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Removal of azo dyes from aqueous solutions using chitosan based composite hydrogels

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ABSTRACT

Some cationic composite hydrogels based on chitosan (CS) and poly (N-2-aminoethyl acrylamide) (PAEA) covalently cross-linked with glutaraldehyde (GA) were tested as novel sorbents for two dis-azo dyes: Congo Red and Direct Blue 1. Three CS-based composite hydrogels having different molar ratios between the primary amine groups and the cross-linking agent (GA/NH₂ = 5.3 and 12.5), the same total concentration of polycations ($C_{PC} = 2$ wt%) and two molar ratios between polycations (PAEA:CS = 0.25 and 1.2) were used for this study. Pseudo-first order model, pseudo-second order model and the intraparticle diffusion model were used to analyze the experimental data in order to establish the mechanism of adsorption. The adsorption kinetics has been well described by the pseudo-second order model. The effect of temperature on the adsorption of both dyes has been also investigated.

Keywords: adsorption, azo dyes, chitosan, composite hydrogels, poly (N-2-aminoethyl acrylamide)

INTRODUCTION

In recent years, the pollution of the wastewaters with dyes is becoming a major environmental problem due to the growing use of a variety of dyes. Dyes usually have a synthetic origin and complex aromatic molecular structures which are more stable and more difficult to biodegrade. It is known that wastewaters containing dyes are very difficult to treat, since the dyes are recalcitrant molecules (particularly azo dyes), resistant to aerobic digestion, and are stable to oxidizing agents. Textile, paper, plastics, and cosmetic industries use a wide variety of dyes to color their products and discharge large amount of effluents including dyes which are very toxic and could cause serious ecological problems. Therefore, dye pollution in water stream is a major environmental problem. The methods of dye removal from industrial wastewaters could require many processes such as biological treatment, coagulation, electrochemical techniques, adsorption, and oxidation. Among these methods, adsorption is considered an effective and economical method to remove dyes

from wastewaters.¹⁻⁶ It has been reported that many different types of adsorbents are effective in removing color from aqueous effluents. Natural polymeric materials are gaining more and more interest for application as adsorbents in wastewater treatment due to their biodegradable and non-toxic nature. As a functional biological polymer, chitosan (CS) offers an interesting set of characteristics, including non-toxicity, biodegradability, biocompatibility, and bioactivity. This material also exhibits remarkable physicochemical properties such as the hydrophilic character, the flexibility of the linear chain, capability to interact and to adsorb various compounds, and cationic properties which are unique among the abundant polysaccharides.

Chitosan and its derivatives have been extensively investigated as biosorbents for removal of heavy metals and dyes.⁷⁻¹⁹ The knowledge and control of the permeability and swelling properties of the CS-based composite materials is crucial for such applications.^{20,21} The aim of this study is to investigate the adsorption behavior of the CS-based composite hydrogels

towards two dis-azo dyes: Congo Red (CR) and Direct Blue 1 (DB1).

EXPERIMENTAL

Materials

Chitosan as powder was purchased from Fluka, ash content less than 1%, and used without further purification. The viscometric average molar mass of CS was 235 kg/mol and the degree of deacetylation of around 85%.²² PAEA has been prepared by the aminolysis/hydrolysis reaction of the nitrile groups from poly(acrylonitrile) according to ref. 23. GA as aqueous solution with a concentration of 25% was purchased from Merck. The azo dyes (CR and DB1) from Aldrich were used after they were three times recrystallized from an aqueous methanol solution (methanol/water, 70/30, v/v). Molecular structures of the dis-azo dyes are shown below:





Methods

our investigations on CS-based In hydrogels, a less explored route was employed, i.e., the preparation of composite networks by covalent cross-linking of two different polycations, one natural (CS) and another one synthetic (PAEA), both bearing primary amine groups able to react with cross-linking agents like GA in aqueous medium. The CS solutions, with a concentration of 2%, were obtained by dissolving the CS powder in a 1 vol % acetic acid solution and stirring for at least 24 h. PAEA was used as aqueous solution with a concentration of 5%. GA was used as aqueous solution with a concentration of 2.5%. The homogeneous solution containing both polycations (CS and PAEA) was prepared by mixing CS solution with PAEA aqueous solution,

in different proportions. The molar ratios between PAEA and CS from 0 up to 3.54 and the polycation concentrations from 2 up to 3.5 wt.% were thus varied. After 15 min mixing, the crosslinker GA was added and the mixing went on 15 min. The mixture of polycations and GA were cast onto Petri dishes and maintained at 37 °C, for 24 h, and under vacuum at 37 °C, 48 h. All composite gels were further neutralized by immersing in 1 M NaOH for 1 h, and then repeatedly washed with distilled water several days until the neutral pH was reached, and finally allowed to dry at room temperature. Experimental conditions such as temperature, mixing time and speed were maintained constant throughout the investigations.²²

