



# Slow release fertilizers based on urea/urea–formaldehyde polymer nanocomposites



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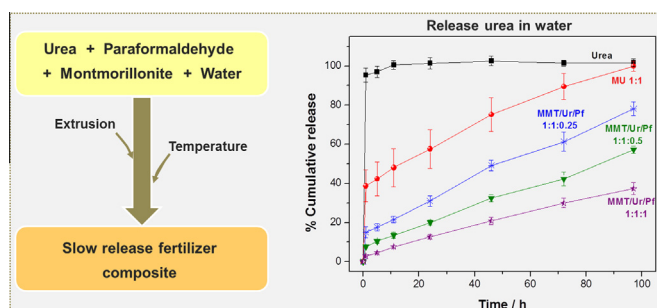
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## HIGHLIGHTS

- Urea–formaldehyde in the presence of MMT is effective to obtain fertilizer.
- Fertilizer nanocomposites were produced by cold plastic extrusion.
- Fertilizer nanocomposites presented good mechanical resistance.
- Efficient results were found in water-solubility and soil incubation tests.
- Intermediate urea–paraformaldehyde molar ratio showed most efficient results.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel nanocomposite material based on the exfoliation of montmorillonite into a matrix of urea/urea–formaldehyde polymer was developed to be used as nitrogen-loaded slow release fertilizers. The nanocomposites were produced by cold plastic extrusion, a simple and high-productive method, using a formaldehyde precursor to accomplish polymerization *in situ* during extrusion processing. Characterizations showed that the extruded fertilizer nanocomposites presented good mechanical resistance, and that the urea release was noticeably controlled by the extent of polymerization. Water immersion experiments demonstrated that the nanocomposite structure was responsible for the effective slow urea release behavior. A dependence of the availability of other nitrogenous compounds ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) on the polymerization degree was also demonstrated by soil incubation tests. The urea/urea–formaldehyde polymer nanocomposites were found to be versatile and smart materials capable of supplying the enormous demand for novel efficient nitrogen fertilizers.

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## 1. Introduction

The growing use of fertilizers has enabled high gains of productivity in agriculture. However, the growing price of these inputs has led to an increasing cost in the crops production. From an economic point of view, urea ( $\text{CO}(\text{NH}_2)_2$ ) is one of the most

important commercially available nitrogenous fertilizers [1]. Its application at a pristine form to soil involves significant losses of nitrogen through volatilization of  $\text{NH}_3$  to atmosphere and emission of greenhouse gases (GHG) [2].

In recent decades, the enormous demand for fertilizers and the urgent need for a more efficient use of these materials, have led to development of various types of so-called controlled or slow release fertilizers (SRFs). SRFs is a class of fertilizers whose fundamental role is to release nutrients to the soil for a period of time

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longer than a conventional fertilizer so that nutrient availability for absorption by plants is substantially prolonged. In an earlier report, we have developed a nanocomposite based on dispersion of montmorillonite (MMT) within a urea matrix, and this hybrid material exhibited slower dissolution compared with pristine urea, which allowed a better control of the fertilizer release due to a hindered diffusion of urea through the nanocomposite structure [3]. The MMT/Urea nanocomposites presented good potential for practical uses, since it was comprised of small granules, thereby being suitable for application as solid material on soil. However, these nitrogenous nanocomposites presented low mechanical strength and poorly understood relationship between clay content and final nitrogen release behavior, which have motivated further research in order to obtain SRF materials with optimized performances.

Urea–formaldehyde (UF) polymer has attracted special interest among other products tested for controlled release of nitrogen to soil. UF-based products belong to the first group of materials especially developed for slow release of nitrogen [1]. It has been shown that agricultural use of this organic polymer occurs at stages similar to those adopted for urea [4–7]. Based on patent search, it was identified some related documents, such as WO2013090287-A1 [8], WO2011137393-A1 [9], WO2010093462-A1 [10], US2008141747-A1 [11], US2006196241-A1 [12], US2005144997-A1 [13]. Some of these patents comprise liquid compositions made up of urea formaldehyde resins, as for example the US2006196241-A1 document, which relates to a fertilizer product corresponding to a liquid composition where urea formaldehyde is one of the possible components; other patents describe formulations of particulate urea formaldehyde polymers (such as the WO2010093462-A1 document); and a third group of patents relates to granulate fertilizers produced by the mixture of different components in urea formaldehyde resin, which are solidified to obtain the final material (US2008141747-A1 document, for instance). Despite these products have some features similar to our proposed material, the main difference lies on the application of a liquid, pre-formulated urea formaldehyde resin. However, the preparation of UF granules at large scale is generally complex because it involves reactions in liquid medium where the control of polymerization is essentially done by the molar ratio between components. Formaldehyde solutions, commonly used as a precursor, contain 70–73% of water (by weight), which hinders their processing by methods such as extrusion. Furthermore, the low solubility of UF polymer has led to extremely low rate of nitrogen release in several practical applications. Therefore, it is highly preferable the development of fertilizer products with complex architectures comprised of partially polymerized urea, urea-rich domains limited by structural barriers and easily available urea. In this sense, the relative contents of UF/unreacted urea could be used to adjust the final profile of urea release for a specific agronomical application, thereby resulting in an intelligent fertilizer. To the best of our knowledge, composite materials based on UF/unreacted urea have not been supplied to the fertilizer market yet.

