

Removal of Reactive Dye from Wastewater by Adsorption Using ECH Cross-Linked Chitosan Beads as Medium

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ABSTRACT

The feasibility of the removal of reactive dye from wastewater using a novel adsorbent, ECH cross-linked chitosan beads, as medium was examined. The effect of the pH and the initial concentration of the dye (RR222) solution on the adsorption capacity of the ECH cross-linked chitosan beads were also investigated. It was found that the initial dye concentration and the pH of the solution significantly affected the adsorption capacity. An increase in initial dye concentration results in the increase of adsorption capacity while an acidic pH was found to be favorable for the adsorption of dye. It was also found that the equilibrium adsorption of RR222 could be adequately described by using the Langmuir model ($r^2 \geq 0.999$). Moreover, results showed that the adsorption rate of RR222 onto ECH cross-linked chitosan beads could be described by using the second-order kinetic model, suggesting that chemical sorption instead of mass transfer was the rate-limiting step for the adsorption process. The maximum monolayer adsorption capacity obtained from the Langmuir model was extremely high as compared to the data reported in literature; 2252 g/kg at 30°C with a pH of 3.0. Therefore, ECH cross-linked chitosan beads could be a feasible medium for the removal of reactive dye from wastewater and potentially an alternative for the decolorization of wastewater.

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INTRODUCTION

Color in textile effluents has become a serious environmental problem. Conventional biological and coagulation/flocculation treatment methods are problematic in the decoloring of such wastewater due to the nature of synthetic reactive dyes. The adsorption process has been considered one of the efficient methods for removing dye pollutants from wastewater. Activated carbon^[1] is the most widely used adsorbent for the adsorption process. However, the adsorption capacity of activated carbon for reactive dyes is not very high, leading to a high operation cost. Consequently, a more effective and cheaper adsorbent with a higher adsorption capacity has stimulated intensive research.

Chitosan is the deacetylated form of chitin, which is a linear polymer of acetylamino-D-glucose. Recently, chitosan used as an adsorbent has drawn attention due to its high contents of amino and hydroxyl functional groups showing a high potential for the adsorption of dyes,^[2-7] including reactive, acid and direct dyes in neutral solutions. However, chitosan is soluble at a low pH, especially in organic acids, and this precludes the use of chitosan as an adsorbent under acidic conditions.^[4] To improve the acidic and chemical stability of chitosan, some cross-linking agents such as Denacol EX841^[4] have been used to stabilize chitosan in acidic solutions. Nevertheless, the adsorption of dyes in acidic solutions using cross-linked chitosan as medium was still limited.

In this study, the feasibility of using the novel Epichlorohydrin (ECH) bead-type cross-linked chitosan as an adsorbent for the removal of the reactive dye, RR222, from wastewater was examined. ECH was selected as a convenient base cross-linking agent because it does not eliminate the cationic amine function of chitosan that was the major adsorption site attracting anion dyes during adsorption. Moreover, the adsorption behavior, including the equilibrium isotherm and kinetics of the dye on ECH cross-linked chitosan beads, was also investigated.

MATERIALS AND METHODS

Materials

The commercial reactive dye-reactive red 222 (RR 222, $\lambda_{\max} = 502$ nm) was supplied by Sumitomo Chemical Co., Ltd, Japan and used with no pretreatment. Figure 1 shows the molecular structure of RR 222.^[2] The sodium acetate-3-hydrate (purity >99%, RDH Co.) and acetic acid (ACS grade, TEDIA Co.) buffer solution was used for adjusting the pH of the dye solutions. Chitosan (α -type, degree of deacetylation: 95.5%, molecular weight: 220 k) was supplied by OHKA Enterprises Co. Epichlorohydrin (ECH, purity $\geq 98\%$) was supplied by Fluka Co. Powered Activated Carbon (PAC) purchased from Merck Co., Taiwan.

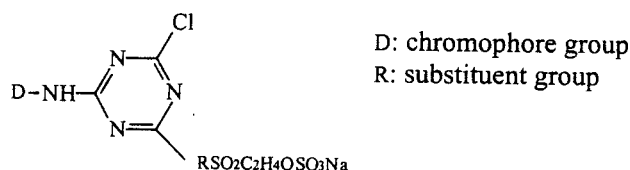


Figure 1. The molecular structure of reactive dye RR222.

