Urea−Montmorillonite-Extruded Nanocomposites: A Novel Slow-Release Material

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ABSTRACT: The present study describes the preparation and characterization of a novel urea slow-release nanocomposite, based on urea intercalation into montmorillonite clay by an extrusion process at room temperature. Nanocomposites with urea contents ranging from 50 to 80 wt % were successfully produced and characterized. Analyses by XRD, DTA, and SEM-EDX confirmed the effectiveness of this simple process to exfoliate the clay lamellae into the urea matrix, forming a product that can be classified as a nanocomposite, due to the exfoliation degree attained. Diametral compression tests showed that the samples were very deformable, and the release rate of active components in water showed that the nanocomposite showed a slow release behavior for urea dissolution, even in low montmorillonite amounts (20% in weight).

KEYWORDS: urea, fertilizer, montmorillonite, extrusion, intercalation

INTRODUCTION

The efficient use of mineral fertilizers to supply the demand for macronutrients (nitrogen, phosphorus, and potassium) is a key aspect in the productivity of agriculture, and several commercial options are available today. Among the molecules widely applied for nitrogen delivery, one of the most interesting from an economic standpoint is urea, $CO(NH_2)_2$. However, effects such as ammonia volatilization and nitrate leaching reduce the effectiveness of this fertilizer when applied to alkaline or coarse-textured soils, respectively .[1] Therefore, several alternatives have been studied to control the urea supply to reduce these losses.

Among the alternatives reported in the literature, the application of zeolites as a control system for urea release is well documented. These materials have, as main characteristics, high surface area and high cation exchange capacity, >2 mequiv g^{-1}. Therefore, these materials can be used to hold exchangeable cations such as ammonium (NH_4^+) derivate from the hydrolysis of urea.[2] Recent works by Zwingmann and collaborators[3,4] have shown the potential of mesolite zeolite in the retention and release of NH_4^+ and also K^+ cations.

However, as the availability and cost of zeolites, particularly in Brazil, may preclude their widespread use, alternative formulations are required to improve the efficiency of applied urea in granular form. Natural aluminosilicate clays, which are cheaper and more widely available than zeolites, also have cation exchange properties that could be usefully substituted for zeolites to improve the efficiency of urea. Clay minerals are hydrated layered silicates, able to exchange cations, and intercalate neutral molecular species between the interlayer regions by interaction with structural water. Montmorillonites are the most abundant minerals within the smectite group (2:1 clay minerals) and the determinant component in bentonites. They can be compact but, mostly, they are foliated.[5−7]

This material, contrary to many zeolites, may be properly processed by extrusion,[8] because this clay presents good plasticity, mainly driven by attraction forces between clay lamellae and the lubricating action of water present between the lamellar particles.[9,10] This process is quite attractive due to the use of minimal amounts of water, which reduces production costs related to drying. In the specific case of such clays, the process may be carried out at low temperatures, which is important in the case of urea due to the undesirable conversion for biuret.[11−13] Finally, the process is also attractive due to its ability of produce granules of adjustable size in a continuous process with very high outputs.

The present study, therefore, describes the preparation and characterization of slow-releasing nanocomposites based on montmorillonite intercalation into an urea matrix by a simple and fast extrusion process at room temperature, which can produce high nitrogen content granules and retard the release of N to various degrees.

MATERIALS AND METHODS

Materials. The raw material used as basis for the nanocomposite formulation was urea ($(NH_2)_2CO$, Synth) and montmorillonite clay without purification (Bentonita, Drescon S/A, Produtos de Perfuração). Clay material (average particle size of 230 nm) was used as received, and the chemical composition obtained by X-ray fluorescence spectroscopy (SGS Geosol Laboratórios Ltda, Brazil) is listed in Table 1. Urea was previously ground in a hammer mill (Tecnal, TE-330) to be used in all of the processes described below.

Table 1. Chemical Composition of Bentonite Clay

component	% component
SiO_2	57.50
Al_2O_3	18.30
Fe_2O_3	8.23
CaO	0.71
MgO	2.62
Na_2O	2.49
trace	1.89
loss of ignition	7.18

Preparation of Nanocomposites. Nanocomposites were prepared at different ratios (w w^{-1} basis) of clay (montmorillonite)/urea, that is, 1:1 (50% urea), 1:2 (66% urea), and 1:4 (80% urea). The preparation of the composites consisted of three steps: mixing, extrusion, and drying.

