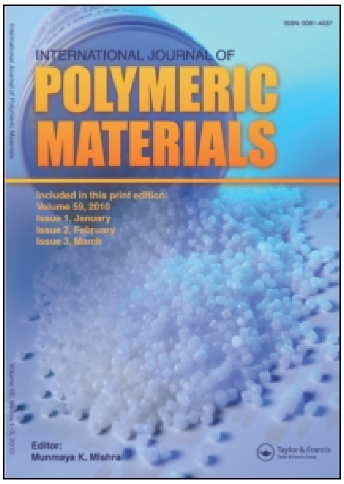

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The interaction between reactive dye containing vinylsulfone group and chitosan microspheres

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THE INTERACTION BETWEEN REACTIVE DYE CONTAINING VINYLSULFONE GROUP AND CHITOSAN MICROSPHERES

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Chitosan microspheres were employed as adsorbent in aqueous medium for the reactive orange 16 containing the vinylsulfone group. Adsorption isotherms were obtained varying pH, contact time, and initial concentration of the dye in the solution. The results from the adsorption experiments were analyzed using Langmuir's isotherm. An increase in the adsorption capacity as the pH decreased could be observed. Maximum adsorption reached 30.4 mg/g and 5.6 mg/g for pH 2.0 and 10.0, respectively. This effect could be mainly attributed to an increase in the contents of the NH_3^+ *group present in acid media, which resulted in a higher electrostatic attraction between the anionic dye and the protonated chitosan.*

Keywords: adsorption, chitosan microspheres, reactive dye

INTRODUCTION

Environmental issues bring major challenges to textile companies, especially concerning the removal of dyes from wastewaters. Adsorption processes used to that end have been extensively described in the literature. Such processes allow recovery of the dye in a concentrated form and reuse of the adsorbent in the process.

Several studies have been carried out on wastewater treatment, employing adsorbents such as activated coal, turf, silica, alumina, cellulose, and more recently, chitin and pulverized chitosan [1–6].

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Yoshida *et al.* [7] investigated the adsorption of anionic dyes on chitosan fibers. Adsorption of the anionic dye was quite extensive, whereas that of the cationic ones were rather limited.

Kim *et al.* [3] reported on the effect of the deacetylation degree of chitosan on the adsorption of four different anionic dyes. Chitosans with deacetylation degrees varying from 10.7% to 67.2% were prepared. Those with deacetylation degrees 36.3% or 46.86% were most effective in dye removal from textile wastewaters.

Many textile wastewaters are highly acid. This limits the use of chitosan as adsorbent for dye removal, as this compound is highly soluble in such environments. This work presents a detailed evaluation on the adsorption of a reactive dye containing the vinylsulfone group using reticulated chitosan microspheres. Crosslinking of chitosan was necessary to stabilize the microspheres in acid medium as well as to grant the material the mechanical strength necessary for the adsorption studies in dynamic systems.

EXPERIMENTAL

Materials and Methods

Reactive Orange 16 (Aldrich Chemical Company, Inc.) was used without previous purification. All other reagents employed herein were of an analytical grade and supplied by Merck. Figure 1 illustrates the structure of the reactive dye containing vinylsulfone.

Synthesis of Chitosan

Chitin (10.0 g) had been previously prepared according to an adaptation of Hackman's method [8]. The compound was submitted to a deacetylation reaction using Broussignac's method [9]. Synthesized chitosan was purified by dissolving it in 3% (m/v) acetic acid followed by filtering to eliminate insoluble residues. The material was then dried in a Mini Spray Dryer Büchi B-191 resulting in particles of approximately 25 μm.

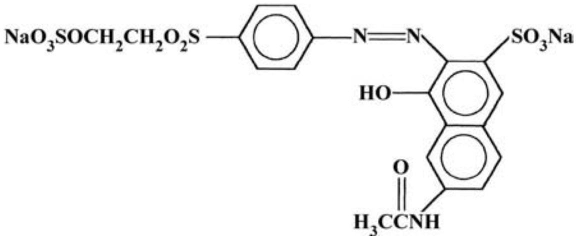


FIGURE 1 Structure of orange 16 reactive dye.

Characterization of Chitosan

Infrared patterns were obtained from 400 to 4000 cm^{-1} using an FT Perkin Elmer 16 PC infrared spectrophotometer. Chitosan films were prepared by dissolving 200 mg of the polymer into 20.0 mL of 3% (m/v) acetic acid in a petry dish. The acid slowly evaporated at ambient temperature. Its absorption band at 3454 cm^{-1} is rather intense as a consequence of OH and water stretching vibrations, whereas the band at 2900 cm^{-1} corresponds to C—H stretching vibrations. The bands at 1654 and 1380 cm^{-1} can be attributed to deformation vibrations of medium intensity of N—H bonds from primary amines and of low intensity from C—H bonds of the CH_3 group. Small contents of residual acetamide groups can be found in the polymeric chain as a consequence of incomplete deacetylation of chitosan. The band at 1068 cm^{-1} corresponds to the stretching vibrational of C—O bonds from primary alcohol [10, 11].