Preparation of Chitosan Bead

The chitosan beads were prepared in accordance with the method reported by Chiou and Li.^[7] In this way, the wet noncross-linked chitosan beads with a diameter of 2.3 ~ 2.5 mm were prepared.

Preparation of ECH Cross-Linked Chitosan Beads

The wet noncross-linked chitosan beads (containing 0.1 g dry chitosan) was put into 50 mL, 1 N sodium hydroxide solution in a flask. Some cross-linking agent, ECH, was added and then it was shaken at 50°C for 6 h in a water bath (Deng Yang corp., Taiwan). The weight ratio of ECH to chitosan was 0.5.

Batch Equilibrium Experiments

To evaluate the effect of pH, the pH of dye solutions was adjusted by buffer solutions of acetic acid/acetate to the desired pH of 3, 4, 5, 6, 7, or 8. Chitosan beads (containing 0.1 g dry chitosan) and a 50 mL of dye solution (approximately 5300 mg/L) with a different pH value were placed in a 125 mL flask, and shaken for two days at a constant temperature (30 ± 1°C). The amount of adsorption at equilibrium q_e (g/kg) was computed as follows

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

where C_0 and C_e are the initial and equilibrium solution concentrations (mg/L), respectively, V is volume of the solutions (L), and W is the weight of chitosan used (g).

For the experiments of the equilibrium adsorption isotherm, a bottle-point technique with a constant shaking speed (100 rpm) was used. The dye (RR222) was diluted in a pH 3 buffer solution to the required concentration. The experiments were performed at a constant temperature (30 ± 1°C) for two days. Two common adsorption isotherms were used for the description of experimental data; The Langmuir isotherm:

$$q_e = \frac{QbC_e}{1 + bC_e} \quad (2)$$

and the Freundlich isotherm:

$$q_e = Q_f C_e^{1/n} \quad (3)$$

where Q (g/kg) is the maximum amount of the dye per unit weight of chitosan to form complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e , and b is the Langmuir constant related to the affinity of binding sites (L/mg). Q represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules and assists in the comparison of adsorption performance. Q_f is roughly an indicator of the adsorption capacity and $(1/n)$ of the adsorption intensity.

Batch Kinetic Experiments

In the batch kinetic adsorption experiments, chitosan beads (containing 0.1 g dry chitosan) and dye solution (50 mL) with a constant pH value of 3.0 were placed in a 125 mL flask and shaken in a water bath at $30 \pm 1^\circ\text{C}$. 0.1 mL of the dye solution was taken out to dilute to 10 mL for analyzing the residual concentration of dye at each preset interval.

The pseudo first-order and pseudo second-order kinetic models were used to investigate the rate of adsorption. The pseudo first-order rate equation is given as

$$dq/dt = k_1(q_e - q) \quad (4)$$

where q_e and q are the amounts of dye adsorbed on the adsorbent at equilibrium and at time t , respectively (g/kg) and k_1 is the rate constant of the first-order adsorption (min^{-1}). After definite integration with the initial conditions $q = 0$ at $t = 0$ and $q = q$ at $t = t$, Eq. (4) becomes

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

The pseudo second-order rate equation is expressed as

$$dq/dt = k_2(q_e - q) \quad (6)$$

by integrating Eq. (6), resulting in

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where k_2 ($\text{kg g}^{-1} \text{min}^{-1}$) is the rate constant of the second-order adsorption. If the second-order kinetics is applicable, the plot of t/q vs. t should show a linear relationship.

Analysis

The residual concentration of RR222 dye solutions was analyzed at wavelength 502 nm using a JASCO Model V-530 UV/Visible spectrophotometer (JASCO Co., Japan). In addition, in order to examine whether any breakdown product of RR222

dye during the adsorption experiments was produced, the solution of RR222 with different contact time was scanned from the wavelength of 220 to 800 nm using the spectrophotometer.

RESULTS AND DISCUSSION

The result showed in Fig. 2 illustrates that no breakdown product was generated in solution because the absorption spectrum of the solution did not shift and there was no new additional peak found in the spectrum. Therefore, it is believed that a decrease in the concentration of dye solution in this study is generally through the mechanism of adsorption.

