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Adsorption Kinetics and Thermodynamics of Cellulose Dinitrobenzoate Prepared in Ionic Liquid for the Removal Of Creatinine

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Creatinine is one of the major toxins in patients suffering from chronic renal failure. In this paper, cellulose dinitrobenzoate, with a degree of substitution (DS) of 0.15, was used as an oral adsorbent for creatinine adsorption. Cellulose dinitrobenzoate was prepared by modification of cellulose with 3,5-dinitrobenzoyl chloride in 1-butyl-3-methylimidazolium chloride (BMIMCl) ionic liquid as a homogenous medium. The effects of contact time, pH, adsorption temperature, and initial concentration of creatinine on the adsorption per unit mass of cellulose dinitrobenzoate were studied, comparatively. Results showed that the maximum adsorption per unit mass for creatinine was 3.88 mg/g. Furthermore, the adsorption process was spontaneous and exothermic. It was determined that the experimental results were well fitted to the pseudo-second-order rate equation and the Freundlich adsorption isotherm. Compared with traditional oral adsorbents, this cellulose-based adsorbent was biocompatible and could remove creatinine from dialysate effectively.

INTRODUCTION

Chronic renal failure (CRF) is a complicated clinical syndrome, resulting from chronic progressive renal damage; it has various causes and results in a dramatic drop in the function of the kidneys making them unable to maintain basic functions (Salmela and Isoniemi 1997). Uremia syndrome is characterized by an accumulation of human metabolism end products in blood, due to the kidney's inability to remove them down to a normal level. Conventional methods, such as kidney transplantation, haemoperfusion, and hemodialysis, have been used to remove these toxins in patients suffering from chronic renal failure, achieved relatively good results (Malik *et al.* 2005; Humes *et al.* 2006; Kute *et al.* 2014). However, the removal of some uremic toxins by oral adsorbent during a dialysis session attracts interest because of the low cost and easy use of adsorbents. Creatinine (2-amino-1-methyl-2-imidazoline-4-one, $C_4H_7N_3O$) is representative for small uremic toxins that are not bound to proteins. The solubility of creatinine is 90 g/L (20 °C), meaning that it can easily be dissolved in water. The ketone structure and enol structure of creatinine could interconvert, and in an alkaline environment the structure will convert into the oxygen anion structure (Scheme 1). About 60% of creatinine can be removed by the gastrointestinal tract (Akizawa *et al*. 2009). Thus, treatment by way of an oral adsorbent

method has been suggested as either an alternative or supplemental treatment for patients with chronic renal failure (Ali *et al*. 2014).

Adsorbents efficient for adsorption in these applications should possess high surface area, stability under physiological conditions, toxicological safety, and some selectivity towards the target toxin. Furthermore, their surface chemistry has to allow for the efficient adsorption from not only aqueous solution, but also under physiological conditions (Berge-Lefranc *et al*. 2009). Oral adsorbent used for the removal of creatinine has attracted significant attention in recent years. Many types of materials have been used as adsorbents for the removal of creatinine, including activated carbon (Teng *et al*. 2006; Deng *et al.* 2007; Zhang *et al.* 2007), cellulose (Li and Liang 2011), chitosan (Jing *et al*. 1997), starch (Yu and Yang 2003a), and other low-cost adsorbents (Gao *et al*. 2008). Nevertheless, the type of activated carbon adsorbent is not specific and adsorbs more or less any molecule that is partially hydrophobic (Rosinski *et al.* 2004). Therefore, it is important to prepare an adsorbent with high selectivity and biocompatibility.

Cellulose, the most widely available and renewable biopolymer in nature, is a very promising raw material available at low cost for the preparation of various functional materials, such as membranes, microspheres, sponges, and non-woven and knitted textiles (Shin *et al*. 2014). Due to high specific surface areas and numerous reactive groups, cellulose also displays excellent adsorption performance. Li *et al*. (2011) prepared dialdehydecellulose-3,5-dinitrobenzoate in a lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMA) solvent system using pyridine as the catalyst. Yu *et al*. (2007) synthesized a series of cellulose nitrates and investigated their adsorption properties for creatinine. The optimal adsorption capacity was 2.04 mg/g, with good selectivity for creatinine. Dai *et al.* (2010) synthesized the carboxymethyl picric acid ester with CMC and picric acid. However, the adsorption capacity of cellulose dinitrobenzoate is relatively low. Due to biocompatibility, biodegradability, and reactive surface properties, cellulose as a raw material is often used in the medical field. Cellulose cannot be digested by the human gastrointestinal system. Otherwise, it can be used as a source of dietary fiber to promote gastrointestinal peristalsis (Torcello-Gomez and Foster 2014). Therefore, cellulose is an ideal resource for oral adsorbents in the pharmaceutical industry.

