Kinetic study on urea uptake with chitosan based sorbent materials

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ABSTRACT

A one-pot kinetic uptake study of urea in aqueous solution with various chitosan sorbent materials such as pristine chitosan, cross-linked chitosan with glutaraldehyde from low (**C-1**) to higher (**C-2**) glutaraldehyde content, and a Cu(II) complex of a glutaraldehyde cross-linked chitosan material (**C-3**) is reported herein. The kinetic uptake profiles were analyzed by the pseudo-first order (PFO) and pseudo-second-order (PSO) models, respectively. The uptake rate constant of urea and the sorption capacity (q_e) of high molecular weight (HMW) chitosan, **C-1**, **C-2**, and **C-3** were best described by the PFO model. The uptake rate constant of urea with the various sorbents is listed in ascending order: HMW chitosan < **C-1** < **C-2** ≈ **C-3**. The q_e values (mg urea/g sorbent) for the sorbent/urea systems are listed in ascending order: HMW chitosan (48.1) ≈ **C-1** (44.7) < **C-2** (51.3) < **C-3** (66.4 mg/g), revealing good agreement with uptake values obtained independently at equilibrium conditions. Cross-linked chitosan displays relatively rapid urea uptake and greater adsorption capacity when compared with pristine chitosan. The observed trends are in agreement with the greater surface accessibility and pore structure properties of cross-linked chitosan based on scanning electron microscopy studies. These results further illustrate the rational design of chitosan-based materials for the controlled uptake of urea in aquatic environments.

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1. Introduction

Urea is an abundant source of nitrogen in inorganic fertilizers and also represents an important metabolic by-product in living systems. A key issue in sustainable management of food production relates to the buildup of oxyanion nutrients such as nitrate and phosphate species in surface aquatic environments, as evidenced by eutrophication problems, where a major point source of contaminants is fertilizer leaching (Cui, Dou, Chen, Ju, & Zhang, 2014; OECD, 2014). Surface water quality is directly connected to climate change, soil quality, nutrient availability, and agriculture activities (Brooks, Williams, & Schmidt, 1998; Sachs et al., 2012; Schindler & Donahue, 2006). Therefore, the uptake of urea in water environments is an important process in many fields of application such as environmental remediation of surface water containing inorganic fertilizers or in cases when hemodialysis is required to lower the urea levels in the blood plasma of patients with chronic kidney disease (Alizadeh, 2010; Grynpas, Rosen, & Sutton, 1984; Humes, Fissell, & Tiranathanagul, 2006; Shimizu & Fujishige, 1983). The fate and transport of N-containing fertilizer species such as nitrate and urea can be modified by adsorption-based removal technologies (Qu & Fan, 2010) using adsorbent materials such as chitosan (Patil,

Husain, & Rahane, 2013). Several chitosan related materials have been developed as sorbents for urea capture (Liang, Feng, Liang, & Meng, 2005; Liu, Chen, Shao, & Zhou, 2003; Liu et al., 2012; Pathak & Bajpai, 2009; Zhou, Yang, Guo, & Chen, 2003). However, the molecular level details of the uptake of urea by chitosan-based materials are poorly reported (Ganesapillai, Venugopal, Ananthkrishna, & Tapankrishna, 2015; Liang et al., 2005; Liu et al., 2012; Long, Zhang, Wang, & Cao, 2009). The limited availability of studies that have examined the relationship between sorbent structure and the uptake mechanism of urea has limited the development of sorbent materials with improved properties. There are relatively few studies that detail the kinetics of the urea uptake process with chitosan-based sorbents. Some selected examples include the use chitosan coated dialdehyde cellulose (Liang et al., 2005), cross-linked chitosan microspheres with immobilized Zn(II) (Liu et al., 2012), and microwave activated carbonized biosorbent materials (Ganesapillai et al., 2015).

In this paper, we report a kinetic uptake study that used a specialized *one-pot* kinetic method for evaluating the *in situ* heterogeneous sorption of urea for macromolecular chitosan sorbents at ambient solution conditions. The sorbent materials include pristine chitosan, glutaraldehyde cross-linked chitosan, and a Cu(II) complex of cross-linked chitosan which were prepared and characterized in a previous study (Wilson & Xue, 2013) along with an equilibrium uptake study of these materials with urea. The significance of this report relates to an improved understanding of the

Table 1
Chitosan–glutaraldehyde materials and their identification (ID), mass ratio (chitosan to glutaraldehyde; chi/glu) and swelling level (%) in water at 295 K and ambient pH conditions.

ID	Cross-linked chitosan[a]	Mass ratio (chi/glu)[b]	Swelling[a,c] (%)
C-1	CP-1 (long)	1:0.0835	277 ± 21
C-2	CP-3	1:0.585	257 ± 19
C-3	CP-1/Cu(II) (long)	1:0.0835	81 ± 8

[a] Defined in the reference by Wilson and Xue (2013).
[b] See Table I in Wilson and Xue (2013).
[c] See Table III in Wilson and Xue (2013).

adsorption properties of chitosan materials through a systematic kinetic study of urea uptake. A systematic variation of the molecular structure of a chitosan adsorbent material enables an improved understanding of the relationship between molecular structure and corresponding physicochemical properties such as adsorption. This study also advances the field of knowledge in adsorption phenomena through the deployment of the *one-pot* kinetic method. The foregoing is understood due to the technical limitations and challenges related to the use of batch methods for the measurement of urea adsorption in heterogeneous solid-solution processes (Kwon, Wilson, & Sammynaiken, 2014; Mohamed & Wilson, 2015).

