

Preparation, characterization and adsorption properties of chitosan nanoparticles for eosin Y as a model anionic dye

Wen Li Du, Zi Rong Xu*, Xin Yan Han, Ying Lei Xu, Zhi Guo Miao

Institute of Feed Science, College of Animal Science, Zhejiang University, The Key Laboratory of Molecular Animal Nutrition, Ministry of Education, Hangzhou 310029, China

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Abstract

The present study dealt with the adsorption of eosin Y, as a model anionic dye, from aqueous solution using chitosan nanoparticles prepared by the ionic gelation between chitosan and tripolyphosphate. The nanoparticles were characterized by atomic force microscopy (AFM), size and zeta potential analysis. A batch system was applied to study the adsorption of eosin Y from aqueous solution by chitosan nanoparticles. The results showed that the adsorption of eosin Y on chitosan nanoparticles was affected by contact time, eosin Y concentration, pH and temperature. Experimental data followed Langmuir isotherm model and the adsorption capacity was found to be 3.333 g/g. The adsorption process was endothermic in nature with an enthalpy change (ΔH) of 16.7 kJ/mol at 20–50 °C. The optimum pH value for eosin Y removal was found to be 2–6. The dye was desorbed from the chitosan nanoparticles by increasing the pH of the solution.

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1. Introduction

Dyes are widely used in textile industries. The wastewaters from these industries are important sources of water pollution. It has been estimated that worldwide annual production of dyes is around 7×10^5 t, 5–10% of which is discharged into water by the textile industries [1]. Dyes in wastewater undergo chemical changes, consume dissolved oxygen, and destroy aquatic life. Moreover, some dyes and their degradation products may be carcinogenic and/or toxic. So the wastewaters from the textile industries should be treated before their discharge into environment.

Many investigators have made great effort to study different techniques for removal of dyes in wastewater. Now, various types of technology are available such as chemical coagulation, cold point extraction [2–4], micellar enhanced ultrafiltration [2–4], nanofiltration [5], and adsorption on to kaolinite [6], activated agricultural solid waste [7], various types of activated carbon

[8,9], and magnetic nanoparticles [10]. The activated carbon generally used for dye adsorption is very expensive.

Biosorption, which uses waste biomaterials as sorbents, is a newly developed technique [11,12] for the removal of harmful substances from water bodies, but suffers serious limitations in the case of anionic dyes as most of the biomaterials contain negatively charged cellulosic moieties, which lower adsorption due to coulombic repulsion.

Chitosan, a cationic polysaccharide, is easily obtained by partially deacetylation of chitin, which is the second most abundant biopolymer on earth only after cellulose and commonly found in the exoskeleton or cuticles of many invertebrates and in the cell wall of most fungi and some algae. Due to the unique polycationic nature, chitosan and its derivatives have been used for various applications in many different fields including biomedicine, food, agriculture, biotechnology and pharmaceuticals [13]. Recent studies indicated that chitosan showed a higher capacity for adsorption of anionic dyes [14].

In the present study, chitosan nanoparticles were prepared with a narrow size distribution based on ionic gelation between positively charged chitosan and negatively charged tripolyphosphate. The nanoparticles were further used for the removal of

* Corresponding author. Tel.: +86 571 86022298; fax: +86 571 86994963.
E-mail address: wenlidu@126.com (W.L. Du).

eosin Y as a model anionic dye, to obtain information for treating effluents from the dye industry.

2. Materials and methods

2.1. Materials

Chitosan, from shrimp shell with a molecular weight of 150 kDa and deacetylation degree of 90%, was purchased from Yuhuan Ocean Biochemical Co. (Zhejiang Yuhuan, China). Tripolyphosphate (TPP) and eosin Y were obtained from Sigma Chemical Co. (USA). The water used throughout this work was the reagent-grade water produced by Milli-Q SP ultra-pure-water system of Nihon Millipore Ltd., Tokyo. All other chemicals used were of analytical grade reagents commercially available and used without further purification.