Study of the dye removal properties of the cationic composite hydrogels was carried out using a batch equilibrium procedure. Thus, 0.025 g of dry composite hydrogel was placed in a flask and contacted with 10 mL of aqueous solution of each dye: CR and DB1 at the concentration of 2×10^{-5} mol/L, the initial solution pH being 5.5. For kinetic study, the flask containing the mixture of composite hydrogel and dye solution was placed in a thermostatic bath at 40 °C. The experiments concerning the effect of temperature on the dye removal were carried out in 10 mL of dye solutions (C = 2×10^{-5} mol/L) with 0.025 g adsorbent for 24 h. After 24 h composite hydrogels were filtered off and the residual concentration of CR and DB1 remained in the filtrate was measured by the UV-Vis spectroscopy at 497 nm for CR and at 620 nm for DB1.

RESULTS AND DISCUSSION

Adsorption kinetics of dyes onto hydrogels

The CS-based composite hydrogel having the molar ratio between the primary amine groups and the cross-linking agent (GA/NH₂) of 5.3, the total concentration of polycations (C_{PC}) of 2 wt%, and the molar ratio between polycations of 0.25 was used for the study of the influence of contact time. The effect of the contact time on the adsorption capacity of composite hydrogel for CR and DB1 is shown in Figure 1. The contact time varied in the range 0 -900 min, and the initial concentration of dyes was fixed at 2×10^{-5} mol/L. As Figure 1 shows, the time required to achieve the equilibrium at temperature 40 °C was about 400 min. The kinetics of dyes adsorption on the CS/ PAEA composite hydrogel was determined with three different kinetic models, i.e., the pseudofirst order, pseudo-second order and the intraparticle diffusion model.



Figure 1. Adsorption of dyes (CR, DB1) onto composite hydrogel as a function of contact time.

The pseudo-first order equation of Lagergren (Eq. (1)) is one of the most widely used equation, being the first rate equation developed for sorption in solid/liquid systems.²⁴

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$
(1)

where: q_e and q_t are the amounts of dyes adsorbed at equilibrium and at time t, respectively (mmol/g), k_1 (min⁻¹), is the rate constant of the pseudo-first order kinetics. The slopes and intercepts of the plots log ($q_e - q_t$) versus t (Figure 2) were used to determine the pseudo-first order rate constant, k_1 , and q_e , the values obtained being presented in Table 1.



Figure 2. *Pseudo-first order model fitted for the adsorption of CR and DB1 on the CS-based composite hydrogel.*

Table 1. Kinetic data for the adsorption of dyes onto CS/PAEA composite hydrogel obtained using pseudo-first order model.

	q _e exp,	q _e exp, Pseudo-first order constant		
Dye	mmol/g	k ₁ ,	q _e calc,	\mathbb{R}^2
		min ⁻¹	mmol/g	
CR	$78.63 \cdot 10^{-4}$	4.72 ·	46.20 ·	0.9953
		10^{-3}	10^{-4}	
DB1	$79.46 \cdot 10^{-4}$	3.54 ·	46.40 ·	0.9982
		10^{-3}	10-4	

The theoretical q_e values estimated from the pseudo-first order kinetic model gave significantly different values compared to experimental values (Table 1). These results showed that the pseudo-first order kinetic model did not describe well these adsorption systems.

The adsorption data were also treated according to the pseudo-second order kinetics using the (Eq. (2)), which is proposed by Ho and McKay:²⁵

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(2)

where: k_2 [g/(mmol × min)] is the rate constant of the pseudo-second order kinetics. The values of k_2 and q_e were obtained from the intercept and slope of the straight lines resulted by plotting t/q_t against t (Figure 3) and were presented in Table 2.



