Research article

Evaluation of the interactions between chitosan and humics in media for the controlled release of nitrogen fertilizer

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ABSTRACT

The aim of this study was to evaluate the interactions of peat, humic acids, and humin with urea dispersed in chitosan, in systems intended for the controlled release of urea. Spheres of chitosan with humic material and urea intentionally added to the media were prepared and characterized by means of elemental analysis (CHN), electron paramagnetic resonance (EPR), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). The spheres possessed functional groups related to humic substances that interacted with the chitosan, and the presence of urea in the media was also confirmed after it has been added. Release experiments demonstrated that the samples released urea in a controlled manner that was dependent on pH, increasing in the order: pH 2.5 < pH 4.0 < pH 9.0. In soil experiments, the degree of release of urea (α) increased over time, with values of 0.44 for chitosan-humic acids-urea (CHAU), 0.48 for chitosan-peat-urea (CPTU), and 0.67 for chitosan-humin-urea (CHMU) obtained in the first day of the experiment. The release of urea did not exceed 70% after 7 days. The results demonstrated the potential of using peat, humic acids, and humin, in combination with chitosan, in order to manufacture controlled release urea fertilizers and contribute to reducing adverse environmental and economic impacts.

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1. Introduction

According to the report of the Population Reference Bureau (PRB), the global population reached more than 7.1 billion in 2013, and is expected to reach 8.1 billion in 2025 and 9.7 billion in 2050 (PRB, 2013). Given these figures, the agricultural sector will play an important role in reducing and preventing hunger, linking population growth to the search for strategies to increase food production, which requires maximization of production yields. In intensive production systems, this involves greater inputs of chemicals for pest control and improvement of soil fertility. However, in excess, the substances used can have environmental impacts including the contamination of soils, freshwater, and oceans, as well as effects on biodiversity.

The improvement of soil fertility requires the use of fertilizers, which now play a key role in agricultural productivity and food security. Globally, experience has shown that fertilization is the most effective way of increasing food production (Xiang et al.,

2008; Yan et al., 2016). Among the types of fertilizers used, those that contain nitrogen are especially important because nitrogen (N) is one of the most limiting nutrients in soil and is essential for achieving high crop yields (Grant et al., 2012). Urea is one of the nitrogen fertilizers most widely used in agriculture, due to its low production costs, high N content (~46% N in the molecule) and low costs associated with transport and storage (Trenkel, 2010). According to the International Fertilizer Industry Association, around 60,700 tons of urea fertilizer were used globally in 2012 (IFA, 2015). Brazil was responsible for the consumption of around 1800 tons, corresponding to 2.9% of the total.

When excess nitrogen is present in the soil, it is liable to losses by volatilization, immobilization, denitrification, and leaching, before it can be absorbed by plants, leading to increased usage of fertilizers and detriment to the wider environment (van Loon and Duffy, 2011; Civardi et al., 2011; Ha et al., 2015). Given that the use of fertilizers in agricultural production systems is inevitable, technologies are required to improve the efficiency of nitrogen fertilizer use. A promising way to reduce the high costs associated with intensive application of this type of fertilizer and minimize environmental impacts is to use slow-release or controlled release

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fertilizer products (Xiang et al., 2008). Coating of fertilizer with hydratable, soluble, or biodegradable polymers is an effective way of providing controlled release of nutrients to the soil (Fukamachi et al., 2007; Roberts, 2008). However, drawbacks are the high costs involved, complex preparation procedures, and the fact that many commonly used polymer matrices are not biodegradable.

Chitosan, a copolymer of β-(1-4)-2-amino-2-deoxy-D-glucose and β-(1-4)-2-acetamide-2-deoxy-D-glucose, is obtained by alkaline deacetylation of chitin (2-acetamido-2-deoxy-β-D-glucose), which is found in crab and shrimp shells, exoskeletons of insects, and the cell walls of some fungi (Demetgul and Serin, 2008). Chitosan is inexpensive, biodegradable, and non-toxic, and is promising for use in controlled fertilizer release systems, especially when combined with materials with hydrophobic properties, such as humic substances.

Humic substances are complex heterogeneous mixtures of substances formed by chemical and biochemical reactions during the transformation of plant, animal, and microbial residues in a process called humification, with components such as polysaccharides, proteins, lipids, nucleic acids, and fine carbon particles participating in the process (IHSS, 2015). When the decomposition of tree and plant residues by microbial oxidation and humification occurs in flooded environments, such as swamps and marshes, an organic soil (peat) is continuously formed over millennial time periods (Orru and Orru, 2006; Romão et al., 2007).