Hence, we report in this paper a strategy to prepare nanocomposite fertilizers based on urea–formaldehyde polymer (UF)/unreacted urea and montmorillonite (MMT) exfoliated at nanoscale using a formaldehyde precursor (paraformaldehyde) to polymerize UF *in situ*. This hybrid nanocomposite fertilizer was prepared through cold plastic extrusion, a simple and high-productive method, where MMT not only acted as a processing agent (plasticizer), but also as a structural component and diffusional barrier against urea dissolution. Our results show that this intelligent material, due to its easy processing and versatile polymerization control, may be a promising strategy to produce complex granules with adjusted dissolution, and possibly to be used as a carrier of other nutrients such as  $K^+$  and  $PO_4^{3-}$ .

## 2. Materials and methods

### 2.1. Materials

The raw materials used in the nanocomposite formulations were: urea AP (Synth), paraformaldehyde (Sigma–Aldrich) and montmorillonite clay (Bentonita, Drescon S/A – Produtos de Perfuração). Urea was previously milled to a mesh grain size of 300  $\mu$ m in a TE-330 hammer mill (Tecnal, Brazil). All the other materials were used as received.

### 2.2. Preparation of nanocomposites

Nanocomposites were prepared with a fixed montmorillonite: urea (M/U) weight ratio of 1:1, and at different urea:paraformaldehyde (U/Pf) molar ratios of 1:0.25, 1:0.5, and 1:1. Urea–formaldehyde polymer is formed by reaction of formaldehyde with an excess of urea with conditions of pH, temperature, molar ratio, reaction time, etc., well controlled [1]. This reaction basically consists in a stepwise mixing of urea and formaldehyde with subsequent release of water. Urea suffers hydroxymethylation under both acidic and alkaline conditions, and the formation of urea–formaldehyde (UF) occurs by condensation of these hydroxymethylated compounds. Paraformaldehyde is the polymer of formaldehyde with a degree of polymerization between 8 and 100. This polymer depolymerizes into formaldehyde in presence of water and heating [14]. Thus, the use of paraformaldehyde allows minor addition of water to the MMT/Urea formulations, leading to a better control of plasticity in the extrusion process.

The nanocomposites were prepared through the following steps: pre-mixing, extrusion, shaping and curing. The precursor materials (montmorillonite, urea and paraformaldehyde) and water (15 wt.%) were pre-homogenized and then extruded at 35 °C in a counter-rotating double screw extruder (Coperion Werner and Pfleiderer) running at 60 rpm. Part of the extruded mass was pelletized and another part was molded into standardized specimens to conduct mechanical test. The optimum amount of water used in the preparation of nanocomposites, to achieve adequate plasticity, was beforehand determined by torque rheometry. After shaping, the samples were cured at 80 °C in an oven for 12 h, and subsequently stored at 90 °C until complete drying. The nomenclature given to each composition is listed in Table 1.

### 2.3. Characterizations

#### 2.3.1. X-ray diffraction (XRD)

X-ray diffractograms were registered using a XRD 6000 diffractometer (Shimadzu, Japan), in order to verify occurrence of montmorillonite exfoliation due to the shear processing. Relative intensity of diffraction was registered in the angular range ( $2\theta$ ) of 3–40°, using a Cu K $\alpha$  incident beam ( $\lambda = 0.1546$  nm) and scanning speed of 1° min<sup>-1</sup>. The voltage and current of the X-ray tube were 30 kV and 30 mA, respectively. The basal spacing ( $d$ ) of montmorillonite was calculated using the Bragg equation,  $n \cdot \lambda = 2 \cdot d \cdot \sin \theta$ , where  $n$  ( $= 1$ ) is the reflection order and  $\theta$  angle of diffraction.

**Table 1**

Nanocomposites and their nomenclatures. The raw materials used were identified by their initial letters: M – montmorillonite, U – urea and Pf – paraformaldehyde.

Nomenclature	Mass ration M:U	Molar ration U:Pf
M/U 1:1	1:1	–
M/U/Pf 1:1:0.25	1:1	1:0.25
M/U/Pf 1:1:0.5	1:1	1:0.5
M/U/Pf 1:1:1	1:1	1:1

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