

Kinetic of Adsorption of Urea Nitrogen onto Chitosan Coated Dialdehyde Cellulose under Catalysis of Immobilized Urease

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Abstract: The adsorption of urea nitrogen onto chitosan coated dialdehyde cellulose (CDAC) under catalysis of immobilized urease in gelatin membrane (IE) was studied in batch system. The pseudo first-order and second-order kinetic models were used to describe the kinetic data, and the rate constants were evaluated. The experimental data fitted well to the second-order kinetic model.

Keywords: Adsorption, kinetic, urea nitrogen, chitosan coated dialdehyde cellulose, immobilized urease.

Urea is one of the major metabolic end products, and the removal of excess urea nitrogen has been a major problem for patients suffering from chronic renal failure (CRF). Haemodialysis is the conventional treatment for CRF. However, It is bulky, cumbersome, expensive, time-consuming, and difficult to handle¹. Oral urea nitrogen adsorbents, such as active charcoal² and oxystarch³, could potentially delay the onset of haemodialysis therapy in the patients who still have some renal function and reduce haemodialysis treatment times². However, the adsorption capacity of the adsorbents is not very large, and no study on kinetic of adsorption of urea nitrogen onto adsorbents has been made.

In this work, complex of the type urea nitrogen adsorbent, which consisted CDAC and IE, was prepared. Kinetic of adsorption of urea nitrogen onto CDAC under catalysis of IE was firstly investigated. The results will be useful for further applications in the clinic for removal of urea nitrogen by oral administration.

Preparation of dialdehyde cellulose (DAC) and determination of its percentage degree of oxidation (DO) based on glucose monomer units followed the methods previous reported⁴. The DACs with the different DO (53, 78 and 95%) were obtained by adjusting the quantity of oxidizing agents. The resulting DAC was grinded into paste in 100 mL deionized water, and then added in the chitosan solution of mass concentration 2 g/L with constant stirring for 1 h at 25°C. The pH of the solution was adjusted to 7.0-7.5 with 20 g/L sodium hydroxide solution and then was gelized for 0.5 h at 25 °C. The resulting CDAC was filtered and washed with deionized water, and then

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dried at 40 °C. Preparation of IE and determination of its enzymatic activity followed the methods previous reported⁵. 2 g urease was dispersed in 100 mL gelatin solution of mass concentration 10 g/L with stirring for 20 min. The mixed solution was spread over the plastic wrap and allowed to dry at 40°C overnight. The resulting dried membrane was grinded. IE contained 528 IU/g support enzymatic activity.

The urea was dissolved in deionized water to the required urea nitrogen concentration. In experiments of batch kinetic adsorption, 0.5 g CDAC (DO 53 - 95%), IE (20 - 60 mg) and 75 mL urea nitrogen solution (395.2 - 767.3 mg/L) were placed in a 150 mL Erlenmeyer flask and shaken by a shaker in a water bath to control temperature. Every other period of time, the supernatant liquid 2 mL was taken out and placed in a 50 mL flask containing desired amount urease and residual urea were hydrolyzed to ammonia and carbon dioxide by urease catalyzing for 12 h. The concentration of unadsorbed urea nitrogen was analyzed by measuring the amount of ammonia liberated from the hydrolysis of urea.

Figure 1 shows that the effect of initial urea nitrogen concentration on adsorption kinetics of CDAC with DO 95% at CDAC/IE weight ratio 10:1 and 37°C. An increase in the initial urea nitrogen concentration leads to an increase in adsorption capacity of the urea nitrogen onto CDAC. This is due to the increase in the concentration gradient between the bulk and the surface of the DACs with the increase in initial urea nitrogen concentration. **Figure 2** shows the effect of CDAC/IE weight ratio on adsorption of urea nitrogen onto CDAC with DO 95% at initial urea nitrogen concentration 648.8 mg/L and 37°C. The results suggest that increasing IE amount leads to increase ammonia concentration and enhance the reaction between ammonia and aldehyde group of CDAC. **Figure 3** shows the effect of DO of CDAC on adsorption of urea nitrogen onto CDAC at initial urea nitrogen 648.8 mg/L, CDAC/IE weight ratio 10:1 and 37°C. It is seen that the adsorption capacity increases with increasing DO of CDAC. This suggests that the

Figure 1 Adsorption kinetics of urea nitrogen onto CDAC with DO 95% at different initial concentration

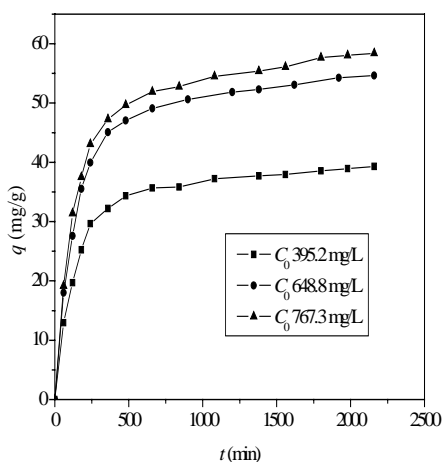


Figure 2 Adsorption kinetics of urea nitrogen onto CDAC at different CDAC/IE weight ratio