Cellulose is extremely difficult to dissolve in water and in most common organic solvents, which presents a major obstacle for cellulose application. At present, only a limited number of solvent systems, such as DMAc/LiCl, DMF/N_2O_4, NMNO, DMSO/TBAF, and some molten salt hydrates like $LiClO_4 \cdot 3H_2O$, have been found efficient for cellulose dissolution. However, these solvent systems currently used for cellulose dissolution suffer drawbacks such as generation of poisonous gas or volatility, difficulty for solvent recovery, or instability in application and processing (Liu *et al.* 2009). Ionic liquids (ILs) are organic salts that have low melting points (ca. 373 K) and have been a topic with growing interest in chemistry and engineering (Qi *et al.* 2014). In the last decade, ionic liquids have received increasing interest for use in the preparation of cellulose-based functional materials (Ramli and Amin 2014). The ionic liquids are green solvents for the dissolution of cellulose because they are non-volatile, non-flammable, and have a high thermal stability. In the ionic liquid system, hydrogen bonds between cellulose can be destroyed to form a homogeneous system. Then, the target reagents can react with the active groups of cellulose more easily in the homogeneous system to form cellulose-based materials with functional groups (Reddy *et al*. 2014). The ionic liquids could be

recycled after the extraction of products. Thus, it is significant to develop the green chemical synthesis pathway and high-valued cellulose-based materials for the sustainable development of pharmaceutical materials.

Cellulose-based materials, for the removal of creatinine mentioned above, were prepared in the pyridine system or LiCl/DMA system, which are not eco-friendly solvents. It has been reported that a special complexation reaction could occur between creatinine and carbazotic acid, 3,5-dinitrobenzoic acid or 3,5-dinitrobenzoate (Yu and Yang 2003a; Gao *et al*. 2008; Yang *et al*. 2008). Therefore, in this study, 1-butyl-3-methylimidazolium chloride (BMIMCl) ionic liquid, as representative of a class of environmental friendly green solvents, was applied to dissolve cellulose and to provide a homogenous system for the acylation of cellulose with 3,5-dinitrobenzoic acid chloride (Scheme 2). The resulting product (cellulose dinitrobenzoate) was employed as an oral adsorbent for the removal of creatinine in dialysate. Physicochemical properties of the obtained products were characterized using solid-state nuclear magnetic resonance (NMR) spectroscopy and elemental analysis. The adsorption per unit mass of cellulose dinitrobenzoate was investigated by varying the adsorption conditions, such as pH, contact time, contact temperature, and initial concentration of creatinine. In addition, kinetic and thermodynamic studies were conducted to evaluate the adsorption per unit mass of cellulose dinitrobenzoate.
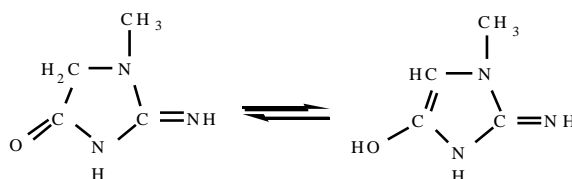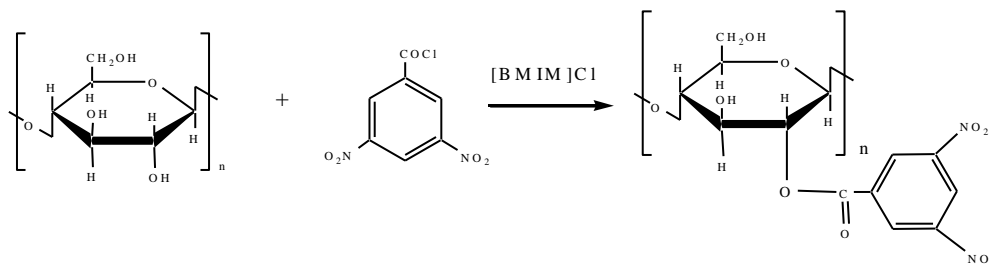

Ketone structure and enol structure interconvert of creatinine
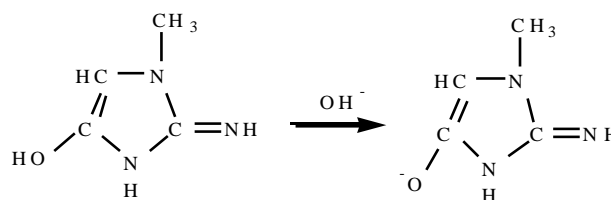
Oxygen anion structure of creatinine in alkaline environment