2.2. Preparation of chitosan nanoparticles

Chitosan nanoparticles were prepared based on the ionic gelation of chitosan with TPP anions. Briefly, chitosan was dissolved in 1% (v/v) acetic acid to obtain a 0.2% (w/v) chitosan solution. TPP was dissolved in water to a concentration of 1%. Under magnetic stirring at room temperature, 1 ml of tripolyphosphate solution was added dropwise to 25 ml of chitosan solution. The mixture was stirred for a further 20 min followed by sonication. The resulting suspension was subsequently centrifuged at $12,000 \times g$ for 10 min. The precipitate was suspended in water, centrifuged again and then freeze-dried. Then the freeze-dried chitosan nanoparticles were resuspended for characterization or directly used for adsorption experiments.

2.3. Characterization

Chitosan nanoparticles were visualized with atomic force microscopy (AFM, SPM-9500J3, Shimadzu CO., Japan) in the contact mode. Samples dissolved in water were placed onto freshly cleaved mica and dried in air at room temperature. AFM image was performed with a spring contact of $k = 0.03$ N/m using a nanoprobe cantilever made of silicon nitride (Si_3N_4).

Particle size distribution and zeta potential of chitosan nanoparticles were measured by Zetasizer Nano-ZS-90 (Malvern Instruments). The analysis was performed at a scattering angle of 90° at 25°C . For zeta potential measurements, samples were diluted with 0.1 mM KCl and measured in the automatic mode.

2.4. Adsorption and desorption studies

The adsorption of eosin Y onto chitosan nanoparticles was carried out in a batch process by using aqueous solutions of eosin Y. The variable parameters were tested including contact time, initial dye concentration, pH of the medium and temperature. In each experiment except for the initial concentration experiment, 100 mg chitosan nanoparticles were added to 100 ml water solution of eosin Y with a known concentration. The pH value was adjusted by adding a few drops of dilute NaOH or HCl if neces-

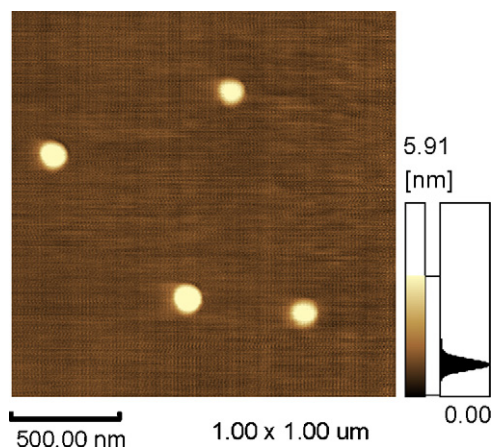


Fig. 1. AFM image of chitosan nanoparticles.

sary. The mixture, loaded in a 250 ml conical flask, was shaken at 100 rpm in the water bath of a thermostat at a particular temperature for different time intervals. Nanoparticles were removed by centrifuge at $12,000 \times g$ for 10 min. The adsorption amounts of eosin Y were determined by the concentration change of eosin Y in solution after adsorption using spectrophotometric method at 517 nm (Pharmacia Biotech Ultrospec 2000).

Desorption of eosin Y was performed by putting the removed nanoparticles into a clean 250 ml conical flask containing 100 ml water, and the pH was adjusted to 10.0, 11.0, and 12.0. The flasks were shaken at 100 rpm up to 20 h at 20°C . The concentration of the eluted dye was determined at different time intervals by the same method described above.

3. Results and discussion

3.1. Characterization of chitosan nanoparticles

Chitosan solution changed from a clear solution to an opalescent suspension when TPP was added. This transformation indicated that ionic gelation occurred between chitosan and TPP, and nanoparticles formed. The chitosan nanoparticles prepared took on a white powder and could disperse in water, dilute acidic and alkali solutions without aggregation.

