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Adsorption Equilibria of Reactive Dye onto Highly Polyaminated Porous Chitosan Beads

Tae Young Kim and Sung Yong Cho*,†

Engineering Research Institute, *Biohousing Research Institute, Chonnam National University, Gwangju 500-757, Korea

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Abstract−The adsorption of vinyl sulfone type reactive black 5 (RB 5) in aqueous solution onto chitosan beads and cross-linked chitosan beads with glutaraldehyde has been investigated in terms of initial pH and temperature of the solution. The adsorption equilibrium data were correlated with three adsorption models, such as Langmuir, Freundlich and Sips isotherms. Among them, the Freundlich isotherm best fit the data over the entire pH and temperature range of the solution. The adsorption capacity of RB 5 onto chitosan beads and cross-linked chitosan beads increased with decreasing initial pH and with increasing temperature. Equilibrium amount of RB 5 on chitosan beads was greater than that of cross-linked chitosan beads at the same initial pH values. Thermodynamic studies have also been carried out and values of standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were calculated.

Key words: Adsorption, Reactive Dye, Chitosan Beads, Cross-linking

INTRODUCTION

Dyes are widely used in such industries as textiles, leather, paper, and plastics to color their final products. Since many organic dye compounds are harmful to human beings, the removal of color from waste effluents has become environmentally important [Chiou and Li, 2002; Choi et al., 2004].

The vinyl sulfone and chlorotriazine dyes are the most reactive and versatile among the fiber reactive dyes, which means that the dye molecules readily react with fabric molecules [Juang et al., 1997]. In other words, reactive sites of dye react with functional groups on a fibre to bind the dye covalently under the influence of heat and pH (alkaline) [O'Neill et al., 1999]. These dyes can be used for cotton, silk, wool, rayon, paper and wood but not for synthetic fibers. Although most of these dyes are non-toxic at the discharge concentration into the receiving waters, the color they impart is very undesirable to the water user. Hence, color removal from such effluent is a major environmental problem because of the difficulty of treatment by conventional chemical coagulation/flocculation, biological and adsorption methods [Juang et al., 2002].

The adsorption process is one of the efficient methods to remove pollutants from wastewater. A number of articles have been published on the use of maize cobs, palm-fruit bunch particles, eucalyptus bark, cotton, sunflower stalks, and wheat straw [Davila-Jimenez et al., 2005; Kim et al., 2005; Choi et al., 2004;] as sorbents for dye removal. The adsorption of dyes is mainly dependent on the dye's properties and structure, and to an equal extent on the surface chemistry of the adsorbents. However, the adsorption capacity of the adsorbents is not very large and endeavors to improve the adsorption performance with new absorbents are still in progress.

Chitosan is a partially acetylated glucosamine biopolymer which exists in the cell wall of some fungi such as the Mucorales strains. In fact, it can be obtained from deacetylation of chitin. Chitosan is a widely used sorbent for transition metals and organic species because both amino ($-NH_2$) and hydroxyl ($-OH$) groups on chitosan chains can serve as coordination and reaction sites [Son et al., 2004; Wu et al., 2001]. The acidic effluent could severely limit the use of chitosan as adsorbent in removing dyes and metal ions due to the dissolution tendency of chitosan in the acidic solution. To overcome this problem, a cross-linked agent was used to stabilize chitosan in acidic solutions [Zheng and Xiao, 2004].

In this study, focusing on the reactive dye with vinyl sulfone groups, we studied the adsorption equilibrium of reactive dye using chitosan beads for different initial pH and temperature of the solution. Glutaraldehyde (GA) was chosen as a cross-linking agent and adsorption behaviors of reactive black 5 (RB 5) on cross-linked chitosan beads were examined in both acidic and alkaline solutions (pH=3, 6, 9 and 12) to evaluate the effect of pH. Langmuir, Freundlich and Sips isotherm models were used for the mathematical description of the adsorption equilibrium. Isotherm constants were evaluated for different initial pH and temperature of the solution. These results can be useful for the development of new adsorption technology to remove color from wastewater.

