Particuology 30 (2017) 73–82

Contents lists available at ScienceDirect

Particuology

journal homepage: www.elsevier.com/locate/partic

Swelling and diffusion model of a hydrophilic film coating on controlled-release urea particles

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ARTICLE INFO

Article history:
Received 15 December 2015
Received in revised form 14 March 2016
Accepted 27 March 2016
Available online 20 July 2016

Keywords:
Coating
Controlled-release
Particle
Permeability
Swelling
Urea

ABSTRACT

Controlled-release urea was fabricated by coating urea particles with a polymer latex in a fluidized bed. The latex film coated on the urea particle surface was hydrophilic and swelled in water. The film swelling in water and urea solution and properties of the swollen film were studied. The film swelling in urea solution followed the Lagergren's pseudo-first order kinetics with the swelling coefficient depending on the film material and experimental conditions. The effects of swelling on film structure and permeability were studied. The film permeability coefficient decreased with increasing swelling ratio with an approximately linear relationship. Based on the film formation process and structure of the swollen film, a film structure model consisting of dense and swollen phases was proposed. The permeability coefficient of the spherical film and cumulative release of urea from the coated particles were calculated from the swelling ratio of the spherical film, which was determined from the expansion curve of the coated particle during the release process. The calculated and measured release curves agreed well. This research indicates that the swelling of the hydrophilic film and the controlled-release mechanism are important factors in the development of controlled-release urea.

Introduction

The inefficient use of fertilizers has caused serious environmental pollution. The use of controlled-release fertilizers is an effective measure to increase their utilization efficiency and lower pollution. Controlled-release fertilizers are usually produced by coating the fertilizer particles with a synthetic polymer. Using polymer latex as a coating material, in which the continuous phase is water, and the latex is sprayed onto urea particle surfaces and forms a film after dehydration, is a promising green process for controlled-release fertilizer production (Du, Shen, & Zhou, 2013; Lan et al., 2011; Tzika, Alexandridou, & Kiparissides, 2003; Yin et al., 2015).

Unlike slow-release drugs (Dekyndt, Verin, Neut, Siepmann, & Siepmann, 2015; Li, Guo, Meng, & Zhang, 2011), controlled-release fertilizers require a long release period and low cost. Therefore, characterization of the release properties of controlled-release fertilizers is very important. Because of the long release period, measurement of their release curves usually takes tens of days or longer. Methods to shorten the measurement time have been explored; e.g., measuring the release curve in hot water or/and at low/high pH, and then calibration with the results for release characteristics under normal conditions (Chen, Ge, Sun, Wang, & Zhang, 2012; Duan, Zhang, Liu, Yang, & Shang, 2009; Xie, Yang, Cao, Jiang, & Zhang, 2007). However, these methods could not reproduce the mechanism of the actual release process, so they usually have a large error compared with those measurements obtained under ambient conditions, and the measurement time is still long. Therefore, it is important to understand the release process and establish a release process model to allow efficient prediction of the release characteristics of controlled-release fertilizers. The effects of preparation conditions on fertilizer release properties and a release process model have been reported (Lan et al., 2013).

Film structure strongly affects the release of fertilizer particles. In the existing literature, the film structure and permeability coefficient (P), which is defined as the permeation flux under a unit concentration gradient across the film, were assumed to be constant during the release process (Al-Zahrani, 1999; Gambash, Kochba, & Avnimelech, 1990; Shaviv, Raban, & Zaidel, 2003). Lan et al. (2013) proposed a diffusion model for film with a multilayer and random defect structure based on the film formation process by spray coating. From the measured structural parameters and nutrient diffusion rate in this film structure model, P and the release curve of the film were calculated. The calculated release curve agreed well with that measured.

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http://dx.doi.org/10.1016/j.partic.2016.03.005

Symbols used

A	permeation area of the film (m^2)
A_s	average surface area for single particle (m^2)
C	urea concentration (g/L)
ΔC	concentration difference across the film (g/L)
C_1	low concentration of urea (g/L)
C_2	high concentration of urea (g/L)
C_i	urea concentration inside the particle (g/L)
C_o	urea concentration outside the particle (g/L)
C_s	urea concentration of saturated solution (g/L)
C_w	urea concentration in the water tube (g/L)
J	permeation flux (g/(m^2 s))
k	swelling coefficient (s^{-1})
Δm	penetration amount of urea through the film (g)
m_0	initial mass of coated urea in the release process (g)
m_L	coating amount of latex on a single urea particle (g)
M_o	mass of the urea solution outside of the particles in the vessel (g)
m_s	urea mass in a single coated urea particle (g)
N	number of particles
P	permeability coefficient of the film (m^2/s)
P_0	permeability coefficient for unswollen film (m^2/s)
P_a	apparent permeability coefficient (m^2/s)
P_x	permeability coefficient of the infinitesimal cross-section (m^2/s)
R^2	correlation coefficient
R_{ac}	accumulated quantity released from a single particle (%)
t	time (s)
Δt	time interval in measurement (s)
V	total volume of the expanded particles (m^3)
V_s	volume of a single particle (m^3)
W	mass of the swollen spherical film (g)
W_0	dehydrated mass of the swollen spherical film (g)
w_i	mass of the ith plane film (g)