Figure 3. *Pseudo-second order model fitted for the adsorption of CR and DB1 on the CS-based composite hydrogel.*

Table 2. Kinetic data for the adsorption of dyes on CS/PAEA composite hydrogel obtained using pseudo-second order model.

	q _e exp,	Pseudo-second order constants		
Dye	mmol/g	k ₂ ,	q _e calc,	\mathbf{R}^2
		g/(mmol	mmol/g	
		× min)		
CR	78.63 ×	2.00	$82.78 \times$	0.9990
	10^{-4}		10^{-4}	
DB1	79.46 ×	2.04	79.72×	0.9971
	10-4		10-4	

As Table 2 shows, the theoretical q_e values, estimated from the pseudo-second order kinetic model, are very close to the experimental values (Table 2). Furthermore, the correlation coefficients are high for CS/PAEA composite, this indicating the validity of the pseudo-second order model for the adsorption of the dyes CR and DB1 on the composite hydrogel.

In order to assess the nature of the diffusion process reasonable for the adsorption of dyes onto the CS-based composite hydrogels, attempts were made to calculate the pore diffusion coefficients. The intra-particle diffusion model was proposed by Weber and Morris,²⁶ the initial rate of intra-particle diffusion is calculated by linearization of the curve $q = f(t^{0.5})$ (Eq. (3), Figure 4):

$$q_t = k_{id} t^{0.5} \tag{3}$$



Figure 4. Weber and Morris intra-particle diffusion model fitted for the adsorption of CR and DB1 on the CS-based composite hydrogel.

Generally, the intercept of the plot of q_t versus $t^{0.5}$ gives an idea about the boundary layer thickness, the larger the value of the intercept, the greater the boundary layer diffusion effect is.²⁷ The values of intra-particle diffusion rate constant, k_{id} , are presented in Table 3.

Table 3. Kinetic data for the adsorption of dyes

 onto
 CS/PAEA
 composite
 hydrogel
 obtained

 using intra-particle diffusion model.

Dye	q _e exp, mmol/g	Intra-particle diffusion constants		
		k _{id} , mmol/(g× min ^{0.5})	\mathbb{R}^2	
CR	78.63 ×10 ⁻⁴	1.82×10^{-4}	0.9523	
DB1	79.46 ×10 ⁻⁴	1.81×10^{-4}	0.9881	

If the regression of q_t versus $t^{0.5}$ is linear and passes through the origin, then the intraparticle diffusion is the sole rate-limiting step.²⁶ The deviation of the straight line from the origin indicates that this process is not the rate-limiting step. The values of the correlation coefficients in Table 3 also support this conclusion.

Some data selected from literature for the pseudo-second order constant concerning the sorption of CR on CS as beads were presented in Table 4 compared with the constant found in this study.

Table 4. Comparative values of the pseudo-second order constants for the adsorption of CR

Concentration of	k ₂ ,	Ref.
CR, mol/L	g/(mmol×min)	
2.8×10^{-4}	0.1142	[9]
7.2×10^{-5}	3.2643	[13]
2.9×10^{-4}	0.1798	[13]
2×10^{-5}	2.00	This
		study

As Table 4 shows, the pseudo-second order constant found in this study for the adsorption of CR on the CS/PAEA composite is in the same range with the values reported in literature for the adsorption of this dye on the CS beads.

The effect of temperature on the adsorption of dyes (CR, DB1) onto composite hydrogels

Figure 5 illustrates the effect of temperature on the removal of dis-azo dyes (CR and DB1) by the composite hydrogels. The color removal efficiency CRE (%) was calculated according to Eq. (4):

 $\begin{aligned} & \text{CRE (\%)} = (1 - A_c/A_i) \text{ x } 100 \end{aligned} \tag{4} \\ & \text{where } A_i \text{ and } A_c \text{ are the adsorbance of the dyes} \\ & \text{before } \text{ and } \text{ after the adsorption process,} \end{aligned}$

respectively.



Figure 5. *Effect of temperature on the removal of CR and DB1 by composite hydrogels.*

Figure 5 shows that the adsorption capacity of the composite hydrogels increased with increasing the temperature from 4 up to 40 °C.

CONCLUSIONS

In this study, the capacity of CS/PAEA composite hydrogels to adsorb CR and DB1 from aqueous solutions was examined. Kinetic data were successfully fitted by the pseudo-second order equation, which gave the best correlation with experimental data, for the studied systems. The increase of temperature led to the increase of the CRE for both dyes.

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