

The Adsorption of Sulphonated Azo-Dyes Methyl Orange and Xylenol Orange by Coagulation on Hollow Chitosan Microsphere

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ABSTRACT: Chitosan (CS) can be used as adsorbent in the treatment of effluents from the textile industry, especially for negatively charged dyes, due to its cationic polyelectrolyte nature. In this work, the adsorption of a model dye, methyl orange, xylenol orange on hollow CS microsphere is analyzed. Adsorption of methyl orange, xylenol orange onto cross-linked CS is realized by means of analysis of pH influence, agitation time, and initial concentration of the dye. The results obtained from the experiment shows that the adsorption capacities of the two dye-hollow CS microsphere systems are higher than those stated in

other literature using CS particles. The difference in the degree of adsorption may also be attributed to the size and chemical structure of the dye molecule. The results have demonstrated that monovalent and smaller dye molecular sizes have superior capacities due to the increase in dye/CS surface ratio in the system and deeper penetration of dye molecules into the internal pore structure of hollow CS microsphere. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2065–2071, 2011

Key words: hollow chitosan microsphere; adsorption; dyes

INTRODUCTION

There are significant amounts of unused dyes remaining in the wastewater from the textile and dyeing industry. Aqueous waste and dye effluents with persistent and high biochemical oxygen demand loading is being discharged every day in Mainland. Many industries, such as dyestuffs, textile, paper, and plastics, use dyes to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored waste water. It is recognized that public perception of water quality is greatly influenced by the color. A range of conventional technologies for dye removal, such as carbon adsorption and photo-degradation, has been investigated extensively color is the adsorption-related phenomena involved in a wide range of processes used in carbohydrate research, such as heterogeneous catalysis,^{1–3} stabilization of colloidal dispersions, biocompatibility,⁴

and effluent treatment.⁵ Adsorption in particulate systems has been used for heavy metal uptake, as part of the treatment of pulp and paper mill wastewater,⁶ and in the treatment of effluents from the textile industry.⁷ Chitosan (CS) is a biomacromolecule obtained from the deacetylation of chitin. It can be used as adsorbent for treatment of textile industry effluents as well as for metal uptaking from water.^{8–12} Apart from being biocompatible, it is a polyelectrolyte with polycationic character depending on pH which be able to interact with negatively charged molecules.^{13,14} Spectrophotometry has been employed to quantify CS, using the strong interactions that occur between dye molecules and this biopolymer. Amount of works on the analysis of sorption about dyes on CS has been carried out,¹⁵ which were usually divided into two approaches: one dedicated to the obtaining of adsorption isotherms and the other one on the kinetic analysis of adsorption.^{9,16,17} Physically and chemically modified CS has also been used in some works, for example, the author has employed CS/montmorillonite nanocomposite particles in the adsorption of Congo Red,¹⁸ and Lima has used CS chemically modified with succinic anhydride for methylene blue adsorption.¹⁹ Some recent researches on the adsorption of methyl orange as a model dye, on dry crosslinked CS particles have shown that the usual kinetics description

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TABLE I
Physical and Chemical Characteristics of the Dyestuffs Being Investigated in This Project

| Generic name | Chromophore | Formula weigh | λ_{\max} (nm) | R^2 |
|----------------|-------------|---------------|-----------------------|--------|
| Methyl orange | —N=N— | 327 | 505 | 0.9992 |
| Xylenol orange | —N=N— | 738 | 480 | 0.9990 |

as pseudo-second-order kinetics is not adequate to describe this particular sorption process. It has also been found that diffusion-related phenomena govern the kinetics of sorption in these systems.²⁰ The aim of the proposed work is to conduct experiments on crosslinked hollow CS microsphere and compare the capacity of hollow CS microsphere with conventional CS about the adsorption of two acid dyes, methyl orange, and xylenol orange.