Fig. 1 showed the morphological characteristic of chitosan nanoparticles by AFM image. Chitosan nanoparticles prepared were regular spheres. The mean size, width of distribution and zeta potential are essential parameters for nanoparticles. Fig. 2 showed a typical size distribution profile of the nanoparticles with a mean diameter of 69.33 nm in a narrow size distribution

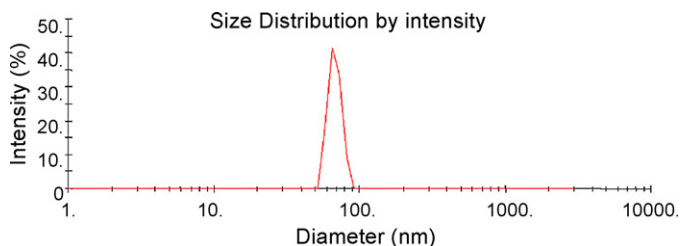


Fig. 2. Size distribution of chitosan nanoparticles.

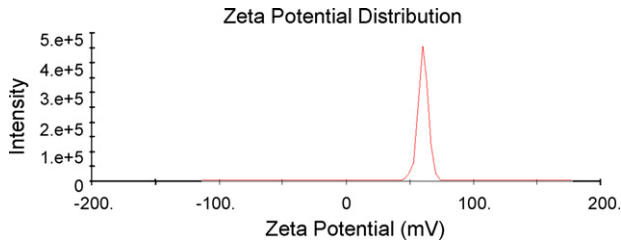


Fig. 3. Zeta potential distribution of chitosan nanoparticles.

(polydispersity index < 1). Particle charge is a stability determining parameter in aqueous nanosuspensions. A zeta potential of ± 30 mV is required as a minimum for a physical stable nanosuspension solely stabilized by electrostatic repulsion [15]. The zeta potential of the nanoparticles is about +65 mV as shown in Fig. 3.

3.2. Effect of contact time and initial dye concentration

The experimental results of adsorption of eosin Y onto chitosan nanoparticles at various concentrations with different contact time were shown in Fig. 4. The percentage of adsorption increased with an increase in the agitation time for any initial dye concentration and attained equilibrium within 4 h. The adsorption percentage decreased with the increase of initial dye concentration, but the actual amount adsorbed per unit mass of chitosan nanoparticles increased with the increase of eosin Y concentration. About 96% adsorption was observed in 2 h for the initial concentration of 100 mg/l. For an initial concentration of 200 mg/l, the adsorption percentage reached about 90% in 3 h. For the initial concentration of 400 mg/l, 81% of the dye was absorbed by chitosan nanoparticles in 210 min. From the above results, it was obvious that the adsorption occurred quickly and reached equilibrium within 4 h.

3.3. Effect of pH

The effect of pH on the percentage of dye adsorption by chitosan nanoparticles was shown in Fig. 5. The adsorption capacity of chitosan nanoparticles decreased with the increase of the solution pH. The adsorption capacity changed slightly from pH 2 to

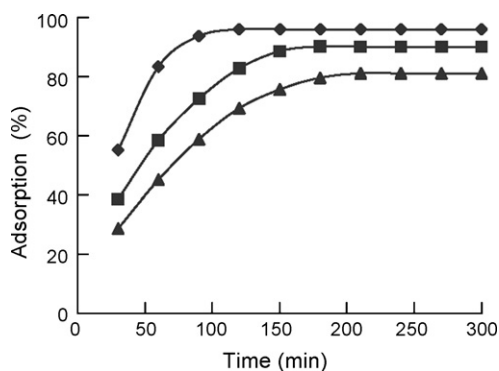


Fig. 4. Effect of contact time and initial dye concentration on eosin Y removal. Conditions: (chitosan nanoparticles: 1 mg/ml; pH: 5; temperature: 293.15 K). (◆) 100 mg/l; (■) 200 mg/l; (▲) 400 mg/l. Results represent averages of five replicated experiments.

