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The sorption of acid dye onto chitosan nanoparticles

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Abstract

The behavior of chitosan nanoparticles as an adsorbent to remove Acid Green 27 (AG27), an acid dye, from an aqueous solution has been investigated with nanochitosan (particle size = 180 nm; degree of deacetylation = 74%). The dye concentration at equilibrium (Q_e, mg/g) was calculated using the weight of the nanoparticles in the mixed solution (Q_{es}) and the weight of chitosan in the nanoparticles (Q_{ep}). The experimental isotherm data were analyzed using the Langmuir equation for each chitosan sample; the Langmuir monolayer adsorption capacity (Q_0) was calculated with Q_{es} and Q_{ep} and the results were 1051.8 mg/g and 2103.6 mg/g, respectively, which were significantly higher than that of the micron-sized chitosan.

Keywords: Chitosan nanoparticles; Adsorption; Langmuir equation

1. Introduction

The environmental protection becomes a difficult task while many industries produce wastes that cause serious pollution. In the textile industry, large quantities of aqueous wastes and dye effluents are discharged from the dyeing process with strong persistent color and high BOD loading that are aesthetically and environmentally unacceptable [1]. Most of these dye wastes are toxic and may be carcinogenic [2], and this poses a serious hazard to aquatic living organisms. As a result, the removal of dyestuffs from effluents becomes important, and many governments have established environmental restrictions with regard to the quality of colored effluents and have forced dye-using industries to decolorize their effluents before discharging. Different kinds of conventional treatment technologies for dye removal have been investigated extensively [3–9], such as the trickling filter, activated sludge, chemical coagulation, carbon adsorption, and photodegradation processes. Among these chemical and physical methods, the adsorption process is fairly effective to produce a high-quality effluent without the formation of harmful substances, such as ozone and free radicals in the photodegradation process using UV. Methods are developed using different sorbents, such as peat [10,11], activated carbon [5], pith [12–16], fuller's earth [17,18], and wood [19,20].

Chitosan, a kind of natural polysaccharide derived from chitin, plays an important role in the adsorption process. The polymer is biodegradable and non-toxic and has extremely high affinity for many classes of dyes such as disperse, direct, reactive and acid dyes [21–28]. In an acidic aqueous medium, the cationized amino groups can adsorb anionic dye molecules by the electrostatic attraction. Yoshida et al. [26–28] studied the sorption of various dyes onto chitosan fibers and reported its high potentials for dye adsorption. Chiou and Li [29] also reported the adsorption of chemical cross-linked chitosan beads to Reactive Red 189 (C.I. 18210) at pH 3.0 and at 30 °C. However, the adsorption of nanochitosan is sparsely reported. It is believed that the nanochitosan should have a larger capacity because of its large surface area. Chang and Che [30] studied the sorption behavior of the carboxymethylated-chitosan-bound Fe_3O_4 nanoparticle to Acid Orange 12 (AO12) and Acid Green 25 (AG25), and found that the adsorption capacities of AO12

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(1883 mg/g) and AG25 (1471 mg/g) were very high due to the large surface area.

The aim of this paper is to explore the potential of nanochitosan in the dye removal area. Chitosan nanoparticles were prepared using a typical gelation reaction between the positively charged amino groups of chitosan and the negatively charged counter-ions of sodium tripolyphosphate (TPP) [31]. The adsorption ability of the nanoparticles was studied using anthraquinone type Acid Green 27 (AG27), which is structurally similar to AG25 (Fig. 1). The equilibrium sorption capacities of the dyes on chitosan were studied using the adsorption isotherm technique. The experimental data were then fitted into the Langmuir equation.

2. Experimental

2.1. Materials

Chitosan (molecular weight: 100,000, 74% DD) was prepared from chitin (Sigma). Other chemicals of reagent grade were from Aldrich.

2.2. Preparation of chitosan nanoparticles emulsion

The emulsion was prepared as reported before [31]. Typically, a TPP solution (95.4 ml, 1.45 mg/ml) was slowly dropped (10 ml/min) into a chitosan solution (150 ml, 2 mg/ml in 0.5% dilute acetic acid) in a 500 ml round-bottom flask under mechanical stirring (1200 rpm/min). After a further stirring of 20 min, a milky emulsion was obtained at pH 5.0.

