



Research paper

Controlled release of nitrate from hydrotalcite modified formulations

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ABSTRACT

Different nitrate controlled release systems based on modified hydrotalcite-like LDH (LDH) have been investigated to reduce environmental pollution derived from nitrogen-fertilizer use. A synthesized nitrate-hydrotalcite was modified with hydroxypropyl methylcellulose (HPMC) in different proportions and two types of systems were prepared: a) granules with a LDH/HPMC 5/1 proportion and three different sizes (200 μm , 500 μm and 1 mm) and b) tablets with three different proportions of LDH/HPMC (5/1, 5/0.5 and 5/0.25). In order to determine the release rate of the active ingredient, we carried out the release experiments as a function of time in water and in a simulated soil solution. In both experimental conditions (decarbonated water and simulated soil solution), the LDH/HPMC 5/0.5 system produces the slowest release rate of nitrate than the other two systems. Using the Ritger and Peppas equation, the T_{50} parameter was calculated. The average values ranged from 8.7×10^{-4} h and 12.3 h for the granules system in simulated soil solution and decarbonated water respectively, up to 17.6 and 54.5 h for the tablet system, in simulated soil solution and decarbonated water, also respectively. From the analysis of these data, it could be deduced that the release rate of nitrate can be controlled mainly through the shape of the formulations, the tablets being more effective than the granules.

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1. Introduction

Almería province (south-eastern Spain) is considered one of the driest regions of Europe. Despite of this, greenhouse intensive agriculture in this area is one of the most evident demonstrations of the change that this region has undergone over the past few decades. This vegetable production system has expanded rapidly along the Spanish Mediterranean coast in the last 30 years. There are currently 45,000 ha of greenhouses, with 27,000 ha in the province of Almería (Castilla and Hernández, 2005).

In order to maintain a high crop production, the use of fertilizers is necessary; so large amounts of synthetic nitrogen fertilizers, such as urea, ammonium nitrate, liquid nitrogen fertilizer or commercial complex fertilizers with different proportions of nitrogen, are applied.

Several reports in recent years indicate a worst water quality and that nitrate contamination is a serious problem that not only affects the aquifers in southeastern Spanish but also is a common problem in rural regions around the world, where the levels of nitrates significantly exceed the established by the Food and Agriculture Organization of the United Nations (FAO) (Kendall and Aravena, 2000; Semaan et al., 2007; WHO, 2006).

Furthermore, it should be noted that the environmental damage owing to the fertilization with nitrates is not just limited to the water environment, but it has been shown that the nitrogen compounds in the soil, play an important role in the emission of nitrous oxide into the atmosphere, thus contributing to climate change with the intensification of the greenhouse effect as well as the destruction of the ozone layer in the stratosphere (Jassal et al., 2008; Meijide et al., 2007; Sanz et al., 2007; Vallejo et al., 2004).

Therefore, it is clearly necessary to develop practices that contribute to a sustainable agriculture, in order to prevent environmental problems arising from the application of nitrogen fertilizers. So, the research aimed to develop low pollutant fertilizers formulations, has an unquestionable interest. In this sense, the technology of controlled release (CR) has emerged as a potential approach to solve the problems associated with conventional applications of agrochemicals (Flores-Céspedes et al., 2004; Pérez-García et al., 2007).

The main objective of controlled release formulations is to maintain the concentration of active ingredient within the optimum limits over a specified period of time. The use of controlled release formulations of agrochemicals has several advantages such as the increase of the effectiveness of the agrochemical, the reduction of number of applications and costs, and the prevention of leaching losses (Fan and Singh, 1989; Peppas, 1986).

Layered double hydroxides (LDHs), also referred to as hydrotalcite like compounds (HDT) or anionic clays, are an important class of ionic layered solids (Cavani et al., 1991; He et al., 2006). The layered

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structure and the anion-exchange properties of the LDHs make them attractive for technological applications such as anion adsorbents (Ahmet-Nedim et al., 2007; Gillman, 2006; Li et al., 2008; Lv et al., 2006; Socías-Viciano et al., 2008), medicine carriers (Khan et al., 2001; Tammaro et al., 2007), ion exchangers (Jobbagy and Regazzoni, 2005; Rhada et al., 2007; Wang et al., 2007), catalyst supports, catalysts and membranes (Aradi et al., 2008; Chen et al., 2006; Neat et al., 2008), reinforcement for polymers and supports for catalysts (Castro et al., 2010; Halma et al., 2009; Marangoni et al., 2008). More recently, interesting researches about the potential use of these compounds as components of controlled release formulations of agrochemicals are being carried out (Cardoso et al., 2006; Gillman and Noble, 2005; Qiu and Hou, 2009).