Scheme 1. Structure of creatinine

Scheme 2. Reaction scheme of DNBZ-Cl with the hydroxyl groups of cellulose in ionic liquids

EXPERIMENTAL

Materials

Cellulose was obtained using sodium hydroxide (17.5%, w/v) at 20 °C for 45 min with a solid to liquor ratio of 1:20 from holocellulose prepared by delignification of bamboo *(Phyllostachys pubescens)* with 6% sodium chlorite in an acidic solution (pH 3.6 to 3.8, adjusted with 10% acetic acid) at 75 °C for 2 h. Then the dried cellulose was milled using a planetary ball mill (Fritsch, Germany) for 4 h under a nitrogen (N_2) atmosphere at 500 rpm with 10 min of rest after every 10 min of milling.

The ionic liquid [BMIM]Cl, with a purity of 99%, was purchased from Lanzhou Institute of Chemical Physics (Lanzhou, China). 3, 5-Dinitrobenzoic acid chloride (DNBZ-Cl) with 99% purity and creatinine with 99% purity were supplied by Aladdin Reagent Co. (Shanghai, China). 4-Dimethyl aminopyridine (DMAP) was provided by Alfa Aesar Co., Ltd (Tianjin, China). Silver nitrate, Sodium chlorite, calcium chloride, magnesium chloride, potassium chloride, sodium acetate with the 99% purity, toluene, and ethyl alcohol were provided by Beijing Chemical Reagent Factory (Beijing, China). All chemicals were of analytical reagent grade and used without further purification.

Preparation of Cellulose Dinitrobenzoate

To ensure complete dissolution of the ball-milled cellulose in the ionic liquid [BMIM]Cl, cellulose (0.27 g, 0.005 mol of hydroxyl groups in cellulose) was added to 10.0 g of [BMIM]Cl in a 50-mL dried three-neck flask. Then, the mixture was placed into an oil bath and heated under vigorous magnetic stirring (500 rpm) at 130 °C for 5 h under N_2 atmosphere (Soheilmoghaddam *et al*. 2014; Zhang *et al*. 2014). After the complete dissolution of cellulose in [BMIM]Cl, the dissolved cellulose was cooled down to 100 °C. DNBZ-Cl (the molar ratios of DNBZ-Cl to glucose units in cellulose is 2:1) and DMAP (5% of the cellulose amount) were added to the flask under stirring (500 rpm) for 30 min. Isolation of the derivative was carried out by the precipitation of the mixture into 100 mL of 50% (v/v) ethanol while stirring for 2 h and then centrifuged at 4000 rpm for 10 min. The precipitate was washed with 70% (v/v) ethanol until there were no chloride ions in the filtrate, which was tested using silver nitrate. Finally, the resulting product was dried in a vacuum for 24 h at 50 °C. The degree of substitution (DS) of cellulose dinitrobenzoate obtained was 0.15, which was determined according to the equation in literature (Yu and Yang 2003b).

(CP/MAS) ^{13}C NMR Spectra

The solid-state cross polarization/magic angle spinning (CP/MAS) ^{13}C NMR spectra of the samples were obtained at 100 MHz using a Bruker AV-III 400M spectrometer (Bruker, Germany).

Adsorption Properties of Cellulose Dinitrobenzoate for Creatinine

All of the adsorption data was measured twice, and the results were calculated to obtain the average.

The dialysate was prepared with Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and Ac^- with concentrations that were 132.50, 1.00, 1.75, 0.50, 98.00, and 40.00 mmol/L (pH=7), respectively, to simulate the physiological conditions in the human body (Yu and Yang

2003a). The adsorption per unit mass of cellulose dinitrobenzoate for creatinine was investigated in batch experiments. A certain amount of creatinine was added into the dialysate to keep the concentration at 100 mg/L. In each experiment, 0.01-g dried adsorbent was added to a 10-mL solution of dialysate of creatinine. The flasks were stirred with a magnetic stirrer at 200 rpm, and the pH values were adjusted using 2.0 mol/L of NaOH and HCl. After equilibrium was reached, the filtrate was measured for creatinine concentration by an ultraviolet-visible spectrometer (TU-1810, Beijing, China) at 510 nm, and the standard curve was detected (Li and Liang 2011). The amount of creatinine adsorbed on the absorbent was calculated according to Eq. 1,

$$Q = \frac{(C_0 - C) \times V}{m} \tag{1}$$

where Q (mg/g) is the adsorption per unit mass for creatinine, C_0 (mg/L) is the initial concentration of creatinine, C (mg/L) is the concentration of creatinine in the dialysate after the treatment, V (L) is the volume of the dialysate of creatinine, and m (g) is the amount of the dry adsorbent.