METHODS

Materials

CS ($M_w = 750,000$) was made and the degree of deacetylation is 55%.²¹ The preparation of the hollow CS microsphere has been reported.²² The adsorbent was applied directly in this project without any prior purification and pretreatment processes. Two different commercially available textile dyestuffs were used in this study and they are both azo dyes: methyl orange and xylenol orange. The selected dyestuffs are commonly used in dye houses nowadays and are regarded as dye contaminants in the discharged effluents. All dye stuffs were obtained from Aldrich Chemical and used without any further purification process. The characteristics of the selected dyestuffs are listed in Table I.

Concentration measurement and calibration

To calculate the concentration of sample from each experiment, a calibration curve of each dye was first prepared. For each dye, different concentrations (0–50 mg/L) were prepared and the absorbance was measured using a Perkin-Elmer UV/VIS Spectrophotometer. The calibration checks maximum absorption occurs, λ_{\max} were carried out repeatedly in Figure 1. Then, the maximum absorbance of each dye was plotted against a range of dye concentration. From the results, the concentrations of the dye samples can be calculated with the following equation Type (1) and the constants for calculations are summarized in Table I.

$$Q_e = V(C_0 - C_e)/W \quad (1)$$

where Q_e = the dye concentration on the adsorbent at equilibrium, C_0 = the initial dye concentration

(mg of dye/g⁻¹ of CS microsphere), C_e = the liquid-phase dye concentration at equilibrium (mg of dye), V = the total volume of dye-hollow CS microsphere mixture, and W = mass of adsorbent used (g).

Adsorption experiments

The adsorptions of the dyes were performed using batch procedures,²³ where the CS quantities specified by the adsorption factorial design were placed in contact with 50 mL of aqueous solutions in 100 mL polyethylene flasks. The suspensions were agitated for sufficient time to reach equilibrium.

pH effects

The hollow CS microspheres were investigated to determine the pH effects of their adsorption of methyl orange and xylenol orange. These were adjusted to pH 2 and 11 with 1.0 M HCl solution and 1.0 M NaOH solution, and then by stirring for sufficient time at room temperature. Their solutions were filtered and their concentrations of methyl

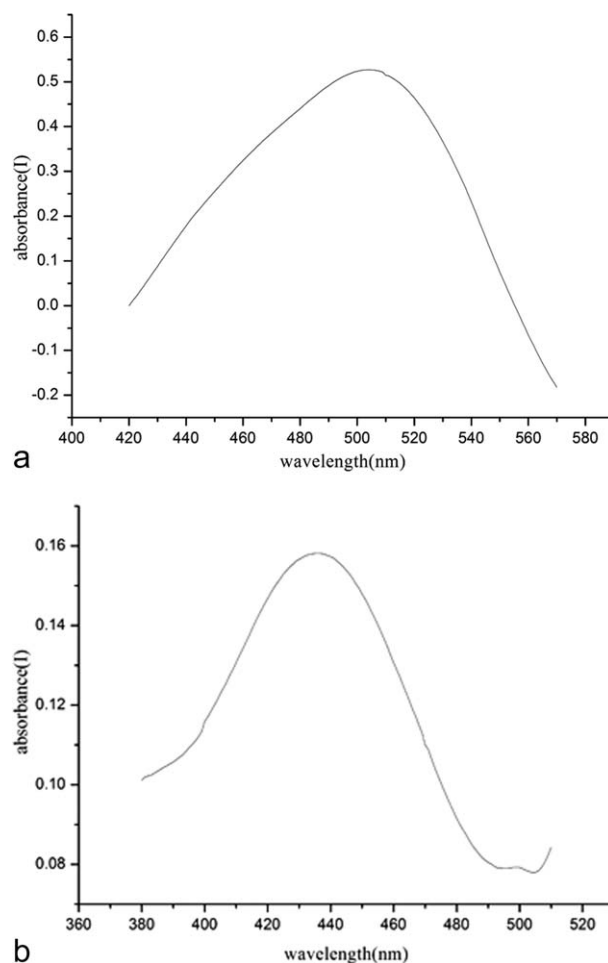


Figure 1 UV spectra of the wavelength of dyes (a, methyl orange; b, xylenol orange).