Equilibrium Adsorption

Effect of pH on the Adsorption Capacity

Figure 3 shows the effect of pH on the adsorption capacity of RR222 on ECH cross-linked chitosan beads and PAC at equilibrium. It was found that the adsorption capacity of RR222 on ECH cross-linked chitosan beads was strongly affected by the pH of solution and increased significantly by decreasing the pH of solution while that on PAC was almost constant. This result was qualitatively consistent with the finding of some previous studies.^[4,8] The q_e value at pH 3.0 was almost twice that of pH 8.0. At pH 3–5, there was little difference between adsorption capacities. This may be due to the amino groups of ECH cross-linked chitosan beads with

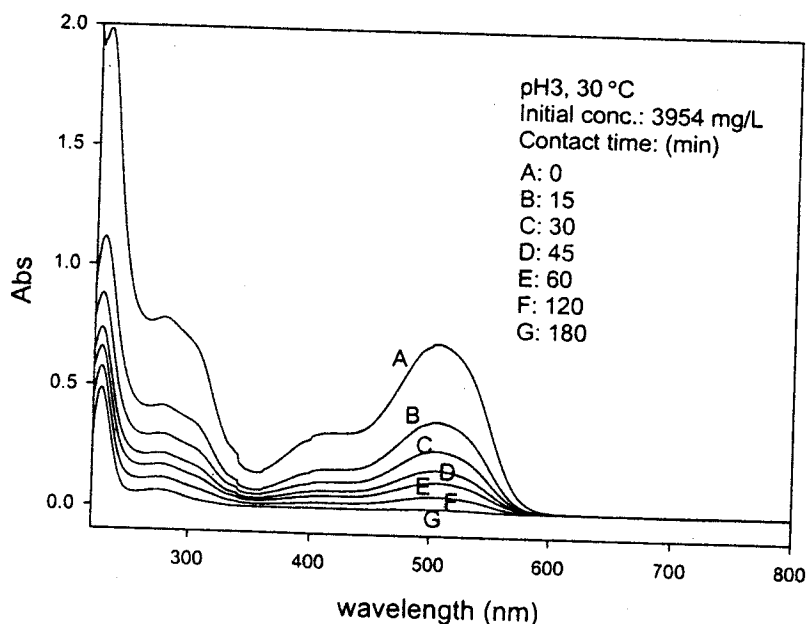


Figure 2. Absorption spectrum of the solution of RR222 during adsorption.

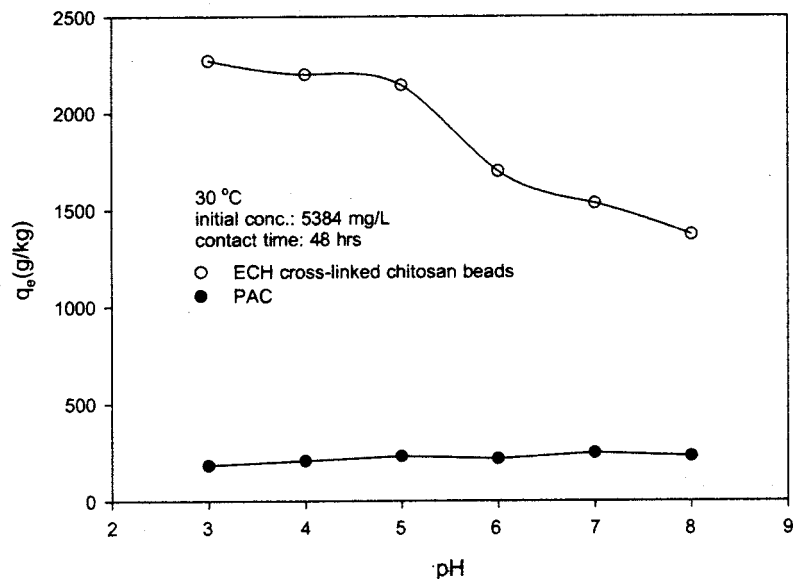


Figure 3. Adsorption capacity of ECH cross-linked chitosan beads and powdered activated carbon (PAC) for RR222 under different pH conditions.

a pH of 3–5 being almost protonated (Eq. (8)) and then adsorbing the dye anion by electrostatic attraction (Eq. (9)). At pH > 6, the formation of protonated ECH cross-linked chitosan beads decreased, resulting in reducing the adsorption capacity. Accordingly, it can be seen that the optimal pH for adsorption of RR222 onto ECH cross-linked chitosan was about pH 3.0.