Kinetic Study

The study on adsorption kinetics was conducted with an initial creatinine concentration of 100 mg/L at pH 7 and 37 °C. The concentration of creatinine in the dialysate was analyzed over a time period of 1 to 24 h. Then the samples were centrifuged and the residual creatinine concentration in the supernatant was analyzed. The adsorption per unit mass for creatinine was calculated according to Eq. (1).

Effects of Adsorbent Dosage

The effects of the adsorbent dosage on the adsorption per unit mass of creatinine was investigated by putting 10-mL dialysate into contact with an initial creatinine concentration of 100 mg/L and different amounts of adsorbent (0.02 to 0.16 g) at pH=7 with a constant stirring speed of 200 rpm. After equilibrium was reached, the samples were centrifuged, and the residual creatinine concentration in the supernatant was analyzed. The adsorption per unit mass for creatinine was calculated according to Eq. (1).

Effects of pH Value

Dry cellulose dinitrobenzoate was immersed in a series of 100-mg/L creatinine dialysate at different pH values (5, 6, 7, 8, 9, 10, and 11) and at 37 °C for 6 h to investigate the optimum pH for the maximum adsorption. The adsorption per unit mass for the amount of creatinine adsorbed onto the adsorbent was calculated according to Eq. (1).

Isotherm Study

To explore the isothermal relationship, the effect of initial concentration of creatinine on the adsorption per unit mass of cellulose dinitrobenzoate was investigated by increasing the creatinine solution concentration to an optimum amount. The adsorption equilibrium of cellulose dinitrobenzoate was achieved at 23 °C, 30 °C, and 37 °C and a pH value of 7.0 for 6 h in the creatinine dialysate at different concentrations of 10, 30, 50, 75, 100, 125, 175, 225, and 300 mg/L. This was used to study the effects of the initial creatinine

concentration on the adsorption per unit mass of cellulose dinitrobenzoate adsorbent and adsorption isotherm. The amount of creatinine adsorbed was determined by Eq. (1).

RESULTS AND DISCUSSION

Solid State CP/MAS NMR Spectra Analysis

The solid state CP/MAS NMR spectra of the native cellulose and cellulose dinitrobenzoate were employed to investigate the homogeneous acylation of cellulose in the [BMIM]Cl ionic liquid system. Figure 1 illustrates the spectra for cellulose dinitrobenzoate sample (a) and native cellulose (b), which exhibits the characteristic signals of carbohydrate polymers. In the spectrum of native cellulose (b), the signals at 104.1, 82.6, and 61.4 ppm were attributed to C-1, C-4, and C-6, respectively. The sharp signal at 73.7 ppm was because of the overlapping signals from C-2, C-3, and C-5 (Andrews *et al.* 2014). In comparison with the native cellulose (b), there were noticeable changes in the number and position of the signals for the cellulose dinitrobenzoate sample. The new signals at 123.2, 146.6, and 123.7 ppm were assigned to the carbons in the benzene ring (Yu and Yang 2003b), indicating the successful attachment of 3,5-dinitrobenzoyl groups onto the backbone of cellulose.
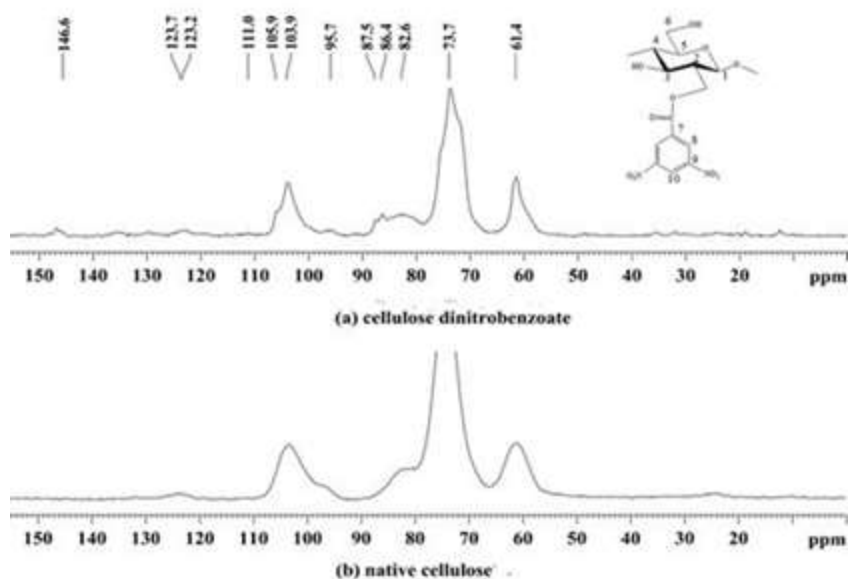