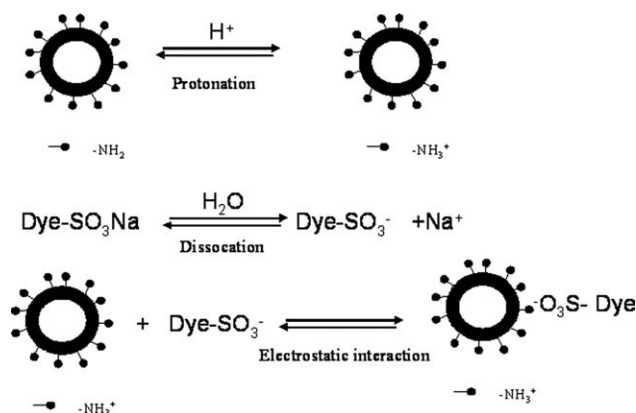


Figure 2 Mechanism of anionic dye adsorption by chitosan under acidic conditions.

orange and xylene orange were measured on a Perkin-Elmer UV/VIS spectrophotometer. The adsorption capacity (Q_e) was calculated by the eq. (1).

Effect of initial concentration

The hollow CS microspheres were investigated to determine the initial concentration effects of their adsorption of methyl orange and xylene orange. These were adjusted to methyl orange and xylene orange solution in the range of 0–600 mg/L at pH 5, and then by stirring for sufficient time at room temperature. Their solutions were filtered and their concentrations of methyl orange and xylene orange were measured on a Perkin-Elmer UV/VIS spectrophotometer. The adsorption capacity (Q_e) was calculated by the following eq. (1).

Effect of agitation time

The hollow CS microspheres were investigated to determine the agitation time effects of their adsorption of methyl orange and xylene orange. These were adjusted to methyl orange and xylene orange solution stirring for period time at room temperature at pH 5. Their solutions were filtered and their concentrations of methyl orange and xylene orange were measured on a Perkin-Elmer UV/VIS spectrophotometer. The adsorption capacity (Q_e) was calculated by the following eq. (1).

RESULTS AND DISCUSSION

Mechanism of adsorption

The mechanisms of the adsorption process of acid dye on hollow CS microsphere are likely to be the ionic interactions of the colored dye ions with the amino groups on the CS in Figure 2.

Preparation and characterization

Presence of CS in the microspheres has been confirmed by FTIR measurements. Curves a–c in Figure 3 are the FTIR spectra of the CS, CS microsphere, and CS microsphere after adsorption xylene orange. The FTIR spectra (4000–400 cm^{-1}) of the CS flakes and CS microspheres are shown in Figure 3(a,b). Usually, the major peaks of the CS flakes are located at around 3400 cm^{-1} for OH stretching vibration and 1650 cm^{-1} for NH_2 stretching vibration. The band observed at 1320 cm^{-1} and 1380 cm^{-1} are assigned to the CH_3 deformation and C–N bond. The broad band at 3433 cm^{-1} was –OH stretching, which overlapped the NH_2 stretching in the same region. The shifts at 1660 and 1597 cm^{-1} were the bands of amide I and II, respectively. For CS microspheres, a new peak at 1635 cm^{-1} can be observed [Fig. 3(c)], which corresponded to stretching vibrations of C=N bond. It indicated that the reactions occurred.

