONS

The initial chitosan concentration is the major determinant of chitosan solution viscosity, which can either be extremely low, results in the formation of small and mechanically weak beads, or too high, results in the formation of big and hard beads. However, both have low adsorption capacities. Therefore, an optimum initial chitosan concentration of 2 wt.% was determined according to the maximum adsorption achieved from the experiments. The chitosan beads prepared from the solution with a low acid concentration have a higher adsorption capacity that those prepared from high acid concentrations. Thus, the optimization concentration of acetic acid is determined to be 1%. The beads synthesized from the solution with low temperature showed a higher adsorption performance. The temperature used for preparation of the beads according to the obtained dye adsorption data was room temperature (30 ± 2°C).

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Persian Abstract

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چکیده

در پژوهش پیش رو، بیدهای کیتوزان در شرایط آماده‌سازی متفاوت تهیه گردید و سپس به منظور جذب ری‌اکتیو بلو چهار (RB4) در یک فرآیند جذب ناپیوسته به کار گرفته شد. اثر پارامترهای مربوط به ساخت بیدها، نظیر غلظت کیتوزان، استیک‌اسید و درجه حرارت در حذف RB4 از محلول مورد بررسی قرار گرفت. مشاهده شد که با افزایش غلظت کیتوزان، استیک‌اسید و دما، بازدهی حذف رنگ کاهش یافت. بیدهای کیتوزان توسط کیتوزان با غلظت دو درصد و استیک‌اسید یک درصد در دمای محیط ، که برای حذف RB4 مناسب‌تر بود، تهیه گردید و مشخص شد که پارامترهای دخیل بر ساخت بیدها بر خواص جذب‌کنندگی جاذب‌های ساخته شده موثر بوده‌اند. بنابراین، تهیه بیدهای کیتوزان تحت شرایط مطلوب، روشی مناسب برای افزایش جذب رنگ‌های آنیونی از محلول آبی می‌باشد.