Fig. 1. CP/MAS ^{13}C NMR spectra of cellulose dinitrobenzoate (a) and native cellulose (b)

Kinetic Study

An initial creatinine concentration of 100 mg/L and the adsorbent dosage of 0.1 g in 10 mL of dialysate at pH 7 were used to determine the equilibration time for maximum removal efficiency and kinetics. The amount of creatinine adsorbed onto cellulose dinitrobenzoate is shown as a function of time in Fig. 2. The adsorption per unit mass of creatinine rose sharply with increasing contact time from 1 to 6 h, after which the adsorption amount for creatinine began to level off. The adsorption equilibrium was achieved within 6 h for creatinine. The adsorption equilibrium time was shorter than the time that food stayed within the gastrointestinal tract (8 to 9 h), indicating that the ingestion

of cellulose dinitrobenzoate adsorbent resulted in a significant reduction in the level of creatinine.

To inspect the controlling mechanism of the adsorption process, the two most commonly used kinetic models, pseudo-first order and pseudo-second-order models, were used to examine the experimental data. And their equations are illustrated as follows,

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \tag{2}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{3}$$

where q_t (mg/g) is the adsorption per unit mass at time t (h), q_e (mg/g) is the adsorption per unit mass at adsorption equilibrium, k_1 (h^{-1}) and k_2 (g/mg/h) are the kinetic rate constants for the pseudo-first-order and pseudo-second-order models, respectively. Table 1 lists the computed results obtained from the first- and second-order kinetic models. Clearly, the correlation coefficient (R^2 in Table 1) for the pseudo-second-order kinetic model is higher than that of the pseudo-first-order kinetic model, which indicates that the pseudo-second-order kinetic model more accurately reflects the adsorption kinetics than the pseudo-first-order kinetic model does (Peng *et al*. 2012). The underlying reason why the pseudo-second-order rate law tends to fit adsorption onto cellulose dinitrobenzoate can be attributed to nano-scale porosity, such that some sites take longer for creatinine molecules to reach (Hubbe *et al.* 2012).

Table 1. Parameters of Adsorption Kinetic Models

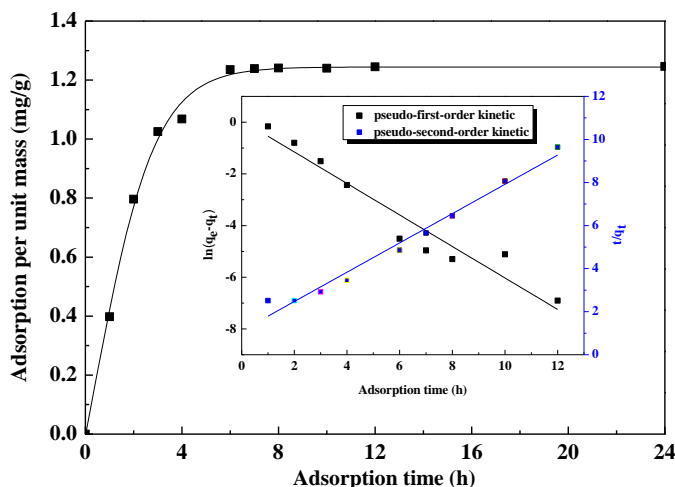| $q_{e(exp)}$	Pseudo-first-order model			Pseudo-second-order model		
	k_1	$q_{e(cal)}$	R^2	k_2	$q_{e(cal)}$	R^2
	(h^{-1})	mg/g		g/mg/h	mg/g	
1.246	0.609	1.069	0.93	0.579	1.471	0.98

Fig. 2. Adsorption kinetics curves of cellulose dinitrobenzoate at 37 °C, pH 7.0, and creatinine concentration of 100 mg/L