Hydrotalcite-like LDH consist of stacked brucite-type $[\text{Mg}(\text{OH})_2]$ octahedral layers with water molecules and anions occupying the space between the layers. The role of the interlayer anions is to compensate the excess positive charge due to the partial substitution of divalent cations for trivalent ions. The general formula of the LDHs can be written as follows: $[\text{M}_{(1-x)}^{2+}\text{M}_x^{3+}(\text{OH})_2]\text{A}_x^{n-} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} represent the divalent and trivalent cations, respectively and A^{n-} designates the interlayer anion. LDHs are a versatile class of compounds; it is possible to modulate their properties by changing the nature of the M^{2+} and M^{3+} cations, their molar ratio, and the size of the A^{n-} anion (Leroux and Besse, 2004). The high anion exchange capacity is one of the most important properties of the anionic clays; for this reason, as indicated above, these clays are being used as components of slow release formulations of fertilizers (Gillman et al., 2008; Komarneni et al., 2003).

In this paper we show the results of the nitrate release study from an Mg/Al-LDH specifically prepared, containing nitrate as interlayer anion. This clay was also modified with hydroxypropyl methylcellulose (HPMC) in different proportions. The results showed that it is possible to slow the release of nitrate with the use of this polymer and that these formulations may be employed in the future as potential nitrate controlled release formulations.

2. Materials and methods

2.1. Chemicals

The reagent NH_3 solution, and salts $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, used in the experiments, were reagent-grade Panreac products (Barcelona, Spain). As the controlled-release agent, a commercially available and water-soluble polymer derived from cellulose, was used in this study: hydroxypropyl methylcellulose ether (HPMC Methocel K 4M Premium USP/EP, Colorcon Iberica S.L, Barcelona, Spain). HPMC polymers are very versatile release agents. They are nonionic, so they minimize interaction problems when used in acidic, basic, or other electrolytic systems.

2.2. Synthesis of hydrotalcite in nitrate form

Hydrotalcite was prepared by the co-precipitation method according to Reichle (Reichle, 1986), but with some modifications. All solutions were prepared using water previously decarbonated by boiling for 1 h. The purpose of this action was to reduce the possibility of incorporation of carbonate into the hydrotalcite. A solution prepared by dissolving 64.1 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 47 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (the amount required for a Mg/Al ratio equal to 2) in 125 ml H_2O was added drop wise, using a peristaltic pump at a rate of 4 ml/min, to 250 ml of NH_3 solution (12 mol/L), under a bubbling constant flow of N_2 in the reaction medium and vigorous stirring. The pH value of the reaction was maintained at about 10 by adding drops of NH_3 solution (12 mol/L). The synthesis was carried out at 25 °C. The precipitates were separated by centrifugation, washed exten-

sively at ambient temperature with decarbonated water to remove any residual soluble contaminant, and dried at 60 °C for 24 h.

2.3. Synthesis of the LDH/HPMC systems

The hydrotalcite previously synthesized (5 g) was added to an emulsion of hydroxypropyl methylcellulose (1 g previously dissolved in ethanol for 1 h), under permanent magnetic stirring at room temperature. After 1 h, 10 ml of decarbonated water was added to the mixture and left stirring for 1 h. Finally, the product was dried at 100 °C for 24 h.

2.4. Preparation of the controlled release formulations based on LDH/HPMC systems

The controlled release systems were prepared in two different shapes: tablets and granules. Tablets were prepared by mixing LDH and HPMC using a TECNO-PRO MATRIX 2.2 Ataena (Vicchio FI, Italy) tablet press, with LDH/HPMC proportions equal to 5/1, 5/0.5 and 5/0.25. Granules were prepared with a proportion LDH/HPMC equal to 5/1 having three different sizes: 200 μm , 500 μm and 1 mm. Nitrate layered double hydroxide formulations (tablets and granules) were also used as blanks.

2.5. Materials characterization

The materials obtained were analyzed chemically by ICP-MS with a Hewlett-Packard ICP-MS 4500 Series instrument (Technical Services, University of Almería).