Montmorillonite and urea were separately weighed and premixed, and water at 25 °C was added to complete the mixture. The optimum water content (appropriate plasticity) was determined by torque rheometry (described under Plasticity Test Using Torque Rheometer). The materials obtained were extruded in a twin-screw extruder (Coperion Werner and Pfleiderer) at 35 °C and converted into pellets with 3 mm diameter per 5 mm height, as illustrates in Figure 1. The materials were dried at room temperature for 48 h in darkness.
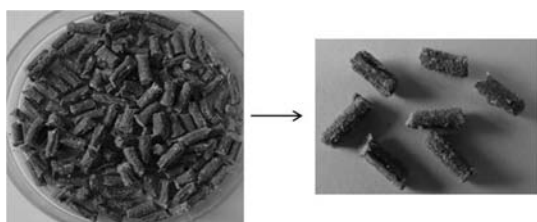

Figure 1. Images of composites obtained in the form of pellets in a twin-screw extruder.

The composites were designated Mt/Ur 1:1, Mt/Ur 1:2, and Mt/Ur 1:4, being the ratio (w w^{-1}) of urea and montmorillonite, respectively. The pure montmorillonite was designated Mt.

Characterization. *Plasticity Test Using Torque Rheometer.* Clay becomes plastic, suitable for extrusion, when it contains minimal amounts of water to develop capillary forces between the individual particles in the mixture. This content was determined by a test based on torque rheometry. Different amounts of water were added to pure Mt and also to the different Mt/Ur mixtures and then placed in the mixing chamber so that the resistance to shear (which is displayed in terms of torque) could be measured as a function of time. The test was performed using an internal chamber mixer Haake, with a base unit Polylab Rheodrive 4, and mixer Rheomix OS4 equipped with rotors of the "roller" type. As the mixing head is volume-sensitive, the amount loaded (about 70 g) was about 50% of the capacity, considering the volume of the cavity and density of the material. The formulations were then processed at 35 °C with the roller-type rotors operating at 60 rpm, for approximately 5 min. The profiles of the torque curves were recorded during the processing using software Polysoft OS. Then a curve of stable torque versus percentage of water for each material was drawn, from which was determined the amount of water to be added to obtain the ideal point of plasticity of the mixture.

X-ray Diffraction. X-ray diffractograms of the composites were obtained using a Shimadzu XRD 6000 diffractometer. The relative intensity was registered in a diffraction range (2θ) of 3–40°, using a Cu Kα incident beam (λ = 0.1546 nm). The scanning speed was 1°/min, and the voltage and current of the X-ray tubes were 30 kV and 30 mA, respectively.

The corresponding d interplanar spacing of the Mt and composites (from the position of a peak) was computed from Bragg's diffraction equation

$$2d \sin \theta = n\lambda \qquad (1)$$

n (= 1) being the order of reflection and θ the angle of refraction.

Thermal Analyses. Thermogravimetric analyses were carried out on TGA Q-500 equipment (TA Instruments, USA). The samples were heated from room temperature to 600 °C, at a 10 °C/min rate, under air flow.

SEM-EDX Measurements. The morphology and relative elemental concentration of the samples were analyzed by means of scanning electron microscopy (SEM) (JEOL microscope, model JSM 6510) equipped with an energy dispersive analysis system of X-ray spectrometer-EDX (Thermo Scientific NSS coupled or linked). The sample was dispersed over a carbon tape pasted on the surface of a metallic disk (stub). Then, the disk was coated with gold in an ionization chamber (BALTEC Med. 020) and analyzed.

Diametral Compression Tests. Diametral compression tests were conducted at a constant rate of 10 mm min^{-1} until a maximum deformation of about 70% or the ultimate limit of the load cell (50 N) (EMIC/DL-3000 equipment). The tests were performed at room temperature. The load values were digitally recorded at the control unit. The results were obtained from an average of 15 specimens, and the standard deviation was calculated for the maximum stress value (σ) and for the elasticity modulus (E) (see Table 3). For this test commercial urea as granules was used as a reference.