Influence of Adsorbent Dosage

The effect of adsorbent dosage was investigated by varying the amount of cellulose dinitrobenzoate (adsorbent) from 2 to 15 mg/mL at the creatinine concentration of 100 mg/L. Figure 3 shows that the adsorption ratio increased with increasing amount of adsorbent. This increase in creatinine removal ratio at higher adsorbent dosage could be attributed to the presence of more active sites for the same number of creatinine molecules (Deng *et al.* 2009). Although the adsorption ratio increased with the increase in adsorbent dosage, the adsorption per unit mass decreased as shown in Fig. 3. This is attributed to the unsaturation of active sites on the adsorbent due to the increase in the ratio of adsorption sites to the creatinine molecules (Batmaz *et al.* 2014). In low adsorbent concentrations of the dialysate, the surface area and the availability of sorption sites were relatively high, and therefore, the creatinine was easily adsorbed. With a higher amount of adsorbent, the available sorption sites per unit mass were limited; however, the total available sorption sites increased (Javadian 2014). The adsorption process was in relation to the functional groups.
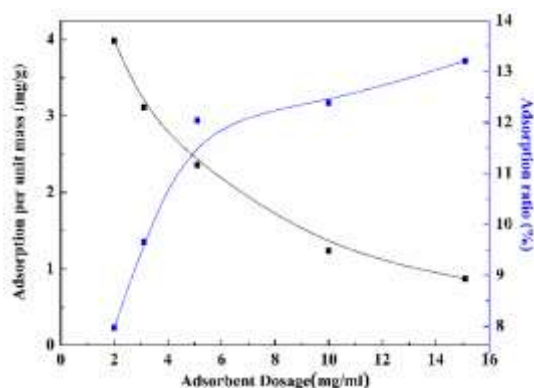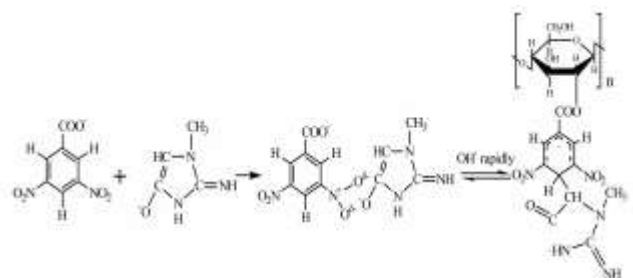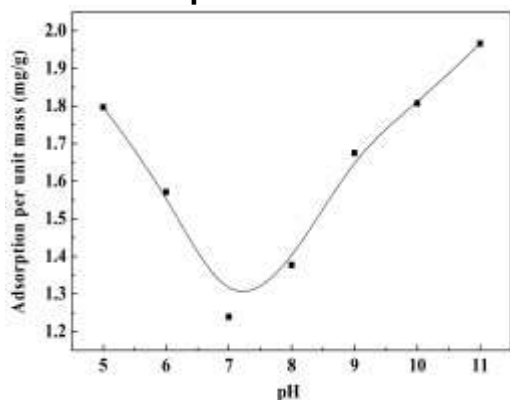

Fig. 3. Effect of cellulose dinitrobenzoate amount at 37 °C, pH 7.0, and creatinine concentration of 100 mg/L

Influence of pH Value of the Solution

The adsorption process of cellulose dinitrobenzoate and creatinine

Fig. 4. Influence of pH on the adsorption per unit mass at 37 °C, adsorption time of 6 h, creatinine concentration of 100 mg/L, and adsorption process of cellulose dinitrobenzoate and creatinine

The effect of pH on the adsorption per unit mass of cellulose dinitrobenzoate and the adsorption process between cellulose dinitrobenzoate and creatinine in the dialysate is

illustrated in Fig. 4. The adsorption per unit mass decreased at first, and then increased when the pH value of dialysate rose from 5 to 11. Within the pH value range of 5 to 7, the adsorption per unit mass for creatinine decreased with the increase of pH value. The pH of the medium affects the surface charge of the adsorbents *via* the protonation or deprotonation of the functional groups. Electrophilic substitution could occur between cellulose dinitrobenzoate and the nitrobenzene ring under acidic conditions, making the amino groups on the outside of the creatinine ring suitable for forming cations with protons. Therefore, the cations could react with the benzene ring by electrophilic substitution. In the pH range from 7 to 11, the adsorption per unit mass for creatinine increased. The most likely reason for that was that creatinine developed the oxygen anion structures in an alkaline environment which could accelerate the complexation reaction between creatinine and the nitrobenzene rings. Moreover, an increase in the –OH group concentration improved the swelling of the cellulose molecule. Accordingly, creatinine could diffuse into a molecule of cellulose quite easily (Yu *et al*. 2007). Therefore, a higher adsorption per unit mass could be achieved.

Isotherms Study

Adsorption isotherms present how adsorbates interact with adsorbents and thus are critical in optimizing the use of adsorbents (Jin *et al*. 2014; Salahi and Ghorbani 2014). For a fixed amount of adsorbent, the adsorption per unit mass (q_e) initially increased and then achieved equilibrium with increasing the initial creatinine concentration as shown in Fig. 5. At low initial concentrations (less than 225 mg/L), adsorption per unit mass of adsorbent increased almost proportionally with the increase in the initial concentration of creatinine, indicating that the adsorption process was highly dependent on the initial concentration of creatinine. However, the adsorption per unit mass slightly increased when the initial concentration was above 225 mg/L. Higher creatinine concentrations (>225 mg/L) had no remarkable effect on the adsorption per unit mass. In this case, the number of available ligands in the adsorbent actually became the limiting factor which controlled the amount of ingestion.