The great diversity of polar and nonpolar functional groups in humic substances enables the formation of chemical bonds with metal and organic species (Batista et al., 2009; Costa et al., 2012). Humic substances can therefore be used to control the dissolution of urea and its subsequent availability in the soil. To date, there have been no reported studies concerning the use of humic substances from peat for the controlled release of urea. The aim of this work was to study the interactions of peat, humic acid, and humin with the chitosan biopolymer, in order to achieve the controlled release of urea fertilizer.

2. Experimental

2.1. Extraction and purification of humic acid and humin

The extraction and purification of humic acid and humin from the peat were performed according to the methodology proposed by the International Humic Substances Society (IHSS, 2015), using alkaline extraction with 0.1 mol L^{-1} NaOH for 4 h (1:10 soil/extractant ratio), under a nitrogen atmosphere. The soluble fraction (humic and fulvic acids) was acidified to pH 1, obtaining a precipitate of humic acid. Subsequently, it was dialyzed and then lyophilized. The humin was washed with deionized water, dried at 60 °C, and sieved through a 0.125 mm prior to the experiments.

2.2. Preparation of chitosan-humic substances spheres

A 4.0 g portion of powdered chitosan (74% deacetylated, Polymar Co., Brazil) was diluted in 100 mL of aqueous 5% (v/v) acetic acid and kept under mechanical stirring. A 2.0 g portion of peat, humic acid, or humin was added to the chitosan solution and then kept under mechanical agitation for 2 h. Subsequently, 5.0 g of urea was added to the medium, with agitation for a further 2 h.

The resulting suspension was added dropwise, using a burette, to an aqueous solution of 5% (m/v) sodium tripolyphosphate for formation of spheres of chitosan-peat-urea (CPTU), chitosan-humic acid-urea (CHAU), and chitosan-humin-urea (CHMU) (Ko et al., 2002). Spheres of chitosan (Ch), chitosan-humic acid (CHA), chitosan-peat (CPT), chitosan-humin (CHM), and chitosan-urea (ChU) were also prepared. All the materials were dried and then

characterized as described in Section 2.6.

2.3. Release experiments

The release of urea from the CHAU, CPTU, and CHMU samples was studied in static mode according to the methodology described by Mangrich et al. (2001), with modifications regarding the mass of the sample and the concentration of the aqueous solution of citric acid. Portions (0.20 g) of the spheres were placed individually in 200 mL of aqueous 0.01 mol L^{-1} citric acid solution at pH 2.5, 4.0, and 9.0 at 25 °C. A 1.0 mL aliquot of the solution supernatant was removed using a pipette at predetermined time intervals (between 5 and 1440 min) and submitted to the derivatization reaction for the determination of urea (described in Section 2.7).

The degree of release of urea (α) was calculated as the ratio of the concentration of urea at time (t) and the maximum urea concentration in the solution, as shown in Eq. (1):

$$\alpha = \frac{C_t}{C_{max}} \tag{1}$$

where C_t is the concentration of urea in the aqueous citric acid solution at time t, and C_{max} is the maximum concentration of urea in the aqueous citric acid solution (Adnadjevic et al., 2007).

2.4. Determination of parameters and release mechanisms

The urea release mechanism was evaluated by the nonlinear least squares and the sum of squares of residuals (SSR) statistical methods, applied to three different release models (Siepmann and Peppas, 2012; Peppas and Narasimhan, 2014) (Eqs. (2)—(4)), performed using Microsoft Office Excel 2010 software.

Higuchi model:

$$\alpha = k_H t^{0.5} \tag{2}$$

where α is the degree of urea release, k_H is the kinetic constant, and t is the release time.

Ritger-Peppas model:

$$\alpha = k_1 t^n \tag{3}$$

where α is the degree of urea release, k_1 is the kinetic constant, t is the release time, and n is the diffusion coefficient, which can be related to the urea release mechanism.

Peppas-Sahlin model:

$$\alpha = k_1 t^m + k_2 t^{2m} \tag{4}$$

where k_1 and k_2 are the kinetic constants, and m is the diffusion mechanism coefficient.

The Akaike Information Criterion (AIC) (Eq. (5)) was used:

$$AIC = N(\ln SSR) + 2p \tag{5}$$

where N is the number of experimental data points and p is the number of parameters of the model. The smaller the AIC value, the better the fit of the data to the model, enabling identification of the most appropriate urea release mechanism (Serra et al., 2006; Yamoaka et al., 1978).

2.5. Application of the of chitosan-humic substances-urea spheres in soil

The release of urea from the CHAU, CPTU, and CHMU spheres was also evaluated in soil, using the methodology proposed by