The nanoparticles were obtained by freezing the emulsion at −4 °C. The frozen emulsion was then thawed in the atmosphere and the nanoparticles were precipitated [32]. After another stirring for 24 h, the nanoparticles were collected after a centrifugation for 24 h. They were then washed with D.I. water and vacuum dried at 60 °C for 24 h.

2.3. Dye adsorption

The nanochitosan emulsion (75 ml) was extracted into a sealable glass vessel, and then mixed with 50 ml of AG27 solution at a specific concentration. The vessel was sealed and shaken in shaker for 24 h at 200 rpm/min and at 25 °C. The mixed solution was then centrifuged (18,000 rpm/min (40,000g); 4 °C for 60 min). The filtrate was analyzed with a visible spectrometer. The dye concentration was calculated with the standard calibration curve obtained from standard AG27 solutions. The experiment was repeated with AG27 at concentrations ranging from 0.4 mg/ml to 2.0 mg/ml.

2.4. Characterization

A Zetasizer 3000HSA was used for the size distribution analysis of the nanoparticles. A Grant OLS 200 shaker was used for the dye adsorption. A Beckman J2-21 centrifuge was used for the ultrahigh speed centrifugation. A Perkin–Elmer Lambda 18 was used to determine the UV–vis absorption of the dye.

3. Results and discussion

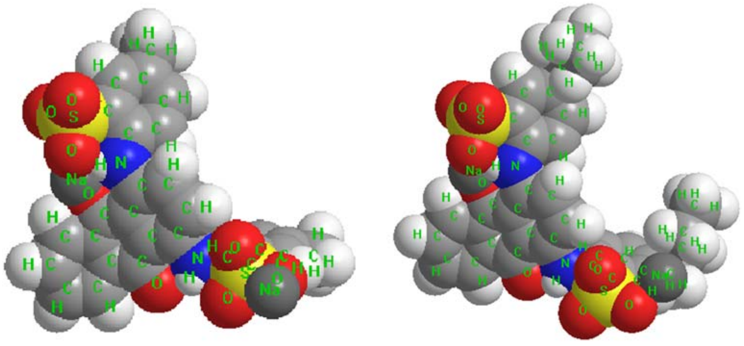
3.1. Nanoparticle characterization

The nanochitosan emulsion had an average size of 180 nm with a polydispersity of 0.519, which indicated that the particle size was narrow. The zeta potential was +30 mV. The positive charge of the chitosan nanoparticles suggested that the emulsion was stabilized by the hydrogen bonding between the amino and hydroxyl groups of the chitosan and the hydroxyl group and oxygen atom of water [33–35].

Fig. 2 shows the spherical profile of the chitosan nanoparticles with sizes from 10 to 100 nm. We added additional TPP into the supernatant after centrifugation and observed a milky emulsion, which implied that not all the chitosan had been converted to nanoparticles. After the freeze–thaw treatment, the nanoparticles were precipitated from the emulsion. The weight of the collected nanoparticles after centrifugation (1.2 mg/ml) was used as the weight of the nanoparticles in the emulsion (particle content) [36].

3.2. Dye sorption

The nanoparticles quickly aggregated after interacting with the dye molecules. The possible mechanism for the adsorption



Acid Green 25 Acid Green 27

Fig. 1. Molecular structures of Acid Green 25 and Acid Green 27.

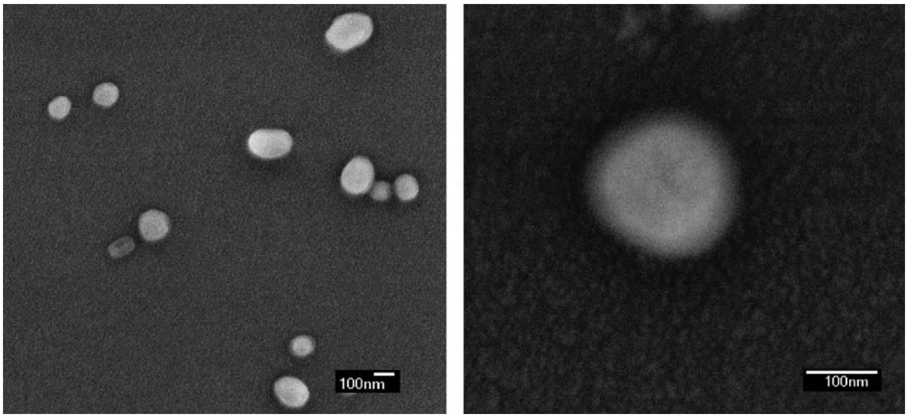


Fig. 2. SEM images of the chitosan nanoparticles.