Solubility and surface morphology

The CS’s microspheres were found to be insoluble in acid and alkaline media as well as distilled water in comparison with native CS. It is well known that high hydrophilicity of CS with the primary amino group makes it easily soluble in dilute organic acids to yield a hydrogel in water. Therefore, the cross-linking treatment of CS reinforces its chemical stability in organic acidic media, making it useful for the removal of chemical pollutants from wastewaters in acidic solution. The SEM of CS microsphere were shown in Figure 4. It shows typical SEM images of the CS microsphere prepared under the standard

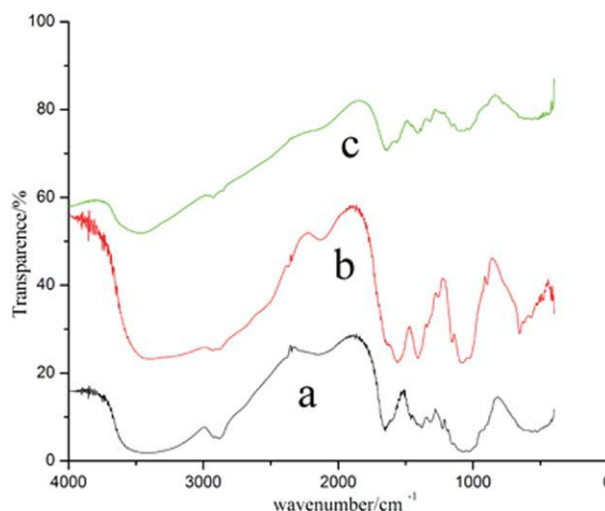


Figure 3 FTIR spectra (a, chitosan; b, chitosan microsphere; c, chitosan microsphere after adsorption xylene orange). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