NMR ^{13}C patterns were obtained using a ^{1}H ^{13}C Nuclear Magnetic Resonance spectrometer Brucker AC-200 F. 100 mg of the polymer were dissolved in a solution containing 0.4 mL glacial acetic acid and 2.5 mL D_2O. The sample was centrifuged and an aliquot was analyzed [12]. The NMR ^{13}C patterns showed that the chemical displacement of the anomeric C_1 carbon at 98 ppm was clearly distinguished from other signals. Two closest signals at 80 ppm corresponded to C_4. The displacement of secondary C_3 and C_5 carbons was 77 ppm. Signals at 60 ppm and 56 ppm could be attributed to C_6 and C_2, respectively [13].

The deacetylation degree (%DD) was estimated by condutometric titration, using a Micronal B 330 condutivimeter and an automatic Schott Geräte T 80/20 titration system. 200 mg of chitosan were transferred to a 600 mL vial containing 450 mL of a solution of 0.001 mol/L NaCl and 5.0 mL of 1.0 mol/L HCl. Titration was carried out following polymer dissolution with the addition of 0.5 mL of 0.100 mol/L NaOH under nitrogen in 20 seconds intervals [14]. The degree of deacetylation estimated thereby was 72.5% (4.50 mmols amino groups/g of chitosan).

Preparation of Chitosan Microspheres

Chitosan (2.5 g) was dissolved into 100 mL of 5% (m/v) acetic acid. A viscous solution was obtained and dripped using an Ismatec peristaltic pump coupled to a bath containing 2.0 mol/L NaOH solution. Gel microspheres were rinsed in distilled water so neutral pH could be reached [15].

Crosslinking of Chitosan Microspheres

Chitosan microspheres were placed in a glutaraldehyde 25% (m/v) solution at a ratio of 1.5 mL of solution per gram of gel microspheres. The mixture was set for 24 hours at ambient temperature. The material was rinsed in distilled water to remove the remainder of the crosslinking agent. Subsequently, the microspheres were placed in acetone during 24 hours and dried at room temperature [15]. Figure 2 illustrates the crosslinked chitosan.

Following crosslinking, the content of free amino groups (NH_2) was determined by acid-base titration. 300 mg of microspheres were placed in 100 mL of a standard HCl 0.100 mol/L solution during 24 hours aiming at the protonation of free amino groups. A 25.0 mL aliquot of the supernant was removed and titrated with NaOH 0.100 mol/L. The results showed the presence of 48.0% of free amino groups (2.98 mmols/g).

Scanning Electron Microscopy (SEM)

The morphology of the microspheres was analyzed under a Philips XL30 Scanning Electron Microscope. The average size of the microspheres was 1.03 ± 0.06 mm and the external surface depicted only limited porosity. Figure 3 show SEM images of chitosan microspheres detailing morphology.

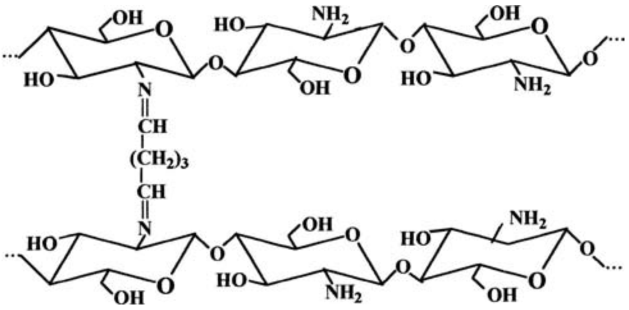
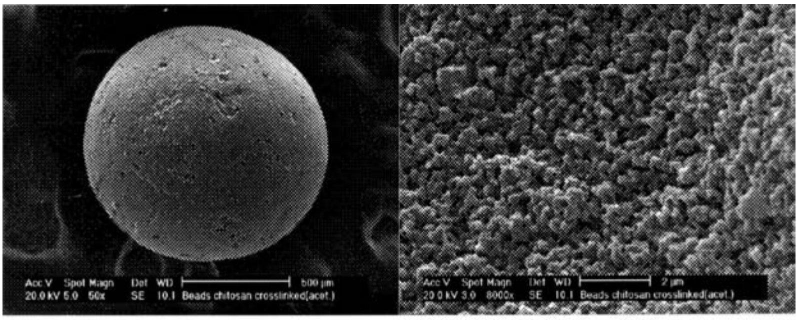


FIGURE 2 Structure of crosslinked chitosan.