Greek letters

α	fitted parameter (%)
β	fitted parameter (%)
γ	fitted parameter (L/g)
δ	film thickness (m)
dx	thickness of infinitesimal cross-section (m)
η	impact factor of swelling (m^2/s)
ρ	density of the swollen film (g/L)
Φ	swelling ratio of the spherical film (%)
φ_e	equilibrium swelling ratio (%)
φ_i	swelling ratio of the ith plane film (%)

Latex films formed from the dehydration of atomized droplets on the surface of fertilizer particles are hydrophilic (Lan, 2012), so such films swell markedly in water. The swelling properties of hydrophilic polymers have been widely studied. Tanaka and Fillmore (1979) used a displacement vector to describe the swelling process of spherical gel particles in water, finding that the displacement of a gel network point depended on swelling time and location. Li and Tanaka (1990) investigated an infinite planar film and reported that the swelling displacement curve of the network increased exponentially. Kostic, Adnadjevic, Popovic, and Jovanovic (2007) proposed that the swelling rate and equilibrium swelling ratio (φ_e) of poly(acrylic acid) gel were higher in pure water than normal saline solution because of ionic osmotic pressure. The swelling ratio of polyacrylamide gel changed exponentially with time in NaCl solution at low concentration (Sivanantham & Tata, 2012). Ataman and Pekcan (2007) calculated P of small molecules in a swollen iota-carrageenan using Fick's law and the Li–Tanaka model (Li & Tanaka, 1990). The calculated activation energies of diffusion and swelling were 20.5 and 28.2 kJ/mol, respectively. Lang, John, and Sommer (2016) studied the network formation and swelling of a cross-linking co-polymer and found the swelling data of most networks agreed with the prediction of the Flory–Rehner model. An additional non-affine contribution to the equilibrium degree of swelling was observed for networks with a low density of active cross-links.

The swelling of a hydrophilic film changes its structure, which changes its nutrient P. The effects of swelling on P have been examined. Yakimets et al. (2007) studied the water uptake of three types of biopolymer films and found that the structural reorganization and elastic properties of the films depended on water content. Zhu and Vesely (2007) reported that swelling has a marked effect on the diffusion and permeation rates of methanol in a polymethylmethacrylate film, and that P can be modified by controlling the swelling ratio. Kim et al. (2009) controlled the release rate of a drug in a capsule by controlling swelling and deswelling. The drug was released very slowly or not at all in pure methanol because the coated film was not swollen. When the capsule was immersed in aqueous methanol with 90% (v/v) water, the drug release rate was fast because of the swelling of the film. When the capsule was reimmersed in methanol, drug release became slow again. Other researchers have also reported that film swelling caused by hydrophilicity accelerated the release rate of particles (Kurek, Guinault, Voilley, Galic, & Debeaufort, 2014). Fan et al. (2008) reported that film swelling and drug permeability were consistently related.

This paper studies the swelling properties and process of a hydrophilic film, and the relationship between the swelling ratio and film permeability. A structure model of the swollen film and a release process model are established to predict the release characteristics of film-coated urea particles.

Experimental

Materials and instruments

Large granular urea with a diameter of 2–3.2 mm (China Blue Chemical Ltd., Beijing, China) was coated with styrene-butyl acrylate copolymer latex with 40% solid content. The latex nanoparticles had an average diameter of 80 nm (Li, Kan, & Liu, 2001) and were synthesized by semi-continuous emulsion copolymerization of butyl acrylate, styrene, methacrylic acid, and crosslinker (Lan et al., 2013). The other chemicals used were urea, ethanol, and hydrochloric acid (analytical grade, Beijing Modern Oriental Fine Chemicals Co., Ltd., Beijing, China), 4-dimethylaminobenzaldehyde (DMAB; analytical grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), and deionized water.

The film structure was characterized by a high-resolution scanning electron microscope (SEM, JSM7401, JEOL, Tokyo, Japan). An ultraviolet–visible spectrophotometer (TU-1900, Beijing Purkinje General Instrument Co., Ltd., Beijing, China) was used to measure the concentration of the urea solution. A precision balance (0.1 mg, PWC214, Adam Equipment Co., Ltd., Milton Keynes, UK) was used to measure the mass of the swollen film. An oven (101-2AB, Beijing Zhongxing Weiye Instrument Co., Ltd., Beijing, China) was used for dehydration and heat treatment of the planar film. A micrometer (0–25 mm, Beijing Blue Light Group, Beijing, China) was used to measure film thickness.