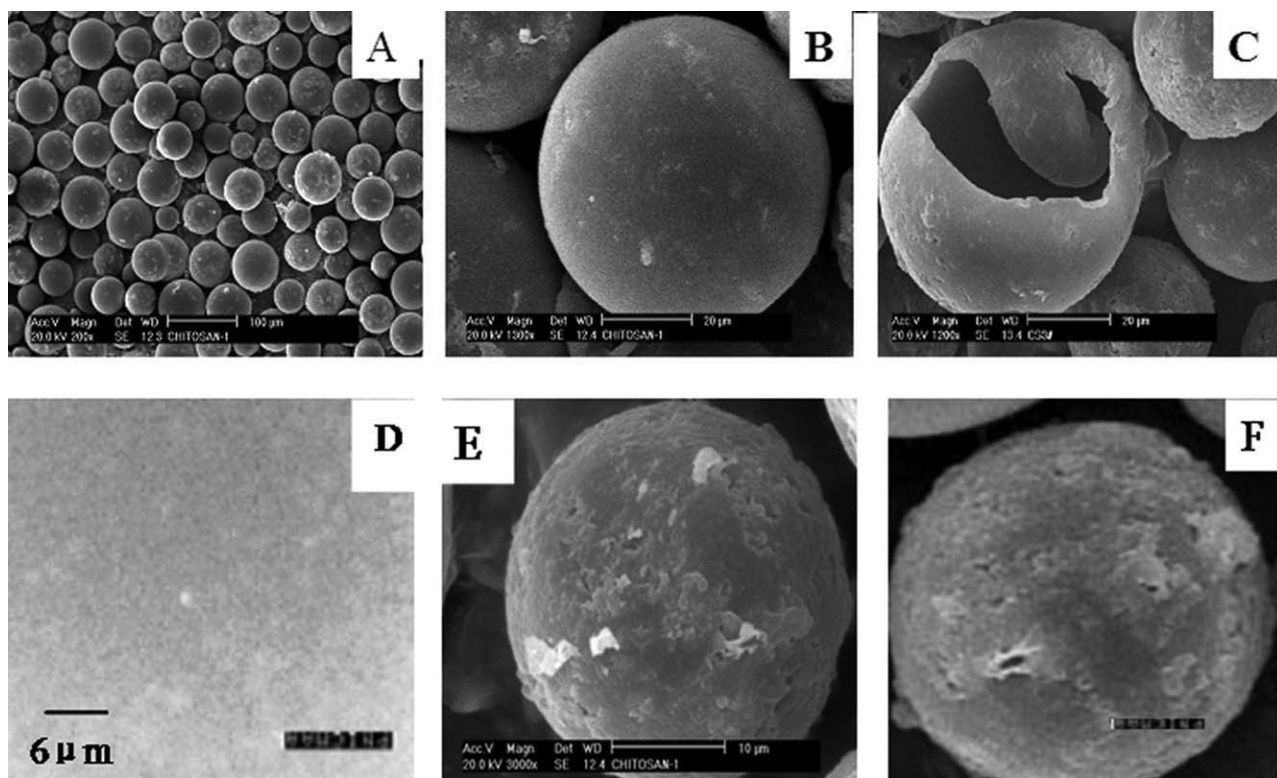


Figure 4 SEM of the CS microsphere (a, $\times 100$; b, $\times 1200$; c, $\times 1500$; d, $\times 10000$; e, $\times 1200$; f, $\times 1200$).

preparative condition,²² and its enlarged surface structure. It can be seen that the microsphere is spherical, and its diameter is about 74 μm [Fig. 4(a)]. The CS microspheres were found to have regular spherical geometry [Fig. 4(b)]. Further study that the microsphere contracts with drying and is swollen after being immersed in water. What's more, the contraction and swelling processes could be repeated for a number of times. The average value is 9/SD. In addition, the size distribution of the composite microspheres is narrow. Figure 4(c) shows the broken CS spherical particle, in which the contrast across the diameter reveals that the thickness of the shell wall is about 2 μm . the comparative analysis of SEM images [Fig. 4(c)] demonstrate that the particles are hollow. What's more, CS microspheres exhibit a smooth surface morphology [Fig. 4(d)]. Figure 4(e) were the CS microsphere after adsorption xylene orange. It can be found the microspheres have regular spherical geometry, whose diameter is about 74 μm . But the microsphere exhibit a roughness surface morphology and the CS microsphere after adsorption methyl orange were shown in Figure 4(f).

Adsorption experiments

The adsorptions of the dyes were performed using batch procedures,²³ where the CS quantities specified by the adsorption factorial design were placed in contact with 50 mL of aqueous solutions in

100 mL polyethylene flasks. The suspensions were agitated for period of time, sufficient time to reach equilibrium.

Effect of pH

Figure 5 shows the effect of pH on the adsorption of methyl orange and xylenol orange by hollow CS microsphere. The adsorption of the dyes increases (i.e., the difference in absorbance increases) with increased pH of the solution. This could be explained by the fact that at low pH (acidic solution), amine groups in the beads easily form protonation. Therefore, competition existed between protons and the dyes for adsorption sites and adsorption capacity was decreased. As pH value was increased, the amino group was free from the protonation for the adsorption behavior in the dyes. At the same time, they were found to be the largest adsorption capacity of methyl orange and xylenol orange at pH 5.0.

Effect of initial concentration

Figure 6 shows the effect of concentration on the adsorption of methyl orange [Fig. 6(a)] and xylenol orange [Fig. 6(b)] by hollow CS microsphere. The adsorption of methyl orange and xylenol orange increases with concentration and attains equilibrium at an initial methyl orange and xylenol orange