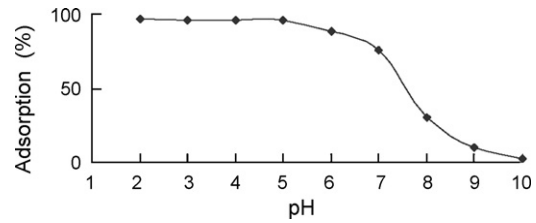


Fig. 5. Effect of pH on eosin Y removal. Conditions: eosin Y concentration, 100 mg/l; chitosan nanoparticles, 1 mg/ml; temperature, 293.15 K; contact time, 4 h. Results represent averages of five replicated experiments.

pH 5, then, decreased sharply when the pH value exceeded 7 and the adsorption percentage reduced to only about 2% at pH 10. The reason was that adsorption of the anionic dye eosin Y by chitosan nanoparticles was a process in which protonated amine group of chitosan interact with the anionic group of the dye. With the pH increasing, protonated amine groups decreased, so did the adsorption capacity.

Chatterjee et al. [14] reported that the chitosan hydrobeads conditioned with ammonium sulfate maintained the maximum adsorption capacity of about 76 mg/g for eosin Y below pH 8.0. However, the adsorption capacity of chitosan nanoparticles for eosin Y was 3.333 g/g below pH 5.0. The adsorption process of conditioned chitosan hydrobeads needed 20 h to reach equilibrium. On the contrary, chitosan nanoparticles reached equilibrium within 4 h. The reason for which chitosan nanoparticles had a large adsorption capacity and a quick adsorption process might be that chitosan nanoparticles had large specific surface area without internal diffusion resistance.

3.4. Adsorption isotherm

The equilibrium isotherm of eosin Y adsorption by the chitosan nanoparticles at pH 5 and 20 °C was shown in Fig. 6. The adsorption behavior could be described by the Langmuir adsorption equation [16].

$$\frac{C_e}{q} = \frac{1}{Kq_m} + \frac{C_e}{q_m} \quad (1)$$

where q is the equilibrium adsorption amount of eosin Y (mg/g), C_e the equilibrium eosin Y concentration in solution (mg/L), q_m the maximum adsorption amount of eosin Y per mg of adsorbent (mg/g) and K is the Langmuir adsorption equilibrium constant (L/mg). As shown in Fig. 7, the plot of C_e/q versus C_e yielded a straight line. From the slope and intercept, the values of q_m and K might be estimated to be 3.333 g/g and 7.69 ml/mg, respectively.

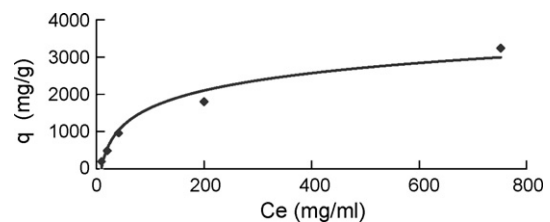


Fig. 6. Adsorption isotherm of eosin Y on chitosan nanoparticles. Conditions: chitosan nanoparticles, 1 mg/ml; eosin Y, 20–400 mg/l; pH: 5; temperature, 293.15 K.

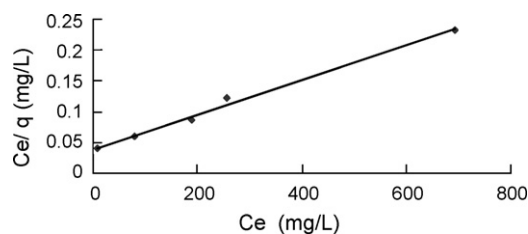


Fig. 7. A plot of C_e/q against C_e for the adsorption of eosin Y on chitosan nanoparticles. Conditions: Chitosan nanoparticles, 1 mg/ml; eosin Y, 20–400 mg/L; pH: 5; temperature, 293.15 K.