Release Rate of Active Components in Water. A test in aqueous medium was performed, adapted from Tomaszewska and Jarosiewicz,[14] where the release rate of urea as a function of time at room
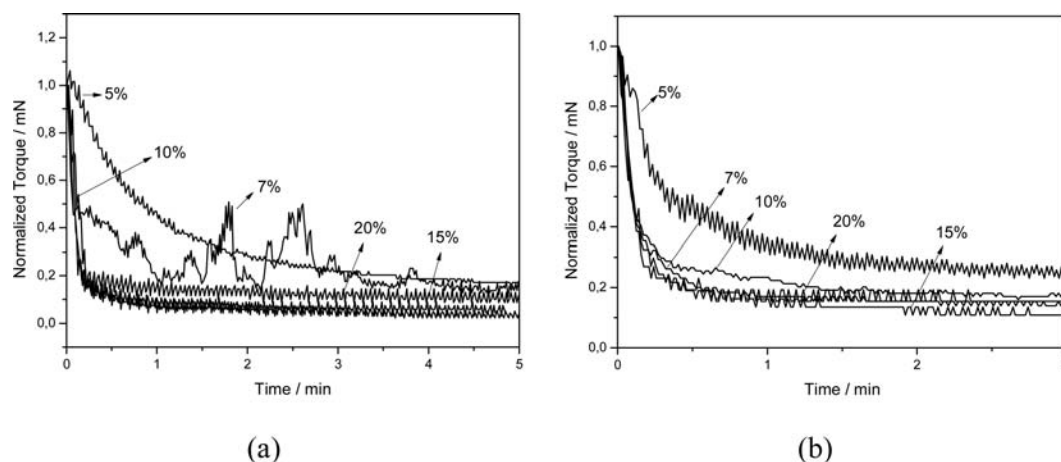

Figure 2. Curves of torque versus time, Mt (a) and Mt/Ur 1:1 (b), varying the percentage ratio by mass of water.

temperature was compared for each of the composites. An apparatus was designed in which a known mass of the material was placed in a beaker immersed in aqueous medium, with external stirring to beaker, to ensure that the content of urea measured in the liquid medium corresponded to the diffusion into the middle and not the mechanical action of the stirrer. The beakers were sealed with plastic wrap to reduce evaporation losses. Aliquots of 1 mL were collected and centrifuged (15 min at 14000 rpm, MiniSpin Plus) at different time intervals, over 5 days. The maximum level of urea added in each experiment was the same; that is, different mass values for the composites were calculated so that each experiment had the same amount of urea. For comparison, a test with pure urea also was performed as a control experiment. The determination of urea concentration in solution was done by UV–vis spectrophotometry (Shimadzu-1601PC), according to the method of With et al.[15] Thus, a curve of urea concentration in solution versus release time was obtained. Each experiment was replicated for five samples of each system, in simultaneous measurements done under the same laboratory conditions for all of the samples, to guarantee identical laboratory conditions. As a reference, for pure urea and for the 1:1 nanocomposite, a second similar experiment was performed, however, separating the granule from the water by a dialysis membrane (Cellulose MC-30, Sigma-Aldrich) to avoid the clay dissolution and separate possible solution equilibrium effects.

■ RESULTS AND DISCUSSION

The first analysis was the Mt plasticity, using a torque reomether, which is shown in Figure 2. Urea significantly increased the plasticity of the montmorillonite and reduced the water required for processing. It is observed by the final torque for each condition that for pure Mt (Figure 2a), the stable torque was attained for the mixtures with 10% humidity, whereas in 7% humidity the system presented a very unstable behavior, characteristic of the minimum water necessary for plasticity development.[16,17] On the other hand, a 1:1 mixture (Figure 2b) showed a very stable and plastic behavior with 7% water, indicating the plasticizing effect of urea. For higher proportions (1:2 and 1:4) plasticity was observed even for mixtures with 5% humidity (not shown here). This plasticity induced by urea is a good indication of the intercalation of the urea into the interlamellar spaces. The urea intercalation alters the system "clay + water" because the forces of interaction or binding between particles are altered,[10] changing the necessary applied shear and, consequently, the viscosity.