process of the chitosan and the acid dye is the electrostatic interactions between the anionic dye and the positive amino group on the chitosan. In this study, the anionic dye ions are believed to replace the hydrogen bonds between the chitosan nanoparticles and water with electrostatic interactions, which cause the aggregation of these nanoparticles. The colorants could be desorbed in an alkaline medium [29] but not in a neutral medium. On the other hand, no precipitate was observed in the mixture of dye solution and chitosan solution when TPP was not present. The affinity between the nanochitosan and the chemicals used can be summarized: the order of attractive forces was TPP > H_3O^+ > SO_3^- (in dye) > the hydrogen bonds in acidic conditions; and OH^- > TPP > SO_3^- (in dye) > H_2O in alkaline conditions.

Table 1 summarizes the sorption results. The sorption was performed with eight concentrations of Acid Green 27. When the dye concentration was below 1.0 mg/ml, all the dyes were adsorbed by the chitosan. Because TPP has no contribution to the adsorption of dye, we calculated the solid-phase adsorbate concentration at equilibrium (Q_e, mg/g) with Eqs. (1) and (2) using both the weight of nanoparticles in the emulsion (Q_{es}) and the weight of chitosan in the nanoparticles (Q_{ep}) to investigate the adsorption ability of the nanoparticles and nano-scale chitosan in the nanoparticles. The weight of chitosan in the nanoparticles was calculated by reducing the weight of the nanoparticles with the weight of TPP according to the original TPP concentration, which was 0.6 mg/ml.

Table 1
Adsorption of Acid Green 27 onto chitosan at different concentrations

Sample	Original dye concentration C_o (mg/ml)	Final dye concentration C_e (mg/ml)	Q_{es} (mg/g)	Q_{ep} (mg/g)
A	0.4	0.0000	555.6	1111.1
B	0.8	0.0000	1111.1	2222.2
C	1.0	0.0234	1356.4	2712.8
E	1.2	0.0587	1585.2	3170.3
F	1.4	0.2515	1595.2	3190.3
G	1.5	0.3437	1576.4	3211.9
H	1.8	0.6382	1613.6	3227.2
I	2.0	0.8352	1617.8	3235.6

$$Q_{es} = \frac{\text{weight of adsorbed dye}}{\text{weight of nanoparticles}} = \frac{(C_o - C_e)V_{\text{the mixed solution}}}{1.2V_m}\ (\text{mg/g}) \tag{1}$$

$$Q_{ep} = \frac{\text{weight of adsorbed dye}}{\text{weight of chitosan in the nanoparticles}} = \frac{(C_o - C_e)V_{\text{the mixed solution}}}{0.6V_m}\ (\text{mg/g}) \tag{2}$$

where C_o is the original dye concentration in the mixing solution, C_e is the dye concentration in the solution after centrifugation, V_m is the used volume of the emulsion in sorption test.

Both Q_{es} and Q_{ep} increased non-linearly with the increase of C_o and then reached a maximum. The nanoparticle adsorption capacities derived from Eqs. (1) and (2) have a significant difference because TPP cannot precipitate all the nanoparticles in the chitosan emulsion.

3.3. Langmuir equilibrium isotherms

Adsorption isotherms are critical in optimizing the use of adsorbents because they describe how adsorbates interact with adsorbents. The correlation of equilibrium data, either by theoretical or empirical equations, is essential for the practical design and operation of adsorption systems. In our previous work, the Langmuir equation has been found to provide the best prediction for the adsorption of AG25 in the entire concentration range [37], it is used in this study because AG27 has a similar molecular structure to AG25.