Adsorption Isotherm

Figure 4 shows the equilibrium adsorption of RR222 on the ECH cross-linked chitosan beads at pH 3.0. The shape of the isotherm seems rectangular because at low equilibrium dye concentrations C_e , the equilibrium adsorption densities q_e of the ECH cross-linked chitosan beads reached almost the same q_e as those at high equilibrium dye concentrations. This indicates that the ECH cross-linked chitosan beads have a high adsorption density even at low equilibrium dye concentrations. The rectangular shape of the isotherm usually results from strongly electrostatic binding between cross-linked chitosan molecule and dye molecule. The equilibrium adsorption isotherm is fundamental to describe the interactive behavior between solutes and adsorbent and is important in the design of an adsorption system. In this study, two common adsorption isotherm models, the Langmuir isotherm and the Freundlich isotherm, were used for description of experimental data

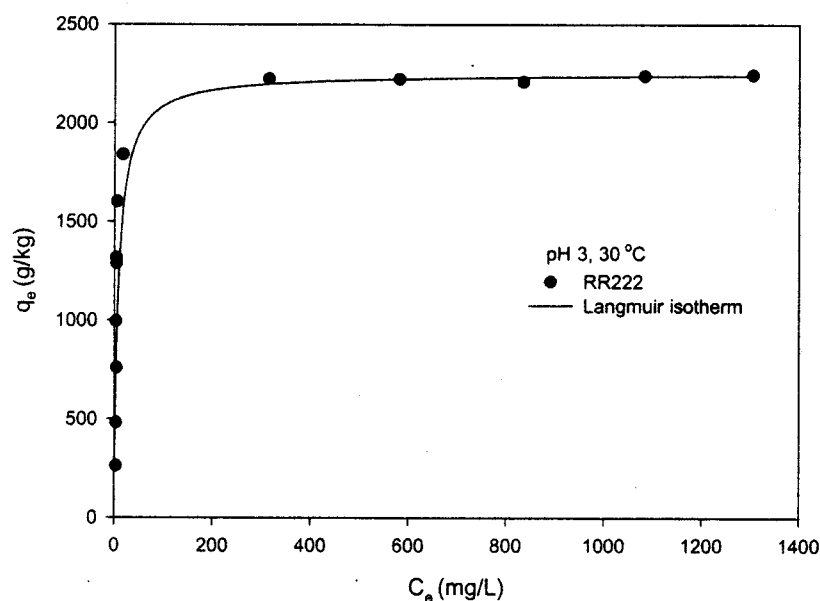


Figure 4. Equilibrium adsorption of RR222 on ECH cross-linked chitosan beads.

Table 1. Adsorption isotherm constants.

Dye	Langmuir Isotherm		Freundlich Isotherm			
	Q (g/kg)	b (L/mg)	r^2	Q_f	n	r^2
RR222	2252	0.125	0.999	663.8	5.305	0.522

shown in Fig. 4. Table 1 summarizes the best-fit model parameters of these two isotherms. According to the values of correlation of coefficient (r^2), the isotherm has a better fit with the Langmuir model. The calculated Q value (2252 g/kg) listed in Table 1 indicates that the maximum monolayer adsorption capacity of RR222 on ECH cross-linked chitosan beads is very large. Compared with some data shown in Table 2, it was found that the ECH cross-linked chitosan beads used in this study have much higher adsorption capacity for adsorbing RR222 than other adsorbents such as noncross-linked chitosan, chitin, and activated carbon.