Specific surface area was determined from N_2 adsorption isotherms at 77.4 K, in a volumetric adsorption system, Geminis II-2375 (Micromeritics, Bonsai Technologies Group, S.A., Madrid, Spain). The nitrogen used was 99.998% pure and the sample was degassed previously at 200 °C for 24 h.

The XRD patterns were obtained on a Bruker D8 Advance diffractometer provided with energy dispersive Sol-X detector using graphite-monochromated $\text{Cu K}\alpha$ radiation (1.5405 Å), time for step 1 s, and 0.02° for the step. (Bruker Biosciences Española, S.A., Madrid, Spain).

The FTIR spectra of the samples were recorded using KBr pellets on a Vertex 70 FT-IR spectrometer with Raman RAM II Module (Bruker) over a range of 4000–400 cm^{-1} . For each sample spectrum, 16 accumulated spectra were collected at a resolution of 4 cm^{-1} in transmittance mode. The samples were mixed with KBr (1/120 ratio) and pressed during 1.5 min at 1.01 MPa for obtaining the pressed KBr disk used for the FTIR analyses. The FTIR spectra were examined using OPUS 6.5 software.

The morphology of the samples was studied using a Hitachi S-3500N scanning electron microscope (SEM) at 20 KeV. Before the SEM micrographs were obtained, the samples were coated with gold (15 nm thickness) for electron reflection and kept under vacuum.

2.6. Analysis of nitrate

In order to determine the nitrate incorporation efficiency to the LDH prepared, 50 mg of the samples (tablets and granules) were treated with 0.1 M HCl (25 mL) under shaking for 24 h. After this time, the solution was diluted with decarbonated water, filtered and analyzed by ionic chromatography using a Vertex Technics S.L. DX 120 equipment (Barcelona, Spain). Separation was performed on an AS9-HC 4 × 250 mm Dionex IonPac column. The mobile phase was a 0.5 mol/L solution of Na_2CO_3 and a Dionex ASRS ULTRA II-4 mm was used as suppressed column. The results indicated that the nitrate incorporation efficiency was 90%. The same analytical procedure was used for the LDH/HPMC formulations obtaining the same result, that

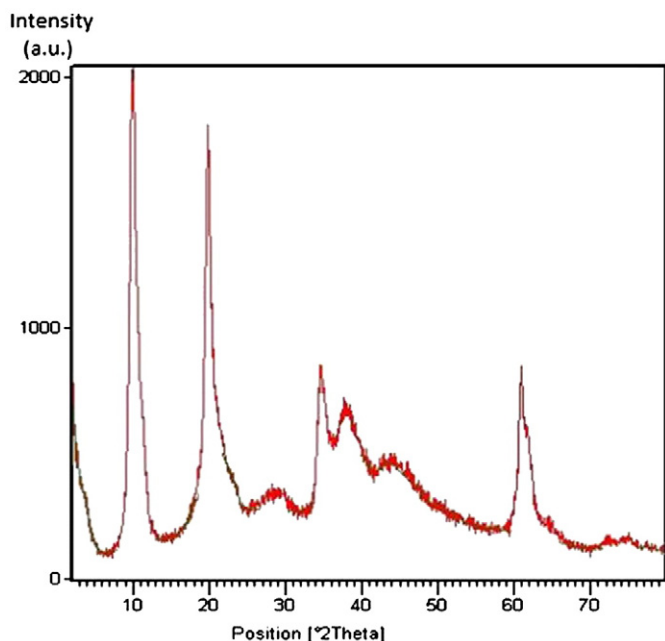


Fig. 1. X-ray diffraction pattern of the unmodified hydrotalcite.

is, the incorporation of HPMC in the used proportions did not affect the nitrate incorporation efficiency.

2.7. Nitrate release experiments

Nitrate release as a function of time was carried out by using tablets (0.35–0.40 g) and granules (0.1 g) of the LDH/HPMC systems as indicated above. Moreover, the unmodified LDH was used as comparative purposes. The systems were added to 250 mL of decarbonated water (used as a blank) or 0.006 mol/L simulated soil solution containing NaCl, Na₂SO₄ and Na₂CO₃; these solutions were shaken at 25 °C in a HT INFORS Unitron thermostatic shaker. At different time intervals, aliquots were taken and filtered by using 0.2 μm Millipore filters. The nitrate concentration was determined by ionic chromatography as indicated above. The amount of nitrate

released was calculated from the difference between the initial and final solution concentration. Blanks containing no KNO₃, and two replicates of each point were used for each series of experiments.