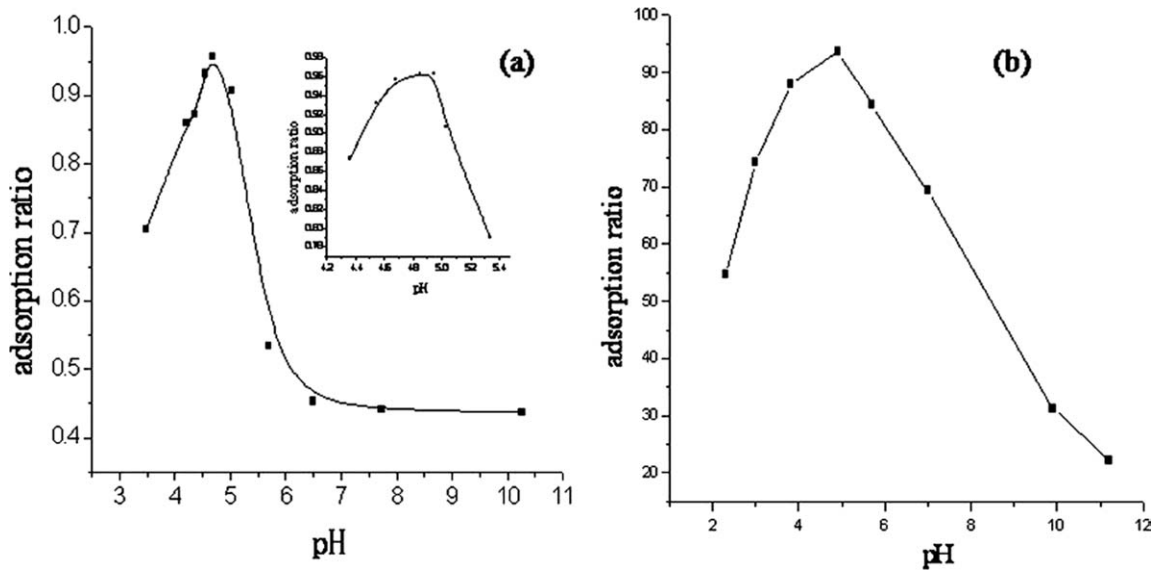


Figure 5 The effect of pH to the adsorption (a, methyl orange; b, xylenol orange).

concentration of 200 mg/L, 32 mg/L for hollow CS microsphere, respectively.

Effect of agitation time

The optimum period (Fig. 7) for the adsorption of methyl orange and xylenol orange on hollow CS microsphere can be observed at the different time. The adsorption of methyl orange and xylenol orange increases with agitation time and attains equilibrium at about 40 mins, 120 mins for CS microsphere for an initial methyl orange and xylenol orange concentration of 200 mg/L and 32 mg/L. It shows that the adsorption of methyl orange and xylenol orange remains constant after 40 mins, 120 mins for hollow CS microsphere, implying that equilibrium has been

reached. Therefore the optimum agitation time for adsorption of methyl orange and xylenol orange was about 40 min and 120 mins, respectively.

Effect of inorganic salts

Apart from dyes, the waste waters from textile manufacturing also contain various types of dissolved compounds, such as acids, alkalis, salts, surfactants, etc. Anions such as chloride, sulphate, carbonate and nitrate, etc. are the most common ions present in textile effluents. An experiment was carried out on the effect of Cl^- , NO_3^- , SO_4^{2-} , and HCO_3^- on the adsorption of methyl orange and xylenol orange by a coagulation flocculation process. A quantity of 1 g/L of an appropriate salt was added to the dye