Kinetics of Adsorption

Figure 5 shows the adsorption kinetics of the ECH cross-linked chitosan for different initial RR222 concentrations. A rapid equilibrium was observed; reached about 4 h for each case. To more quantitatively investigate the rate of dye adsorbed on cross-linked chitosan beads, the pseudo first-order and pseudo second-order model as expressed by Eqs. (4) and (6), respectively, were applied to obtain rate constants. Table 3 lists the calculated rate constants of two models. As listed

Table 2. Comparison of the maximum monolayer adsorption capacities of RR222 on various adsorbents.

Dye	Adsorbent	Maximum monolayer adsorption capacity (g/kg)	Reference
RR222	Chitosan (ECH cross-linked)	2252	This study
	Chitosan (noncross-linked)	1026–1106	[5]
	Chitosan (noncross-linked)	1653	[6]
	Chitosan (noncross-linked)	1009	[6]
	Chitosan (noncross-linked)	299–380	[2]
	Chitosan (noncross-linked)	54–87	[2]
	Chitin	~100	[2]
	Powdered activated carbon	~200	This study
Granular activated carbon	~50	[2]	

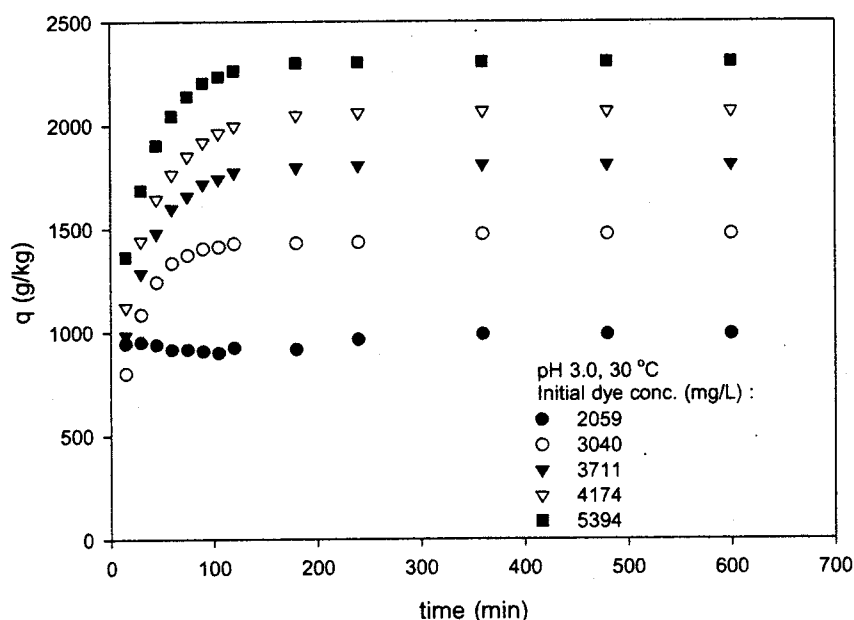
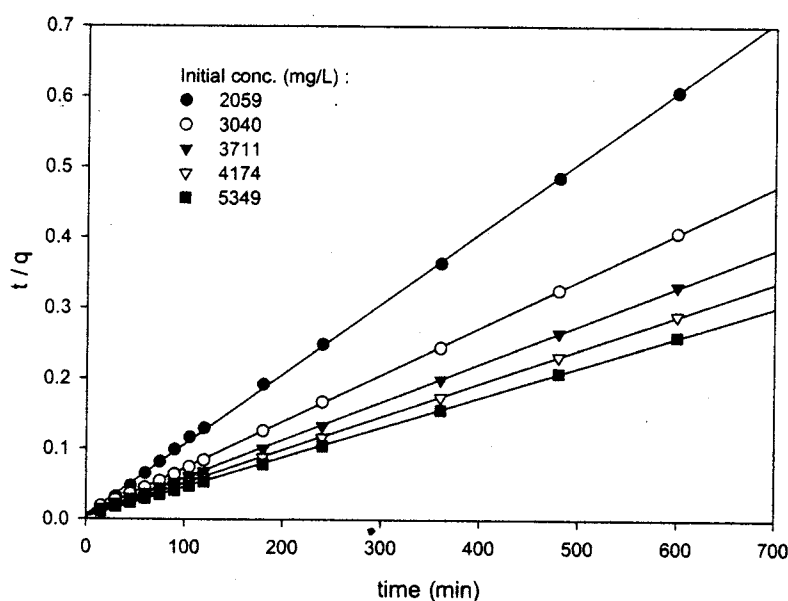


