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Research Paper

Parametric evaluation using mechanistic model for release rate of phosphate ions from chitosan-coated phosphorus fertiliser pellets

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Evaluation of nutrient release from a controlled-release fertiliser (CRF) using mechanistic model is important in order to increase the understanding towards the mechanism that might involve in a release process. In this study, a mechanistic model was used to evaluate the parameters that govern the phosphate release rate through chitosan-coated phosphorus fertiliser. The model considers the phenomena of boundary layer formation on the external surface of the coat and the coating thickness changes due to erosion. Static release experiments were conducted in order to study the effect of the number of coatings and pH conditions to the release rate of phosphate ions. The respective parameters of the phosphate release such as diffusion coefficient were evaluated using the model in both cases. The diffusivity of the phosphate was found to increase as the number of coatings and pH values of the medium decreased. Regeneration of the released data for the phosphate ions using the model indicated a very satisfactory fit with the experimental data.

1. Introduction

The application of controlled-release fertilisers (CRF) in agricultural sector is one of the methods that can be used to enhance the nutrient consumption efficiency as well as minimising the environmental problems due to leaching of uncontrolled nutrient released (Al-Zahrani, 2000). Among these CRF types, coated fertilisers are more commonly used in practice (Shaviv, 2000). The nutrients release rate is controlled by encapsulating the fertiliser granules or pellets into a type of coating material. Various coating materials have been used to coat different types of fertilisers, but the current trend shows that polymer coated fertilisers are the most popular types of CRF and having great advantages over conventional types of coatings (Du, Tang, Zhou, Wang, & Shaviv, 2008). However, the use of conventional polymer coating usually deals with the high cost of material and accumulation of undesired synthetic residues in soil (Golman, 2011; Trenkel, 2010). Recently, a number of studies have been focused on the use of biodegradable polymers as the promising coating materials for fertilisers (Chen, Xie, Zhuang, Chen, & Jing, 2008; Han, Chen, &

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Nomenclature

R	rate of phosphate release, g min^{-1}
Z	thickness of the pellet, m
A	area of the nutrient mass transfer, m^2
C_{av}	average nutrient concentration released at time t, g m^{-3}
k_c	mass transfer coefficient for external surface of the coat, m min^{-1}
C_2	nutrient concentration at the outer surface of the chitosan coat at a time t, g m^{-3}
C_a	nutrient concentration outside the pellet at a distance ∞ from the inner boundary of the chitosan coat, g m^{-3}
C_1	nutrient concentration within the pellet, g m^{-3}
$C_2(x,t)$	concentration of nutrient outside the pellet at a distance x from the inner boundary of the coat at a time t, g m^{-3}
C_m	nutrient concentration within the membrane, g m^{-3}
x	distance from the membrane surface, m
C_o	original concentration of nutrient within the pellet, g m^{-3}
D	diffusion coefficient of nutrient within the membrane or coating layer, m^2 min^{-1}
D_f	diffusion coefficient of nutrient within the bulk, m^2 min^{-1}
l	coating thickness at time t, m
r	$K(D/D_f)^{0.5}$
K	solute partition coefficient
l_o	initial thickness of the chitosan coat, m
m	dissolution rate constant of the coating film, m min^{-1}
t	time, min

Hu, 2009; Ni, Liu, Lu, Xie, & Wang, 2011; Ni et al., 2010; Wu, 2008).

Chitosan is one of the biodegradable polymers, which is available in abundant in nature. This natural polysaccharide has been widely used in biomedical, pharmaceutical and agricultural fields due to its biocompatibility, non-toxicity and biodegradability (Aranaz et al., 2009; Sionkowska, 2011). The application of chitosan can be found in the form of gels, membranes, coatings and beads (Krajewska, 2005). However, chitosan-based materials are hydrophilic in nature and make it less stable to be used in its pure form. Cross-linking reaction is one of the modification methods, which can be used to improve its stability, including the water vapour barrier properties (Rinaudo, 2006; Tsai & Wang, 2008). Several studies have been reported on the chitosan-coated fertilisers, which mainly focused on encapsulating urea and nitrogen–phosphorus–potassium (NPK) compound fertilisers (Chen, Lu, Zhang, Wu, & Deng, 2005; Teixeira et al., 1990; Wu & Liu, 2008; Xia, Zhang, Zhao, & Wang, 2009). Nevertheless, none of them reported on the applicability of coating phosphorus fertiliser using the chitosan film.

The application of mathematical model in the controlled-release fertiliser systems is very important in order to optimize the design of CRF and later to produce fertilisers that can meet the nutrients requirement by plants (Shaviv, 2000; Zheng, Liang, Ye, & He, 2009). Mechanistic model is a type of model derived based on a real physical phenomenon, which takes place during a release process (Siepmann & Siepmann, 2008). Unfortunately, the evaluation of nutrient release kinetics from the chitosan-coated fertilisers using mechanistic model equations is yet to be extensively explored. Some of the previous studies only assessed the parameters of nutrient release using the empirical model, which does not provide a better insight on the actual mechanisms (Wu & Liu, 2008). For the case of chitosan membrane system, capillary pore model and free volume model have been used to investigate the solute diffusional properties across the membrane (Krajewska, 2001a, 2001b). There have been several mechanistic models reported on the controlled-release systems, however, most of them have not taken into account the effect of boundary layer formation occurred on the surface of the external coat (Du, Zhou, Shaviv, & Wang, 2004; Ko, Cho, & Rhee, 1996; Koizumi, Ritthidej, & Phaechamud, 2001; Langer & Peppas, 1983; Shaviv, Raban, & Zaidel, 2003). In fact, in the real application of controlled-release of nutrients into a static release medium, the presence of such a boundary layer could impart additional resistance for the solute fluxes and can affect the transport parameters across the membrane layer (Dworecki, Slezak, Ornal-Wasik, & Wasik, 2005).

The purpose of this study is to investigate the phosphate ions release rate from the chitosan-coated phosphorus fertilisers based on the variation of pH conditions and number of coatings. The parameters of release kinetics were evaluated using a carefully derived mechanistic model. The model was developed by considering the formation of boundary layer on the external surface of the coat. It also considered the effect of coating thickness to the release rate. Coated fertilisers could be custom-designed if the factors affecting the release of nutrients could be parameterized so that the release rate could be estimated, prior to manufacturing of such coatings.

2. Materials and method

2.1. *Materials*

Calcium dihydrogen phosphate was purchased from Acros Organics (Geed, Belgium) and of analytical grade. Calcium oxide powder was supplied by Hamburg Chemical GmbH (Germany). Chitosan (degree of deacetylation > 85%, molar mass is 100–1000 kDa) was purchased from Chito-Chem, Malaysia. Sodium carbonate, glacial acetic acid, and citric acid were purchased from Fisher Scientific (Malaysia). Aqueous solutions of different pH values were prepared using citric acid and sodium carbonate.