3. Results and discussion

3.1. Materials characterization

The Mg and Al contents determined by ICP-MS gave a molar ratio (Al/(Mg + Al)) equal to 0.33 which confirms that the hydrotalcite synthesized (LDH) is in the range corresponding to the pure hydrotalcite (Roy et al., 2001).

Surface area (S) of the samples available to the N₂ molecules were calculated by applying the Brunauer, Emmett and Teller equation (B.E.T.) to the experimental data points obtained in the N₂ adsorption process. The values of the specific surface area obtained were 4.5 m²/g for LDH and 5.7 m²/g for the LDH/HPMC samples. In all cases, the correlation coefficients were higher than 0.999 and the values obtained are very similar and in the same order of magnitude that other values found in literature, these BET surface areas having been mainly attributed to the outer surface area of the samples (Olf et al., 2009).

In relation to the X-ray diffraction patterns, Fig. 1 only shows the corresponding to the original LDH sample as those corresponding to the LDH/HPMC samples are very similar. The observed reflections and relative intensities in the X-ray diffraction pattern were consistent with pure LDHs. So, the hydrotalcite sample shows the reflections (003), (006), (012), (015) and (110), the basal spacing being of 8.8 Å, which fits within the range of values reported in the literature for samples containing interlayer nitrate ions (Jobbagy and Nobuo, 2010; Olf et al., 2009; Wang and Wang, 2007).

The FTIR spectra of the unmodified hydrotalcite and the LDH/HPMC 5/1 sample as an example are shown in Fig. 2. The characteristic bands of hydrotalcite-type compounds are indicated in Fig. 2a, similar to those appearing in the literature (Kustrowski et al., 2005). Thus, the following characteristic bands can be seen for the LDH sample, centered at: a) 3460 cm⁻¹, corresponding to the ν_{O-H} mode of free and hydrogen-bonded hydroxyl groups and water molecules; b) 1634 cm⁻¹ corresponding to the bending mode of the interlayer and adsorbed water molecules; c) the intense absorption band centered at 1384 cm⁻¹ which is related to the anti symmetrical stretching

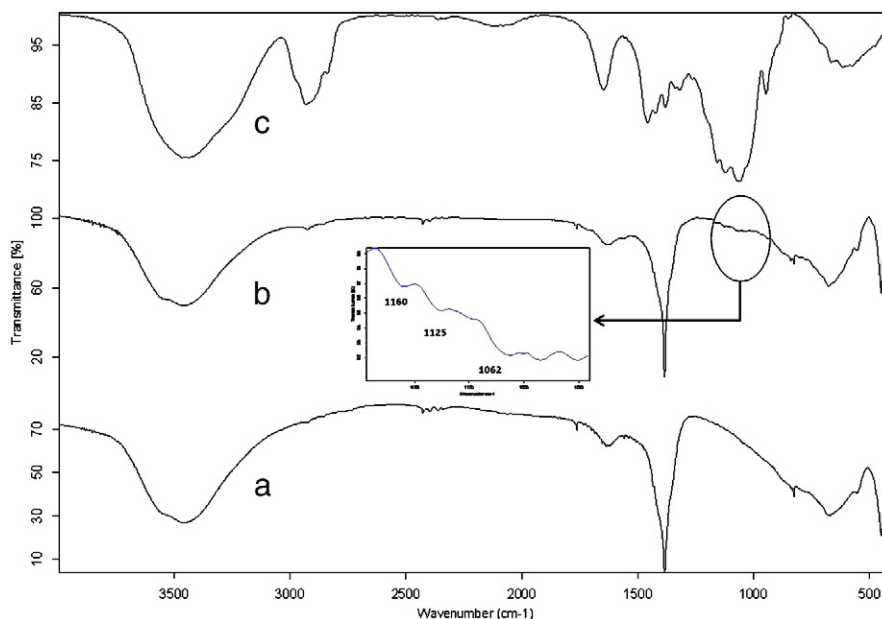


Fig. 2. FTIR spectra of the (a) unmodified hydrotalcite, (b) LDH/HPMC 5/1 system, (c) HPMC.

