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# Nitrogen release characteristics of polyethylene-coated controlled-release fertilizers and their dependence on membrane pore structure

Xiangdong Yang[a,b,*], Rongfeng Jiang[b], Yangzheng Lin[c], Yanting Li[a], Juan Li[a], Bingqiang Zhao[a]

[a] Key Laboratory of Plant Nutrition and Fertilizer, Ministry of Agriculture/Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, Beijing 100081, China
[b] College of Resources and Environmental Sciences, Centre for Resources, Environment and Food Security, China Agricultural University, Beijing 100193, China
[c] Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA

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ABSTRACT

In this study, controlled-release fertilizers (CRFs) with five different nitrogen release periods were prepared by coating large urea particles with polyethylene (PE) membranes under various experimental conditions. The preliminary and differential solubility rates, release periods, and membrane pore sizes of the obtained CRFs were measured using water immersion, scanning electron microscopy, and mercury porosimetry. For all CRF samples, the median pore diameters of the membranes were equal to 4.5–5.3 nm and pores with sizes smaller than 10 nm accounted for 86–96% of the total pore surface area. The obtained pore diameter distributions differed for the five studied types of CRF, having release periods of 1, 2, 4, 6, and 8 months. Thus, for the CRFs with a 1-month release period, the maximum pore diameter reached a magnitude of 4000 nm, while this value did not exceed 30 nm for the CRFs with a release period of 8 months. Hence, we have established a relationship between the release period of CRFs and their effective maximum pore sizes.



## Introduction

Controlled-release fertilizers (CRFs) can improve the nutrient use efficiency of plants by increasing their nutrient uptake, which decreases fertilization frequency and, therefore, substantially reduces the consumption of human resources and possible adverse effects on the environment (Chu, Hosen, & Yagi, 2007). Despite the relatively large number of CRFs utilized in agriculture, the mechanism of nutrient release through membranes and its related parameters have not been elucidated yet. Hence, various experimental methods have been developed to determine the CRFs' nutrient release rate in water and examine the pore structure characteristics of CRF membranes.

Immersion is a widely used method for estimating the time-dependent volume of nutrients that have been previously released into water or soil by CRFs (Oertli & Lunt, 1962; Shaviv & Mikkelsen, 1993; Trenkel, 2010). As a result, the preliminary solubility rate, differential solubility rate, and release period of a fertilizer can be obtained from the volume-time relationship determined via a water immersion method (Fujita, 1996). These parameters reflect the functionality of the CRFs membrane, nutrient release characteristics, and the CRFs' applicability to a particular plant (Yang, Cao, Jiang, & Zhang, 2005). For example, Shavit, Reiss, and Shaviv (2003) studied the wetting mechanisms of gel-based CRFs using a controlled-release experimental device, which consisted of a glass tube and a porous plate. They concluded that the entire CRF release process could be divided into the following three stages: penetration of water vapor, nutrient dissolution, and nutrient release through a membrane (Shavit, Shaviv, & Zaslavsky, 1995; Shavit et al., 2003). Du, Zhou, Shaviv, and Wang (2004) used a mathematical model based on Fick's second diffusion law to describe the potassium release from a polymer-coated CRF and concluded that

* Corresponding author at: No. 12 Zhongguancun South St., Haidian District, Beijing, China. Fax: +86 10 82108664.
*E-mail address:* yangxiangdong@caas.cn (X. Yang).

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**Nomenclature**

| | |
|---|---|
| $A_{<10}$ | Cumulative surface area of pores with sizes less than 10 nm, % |
| $D_A$ | Average pore diameter (4 V/A), nm |
| $D_M$ | Median pore diameter, nm |
| $J$ | Molar flux, mol/(m$^2$ s) |
| $k$ | Conversion quotiety |
| $K$ | Hindrance factor for diffusion |
| $r$ | Average pore semi-diameter (8 V/A), nm |
| $T$ | Release duration, day |
| $V_T$ | Total intrusion volume, mL/g |
| $\varepsilon$ | Porosity, % |
| $\eta_1$, $\eta_{\Delta t}$, $\eta_{28}$ | Preliminary solubility rate, differential solubility rate, and cumulative solubility rate after 28 days |

the release of nutrients was mainly affected by the diffusion coefficient, membrane thickness, and granule radius. Al-Zahrani (1999) studied various CRFs with spherical particles and found that their release characteristics depended on their fertilizer formulation. The mathematical models' formulation determined the release characteristics of CRFs.