MATERIAL AND METHOD

1. Adsorbents and Adsorbate

Chitosan flake (degree of deacetylation: 85%, average molecular weight: 520,000) was supplied by Se-Hwa Ind., Korea. Glutaraldehyde (25%), used as a cross-linking agent, was purchased from Aldrich Co., USA. Fig. 1 shows the structure of chitosan and cross-linked chitosan with glutaraldehyde. Adsorbent used for comparison with chitosan beads was granular activated carbon (GAC), F-400, manufactured by Calgon Co. And physical properties of the two different adsorbents are shown in Table 1. The commercial reactive dye was supplied by a local manufacturer, Fine Chem. Co., Korea. The molecular area of the dye was 779 Å^2, which was calculated by the software Physical Properties Pro 3.27 From ChemSW Inc. One well-known dye classification system of internationally used is the Colour Index, devised by the Society of Dyes and Colourists in 1924. This classifies dyes by assigning a generic name, firstly,

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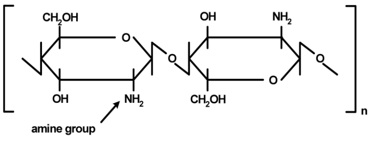
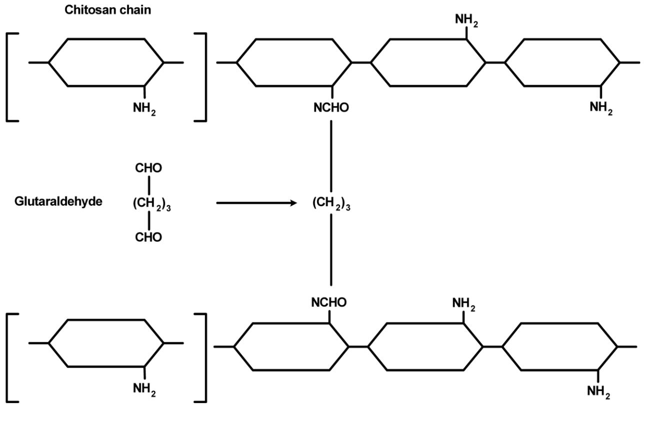
† To whom correspondence should be addressed.
E-mail: syc@chonnam.ac.kr



(a) Chitosan



(b) Cross-linked chitosan

Fig. 1. Structure of chitosan and cross-linked chitosan.

Table 1. Physical properties of the adsorbents

Physical properties	Unit	F-400	Chitosan bead
Particle diameter	mm	0.37-0.54	2.0
Particle density	kg/m^3	682	105
Particle porosity	-	0.62	0.94
BET surface area	m^2/g	800	350
Average pore diameter	Å	19.02	560

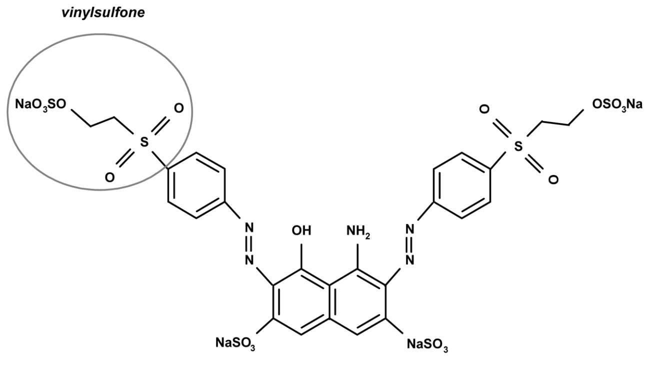


Fig. 2. Structure of the reactive dye used (RB 5).

determined from its application characteristics, and then assigning a CI constitution number based on its chemical structure if known. Dyes can be classified by their chemical structure or application method. In this study, the dye investigated is Polazol Black B and whose CI number is reactive black 5 (RB 5). Fig. 2 displays the structure of reactive dye (RB 5).

