가교결합된 키토산 비드를 이용한 반응성 염료의 흡착에 관한 연구

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Adsorption of reactive dye using cross-linked chitosan-silica beads

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Introduction

Synthetic dyes are used extensively by industries including dyehouses, paper printers and textile dyers. The effuents of these industries are highly coloured and disposal of these wastes into the environment can be extremely deleterious. Their presence in watercourses is aesthetically unacceptable and may be visible at concentrations as low as 1 ppm[1]. Morevoer, they may also affect photosynthetic activity in aquatic systems by reducing light penetration[2]. More importantly, while most are considered relatively non-toxic, several commonly used dyes have been reported to be carcinogenic and mutagenic[3].

Textile dyes are designed to be resistant to degradation or fading by chemicals and light. They must also be resilient to both high temperatures and enzyme degradation resulting from detergent washing. For these reasons, biodegradation of dyes is typically a slow process. Adsorption techniques are seen as an economic alternative. Many studies have been made on the possibility of adsorbents using activated carbon, peat, silica and others. However, the adsorption capacity of the adsorbents is not very large and new adsorbents are still under development to improve adsorption performance.

Chitosan beads used as an adsorbent were prepared with a sol-gel method and by using silica particles as a porogen[4]. A porogen is an inorganic or organic substance with the capability of creating pores. The method uses pH differences as the solvent-non-solvent system. At a low pH, chitosan dissolves in water and silica does not; at a high pH chitosan precipitates and silica dissolves, creating a porous structure with porosity and pore size depending on the amount and size of the silica particles present. In this study, the adsorption of reactive dye (Reactive Orange 16) from aqueous solutions on chitosan beads was investigated. and cross-linked chitosan beads were also used to remove reactive dye in acid effluent.

Experimental Section

- *Chemicals*

Chitosan (degree of deacetylation: 91.6%, molecular weight: 4.9×10^5) was supplied by . Reactive Orange 16(Remazol Brilliant Orange 3R, CI 17757), whose structure is shown in Fig. 1, was anionic, reactive dye and was obtained from Sigma-Aldrich chemical company.

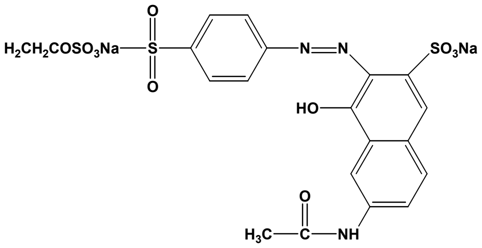

Fig. 1 The chemical structure of Reactive Orange 16

- *Chitosan-Silica beads*

Silica particles constitute such a porogen. In contrast to chitosan, the silica particles are insoluble in acidic media but soluble in alkaline solutions. These opposite properties allow us, using silica particles of various sizes, to control the size of the pores in the chitosan beads. The chitosan beads were prepared by dropping a chitosan solution in dilute acetic acid containing silica particles in an aqueous NaOH solution. Then, the silica particles were extracted by immersing the beads in NaOH solution for 24hr. Finally, the porous chitosan beads were washed with distilled water to remove the remaining NaOH.

- *Cross-linked chitosan-silica beads*

The chitosan-silica beads were shaken in 2.5wt% glutaraldehyde solution for 10min to recover reactive dye from acidic solution. Then, the beads were taken out of the solution and extensively rinsed with hot and cold distilled water to remove any unreacted glutaraldehyde.

Results and Discussion

In this study, chitosan-silica beads were used to remove reactive dye. The adsorption capacity of chitosan-silica beads with the amount of the silica gel is shown in Fig. 2. The equilibrium adsorption amounts of reactive dye on chitosan-silica beads is much higher than them on chitosan beads. However, it can be seen from Fig. 1 that the effect of amounts of the silica gel is insignificant. Three isotherm models - Langmuir, Freundlich, Sips - were used to correlate the experimental equilibrium data. Sips model was fitted successfully for all of data.

Fig. 3 shows the effect of pH on adsorption of reactive dye onto chitosan-silica beads. It indicates that the adsorption capacity increases significantly in low pH of solution. The enhancement of adsorption of reactive dye at acidic pH may be explained in terms of electrostatic interactions between the protonated amine groups($-NH_3^+$) of chitosan and anionic dye. At lower pH, most amine groups are protonated to form groups $-NH_3^+$. Thereby these active sites become more available for binding reactive dye and cause the observed increase in dye adsorption.