Langmuir's theory describes the adsorption of gas molecules onto metal surfaces [38], when it is successfully applied to other real sorption processes of monolayer adsorption. The Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent. Theoretically, the adsorbent has a finite capacity for the adsorbate. Therefore, a saturation value is reached beyond which no further sorption can take place. The saturated or monolayer capacity can be represented by the expression

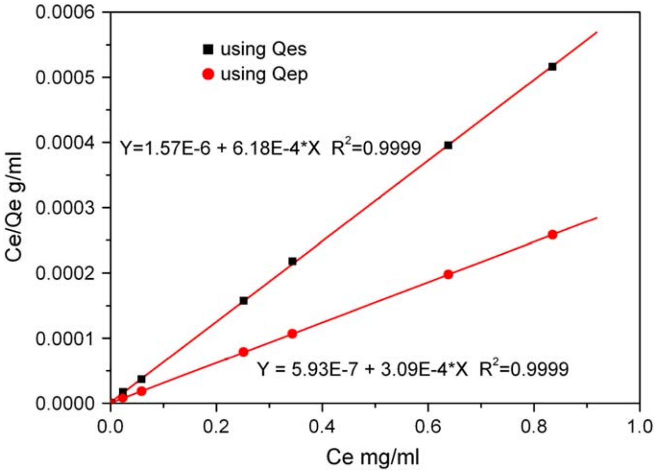


Fig. 3. Isotherms for the sorption of AG27 onto the nanochitosan at temperature = 25 °C, pH = 5.

$$Q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (\text{as } C_e \rightarrow \infty) \tag{3}$$

where Q_e is the solid-phase adsorbate concentration at equilibrium (mg/g), C_e is the aqueous phase adsorbate concentration at equilibrium (mg/ml), K_L is the Langmuir isotherm constant (ml/g), and a_L is the Langmuir isotherm constant (ml/mg).

Therefore, plots of C_e/Q_e versus C_e give a straight line of slope a_L/K_L and intercept $1/K_L$, where K_L/a_L gives the theoretical monolayer saturation capacity, Q_0. The adsorption data, Q_{es} and Q_{ep} as summarized in Table 1, were analyzed with Eq. (3). The linear plots of specific sorption C_e/Q_e against the equilibrium concentration C_e are shown in Fig. 3. The isotherms were found to be linear over the whole concentration range with high correlation coefficients which indicated that the dye–nanochitosan sorption followed the Langmuir model.

Fig. 4 summarizes the equilibrium capacities of AG27, showing that the monolayer saturation or maximum adsorption was reached. The Langmuir isotherm was found to provide a good prediction for the sorption in the study. As the dye purity was 65%, the Langmuir equilibrium monolayer capacities, Q_0, were 1051.8 mg/g and 2103.6 mg/g when derived from Q_{es} and Q_{ep} using Eqs. (1) and (2). The two values had a big difference due to the large difference between Q_{es} and Q_{ep} as discussed. In our previous work [37], Q_0 of Acid Green 25 onto the chitosan (degree of deacetylation = 54%; particle size: 355–500 μm) was 645.1 mg/g. The nanochitosans had a significantly higher capacity for the acid dye than that of the powdered chitosan. Further work on the relationship between the surface area and the sorption capacity is being undertaken.

4. Conclusion

The behavior of the chitosan nanoparticles as an adsorbent to remove Acid Green 27 from its aqueous solution was investigated. The affinity between the nanochitosan and the chemicals used can be summarized: the order of attractive forces was TPP $>$ H_3O^+ $>$ SO_3^- (in dye) $>$ the hydrogen bonds in acidic conditions; and OH^- $>$ TPP $>$ SO_3^- (in dye) $>$ H_2O in alkaline conditions. The equilibrium isotherm was measured to determine the capacities of the nanochitosan for the dye and analyzed using the Langmuir equation. It was found that the sorption well fitted in the Langmuir model, especially when the dye concentration was high.

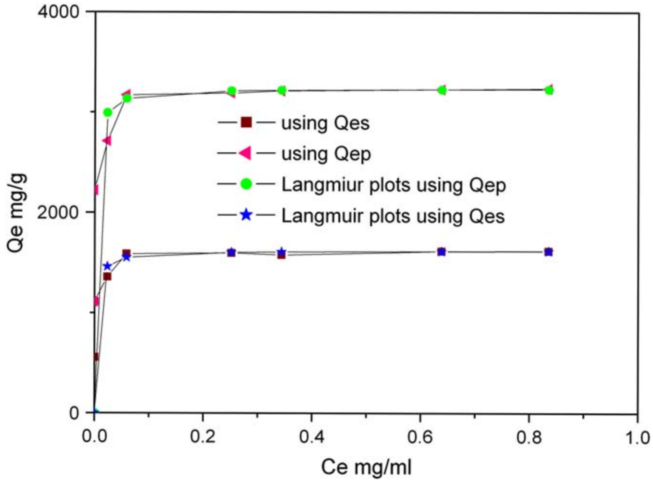


Fig. 4. Langmuir isotherms of Acid Green 27 onto the chitosan nanoparticles at temperature = 25 °C, pH = 5.