2. Preparation of Chitosan Bead and Cross-Linked Chitosan Beads

Fig. 3 represents a schematic diagram of the manufacturing process of chitosan beads. Chitosan solution was prepared by dissolving 15.0 g of chitosan flakes in 500 cm^3 of 2 wt% acetic acid solution. The solution was poured into a 30 cm^3 syringe equipped with a pump and dropped into aqueous solution containing sodium hydroxide (2 mol/L). The chitosan droplets formed beads in the solution, and were left in the aqueous solution for more than 24 h. Then the chitosan beads were washed by deionized water and stored in distilled water. The diameter of the beads was controlled by the size of the injection syringe, approximately 2.0 mm in diameter.

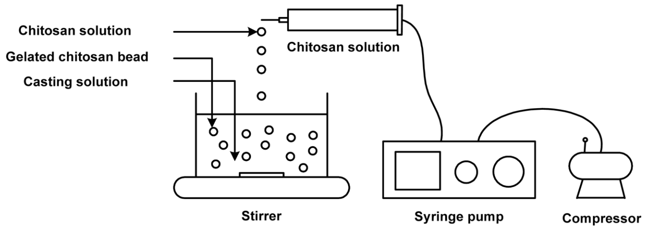


Fig. 3. Schematic diagram of chitosan bead manufacturing process.

The reaction of 15 ml of glutaraldehyde (2.5 wt%) with 10 g of chitosan gelled beads corresponded to that of 0.8 of –CHO (aldehyde) groups per 1.0 of $-NH_2$ (amine) groups, that is a reagent molar ratio, $-CHO/-NH_2$, of 0.8 : 1. Cross-linked chitosan beads at this condition were prepared with reaction time of 10 min, 30 min and 60 min, respectively.

3. Adsorption Equilibrium Studies

The RB 5 was dissolved in deionized water to the required concentration. The pH of dye solutions was adjusted to 3, 6, 9 and 12 using HCl or NaOH, respectively. For adsorption equilibrium experiments, the chitosan beads (0-0.7 g) and the dye solution (200 cm^3) were placed in a 300 cm^3 flask and then shaken for 5 days in a shaking incubator. The dye concentration of the solutions was analyzed with UV-VIS spectrometer (UV-1601, Shimadzu) at a wavelength of 598 nm. The amount of adsorption at equilibrium, q_e (mol/kg), was obtained as follows:

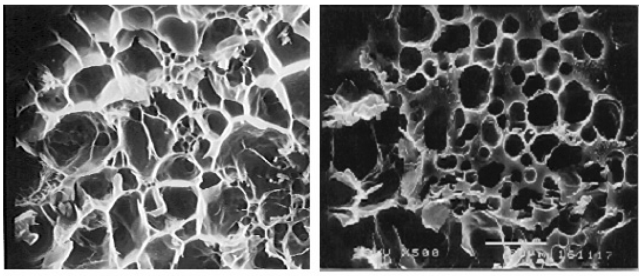
$$q_e=\frac{(C_0-C_e)V}{W} \tag{1}$$

Where C_0 and C_e are the initial and equilibrium solution concentrations (mol/m^3), respectively, V is the volume of the solutions (m^3) and W is the weight of chitosan beads used (kg).