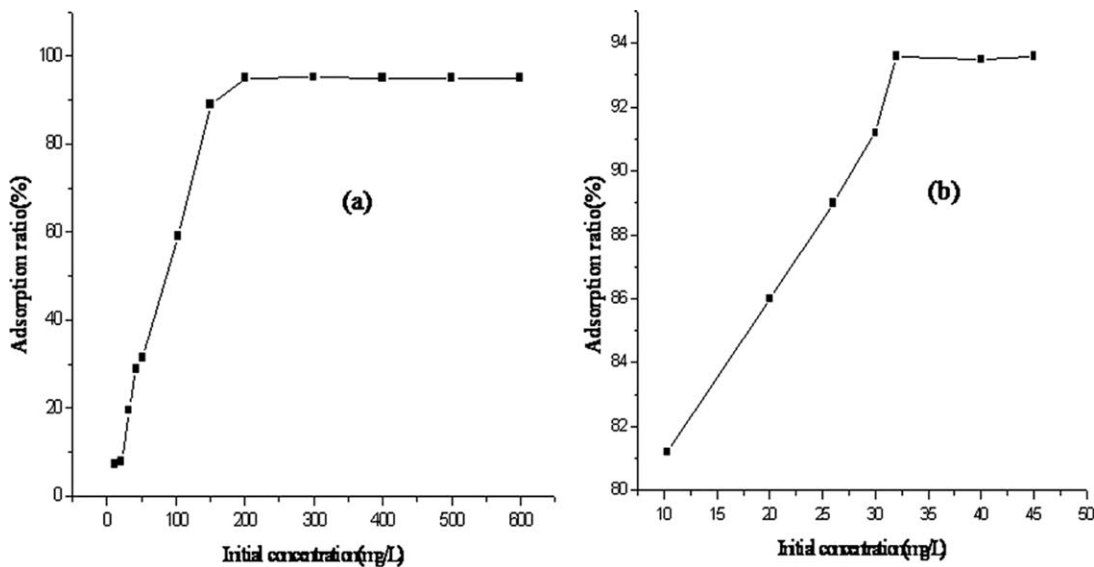


Figure 6 The initial concentration effect to the adsorption (a, methyl orange; b, xylenol orange).

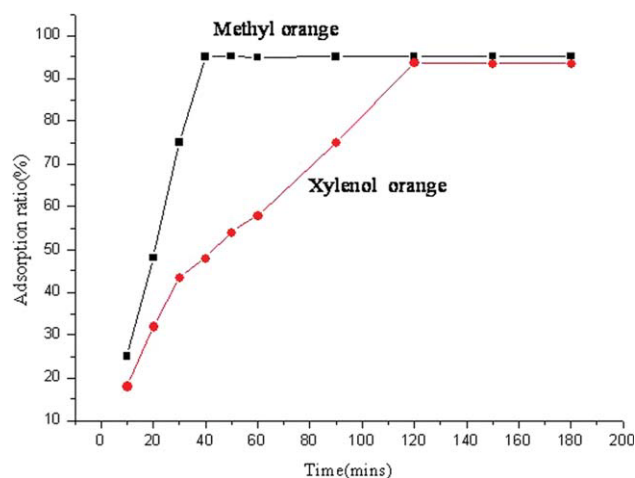


Figure 7 Effect of agitation time to the adsorption. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solution under optimal experimental conditions (initial dye concentration: 200 mg/L, 32 mg/L) at pH 5 (Fig. 8). Since the common cation of all the added salts, i.e., Na^+ , did not react with CS or with the dyes, only relevant anions were involved in the inhibition effect. As shown in Figure 8, the addition of such anions as Cl^- and NO_3^- to the solution did not influence the removal of the studied dyes. The percentage of removal remained constant at a high salt concentration, 10-fold exceeding the concentration of the dyes. On the other hand the removal of methyl orange and xylenol orange was more influenced by the SO_4^{2-} . In this case, the efficiency decreased about 30% in the presence of Na_2SO_4 . The removal of methyl orange and xylenol orange was significantly lower in the presence of Na_2SO_4 than in the presence of NaCl and NaNO_3 . The impact of sulphate anions may be explained by the precipitation effect of these ions on CS: the interactions of the sulphate anions with protonated amine groups contributed to reducing the polymer solubility (dehydrating effect) and decreasing the availability of protonated amine groups. In the case of NaHCO_3 , a drastic increase of the pH was observed (up to 7.1 for methyl orange and up to 8.8 with and xylenol orange). This increase of the pH entrained a significant decrease in the protonation of the amine groups and consequently also their affinity for the sulphonic groups of the dyes was reduced. In addition, the increase in