Figure 5. Adsorption kinetics of RR222 with various initial concentrations on ECH cross-linked chitosan beads.

in Table 3, the correlation coefficients for the first-order kinetic model are low, especially at low initial concentrations of the dye solution. Also, the calculated q_e values obtained from the first-order kinetic model do not give reasonable values, which are too low compared with the experimental q_e values. This suggests that the adsorption rate of dye RR222 onto ECH cross-linked chitosan does not follow the pseudo first-order kinetics. On the other hand, the straight lines in the plot of t/q vs. t (Fig. 6) show a good agreement of the experimental data with the second-order kinetic model for different initial dye concentrations. Table 3 shows that the correlation coefficients for the second-order kinetic model almost approached to 1.000 for all cases. In addition, the calculated q_e values also agree very well with the

Table 3. Adsorption rate constants of RR222 on cross-linked chitosan.

Initial concentration of dye (C_0) (mg/L)	$q_{e, exp}$ (g/kg)	Pseudo first-order rate		Equation	Pseudo second-order rate		Equation
		k_1 (min^{-1})	$q_{e, cal}$ (g/kg)	r^2	k_2 (kg/g/min)	q_e (g/kg)	r^2
2059	988	0.19×10^{-2}	66	0.113	16.4×10^{-5}	997	0.999
3040	1472	1.21×10^{-2}	345	0.713	7.95×10^{-5}	1497	0.999
3711	1807	2.42×10^{-2}	929	0.986	6.39×10^{-5}	1842	0.999
4174	2065	2.20×10^{-2}	884	0.996	5.91×10^{-5}	2104	0.999
5349	2305	3.01×10^{-2}	1515	0.995	5.70×10^{-5}	2345	0.999

**Figure 6.** The pseudo second-order adsorption kinetics of RR222 with various initial concentrations on ECH cross-linked chitosan beads.

experimental data, which shows that an increase in the initial concentration of dye leads to an increase in the adsorption capacity of dye on adsorbent. The adsorption density at a 5349 mg/L of initial dye concentration is almost 2.3 times that of 2059 mg/L. This indicates that the adsorption kinetics of RR222 basically belongs to the second-order kinetic model. Similar phenomena were also observed in the biosorption of dye RB2, RY2, and Remazol Black B on biomass.^[9,10] According to the pseudo second-order model, the adsorption rate dq/dt is proportional to the second-order of $(q_e - q)$. Since the ECH cross-linked chitosan beads used in this study have relatively high equilibrium adsorption density, q_e , even at a lower initial concentration of dye solution, the adsorption rates become very fast and the equilibrium times are quite short. Such short equilibrium times coupled with high adsorption capacity indicate a high degree of affinity between dye RR222 and the

ECH cross-linked chitosan beads, and chemical sorption instead of mass transfer was the rate-limiting step for the adsorption process.

CONCLUSIONS

ECH cross-linked chitosan beads were able to successfully adsorb reactive dye RR222 from wastewater. Both the initial concentration of dye and the pH of the aqueous solution significantly affected the adsorption capacity of dye RR222 on ECH cross-linked chitosan. An increase in the initial dye concentration resulted in the increase of the adsorption capacity while an acidic pH was found to be favorable for the adsorption of dye. Also, the adsorption of RR222 on ECH cross-linked chitosan beads was found to exhibit nonlinear favorable equilibrium behavior that could be adequately characterized by the Langmuir isotherm model. Moreover, the adsorption rate of RR222 onto ECH cross-linked chitosan beads was described by using the second-order kinetic model, suggesting that the chemical sorption instead of mass transfer was the rate-limiting step for the adsorption process. The maximum monolayer adsorption capacity obtained from the Langmuir model was extremely high as compared to the data reported in literature; 2252 g/kg at 30°C with a pH of 3.0. Compared with conventional adsorbents, the novel ECH cross-linked chitosan beads are much more effective and faster for decoloring of wastewater. Therefore, ECH cross-linked chitosan beads used as medium for removing the reactive dye from wastewater can be a feasible and potential alternative for the decolorization of wastewater.

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