In Fig. 5, cellulose dinitrobenzoate showed a higher adsorption per unit mass for creatinine at lower temperature, implying that the adsorption process for creatinine was an exothermic process. The maximum adsorption per unit mass of adsorbent at 23, 30, and 37 °C were 3.88 mg/g, 3.64 mg/g, and 3.33 mg/g, respectively. The widely used Freundlich isotherm (Eq. 4) was used in the adsorption processes (Thiele and Leinweber 2001). An experimental and data-based Freundlich equation could be attained based on the sorption on a heterogeneous surface which assumes a logarithmic decline in the enthalpy of adsorption as the fraction of occupied sites increases (Javadian 2014),

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{4}$$

where C_e (mg/L) is the equilibrium concentration of adsorbate, q_e (mg/g) is the amount of creatinine adsorbed by the adsorbents per unit mass at equilibrium, K_f (L/mg) is the Freundlich equilibrium constant, and n is the Freundlich equilibrium constant.

The linearized form of Freundlich isotherm for the adsorption of creatinine onto cellulose dinitrobenzoate is shown in Fig. 6(a). The parameters of the adsorption isotherm model are given in Table 2. The values of k and n decreased with increasing temperature,

which indicated that better adsorption occurred at lower temperatures (Batmaz *et al*. 2014). The high correlation coefficient ($R > 0.98$) of the linearized Freundlich equation suggested that the adsorption of creatinine onto cellulose dinitrobenzoate was multilayer adsorption and that the adsorption surface was heterogeneous (Yan *et al*. 2014). The values of the Freundlich adsorption isotherm constant *n* were 1.126, 0.937, and 0.939 at 23 °C, 30 °C, and 37 °C, respectively. All the values were within 0 to 2, indicative of the favorable adsorption for creatinine by cellulose dinitrobenzoate adsorbent. As a result, the Freundlich adsorption model, which was considered to be uneven adsorption mainly via monolayer chemical adsorption and a small amount of physical adsorption on the surface of the adsorbent, could be applied in the adsorption process for creatinine.
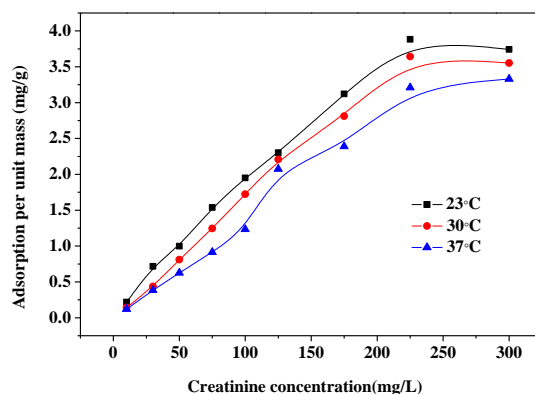

Fig. 5. Effects of initial creatinine concentration and adsorption temperature on the adsorption per unit mass for creatinine at 23 °C, 30 °C, and 37 °C

Table 2. Parameters for Freundlich Adsorption Isotherm Model

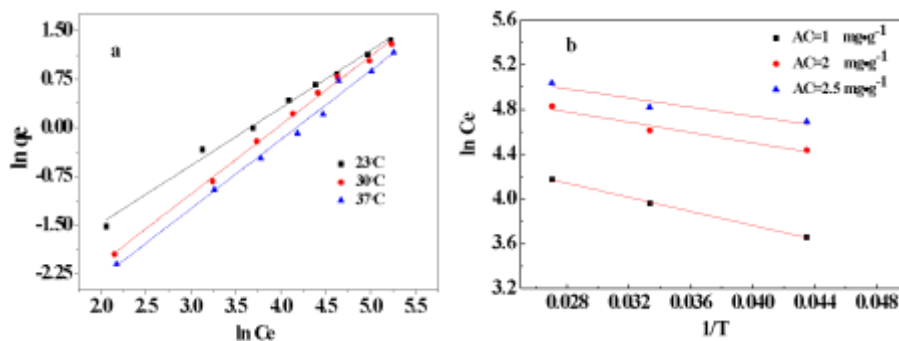| Temperature（ºC）	K	n	R^2	Freundlich equation
23	0.0388	1.126	0.994	$q_e=0.0388C_e^{0.888}$
30	0.0146	0.937	0.997	$q_e=0.0146C_e^{1.067}$
37	0.0117	0.939	0.990	$q_e=0.0117C_e^{1.065}$

Fig. 6. Freundlich isotherms model (a) and Adsorption thermodynamics curve (b)

Adsorption Thermodynamics

The thermodynamic data is presented in Table 3 showing Gibbs free energy, the enthalpy, and the entropy of the binding system. The change in Gibbs free energy (ΔG) was calculated for creatinine based on the relationship between the distribution coefficient or equilibrium constant between creatinine and the adsorbent. The relationship was shown in Eq. 5,

$$\Delta G = -nRT \tag{5}$$

where ΔG is the calculated change in the Gibbs free energy, R is the gas constant (8.314 $J\cdot mol^{-1}K^{-1}$), T is the absolute temperature in Kelvin, and n is the distribution coefficient.