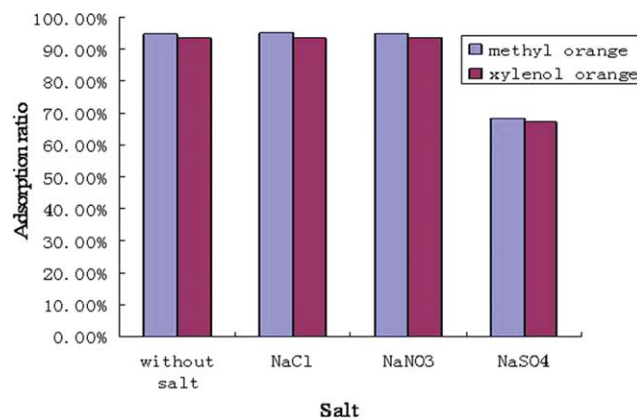


Figure 8 Influence of the presence of inorganic salts (1 g/L) on the adsorption of methyl orange, xylenol orange under optimum experimental conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ionic strength may affect the distribution of the charge on the CS molecules due to a charge screening effect²⁴ or the contraction of the thickness of the double layer surrounding the CS molecules. This, in turn, has an influence on the interaction of CS molecules with the dyes. In a different field, Tixier et al. investigated the effect of the ionic strength on the viscosity of an activated sludge suspension²⁵ and observed that the simultaneous decrease in the particles' double layer thickness and surface charge contributed to the decrease in intraparticle interactions.

Comparison of adsorption capacities

The adsorption capacities of the two dye-hollow CS microsphere systems are higher than those stated in other literature using CS particles²⁶ because of the increased surface area available for adsorption as a result of using hollow CS microsphere. The particle diameter of hollow CS microsphere as measured by SEM and it is found to be average 74 μm . The difference in the degree of adsorption may also be attributed to the size and chemical structure of the dye molecule. Methyl orange has the smallest molecular size which implies smaller surface area and protonated amino groups of the adsorbent being occupied by each dye molecule. The small molecular size not only increases the concentration of dye on the surface of the CS particle but also enables a deeper

TABLE II
Comparison of Chitosan Microsphere for Acid Dyes

| Dye | Adsorption ratio | General conditions | Reference |
|----------------|------------------|---|-----------|
| Methyl orange | 95% | 25°C, pH = 4.9, 45 mins 74 μm , 200 mg/100 mL | 24 |
| Xylenol orange | 93.6% | 25°C, pH = 4.9, 2 h, 74 μm , 32 mg/100 mL | 25 |

penetration of dye molecules into the internal pore structure of CS microsphere. The monovalent nature of methyl orange dye molecules makes more protonated amino groups on the CS particle available for adsorption of xylenol orange. It also reduces the electrostatic repulsion of adjacent dye molecules, which is significant in hollow CS microsphere, on the adsorbent surface when compared with xylenol orange, enabling dye molecules to be packed more closely on the CS surface. The possible reason for the inconsistent results in the present study is the inaccurate initial pH adjustment, which will be explained further in the recommendations and suggestions section. As the hollow CS microsphere available for the experiment was in suspension form, the initial pH adjustment had to be carried out after the mixing of suspended hollow CS microsphere and dye solution. The pH adjustment had to be performed as soon as possible because once HCl was added into the mixture, the amino group on the CS particles were immediately protonated by the H⁺ ions added. Although problems can be minimized by rapid pH adjustment, the experimental error caused cannot be eliminated completely. A comparison of the adsorption capacities of the hollow CS microsphere is shown in Table II.

CONCLUSION

The performance of hollow CS microsphere (with particle size average 74 μm) as an adsorbent to remove acid dyes: methyl orange, xylenol Orange from aqueous solution has been investigated. The differences in capacities may be due to the differences in the particle size of dye molecules and the number of sulfonate groups on each dye molecule. The results have demonstrated that monovalent and smaller dye molecular sizes have superior capacities due to the increase in dye/CS surface ratio in the system and deeper penetration of dye molecules

into the internal pore structure of hollow CS microsphere.

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