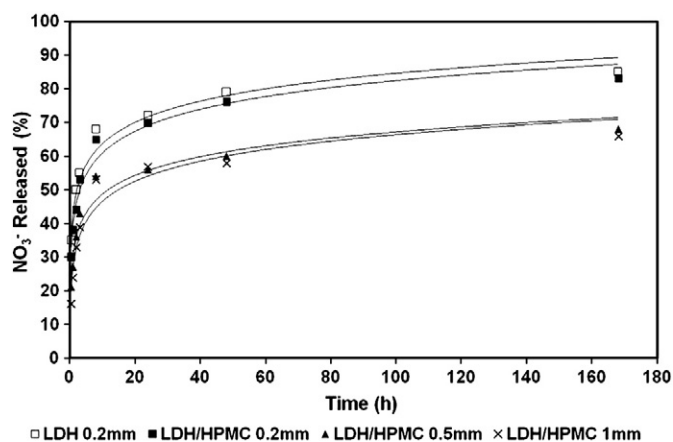


Fig. 3. Cumulative release as a function of time of nitrate from LDH/HPMC 5/1 granules prepared (200 μm , 500 μm and 1 mm) and the unmodified hydrotalcite (200 μm) in decarbonated water.

mode (ν_3) of the nitrate ion together with the presence of the band centered at 827 cm^{-1} caused by the ν_2 mode of the same anion, and that broad band centered at 675 cm^{-1} which could be assigned to the bending angular mode (ν_4) of the nitrate ion although it is largely obscured by the hydrotalcite lattice modes (Kloprogge et al., 2002; Mahamudur and Rajkishore, 2009; Wang and Wang, 2007). The FTIR spectrum of the LDH/HPMC 5/1 sample (Fig. 2b) is very similar to that obtained for the unmodified hydrotalcite. Nevertheless, a new group of bands can be observed in the 1000–1200 cm^{-1} range which are characteristics of the polymer used, such as those centered at 1160, 1125 and 1062 cm^{-1} assigned to the C–O–C stretching mode (Mruthyunjaya Swamy et al., 2009).

The morphologies observed by SEM for the original LDH sample and LDH/HPMC systems are rather similar. So, the original sample appears as well-developed, thin flat crystals with obvious edges indicating the layered structure. Such flat structure was still observed in the modified samples with the polymer appearing amalgamated between the clay particles.

3.2. Nitrate release kinetics

Figs. 3 and 4 show, respectively, the cumulative release of nitrate from LDH/HPMC 5/1 granules prepared (200 μm , 500 μm and 1 mm) and LDH/HPMC tablets formulations with different proportions (5/1, 5/0.5 and 5/0.25) in decarbonated water, whereas Figs. 5 and 6 show, also respectively, the cumulative release of nitrate from LDH/HPMC

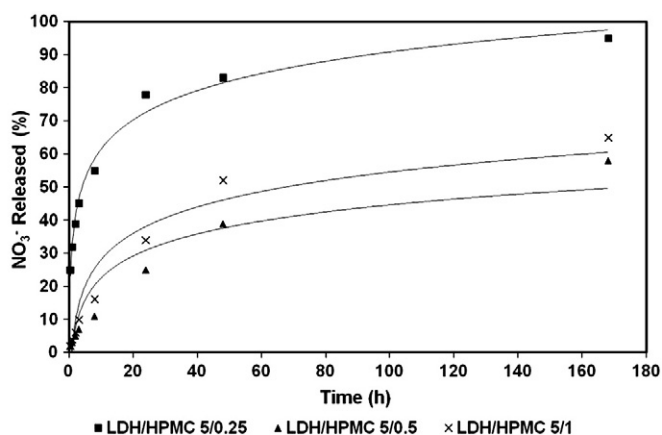


Fig. 4. Cumulative release as a function of time of nitrate from LDH/HPMC tablets formulations with different proportions (5/1, 5/0.5 and 5/0.25) in decarbonated water.