Because the stable torque was observed for humidity values below 8% for the 1:1 mixture, this value was arbitrarily assumed for a production of the composites. To monitor the exfoliation and intercalation of urea into the clay after the processing, the materials were analyzed by XRD, as shown in Figure 3. The analyses were conducted to study the interlamellar distance, monitored by the displacement of the diffraction angle d_{001} characteristic of basal separation on Mt. According to Bragg's law, the diffraction angle θ and the interplanar distance d are inversely proportional; a decrease in diffraction angle means an increase in the interplanar distance. As shown in Figure 2 the position of the d_{001} peak ($2\theta = 6.6°$) showed a substantial shift to low angle, suggesting a change in the interplanar spacing of the matrix clay.[18] The interplanar expansion observed, with respect to Mt ($d = 1.34$ nm) for all of the composites ($d = 1.93$ nm, independent of the ratio Mt/Ur), was about 0.59 nm. This expansion confirmed the intercalation of urea in the inter-lamellar spaces.[19] However, it is important to note that the absence of any difference between 1:1 and 1:4 mixtures indicates that the separation of lamellar structures was maximized using 1:1 mixtures.
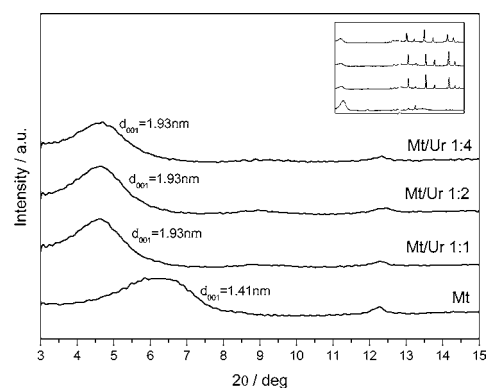

Figure 3. X-ray diffraction (XRD) patterns of the Mt and of the nanocomposites Mt/Ur 1:1, Mt/Ur 1:2, and Mt/Ur 1:4.

Thermogravimetry was used to evaluate the thermal stability of Mt and urea intercalated samples during thermal decomposition of solid materials. The thermogravimetric (TG) and derivative thermogravimetric curves (DTG) are shown in Figure 4, panels a and b, respectively. Chen and Isa[20] applied simultaneous thermogravimetry and mass spectrometry to the investigation of the decomposition of urea and concluded that this compound has a complicated behavior of thermal decomposition. In Figure 4a the four most significant stages of decomposition are observed, which starts before the melting point (132.5 °C) until the complete oxidation of the sample. With regard to pure Mt, it hardly decomposes at temperatures below 600 °C, and about 95 wt % residues are left at 600 °C. The initial loss (between 25 and 150 °C) is related to dehydration of adsorbed water (nonconstitutional water), interlayer water, and water coordinated to exchangeable cations (structural water). The mass loss above 350 °C corresponds to elimination of structural hydroxyl and organic matter.[10,21] However, on the nanocomposites the thermal degradation behavior is almost dominated by the urea degradation, showing the same degradation temperatures on DTG curves, except for the 1:1 mixture. In this condition, which is the maximum Mt content with regard to urea in this study, a significant reduction of 17 °C (from 212 to 195 °C) in the first degradation temperature was observed, indicating that the interaction with Mt reduced the urea crystallinity, imposing a slight reduction of the melting temperature. Actually, in higher urea contents, a large part of the material is unlinked to Mt, and free degradation was observed. Also, it is important to note that in all of the nanocomposites, the final residue after 600 °C corresponds to the initial Mt content expected.