2. Experimental

2.1. Materials

High-molecular-weight (HMW) chitosan (150–375 kDa, ≥75% deacetylated), urea, and *p*-dimethylaminobenzaldehyde (PAB) were obtained from Sigma–Aldrich. All materials were used as received unless specified otherwise.

2.2. Preparation of cross-linked materials

CP-1 (long), CP-3, and CP-1/Cu(II) (long) cross-linked materials were prepared according to a published procedure (Poon, Younus, & Wilson, 2014; Wilson & Xue, 2013). The results in Table 1 summarize the composition of the various chitosan adsorbent materials studied herein which are hereafter denoted as **C-1**, **C-2**, and **C-3**. Scheme 1 illustrates the conceptualized structure of chitosan with low to high levels of cross-linking, along with a cross-linked chitosan polymer complexed with Cu(II).

2.3. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) images were obtained with a JSM-6010LV at 1000× magnification with 508 dpi resolution. The surface of the adsorbent materials was sputter coated with gold by using an Edwards S150B sputter coater for enhanced imaging of sample surfaces with the scanning electron microscope.

2.4. One-pot adsorption kinetics

A schematic of the *one-pot* kinetics setup is shown in Fig. 1. An aqueous urea solution (~10 mM, 500 mL) was prepared in a 500 mL Pyrex beaker. The sorbent (*ca.* 0.25 g) material was added into the beaker (Region B; *cf.* Fig. 1) while the urea solution was stirred at 510 rpm at room temperature. 1.00 mL aliquots were taken from the inner portion of a conical filter paper (Region A; *cf.* Fig. 1) where a Whatman No. 42 filter paper was used as a semi-permeable membrane barrier to separate the solid phase adsorbent from Region A. Sampling of aliquots was carried out in Region A at 2-min intervals for the first 20 min. Then, 1.00 mL aliquots were taken at 10-min intervals up to a 60-min duration. The colorimetric analysis of the urea solutions required 500 μL aliquots which were mixed with
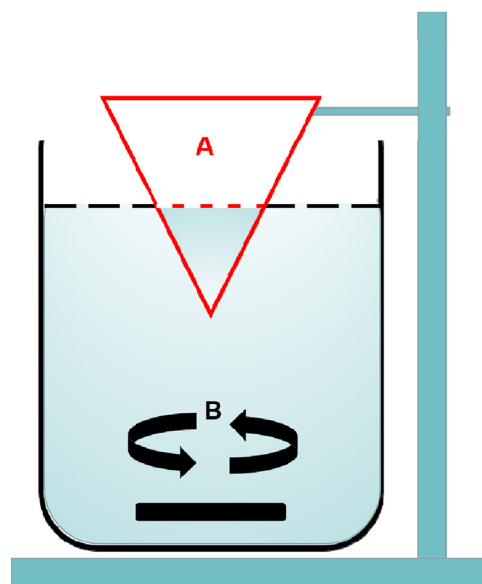

Fig. 1. *One-pot* set-up for the *in situ* measurement of urea uptake kinetics for a heterogeneous solid-solution system. (Region A is the inner sampling compartment with a semi-permeable filter-paper barrier (No. 42 Whatman filter) for the removal of unbound urea; Region B is outer compartment containing the urea solution with the adsorbent phase.)

500 μL of Millipore water and 250 μL of PAB dye development solution to form the blue colored urea-dye complex for quantitative UV–vis analysis of urea, as described elsewhere (Wilson & Xue, 2013). The adsorptive uptake of urea for each time interval (q_t; mg/g) was calculated from Eq. (1) at variable time (t), where C_0 (mM) is the initial urea concentration ($t = 0$) before adsorption, C_t (mM) is the urea concentration at any time (t) after adsorption, V (mL) is the volume of solution, and m is the amount of sorbent (mg) used in the *one-pot* kinetic experimental setup.

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

2.5. Data analysis

The kinetic results of the uptake of urea for the various sorbent/urea systems were analyzed using two models; the pseudo-first-order (PFO) model (*cf.* Eq. (2)) (Lagergren, 1898) or the pseudo-second-order (PSO) model (Eq. (3)) (Azizian, 2004; Blanchard, Maunaye, & Martin, 1984; Ho & McKay, 1999). The "apparent" uptake rate constants for the PFO (k_1; min^{-1}) and the PSO model (k_2; g mg^{-1} min^{-1}) are defined; whereas, q_t (mg/g) is the amount of uptake at time (t), and q_e (mg/g) is the relative uptake at pseudo-equilibrium conditions. The "apparent" rate constants (k_1 and k_2) and q_e (mg/g) were estimated using non-linear fitting procedures according to Eqs. (2) and (3). The criterion of "best fit" between the experimental data and the two models was found by minimizing the absolute sum of squares of error (SSE) according to Eq. (4).

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2}$$

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

$$SSE = \sum \sqrt{\frac{(Q_{e,i} - Q_{c,i})^2}{N}} \tag{4}$$