(a) (b)

FIGURE 3 SEM photomicrographs: (a) whole chitosan microsphere at 50X; (b) external surface of microsphere at 8000X.

Determination of Reactive Dye in Solution

The concentration of reactive Orange 16 in solution was carried out from analytical curve obtained in a UV-Vis Hitachi U3000 spectrophotometer with $\lambda_{max} = 490\,nm$.

Effect of pH on Adsorption

100 mg samples of chitosan microspheres were placed in 50.0 mL of a 20.0 mg/L solution of a reactive dye with ionic strength constant ($\mu = 0.100\,mol/L$). The solution pH was adjusted using several buffer solutions. The solutions were transferred to a Shaker Bath Lab-Line Instruments 3540 mechanical stirrer with a Microquimica MQTZ99-20 thermostatic bath maintained at 25.0 ± 0.5°C. The samples were stirred during 24 hours at 150 rpm. The supernant of each flask was centrifugally separated and the amount of adsorbed dye was determined using the following equation:

$$q = \frac{(C_o - C_e)V}{W} \tag{1}$$

where, q is the amount of adsorbed dye in (mg/g), V is the volume of the solution in (L), W is the mass of microspheres in (g), C_o is the initial concentration of the solution in (mg/L) and C_e is the equilibrium concentration of the dye in solution in (mg/L).

Kinetics of Adsorption

The time necessary for the adsorbate/adsorbent system to reach equilibrium conditions was determined adding 100 mL of reactive dye solution (50.0 mg/L) in a sealed flask containing 1.0 g of microspheres. The solution pH was adjusted to 2.0 and the ionic strength to ($\mu = 0.100\,mol/L$). The flask was continuously stirred at 150 rpm during 55 hours at 25.0 ± 0.5°C. 3.0 mL aliquots were extracted at preset intervals and the concentration of the dye in the solution was determined by UV-Vis spectrophotometry.

Adsorption Isotherms

Isotherms were obtained by the batch method. Flasks were maintained at 25.0 ± 0.5°C and contained 100 mg of chitosan microspheres, and 50.0 mL dye solution (10.0 – 70.0 mg/L). The ionic strength of the solution was controlled with NaCl ($\mu = 0.100\,mol/L$) and pH adjusted with a buffer solution. The system was continuously stirred at 150 rpm during 24 hours. The material was centrifugally separated from the solution and the presence of dye in solution was determined by UV-Vis spectrophotometry. The amount of dye adsorbed by the chitosan microspheres was calculated from Eq. (1).

RESULTS AND DISCUSSION

Figure 4 illustrates the adsorption isotherm of chitosan as a function of the pH of the solution. The adsorption of reactive Orange 16 by chitosan microspheres was improved as the pH decreased, revealing that the chitosan was fully protonated at pH < 3.0 and that adsorption was assisted by electrostatic interaction. The decrease in the adsorption capacity by the adsorbent in alkaline media could be attributed to the deprotonation of amino groups. The polymeric chain was not positively charged and could not interact with the negative charge of the anionic dye.

Figure 5 shows a decrease in the concentration as a function of time. Though abrupt during the initial hours, the concentration gradually reached equilibrium conditions after 24 hours.

Figure 6 shows the plots of the solid phase concentration (q) as a function of the concentration of the adsorbate in liquid phase (C_e). Experimental adsorption results could be interpreted using Langmuir's isotherm, which is represented by:

$$q = \frac{Kq_mC_e}{1 + KC_e} \tag{2}$$

where, K is Langmuir's constant; C_e is the concentration of the dye in equilibrium (mg/L) and q_m is the maximum adsorption capacity in units of