The Langmuir monolayer adsorption capacities (Q_0) were calculated using the weight of the nanoparticles and the weight of chitosan in the nanoparticles. The capacities were 1051.8 mg/g and 2103.6 mg/g. The values were significantly higher than that of the micron-sized chitosan. The study on dye–nanochitosan sorption is worth to be further investigated to explore its high capacity advantage.

Acknowledgement

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References

[1] Annadurai G, Krishnan MRV. Iran Polym J 1997;6:169–75.
[2] Vandevivere PC, Bianchi R, Verstraete W. J Chem Technol Biotechnol 1998;72:289–302.
[3] Lin SH, Lin CM. Water Res 1993;27:1743–8.
[4] Ganesh R, Boardman GD, Michelsen D. Water Res 1994;28:1367–76.
[5] Walker GM, Weatherley LR. Water Res 1997;31:2093–101.
[6] Chu W, Tsui SM. Chemosphere 1999;39:1667–77.
[7] El-Geundi MS. Water Res 1991;25:271–3.
[8] Grau P. Water Sci Technol 1991;24:97–103.
[9] Lucarelli L, Nadtochenko V, Kiwi J. Langmuir 2000;16:1102–8.
[10] Poots VJP, McKay G, Healy JJ. Water Res 1976;10:1061–6.
[11] Ho YS, McKay G. Chem Eng J 1998;70:115–24.
[12] McKay G, Elgeundi M, Nassar MM. Water Res 1987;21:1513–20.
[13] Namasivayam C, Prabha D, Kumutha M. Bioresour Technol 1998;64:77–9.
[14] Ho YS, McKay G. Resour Conserv Recy 1999;25:171–93.
[15] Namasivayam C, Radhika R, Suba S. Waste Manage 2001;21:381–7.
[16] Namasivayam C, Kavitha D. Dyes Pigments 2002;54:47–58.
[17] Atun G, Hisarli G, Sheldrick WS, Muhler M. J Colloid Interface Sci 2003;261:32–9.
[18] McKay G, Otterburn MS, Aga JA. Water, Air, Soil Pollut 1985;24:307–22.

[19] Poots VJP, McKay G, Healy JJ. Water Res 1976;10:1067–70.

[20] Asfour HM, Nassar MM, Fadali OA, Elgeundi MS. J Chem Technol Biotechnol 1985;35:28–35.

[21] Lim SH, Hudson SM. J Macromol Sci Polym Rev 2003;43:223–69.

[22] Ravi Kumar MNV. React Funct Polym 2000;46:1–27.

[23] Hennen William J. Chitosan. Woodland; 1996.

[24] Giunchedi P, Genta I, Conti B, Muzzarelli RAA, Conte U. Biomaterials 1998;19:157–61.

[25] Illum L. Pharm Res 1998;15:1326–31.

[26] Yoshida H, Okamoto A, Kataoka T. Chem Eng Sci 1993;48:2267–72.

[27] Yoshida H, Takemori T. Water Sci Technol 1997;35:29–37.

[28] Yoshida H, Fukuda S, Okamoto A, Kataoka T. Water Sci Technol 1991;23:1667–76.

[29] Chiou MS, Li HY. Chemosphere 2003;50:1095–105.

[30] Chang YC, Che DH. Macromol Biosci 2005;5:254–61.

[31] Calvo P, Remunan C. J Appl Polym Sci 1997;63:125–32.

[32] Leon TL, Carvalho ELS, Seijo B. J Colloid Interface Sci 2005;283:344–51.

[33] Stockman PA, Bumgarner RE, Suzuki S, Blake GA. J Chem Phys 1992;96:2496–510.

[34] Yeo GA, Ford TC. Can J Chem 1991;69:632–7.

[35] Del Bene JE. J Am Chem Soc 1973;95:5460.

[36] Hu Y, Jiang XQ, Ding Y. Biomaterials 2002;23:3193–201.

[37] Wong YC, Szeto YS, Cheung WH, McKay G. Langmuir 2003;19:7888–94.

[38] Langmuir I. J Am Chem Soc 1918;40:1361–403.