RESULTS AND DISCUSSION

1. Characterization of Chitosan Beads

Although chitosan has an intrinsically high affinity and selectivity for reactive dyes, the raw adsorbent (flake type) is not suitable for aqueous waste stream or ground water treatment. Chitosan is usually obtained in a flaked or powdered form; both are nonporous. The low internal surface area of the nonporous material limits access of adsorbates to interior adsorption sites. Furthermore, the flake or powdered form of chitosan swells and crumbles easily and thus does not behave ideally in a packed column. Thus, porous chitosan bead was obtained by the sol-gel method. The water content of the wet chitosan gel bead was determined by drying the beads in an oven at 100 °C for 48 hrs. The water content was about 92%. Var-



x150 x500

Fig. 4. SEM photography of internal surface of chitosan beads (×150, ×500).

ious methods were tried to remove the water from the chitosan beads, including air drying, oven drying, vacuum drying and freeze drying. Other drying methods except for freeze drying resulted in a collapsed pore structure of the beads, possibly due to hydrophilic interactions between the liquid water molecules on hydroxyl groups in the chitosan biopolymer chain. In contrast, freeze drying preserved the porosity because the water in the bead was frozen prior to its removal by a vacuum evaporator. The pore structure of the beads by freeze drying is shown in Fig. 4. As shown in this figure, the porous structure of the bead can clearly be seen in this figure. The highly reticular, three dimensional porous matrix of the bead cross section is particularly evident at the photograph of 150×.

Pore size distributions for the freeze dried beads were determined by the N_2 desorption method, and the pore diameter range was from 20 to 3,000 Å. The pore size distribution of the beads was in the mesoporous regime, with a mean pore diameter of 560 Å. The internal surface area of the freeze dried chitosan beads determined by the BET method was 350 m^2/g. However, the nonporous chitosan beads dried by other methods were only 3.5 m^2/g. Physical properties of the chitosan beads with drying methods are listed in Table 2.

2. Adsorption Isotherm

Adsorption equilibrium information is the most important in understanding adsorption processes. No matter how many components are present in the system, the adsorption equilibria of pure components are the essential ingredient for an understanding of how much of those components can be accommodated by a solid adsorbent. This information can be used to study the adsorption kinetics of a single component, adsorption equilibria of multicomponent systems, and then adsorption kinetics of multicomponent systems [Do, 1998].

In this study, three isotherm models - Langmuir, Freundlich and Sips- were used to correlate our experimental equilibrium data. To find the isotherm parameters for each adsorption, the linear least squares method and the pattern search algorithm (NMEAD) were used.

Table 2. Characteristics of chitosan beads

Drying type	Size [cm]	BET [m^2/g]	Porosity [%]	Pore radius [Å]	Pore volume [cc/g]
Freeze	0.23	350	97	280	1.4
Others	0.08	3-5	-	7.56	0.014

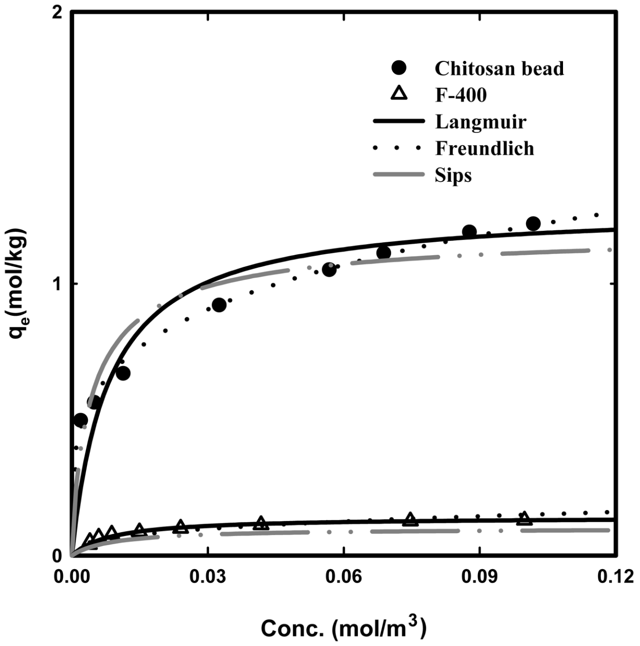


Fig. 5. Adsorption isotherms of RB 5 onto different adsorbents at initial pH 6.0 and 298.15 K.