Fig. 4 and 5 represent the experimental data for reactive dye in a batch adsorber at different pH of solution. The presence of high concentration of hydroxyl ions have much influence on the initial rate of adsorption of reactive dye. The second-order kinetic model is expressed as:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Fig. 5 was used to calculate the second-order rate constant k_2 and q_e. Table 1 lists the results obtained from the second-order kinetic model. The straight lines of Fig. 5 show a good agreement of experimental data with the second-order kinetic model for different pH of solution.

Table. 1 The second-order adsorption rate constants, and calculated and experimental q_e values for different initial pH of solution.

	$q_{e,exp}$ (g/kg)	k_2 (kg/g · min)	$q_{e,cal}$ (g/kg)	R^2
pH 3.5	90.159	1.413×10^{-3}	91.743	0.9998
pH 6.5	88.192	2.558×10^{-3}	90.909	0.9986
pH 6.5 (non cross-linked beads)	80.804	1.140×10^{-4}	81.967	0.9841

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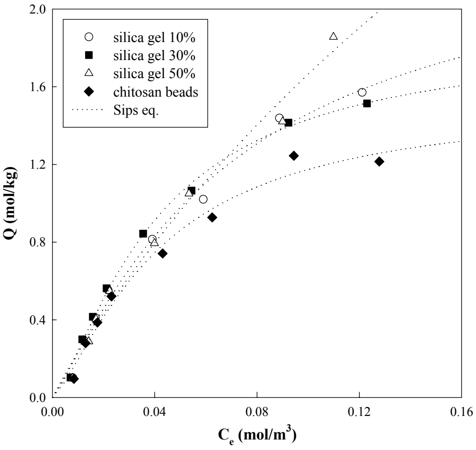

Fig. 1 Comparison of adsorption isotherm of Reactive dye in terms of silica gel ratio in chitosan beads

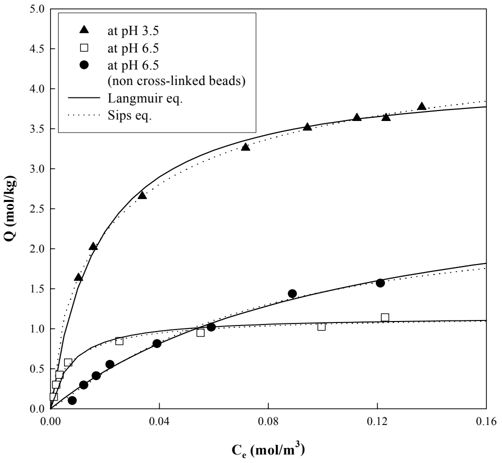

Fig. 2 Adsorption isotherm of Reactive dye on cross-linked chitosan-silica beads in terms of pH (10% chitosan-silica beads)

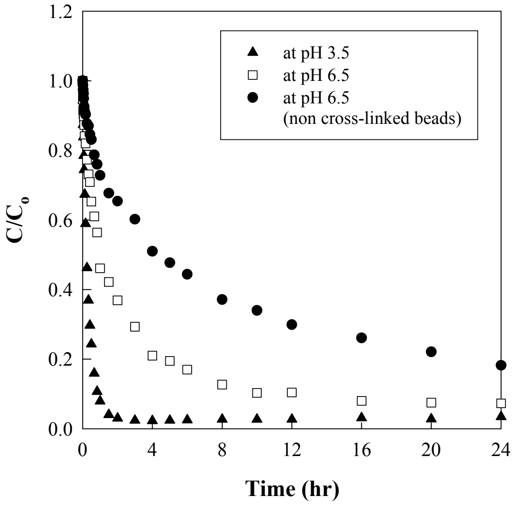

Fig. 4 Observed uptake curves of Reactive dye on cross-linked chitosan-silica beads as initial pH (C_o=0.1619 mol/m^3)

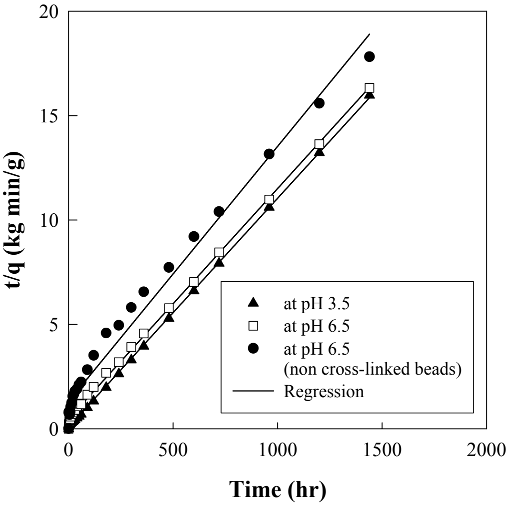

Fig. 5 Plot of the pseudo second-order model at different initial pH of solution