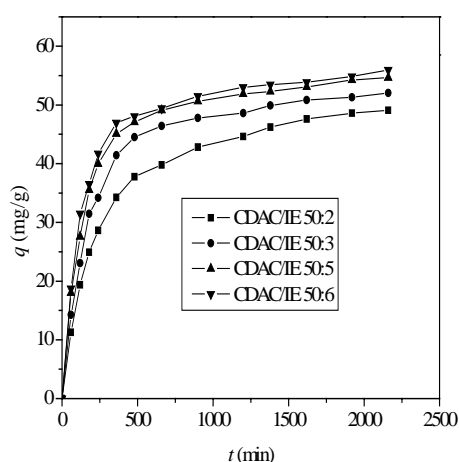
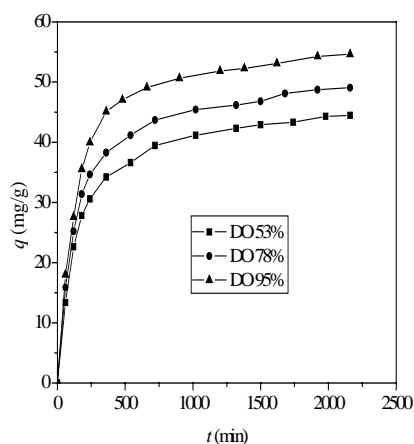
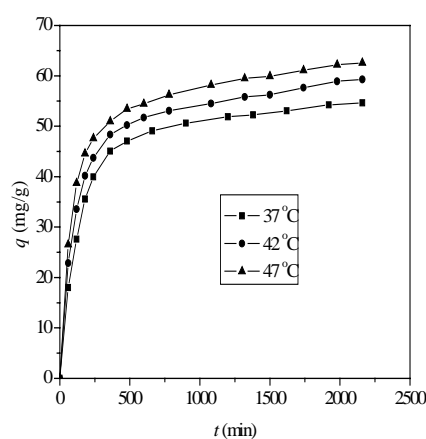


Figure 3 Adsorption kinetics of urea nitrogen onto CDACs with different DO**Figure 4** Adsorption kinetics of urea nitrogen onto CDAC at different temperature

adsorption took place mainly by the reaction between ammonia and aldehyde group of CDAC. **Figure 4** shows the effect of temperature on adsorption of urea nitrogen onto CDAC with DO 95% at initial urea nitrogen concentration 648.8 mg/L and CDAC/IE weight ratio 10:1. It indicates that increase temperature leads to increase in urea nitrogen adsorption rate dq/dt and adsorption capacity q . This suggests that higher temperature enhances the hydrolysis rate of urea to ammonia and carbon dioxide by catalysis of IE and increases the reaction rate between ammonia and group of CDAC.

The pseudo first-order and pseudo second-order equations were used to test the experimental data of initial concentration, temperature, DO of CDAC and CDAC/IE weight ratio. The first-order kinetic model⁶ and the second-order kinetic model⁷ is expressed as follows:

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

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

where q_e and q (mg/g) are the amounts of urea nitrogen adsorbed onto adsorbent at equilibrium and at time t , respectively. k_1 (min^{-1}) and k_2 (g/mg min^{-1}) are the rate constants of first-order and second-order adsorption. The slopes and intercepts of plots of $\log(q_e - q)$ versus t were used to determine the first-order rate constant k_1 and q_e . The slopes and intercepts of plots of t/q versus t were used to calculate the second-order rate constant k_2 and q_e . **Table 1** lists the computed results obtained from the first-order and the second-order kinetic model, and a comparison of results with the correlation coefficients (R^2). The correlation coefficients for the first-order model were low and the calculated q_e values obtained from the first-order kinetic model do not give reasonable value. However, the correlation coefficients for the second-order kinetic model are

higher than 0.9994, and the calculated q_e values obtained from the second-order kinetic model agree with the experimental q_e values for all the cases. These suggest that the adsorption of urea nitrogen onto CDAC under catalysis of IE follows the second-order kinetic model and chemical adsorption might be the rate-limiting step.

Table 1 Comparison of the first-order and second-order adsorption rate constants, and calculated and experimental q_e values at different initial urea nitrogen concentration, temperature, DO of CDAC and CDAC/IE weight ratio

Parameters	$q_{e, \text{exp}}$ (mg/g)	First-order kinetic model			Second-order kinetic model		
		$k_1(\text{min}^{-1})$	$q_{e, \text{cal}}(\text{mg/g})$	R^2	$k_2(\text{g/mg min})$	$q_{e, \text{cal}}(\text{mg/g})$	R^2
Initial urea nitrogen concentration (mg/L)							
395.2	39.30	1.976E-3	29.95	0.9510	2.171E-4	41.09	0.9997
648.8	54.64	2.019E-3	27.28	0.9480	1.514E-4	57.27	0.9997
767.3	58.40	1.994E-3	30.19	0.9487	1.386E-4	61.13	0.9996
DO of CDAC(%)							
53	44.46	2.174E-3	27.62	0.9377	1.546E-4	47.13	0.9997
78	49.05	2.024E-3	27.72	0.9526	1.494E-4	51.63	0.9996
95	54.64	2.019E-3	27.28	0.9480	1.514E-4	57.27	0.9997
CDAC/IE weight ratio							
50/2	49.11	2.023E-3	36.50	0.9757	8.521E-5	53.82	0.9997
50/3	52.04	1.935E-3	28.03	0.9614	1.243E-4	55.37	0.9994
50/5	54.64	2.019E-3	27.28	0.9480	1.514E-4	57.27	0.9997
50/6	55.96	1.644E-3	23.63	0.9398	1.616E-4	58.01	0.9996
temperature(°C)							
37	54.64	2.019E-3	27.28	0.9480	1.514E-4	57.27	0.9997
42	59.29	1.809E-3	27.65	0.9196	1.605E-4	60.86	0.9994
47	62.58	1.858E-3	27.99	0.9411	1.694E-4	64.14	0.9995

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