The value of the mean percentage error has been used as a test criterion for the fit of the correlations. The mean percent deviation between experimental and predicted values is as follows:

$$\text{Error (\%)} = \frac{100}{N}\sum_{k=1}^{N}\left[\frac{|q_{exp,k} - q_{cal,k}|}{q_{exp,k}}\right] \tag{2}$$

Fig. 5 shows the results of adsorption equilibria for RB 5 onto different adsorbents. Adsorption capability of chitosan beads used for removing RB 5 is obviously positive. As can be seen in this figure, the adsorption amount of RB 5 on chitosan beads is much greater than that of activated carbon (F400). Compared with F400, the high efficiency of chitosan beads for the adsorption of RB 5 can be explained by the chemistry of the dyeing process. It is known that reactive dyes can react with fabric molecules (HO-cellulose) and water through either the chlorotriazine or vinylsulfone group, or both [Bonneau, 1995], and accessible to amino groups in the chitosan beads.

The Langmuir, Freundlich and Sips isotherm constants evaluated

Table 3. Adsorption equilibrium constants for different adsorbents (initial pH : 6.0, 298.15 K)

Isotherm type	Equation	Parameter	Adsorbents	
			Chitosan	F-400
Langmuir	$q=\frac{q_m bc}{1+bc}$	q_m	1.28	0.14
		b	122	112
		error (%)	12.4	3.08
Freundlich	$q=kC^{1/n}$	k	2.10	0.34
		n	4.15	2.85
		error (%)	2.91	12.1
Sips	$q=\frac{q_m bC^{1/n}}{1+bC^{1/n}}$	q_m	1.24	0.14
		b	87.5	111
		n	1.17	1.00
		error (%)	10.5	3.13

from the isotherms for different adsorbents are presented in Table 3. As can be seen in the table, the Freundlich model shows better fit to the adsorption data of RB 5 than the Langmuir or Sips models. In the case of GAC (F-400), the Langmuir model gives the best fit of our data among the three models.

3. Effect of Initial pH

The effect of pH may be an important factor on the dye-binding capacity of chitosan because, at low pH, the amino groups in chitosan are much easier cationized and they adsorb the dye anions strongly by electrostatic attraction. Moreover, it is also useful to study the dye-binding capacity of chitosan below pH 7, since acetic acid is often used as a stimulator in the dyeing process, in which the pH of the dye solution is normally adjusted to 3-4. The acid effluent could severely limit the use of chitosan as an adsorbent in removing dyes and metal ions due to the dissolution tendency of chitosan in the acid solution. To overcome such a problem, a cross-linked agent, glutaraldehyde, is used in this study. Cross-linking of chitosan chains with bifunctional groups such as glutaraldehyde has been widely applied to improve the mechanical strength, prevent dissolution in acid solutions, and affect the sorption performance. Adsorption equilibrium data of RB 5 on cross-linked chitosan beads and non- cross-linked chitosan beads are shown in Fig. 6. It is evident that the adsorption capacity of non-cross-linked chitosan beads is greater than that of cross-linked chitosan beads at the same initial pH (6, 10). As shown in Fig. 1, chemical cross-linking of chitosan chains with the bifunctional reagent glutaraldehyde occurs by the reaction of aldehyde (–CHO) groups on glutaraldehyde with amine (–NH$_2$) groups on the chitosan bipolymer chain, thereby resulting in the blocking of adsorption sites, and a decrease in the number of available sites for dye. Similar results are also mentioned in Yoshida et al. [1993] and Kumar [2000]. From pH 7.0 to 9.0, the adsorption capacity of the cross-linked chitosan beads is smaller than that of the non-cross-linked chitosan beads. And as shown in Fig. 6, the adsorption capacity of cross-linked chitosan beads increases significantly with decrease in initial pH. This may suggest that at low pH more protons will be available to protonate amine groups of chitosan molecules to form groups –NH$_3^+$, thereby increasing electrostatic attractions between dye molecules and adsorption sites and causing an observed increase in dye adsorption. The values of adsorption equilibrium constants for different pHs of aqueous solutions of RB 5 are listed in Table 4.