SEM was applied to analyze the morphological aspects of pure Mt and nanocomposites (Figure 5). One may observe morphology changes (Figure 5a) after the formation of the composites (SEM images Figure 5b–d). This modification, after processing, may be related to the urea intercalation in clay, corroborating the XRD data. In fact, the lamellar structure related to Mt is observed even in the condition of 1:4, separated by a large amount of undefined material, identified here as crystallized urea. Actually, in some images it is possible to identify void spaces probably related to the detachment of urea crystals during the sample preparation. It is clear that the urea fraction is crystalline, which supports the hypothesis of a urea matrix with Mt as a disperse phase, consistent with interlamellar displacement observed in XRD analyses (Figure 5). The identification of urea and Mt regions was performed by EDX, as
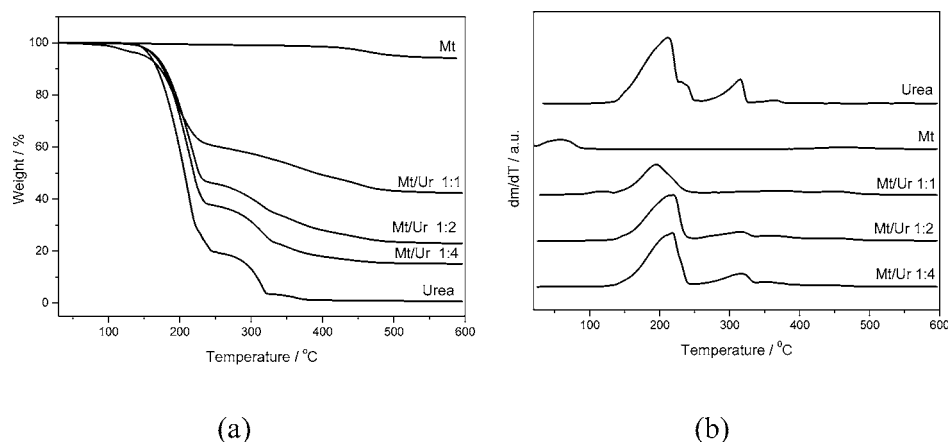
Figure 4. Thermogravimetric curve (a) and derivate thermogravimetric curve (b) of Mt, pure urea, and the nanocomposites Mt/Ur 1:1, Mt/Ur 1:2, and Mt/Ur 1:4.
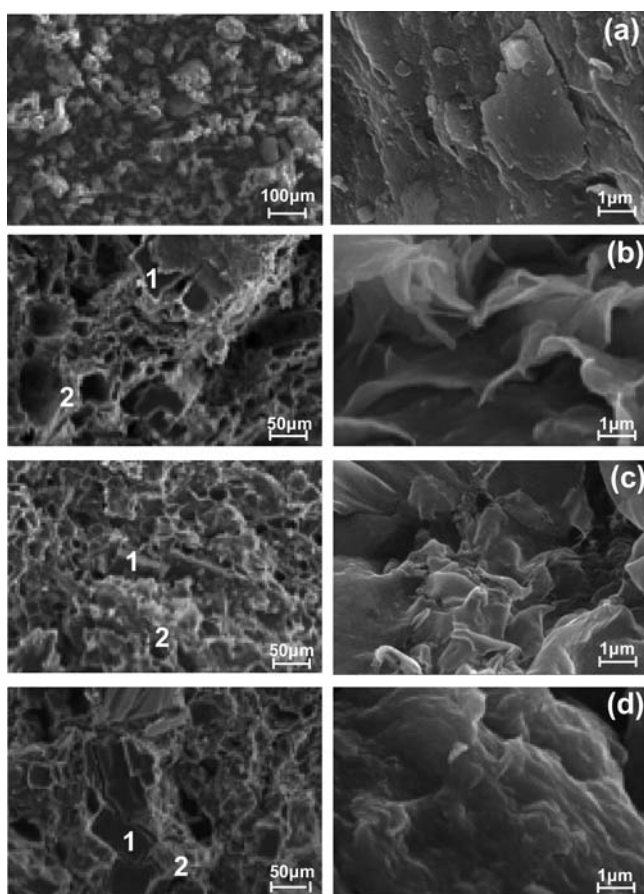

Figure 5. SEM images of (a) Mt and the nanocomposites (b) Mt/Ur 1:1, (c) Mt/Ur 1:2, and (d) Mt/Ur 1:4. Magnification of 500 (left) and 20000 (right).

Table 2. Ratios of C, N, O, Al, and Si in the Composites (Marked by Numbers in Figure 5) Measured by EDX in Atomic Percent

	C	N	O	Al	Si
		Mt/Ur 1:1			
P1	5.2	21.8	14.0	3.9	5.1
P2		1.8	35.1	16.5	33.9
		Mt/Ur 1:2			
P1	3.7	17.7	16.2	7.0	11.2
P2	2.8		23.6[a]	12.8	28.5
		Mt/Ur 1:4			
P1	4.7	21.3	14.3	4.0	6.5
P2	0.2	2.4	25.5	12.6	27.3

[a]The value corresponds to the sum of O and N signals.

Table 3. Values of Mechanical Parameters

	σ^a (MPa)	E^b
urea	2.083 ± 0.4507	3.32 ± 1.45
extruded Mt	12.32 ± 13.71	6.00 ± 1.90
Mt/Ur 1:1	>35.13 ± 3.627	0.99 ± 0.64
Mt/Ur 1:2	>31.24 ± 3.516	1.06 ± 0.51
Mt/Ur 1:4	>33.20 ± 3.495	2.01 ± 0.90

$^a\sigma$ = stress. $^b E$ = elasticity modulus.

By the above results, one may propose a path of the urea intercalation in the extrusion process, as shown in Figure 6. At the first urea loadings, the solubilized material intercalates in clay platelets, properly forming the composite. However, the subsequent additions do not interfere with the Mt separation, but will crystallize independently, forming some small urea crystals, which can grow by adding more urea into the process.