The models utilized in the studies mentioned above were based on phenomenological equations describing the relationship between the permeation flux and chemical potential energy. They could explain some of the observed experimental phenomena but were unable to elucidate the relationship between the membrane structure and the transfer process (Mulder, 1996). The structure of membranes prepared by phase inversion is affected by many factors, such as the concentration of the utilized membrane liquid, solvent type, and additive type (Ma & McHugh, 2007; Siepmann, Siepmann, Walther, MacRae, & Bodmeier, 2008; Van de Witte, Dijkstra, Van den Berg, & Feijen, 1996). Sun, Huang, and Chang (1999) suggested that sprayed membranes were more porous than casted membranes; however, it was difficult for them to predict the type of membrane structure without performing experimental measurements. Scanning electron microscopy (SEM) is a popular technique that allows direct observation of the membrane morphology (Mulder, 1996). Nevertheless, SEM can provide only local and sectional information, and further image analysis is required to determine the distribution, quantity, and sizes of the membrane pores (Hernandez et al., 1997).

Bubble point testing, Brunauer–Emmett–Teller analysis, and mercury porosimetry (MP) are widely used techniques for determining the pore structure of industrial membranes. However, most of these methods are not applicable to studies of the controlled-release membranes formed on the surface of basal granules. In general, MP can be used to evaluate the performance of small particles (Calvo, Hernandez, Pradanos, Martınez, & Bowen, 1995; León y León, 1998; Liu, Du, Zhu, & Xu, 2007; Mohl & Winter, 2004) and thus estimate the pore size distribution of membranes fabricated by a spray phase inversion method since its measuring range spans from 0.36 to 420 mm. However, the use of MP to measure the pore size distribution of CRF membranes has not been reported in the literature.

SEM images of the surface and cross-sectional views were obtained to characterize the pores of the controlled-release membranes fabricated in this study and elucidate the relationship between the pore structure and the nutrient release performance. MP was used to evaluate the membrane pore size characteristics including the pore size distribution, specific surface area, porosity, and other parameters, while the water immersion method was used to determine the preliminary solubility rate, differential solubility rate, and CRF release duration. In total, the pore size distributions of five CRFs types were analyzed in detail to obtain the relationship between their release periods and pore diameters.

## Experimental

### *Materials and equipment*

Five different types of CRFs with release periods of 1, 2, 4, 6, and 8 months were prepared in this study. They were manufactured at the Department of Plant Nutrition of China Agricultural University by spraying the corresponding membrane solutions onto the surface of large urea particles with a fluidized-bed spray coater. The membrane solutions were prepared by dissolving low-density PE (LDPE) and wax reagents in ethylene tetrachloride (TCE) at 120 °C. The coated fertilizer with the mass ratio between different components of urea:LDPE:TCE:wax:dye = 100:8.0:160:1:0.01 was made by changing the concentration of membrane solutions and the spraying rate. PE (1F7B, 25 kg/bag) was purchased from China SINOPEC Yanshan Chemical Corporation. TCE (300 kg/barrel) was obtained from the Dow Chemical Company (United States). Wax (melting point: 60 °C, 25 kg/bag) was acquired from the Fushun Petrochemical Branch Company (China). Urea (40 kg/bag, particle size: 2–4 mm) was obtained from Hebei Cangzhou Dahua Co., Ltd. (China). Both pigment Paliotol® yellow K2270 and Heliogen® blue K6907 dyes (BASF, Germany) were used. The homemade fluidized-bed spray coater (capacity: 1.5 kg urea) utilized a BIMJ2022S303 spraying nozzle manufactured by Ikeuchi (Japan).

A UV-2201 ultraviolet–visible (UV–vis) spectrophotometer (Shimadzu, Japan), JSM-7401F scanning electron microscope (Jeol, Japan), an Autopore IV 9510 mercury porosimeter (Micromeritics, United States), and a PT120 electronic balance (Sartorius, Germany) were used. A biochemical incubator and an HPS-250 incubator with controlled humidity were manufactured by the Harbin Dongming Medical Instrument Factory (China).

### *Pore structure examination*

The prepared CRFs were pretreated before their membrane pore structures were examined. About one eighth of the spherical membrane was cut from each studied CRF particle's surface using a section razor. For each CRF type, 100 membrane pieces were collected from 100 CRF particles and cleaned three times by de-ionized water followed by drying in a vacuum oven at a temperature of 40 °C for 12 h. The dried samples were directly used for SEM observations and MP measurements. Similar to the shortest stave in a bucket, the largest membrane pores were expected to affect the nutrient release rates significantly. The effective maximum pore diameters were determined for all the studied CRF types using the following procedure. First, the CRF samples were immersed in water for 24 h and dried. Next, small membrane pieces were cut from the dried fertilizer particles, leaving parts of the corresponding urea cores exposed. Finally, the maximum pore diameters of the cut membranes were measured using the bubble pressure method (Xu et al., 2016). The obtained maximum pore diameters were considered the effective maximum pore sizes of the membranes.

### *Nitrogen release characteristics*

In this study, water immersion was used to investigate the parameters of the controlled release of nitrogen species by the CRFs. 100 g of the coated CRFs particles was packed in a nylon net bag and placed into a plastic bottle, which was filled with 200 mL of distilled water and covered. Afterward, the temperature of the bottle was maintained at 25 °C using a thermostat for static release. The released amount of nitrogen was determined

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