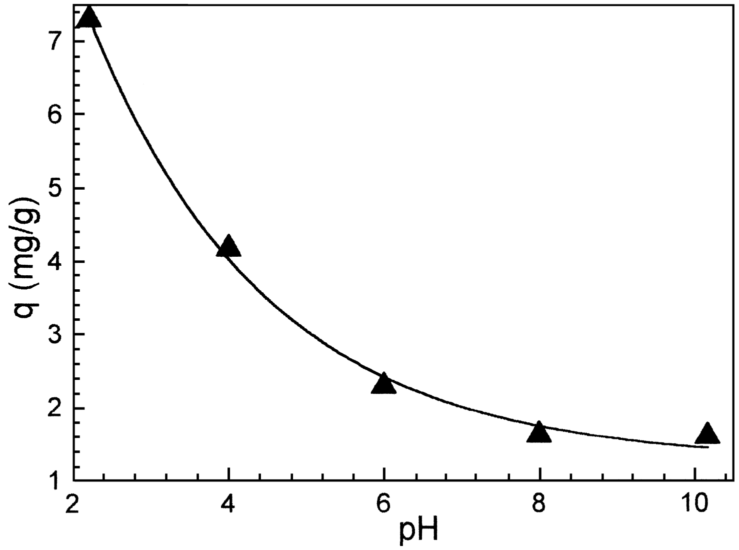


FIGURE 4 Effects of pH on the dye adsorption by chitosan.

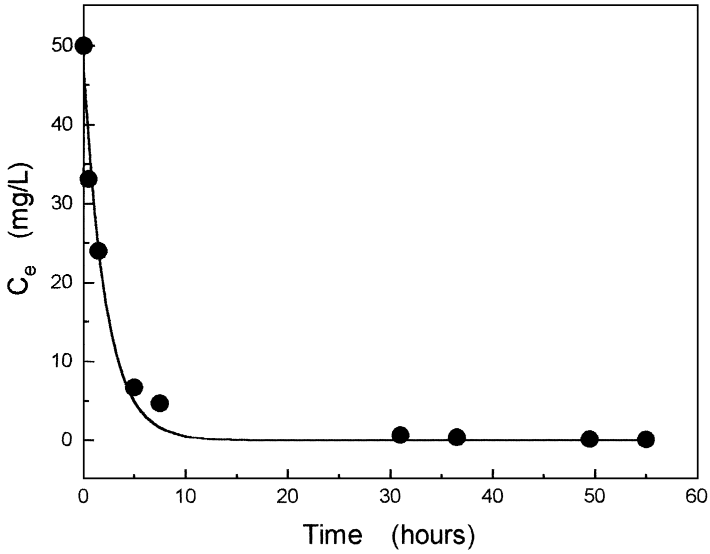


FIGURE 5 Adsorption kinetics of dye by chitosan.

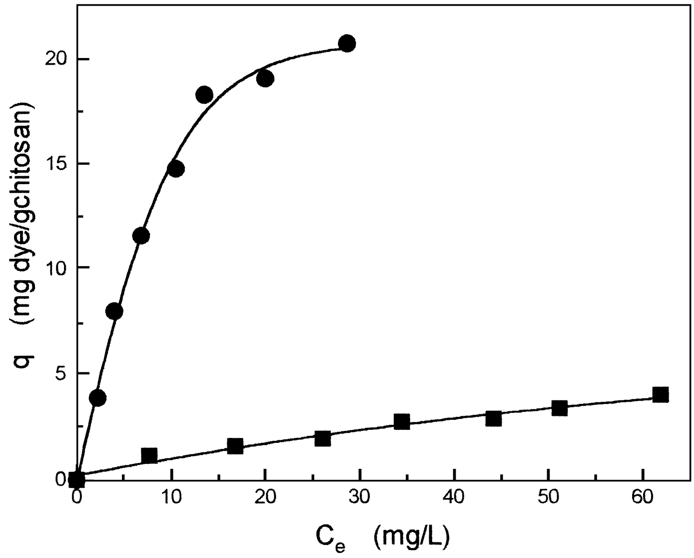


FIGURE 6 Adsorption isotherms of orange 16 reactive by chitosan. (•) pH 2.0 and (■) pH 10.0.

mg of dye per gram of chitosan. Equation (2) was linearized to yield two of Langmuir's parameters. A Figure 7 illustrates a plot of C_e/q as a function of C_e. Table 1 lists the calculated Langmuir's parameters.

At pH 2.0 the saturation capacity (q_m) of the dye by chitosan was 5.4 times greater than at pH 10.0. At pH < 3.0 all amino groups of the polymeric chain of chitosan were protonated ($-NH_3^+$) and they could adsorb anions from the dye by electrostatic attraction.

At pH 10.0, chitosan was deprotonated ($-NH_2$) and the polymer-dye interactions possibly consisted of hydrogen bonds, hydrophobic interactions, and van der Waals bonds.