The determined ΔH and ΔS values for the present study are shown in Table 3 for the binding of creatinine to the adsorbent. The relationship between ΔG, ΔH, and ΔS, and the relationship between ΔG and T are shown in Eqs. 5 and 6, respectively.

$$\Delta S=(\Delta H-\Delta G)/T \tag{6}$$

The following relationship could be determined substituting T into Eq. 5 to develop Eq. 7.

$$\ln C_e=\Delta H/(RT)+K \tag{7}$$

where C_e (mg/L) is the equilibrium concentration of adsorbate, ΔH (J/mol) is the equal amount of adsorption enthalpy, and K is the constant.

The plot of $\ln C_e$ versus $1/\underline{T}$ for the experimental data is shown in Fig. 6 (b). By plotting the $\ln C_e$ against $1/T$, ΔH of the reaction can be determined from the slope of the line. Likewise, from the intercept of the plot, ΔS can be determined according to Eq. 6. Figure 6 (b) shows the plots for $\ln C_e$, determined at the three different temperatures, 27 °C, 30 °C, and 37 °C for the adsorption reaction of creatinine.

Table 3. Parameters of the Adsorption Thermodynamics

AC	-ΔH	-ΔG (kJ·mol⁻¹)			-ΔS (J·mol⁻¹·K⁻¹)		
(mg·g⁻¹)	(kJ·mol⁻¹⁾	23 °C	30 °C	37 °C	23 °C	30 °C	37 °C
1	28.34	2.771	2.360	2.420	86.38	85.74	83.61
2	21.22	2.771	2.360	2.420	62.33	62.24	60.65
2.5	18.92	2.771	2.360	2.420	54.56	54.65	53.23

In Table 3, the negative values of ΔG indicated that the process was spontaneous and feasible in nature. In addition, the spontaneity decreased as the temperature increased from 23 to 37 °C (Zhou *et al*. 2014). The negative values determined ΔH confirmed that the reaction was exothermic (Anirudhan and Rauf 2013). Furthermore, the apparent value of ΔH for the adsorption reaction of creatinine is decreasing with the increase of adsorption per unit mass (q_e). This behavior can be explained that the creatinine adsorbed on the

highest energy site of the adsorbent in the initial stage. With more and more molecules of creatinine absorbed on the adsorbent, the creatinine will be adsorbed on the sites which with lower energy, thus the exothermic energy decreased. Moreover, the dipole moment of the molecule prompted the adsorbed creatinine molecules directionally arranged, thus there will be mutual repulsion between intermolecular. Meanwhile, the apparent ΔH was 18 to 30 kJ/mol, indicating that the reaction was not driven solely though physisorption (Wang *et al*. 2007). For the adsorption reaction of creatinine, it was mainly complexation adsorption on the surface of the adsorbent. The ΔS for the adsorption reaction of creatinine were negative values, suggesting that the decrease of creatinine degree-of-freedom motion and the chaotic degree of system, was due to the limiting motion of creatinine molecules on the adsorbent adsorption sites in the dialysate. With a fixed adsorption per unit mass, the value of ΔS is increasing with the decreasing of temperature, which suggests that the chaos of the adsorption system decreased with the increasing of temperature.

CONCLUSIONS

1. Cellulose dinitrobenzoate, prepared in the green solvent (ionic liquid), was developed as an oral adsorbent for the removal of creatinine in dialysate. Solid-state NMR confirmed that 3,5-dinitrobenzoyl groups were grafted onto the backbone of cellulose.

2. The adsorption per unit mass was related to the adsorption time, adsorption temperature, initial creatinine concentration, and pH value of the medium. The optimum creatinine adsorption per unit mass was 3.88 mg/g at 23 °C, pH 7.0, and creatinine concentration of 225 mg/L. The adsorption process of cellulose dinitrobenzoate for creatinine fit to the Freundlich isotherm very well.

3 Cellulose dinitrobenzoate presented a favorable adsorption capability for creatinine. Studies further indicated the sorption process was controlled by chemical adsorption. However, the detailed mechanism needs further investigation.

ACKNOWLEDGMENTS

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