4. Effect of Temperature

Fig. 7 shows the effect of temperature on the adsorption of RB 5 onto non-cross-linked chitosan beads at pH 6. As shown in this figure, the adsorption amount of RB 5 increased with increasing temperature. The increase in uptake of RB5 on the chitosan bead may be a result of the enhanced rate of intraparticle diffusion of adsorbate, since the diffusion is an endothermic process. The temperature effect

Table 4. Adsorption equilibrium constants for cross-linked chitosan beads at different pH (298.15 K)

Isotherm type	Parameter	pHs			
		3	6	9	12
Langmuir	q$_m$	2.4	0.8	0.6	0.07
	b	165	147	107	65
	error (%)	14.4	14.2	4.0	1.9
Freundlich	k	3.9	1.2	0.8	0.14
	n	4.7	5.5	5.9	3.2
	error (%)	2.9	3.6	2.3	1.6
Sips	q$_m$	2.44	0.68	0.62	0.07
	b	140	92.7	81.8	60.2
	n	1.11	1.09	1.11	1.03
	error (%)	12.0	9.43	3.68	1.72

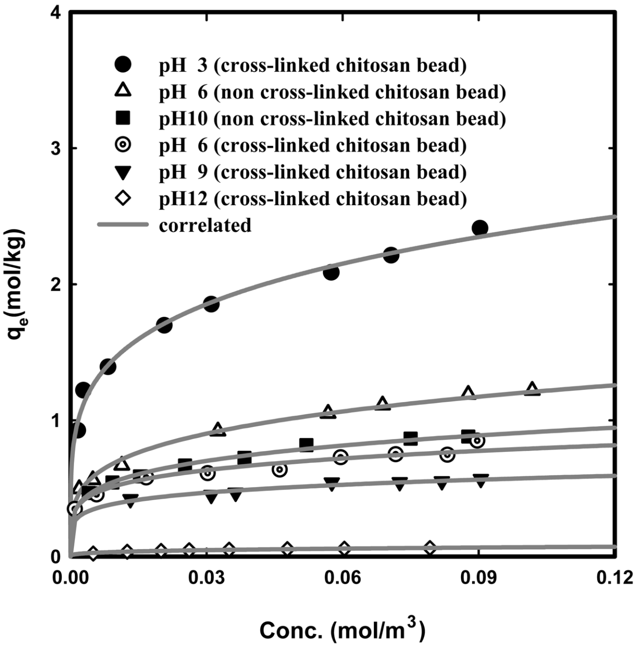


Fig. 6. Adsorption isotherms of RB 5 onto cross-linked chitosan beads at different initial pH (298.15 K).

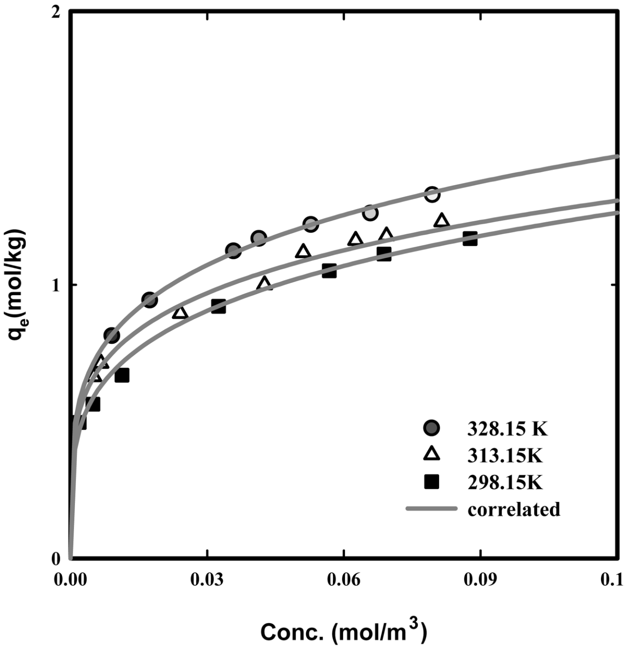


Fig. 7. Adsorption isotherms of RB 5 onto chitosan beads at different temperatures (initial pH : 6.0).