Figure 8 shows a plot of the separation factor (r) for orange 16 reactive dye at pH 2.0 and 10.0. This parameter makes it possible to anticipate whether the adsorption of dyes by chitosan microspheres would be favorable or not. A non-favorable isotherm shows $r > 1$, a linear isotherm $r = 1$, and a favorable isotherm $0 < r < 1$. Finally, for an irreversible

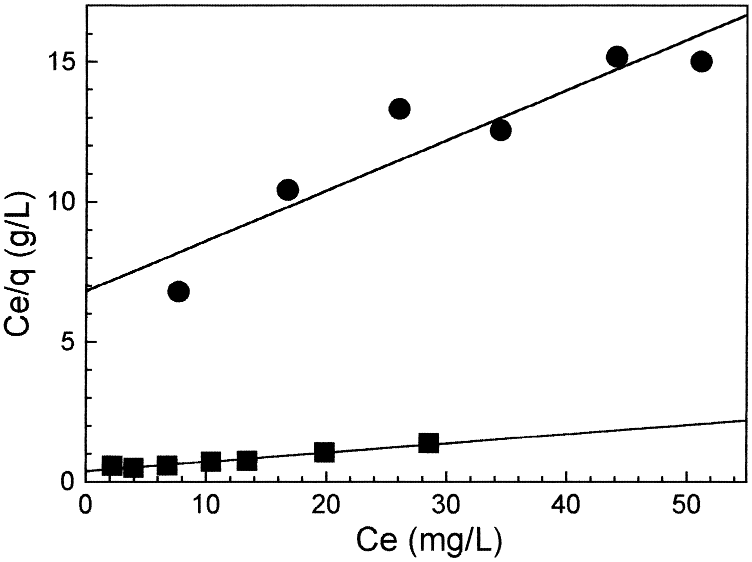


FIGURE 7 Linearization of Langmuir isotherms. (●) pH 2.0 and (■) pH 10.0.

TABLE 1 Values of the adsorption's parameters

Reactive dye	*pH*	*K (L/g)*	*q_m (mg/g)*
Orange 16	2.0	(84.9 ± 12.7)	(30.4 ± 2.8)
Orange 16	10.0	(26.3 ± 7.1)	(5.6 ± 1.1)

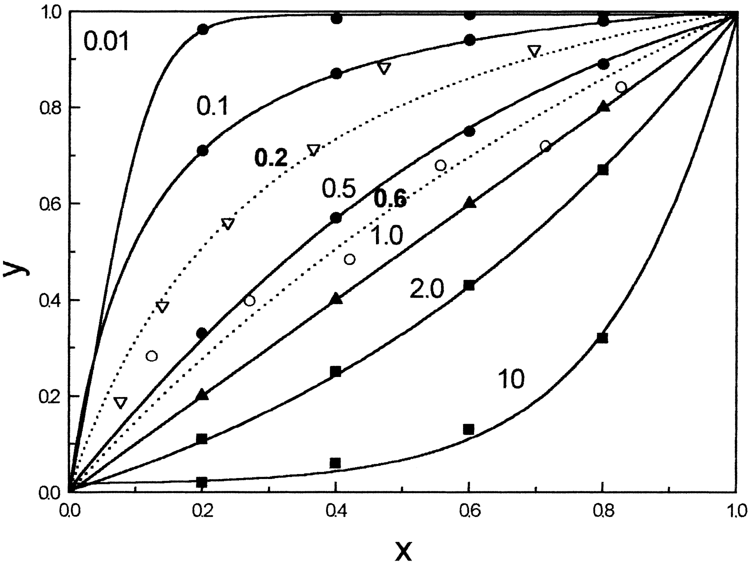


FIGURE 8 Separation factors for orange 16 reactive at pH 2.0 and 10.0.

isotherm $r = 0$. In real adsorption processes, values of r range from 0 to 1. As r approaches zero, adsorption becomes favorable. Values of r can be determined using the relation between Langmuir's isotherm and the parameter defined by (Hall *et al.* [16])

$$y = \frac{x}{r(1 - x) + x} \tag{3}$$

where, x is equal to the ratio of C_e to C_{ref} (equilibrium concentration and maximum equilibrium concentration of the dye in solution, mg/L) and y is equal to the ratio between q and q_{ref} (adsorbed amount to maximum adsorbed amount, mg/g).

At pH 2.0 and 10.0 the separation factor was determined to be 0.2 and 0.6, respectively. The fact that these values were close to zero indicated a favorable adsorption.

CONCLUSIONS

Chitosan microspheres in acid media were more effective in the adsorption of the reactive dye than in alkaline solutions. Acid media are characterized by an increase in the cationic groups (NH_3^+) of chitosan, which act as its main adsorption site. In alkaline environments, adsorption was most likely attributed to hydrogen bonds, hydrophobic interactions, or van der Waals bonds. This new adsorbent support can be used in both static and dynamic adsorption processes. It is highly stable in acid media and can therefore be used to remove dyes from both acid and alkaline textile wastewaters.

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