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Research Paper

Release profile predictions of controlled release fertilisers: Least Squares Support Vector Machines

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Modelling nutrient release profiles from a population of controlled release fertiliser (CRF) is essential for synchronising their release with plant nutrient requirements. A mechanistic model succeeds in describing the release profiles from a single granule. Yet, a large deviation will appear when it is used for a population of CRF due to the large variation in a CRF population. Least Squares Support Vector Machines (LS-SVM) that incorporated the variation were used to predict nutrient release from a CRF population using the photoacoustic spectra of the coating, coating percentage, and frequency distribution of granule radii as inputs. The predicted release profiles were in good agreement with observations both for 'S' and inverse 'L' release patterns. LS-SVM model was effective and accurate in modelling nutrient release from a CRF population.

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1. Introduction

Controlled-release fertiliser (CRF) is used to increase fertiliser efficiency, minimise negative toxic effects of excessive fertilisation, e.g., greenhouse gases and, groundwater pollution, and reduce labour costs associated with fertilisation (Shaviv, 2001; Yang, Zhang, Li, Fan, & Geng, 2012; Xing & Zhu, 2000). Various coating materials have been used on fertiliser. Polymer coated fertilisers are currently the most popular commercialised CRF, as they offer good control over release profiles (Ahmad, Fernando, & Uzir, 2015; Du, Zhou, & Shaviv, 2006; Shen, Du, & Zhou, 2014).

Models are needed to ensure that polymer coated fertiliser is designed to supply available nutrient in synchronous with sequential plant needs. Models can be categorised into theoretical and empirical models. Theoretical models can elucidate the underlying physics, chemistry, and potential biological processes during the entire nutrient release process. They typically simulate nutrient release profiles at the single granule scale using detailed CRF parameters. However, the release profile determined for a CRF population is, in most cases, significantly different from the one expected for one single granule (Du, Zhou, Shaviv, & Wang, 2004; Shaviv, Raban, & Zaidel, 2003a; Shen, Du, Zhou, & Ma, 2015a). The large variation within a CRF population creates the differences, and the variation is primarily reflected in the distribution of granule radii and coating thickness (Shaviv, Raban, & Zaidel, 2003b). The weight of individual CRF granules can vary up to 38% (Takahashi & Ono, 1996). Significant differences in the coating thicknesses are generated if these

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Nomenclature

Symbols

R^2	Coefficient of determination
y_n	Cumulative release of the *nth* day (%)
y_m	Mean value of y_r (%)
y_r	Measured value of the i^{th} observation (%)
n	Number of observations
y_p	Predicted value of the i^{th} observation (%)
γ	Regulation constant
R^2_{cal}	R^2 of calibration
R^2_{pre}	R^2 of prediction
RMSE	Root-mean-square error (%)
RMSEC	Root-mean-square error of calibration (%)
RMSEP	Root-mean-square error of prediction (%)
RMSECV	Root-mean-square error of cross validation (%)
RPD	Ratio of percentage deviation
∂^2	Width of the radical basis function

Abbreviations

ANN	Artificial neural network
CRF	Controlled release fertiliser
FTIR	Fourier-transform infrared
LS-SVM	Least squares support vector model machines
MPO	Modified polyolefin
PULC	Polyurethane
RBF	Radical basis function
SD	Standard deviation

fertiliser granules are not sieved before coating because the coating thickness distribution strongly depends on the initial granule size distribution (Liu & Litster, 1993). In fertiliser release experiments or field conditions, a population of CRF granules, rather than one single granule, are more often used. Some researchers first established a theoretical model for a single CRF granule, and then scaled it to the CRF population by incorporating the distribution of granule radii and coating thickness via population statistics (Ko, Cho, & Rhee, 1996; Zaidel, 1996). However, complex population statistics prevent using these models in practical application.

Empirical models provide estimates of nutrient release from observed relationships between nutrient release profiles and factors influencing their release. These models are developed as first-order kinetic relationships (Hara, 2000; Ishibashi, Konno, & Kilmoto, 1992; Kochba, Gambash, & Avnimelech, 1990), two-stage linear relationships (Jarrell & Boersma, 1979) or simple functions of time (Broschat, 2008; Peppas, 1985). Du, Tang, Zhou, Wang, & Shaviv, (2008) and Lu et al. (2007) predicted urea release profiles from a CRF population based on an artificial neural network (ANN) and unified extreme analysis, respectively. However, these models did not contain the distribution of granule radii and coating thickness. We hypothesise that including both the distribution of granule radii and coating thickness within a CRF population will provide more precise estimates of nutrient release because the broad distribution of granule radii and coating thickness would change the actual nutrient release profile from this population. Existing models have been criticised either because they are too complex for actual applications, or because they have not taken into account the variation within a CRF population. Therefore, it is desirable to construct a simple and comprehensive empirical model to predict nutrient release profiles from a CRF population. The simulation accuracy is enhanced by introducing variation within a population.

The nutrient release profile from a CRF population is directly related to the fertiliser properties, coating material properties, coating percentage, distribution of granule radii, and distribution of coating thickness. There are two factors that influence the coating thickness. The first is the coating percentage between batches, i.e. the mass ratio of coating materials to the fertiliser core. In addition, the coating mass in the same batch is proportional to the initial particle size (Liu & Litster, 1993). Therefore, the distribution of coating thickness in the same batch is included in the distribution of particle size. Here, this study assumes that the fertiliser properties are consistent. The structure of the coating material determines its properties, which have been characterised by the Fourier transform of mid-infrared photoacoustic spectra. Least Squares Support Vector Machines (LS-SVM) have been introduced into the chemometric community to manage the linear and nonlinear problems (Cogdill & Dardenne, 2004; Sukens, Van Gestel, De Brabanter, De Moor, & Vandewalle, 2002). The powerfulness of LS-SVM in infrared spectral analysis has been verified in many studies (Borin, Ferrao, Mello, Maretto, & Poppi, 2006; Lu, Du, Yu, & Zhou, 2014; Shi et al. 2013).

In this study, LS-SVM were used to predict nutrient release profiles from a CRF population using the photoacoustic spectra of the coating, coating percentage, and frequency distribution of the granule radii as inputs, and the output layer was the CRF release profiles vectors. The model performance was evaluated by comparing the predicted release profiles with those obtained from experiments and theoretical models.

2. Materials and methods

2.1. Preparation of controlled release fertiliser

To prepare CRF, 400 g urea granules with diameters ranging from 3.25 to 5.75 mm were loaded into a Wurster fluidised bed equipped with a bottom spray pneumatic nozzle (LDP–3, Changzhou Jiafa Granulation Drying Equipment Co., Ltd., Wujin, Changzhou Shi, Jiangsu Sheng, China). The process parameters were as follows: 45 °C product temperature, 2.5 g min^{-1} spray rate, and 0.1 MPa atomisation pressure. Twenty-seven CRFs were obtained by varying the type of coating materials (polyacrylate-like) and coating percentage (6%, 8%, and 10% of total weight of coated urea granules). The fertiliser core and the coating process parameters were all identical while preparing the 27 CRFs. To remove the remaining water from the coating, the coated granules were tray-dried in an oven at 60 °C for 24 h before further evaluation.

2.2. Characterisation of controlled release fertiliser

Five grams of polymer-coated fertiliser were immersed in 100 ml of deionised water and maintained at 25 °C. Urea solution, 100 mL was removed at 1, 3, 5, 7, 10, 14, 28, 42 d and

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