A comparative analysis of the mechanical resistance of the granules was performed by diametral compression, because this property is very important for the practical application as a fertilizer material. As observed in Figure 7, the behavior of a urea granule is similar to that of a fragile material, with poor plasticity and fracturing at low pressure. On the other hand, all of the nanocomposites were very deformable, without rupture even until the maximum deformation supported by the equipment. It is noticeable that this behavior can not be assumed to be solely due to the Mt structure, because the same analysis in the pure Mt extruded revealed a low mechanical resistance. However, the similarity among the three nano-
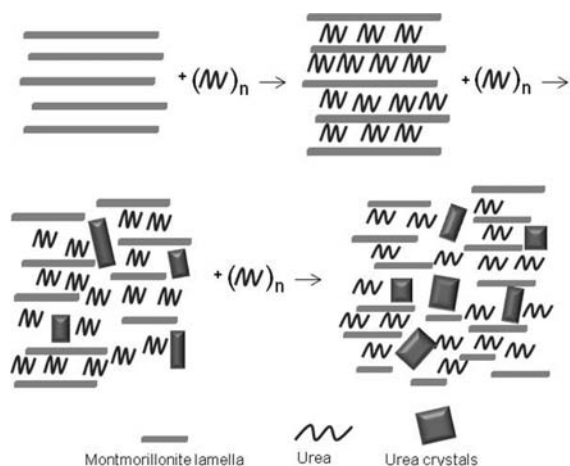
shown in Table 2. The ratios of Si, Al, C, N, and O content in atomic percent in the individual points marked according Figure 5 are summarized in Table 2. The regions labeled "1" in the SEM images correspond to urea crystals redispersed, because the elements detected are predominantly N, C, and O, that is, urea constituents. On the other hand, the regions labeled "2" correspond to urea-intercalated Mt, because significant amounts of Si and Al (clay constituents) and smaller N amounts were detected.

Figure 6. Scheme of the proposed path for urea intercalation in the extrusion process.

Figure 8. Release rate of urea as a function of time for pure urea and each of the composites at pH 7 and room temperature.

composites is noteworthy, with negligible differences observed between them. This suggests that the mechanical behavior is dominated by the intercalated fraction of the material, which deforms continuously when solicited. This is an interesting behavior for the practical use of those materials, because fragile granules are more prone to produce dust during application, which may be avoided or minimized by the nanocomposite materials.

Figure 8 shows the urea release for the three produced nanocomposites compared to urea release. The urea dissolution occurred in <1 h, due to the solution saturation around the urea granule. We performed a reference test, by mixing (without extrusion) a composition of 1:1 montmorillonite/urea, that is, where the clay was not properly exfoliated (not shown here). In this case, the liberation test in the same conditions of the extrude granules did not shown any influence of the clay in urea retention, with almost the same profile of pure urea dissolution, as shown in Figure 8. This profile probably is related to the fact that any interaction of montmorillonite and urea would occur in longer times, because the compound would need to adsorb in montmorillonite platelets after its dissolution. Then, in this very aggressive test condition (immersion in water), any difference could be observed. In fact, this also shows the importance of exfoliation to the controlled release.
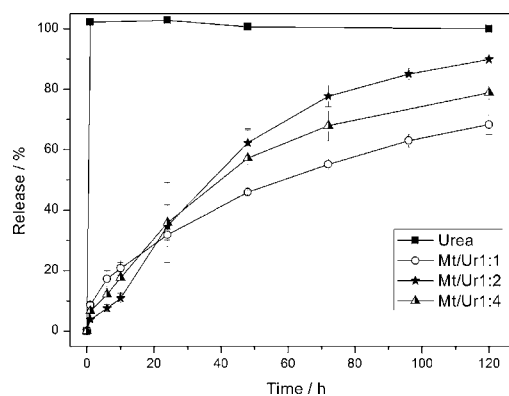
However, by comparing the nanocomposites, one can note that all of the formulations retarded urea release for up to 120 h. It was very important to note that this dissolution experiment was very aggressive, because a complete immersion of the produced materials in water is done. Even in this aggressive condition, the release is comparable to other controlled release systems with very different action principles, as observed by Tomaszewska and Jarosiewicz[14] (for some polymeric coatings applied in urea granules) or in PMMA hydrogels, as reported by Bortolin et al.,[22] denoting that those values obtained for the nanocomposites are promising. In conventional application, the materials would be exposed to low water contents, and one can expect a better retention effect by the nanocomposites.