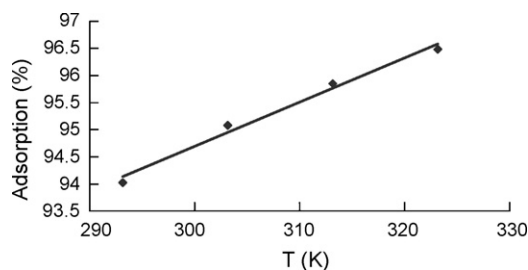


Fig. 8. Effect of temperature on eosin Y removal. Conditions: eosin Y concentration, 100 mg/l; chitosan nanoparticles, 1 mg/ml; contact time, 4 h; pH: 5. Results represent averages of five replicated experiments.

3.5. Effect of temperature

The effect of temperature on the adsorption of eosin Y by chitosan nanoparticles at pH 5 was indicated in Fig. 8. The adsorption amount of eosin Y increased with increasing temperature.

The thermodynamic parameters of the adsorption process were obtained from experiments at various temperatures using the following equation [17]. The plot of $\log(q/C_e)$ versus $1/T$ according to the following equation was indicated in Fig. 9.

$$\log_{10} \left(\frac{q}{C_e} \right) = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (2)$$

where ΔS is the entropy change, R the molar gas constant, ΔH the enthalpy change, T the absolute temperature, and q and C_e are the same as indicated above. The values of ΔH at 20–50 °C was 16.7 kJ/mol determined from the slope of the linear plot of $\log_{10}(q/C_e)$ versus $1/T$. This value revealed that the adsorption process was endothermic in nature.

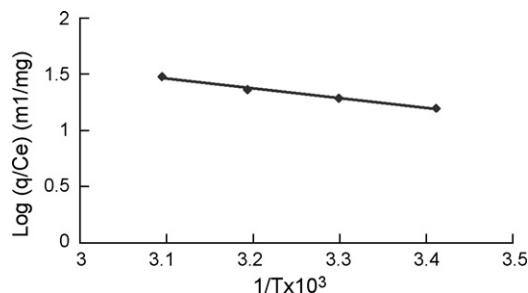


Fig. 9. A plot of $\log(q/C_e)$ against $1/T$. Conditions: chitosan nanoparticles, 1 mg/ml; eosin Y, 100 mg/l; pH: 5.

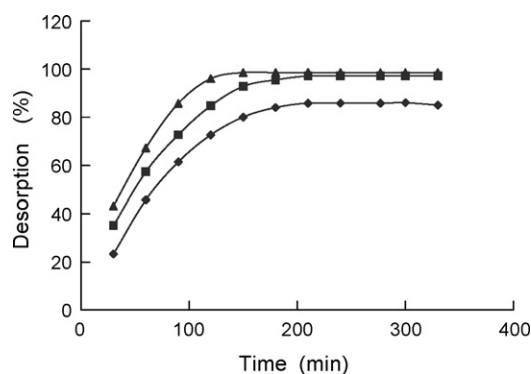


Fig. 10. Desorption of eosin Y from dye-loaded chitosan nanoparticles at different pH and time. Conditions: chitosan nanoparticles, 1 mg/ml; pH: 5; temperature, 293.15 K. (◆) pH 10; (■) pH 11; (▲) pH 12. Results represent averages of five replicated experiments.

3.6. Desorption

As shown in Fig. 10, the percentage of eosin Y desorbed increased with increasing the pH. Eosin Y has been found to be desorbed from the nanoparticles just by increasing the pH of the eluent to the alkaline range. The velocity of desorption also increased with increasing the pH of the eluent. The desorption percentage is about 60% within 60 min at pH 11.0, whereas 98.5% of the dye can be eluted at pH 12 in 150 min.

4. Conclusion

Chitosan nanoparticles showed an excellent capacity for adsorption of anionic dye, eosin Y, due to the large relative surface area and the high zeta potential. The adsorption process was very fast and attained equilibrium within 4 h. The data obtained from adsorption experiments agreed well with the Langmuir's isotherm model. The adsorption amount of eosin Y increased with the increase of temperature. The adsorption process was an endothermic process in nature. The adsorbed eosin Y could be desorbed efficiently using the alkaline solution and chitosan nanoparticles were recyclable.

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