Table 5. Adsorption equilibrium constants for chitosan beads at different temperature (initial pH : 6.0)

Isotherm type	Parameter	Temperatures (K)		
		298.15	313.15	328.15
Langmuir	q_m	1.24	1.28	1.40
	b	138	137	130
	error (%)	12.9	7.36	2.28
Freundlich	k	2.08	2.09	2.38
	n	4.19	4.64	4.40
	error (%)	2.89	2.06	0.74
Sips	q_m	1.24	1.29	1.45
	b	87.4	99.1	92.7
	n	1.17	1.12	1.06
	error (%)	10.5	5.16	2.67

Table 6. Thermodynamic parameters at different temperatures (initial pH : 6.0)

Temperature (K)	Thermodynamic parameters		
	ΔG^o kcal/mol	ΔH^o cal/mol	ΔS^o cal/mol
298.15	−2.88	374.80	10.93
313.15	−3.05	400.33	11.01
328.15	−3.21	-	-

Table 7. Adsorption equilibrium constants of RB 5 onto chitosan beads with cross-linking time (initial pH : 6.0, 298.15 K)

Isotherm type	Parameter	Cross-linking time (min)			
		0	10	30	60
Langmuir	q_m	1.28	0.83	0.64	0.62
	b	122	147	151	73
	error (%)	12.6	14.3	11.8	2.7
Freundlich	k	2.09	1.21	0.88	0.92
	n	4.17	5.47	6.25	4.58
	error (%)	2.55	3.62	3.79	1.54
Sips	q_m	1.24	0.68	0.64	0.62
	b	87.4	92.7	72.4	73.4
	n	1.17	1.09	1.35	1.00
	error (%)	10.5	9.43	8.35	2.68

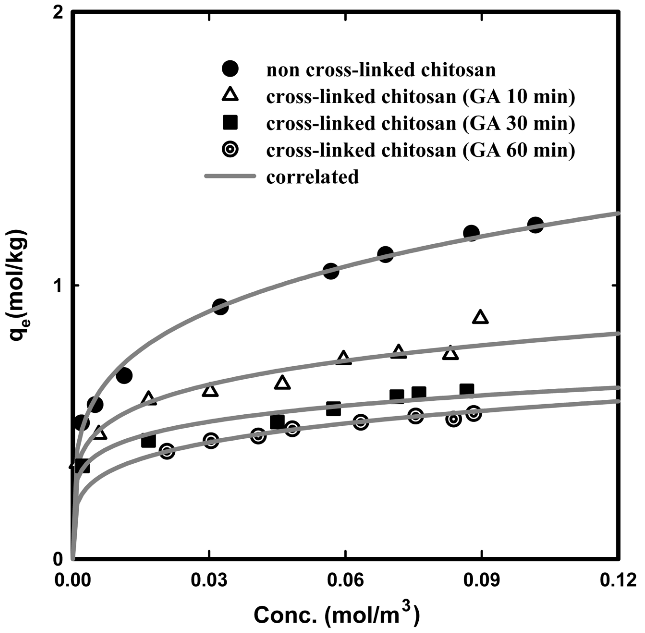


Fig. 8. Adsorption isotherms of RB 5 onto chitosan beads with cross-linking time (initial pH : 6.0 and 298.15 K).

was confirmed through an examination of the thermodynamic parameters calculated, such as changes in standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) during the process. The values are calculated by using the Langmuir equation, using Eqs. (3), (4) and (5), respectively.

$$\Delta G^o = -RT \ln b \tag{3}$$

$$\Delta H^o = -R(T_1T_2)/(T_2 - T_1) \ln b_2/b_1 \tag{4}$$

$$\Delta S^o = (\Delta H^o - \Delta G^o)/T \tag{5}$$

In the equations, R is the gas constant, b, b_1 and b_2 are equilibrium constants at temperature T, T_1 and T_2, respectively.