A particular aspect is the different kinetic behavior observed for each system. There was not a clear correlation between the total Mt in the nanocomposite and the total urea released. In fact, the 1:1 formulation caused higher urea retention, but only small differences were observed using the 1:2 and 1:4 mixtures. This may mean that the effect of the Mt clay in minor quantities is less considerable, but, in any case, it is very important to note that even those nanocomposites showed slower release when compared to pure urea.

To separate possible solution equilibrium effects, a second experiment to measure urea release was performed, comparing pure urea and formulation 1:1 when protected by a dialysis membrane. In this case, one can consider that the osmotic pressure between the inner and outer parts of the membrane
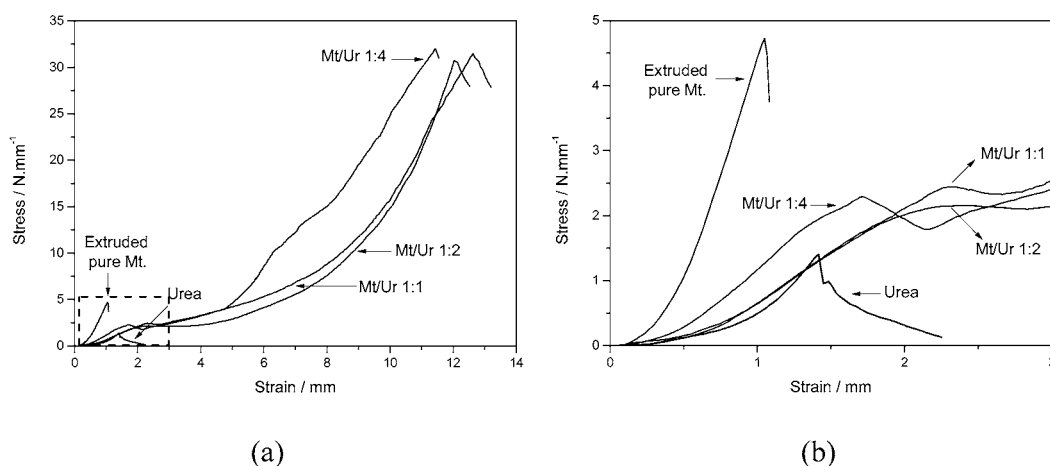

(a)

(b)

Figure 7. Stress–strain curves for the pure urea and for the Mt/Ur composites.

would eliminate the reduction of urea release by equilibrium with the solution. Under these conditions pure Ur dissolution was fast, being complete in <1 h (Figure 9). However, the 1:1
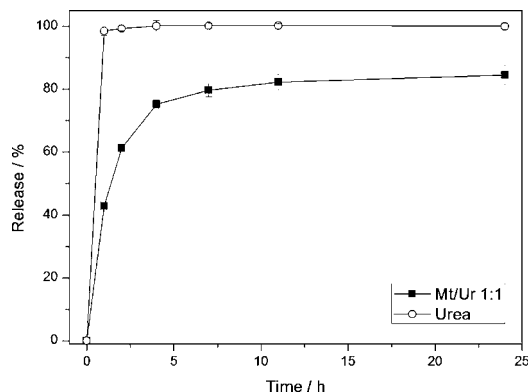

Figure 9. Release rate of urea as a function of time for pure urea and of the composite Mt/Ur 1:1 at pH 7 and room temperature, protected by a dialysis membrane.

formulation had a slower dissolution and was complete only after 8−10 h, indicating the intercalation of the Mt clay was effective. It can be proposed that the Mt action over the urea release is due to weak adsorption, because the compound is not ionic. Then, the interactions should occur due to dipolar interactions over the negative Mt surface.

In summary, we described a simple and fast method to produce a nanocomposite based on the intercalation of Mt clay into urea, at different proportions. The process, based on conventional ceramic extrusion, does not involve application of heating, extensive previous preparation of the Mt/Ur mixture, or addition of granulating or plasticizing agents. Also, the presence of urea acted as a dispersant for Mt clay, requiring only low water contents to be processed. The nanocomposite showed a slow release behavior for urea dissolution, even in low Mt amounts, which is a very important result for its application as a slow-release fertilizer.

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Notes
The authors declare no competing financial interest.

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