The negative values of ΔG^o (Table 6) indicate the spontaneous nature of the process and the positive values of ΔH^o and ΔS^o indicate the endothermic nature of the adsorption of RB 5 on chitosan beads.

The Freundlich equation gives the best fit of our data among the three isotherms. The estimated values of isotherm parameters of RB 5 on chitosan beads at different temperature are listed in Table 5. The accuracy of the values is dependent on the degree of fitness, which can be judged by comparing average percentage error. Comparing the data in Figs. 6 and 7, the effect of pH on the adsorption capacity of RB 5 on chitosan beads was greater than that of temperature.

5. Effect of Cross-Linking

Fig. 8 shows the effect of cross-linking time on adsorption of RB 5 onto chitosan beads at pH 6.0, 298.15 K, and initial concentration 100 g/m^3. Robert and Taylor [1989] determined that the penetration of glutaraldehyde into the gelled bead and fraction of amino groups actually cross-linked, but those were not measured in this work. As can be seen in Fig. 8, an increase in cross-linking time, from 10 to 60 min, decreases adsorption capacity by 20%. The increase in cross-linking time increases the stability of the biopolymer in acidic media. However, it also decreases the number or fraction of free and available amino groups on the chitosan backbone and the accessibility to internal sites of the adsorbent. Chiou and Li [2002] reported that the increase of cross-linking time increases the steric hindrance of the dye molecule diffusion through the chitosan beads. In general, cross-linking reduces the adsorption capacity unless other functional groups are introduced or the diffusion properties are improved [Gukbal et al., 1995; Hsien and Rorrer, 1995]. These might explain that the adsorption capacity of RB 5 is the lowest at the longest cross-linking time of 60 min.

CONCLUSIONS

In this work, the adsorption of a reactive dye, RB 5, on chitosan beads was studied. The effects of adsorbents, initial pHs, temperatures and reaction time with cross-linking agent, glutaraldehyde, were investigated, and the following results were obtained.

1. For the adsorption of RB 5, the adsorption capacity of chitosan beads was much greater than that of a GAC (F-400).
2. The Freundlich equation gives the best fit to the equilibrium data of RB 5 onto chitosan beads. In the case of GAC (F-400), the Langmuir equation gives the best fit to our data.
3. The adsorption amount of RB 5 onto chitosan beads increased with decreasing initial pH and increasing temperature. The effect of initial pH of dye solution was significant on the adsorption capacity compared to that of temperature.
4. Cross-linked chitosan beads were insoluble in low pH solutions. And the adsorption capacity of RB 5 on cross-linked beads decreased with increasing cross-linking react time of the beads.

ACKNOWLEDGMENT

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NOMENCLATURE

a	: isotherm parameter
b	: isotherm parameter
C	: equilibrium concentration of the solution [mol/m^3]
C_i	: initial concentration of bulk fluid [mol/m^3]
G^o	: standard free energy [cal/mol]
H^o	: enthalpy [cal/mol]
k	: isotherm parameter
n	: empirical pressure for the adsorbed phase
q	: equilibrium amount adsorbed on the adsorbent [mol/kg]
q_m	: fixed number of surface sites, i.e. maximum adsorption capacity of adsorbent [mol/kg]
R	: gas constant (=8.314 J/mol·K)
S^o	: entropy [cal/mol]
T	: temperature [K]
V	: volume of solution [m^3]
W	: weight of adsorbent [kg]

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