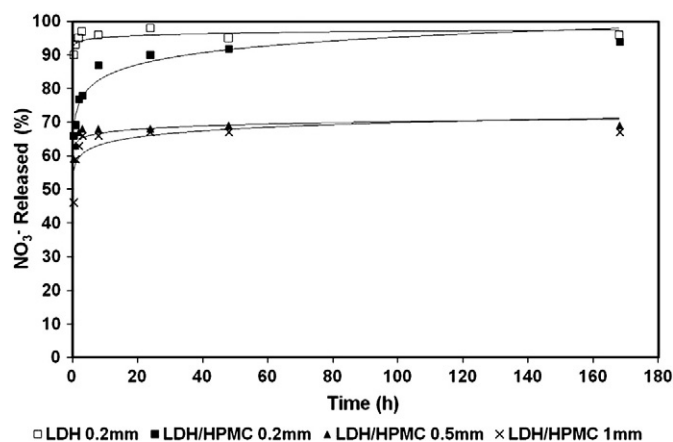


Fig. 5. Cumulative release as a function of time of nitrate from LDH/HPMC 5/1 granules prepared (200 μm , 500 μm and 1 mm) and the unmodified hydrotalcite (200 μm) in simulated soil solution.

granules and LDH/HPMC tablet formulations in simulated soil solution.

In order to observe the effect of the HPMC addition to the prepared systems, the release kinetic curve for the unmodified LDH granules (200 μm) has also been included in Figs. 3 and 5.

Comparing the granules size (200 μm , 500 μm and 1 mm) for the system LDH/HPMC 5/1 in decarbonated water (Fig. 3), we can observe a slower release rate from the larger granules (500 μm and 1 mm). This fact can be explained if we take into account the larger distances over which the active ions must diffuse when granules with the highest size and the highest area/volume ratio are used. It can also be seen, by comparing the curves corresponding to unmodified LDH granules (200 μm) and the LDH/HPMC 5/1 granules (200 μm), that the addition of HPMC to the granules clearly diminishes the percentage of nitrate released in comparison with the unmodified LDH.

On the other hand, by comparing Figs. 3 and 5, it can be seen that the percentage of released nitrate is, in general, lightly higher for the simulated soil solution medium than for the decarbonated water medium. No effects of the granules size on the rate of nitrate release have been observed in these experimental conditions.

Concerning to the tablet formulation system, the influence of HPMC percentage (LDH/HPMC 5/1, LDH/HPMC 5/0.5 and LDH/HPMC 5/0.25), appears clearly defined from Figs. 4 and 6. In both experimental conditions (decarbonated water and simulated soil solution), the LDH/HPMC 5/0.5 system produces the slowest release rate of nitrate than the other two systems, this fact being much clearer

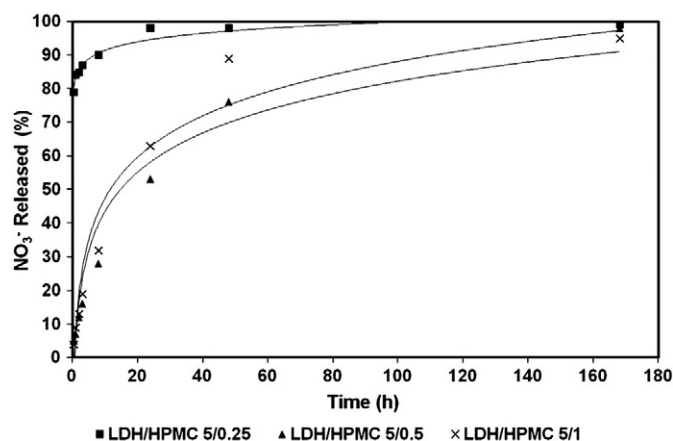


Fig. 6. Cumulative release as a function of time of nitrate from LDH/HPMC tablets formulations with different proportions (5/1, 5/0.5 and 5/0.25) in simulated soil solution.

when the experiment is carried out in decarbonated water. This could be explained if we take into account that, on one hand, the LDH/HPMC 5/0.25 system, that with the lower proportion of HPMC content, produces the quicker and easier release of nitrate ions whereas the LDH/HPMC 5/1 system, although it produces a slower release due to its highest content of HPMC, it has the lower content of nitrate. So, the proportion LDH/HPMC 5/0.5 seems to be the optimum for achieving a controlled release of nitrate in both media.

As can also be seen, the nitrate release percentages in the simulated soil solution (Fig. 6) are also higher than those corresponding to the decarbonated water medium (Fig. 4).

If we now compare the results obtained for the LDH/HPMC formulation tablets with those corresponding to the LDH/HPMC formulation granules, it can be deduced that the formulation tablets show the lower nitrate release rate. This fact could be probably due to the higher homogeneity and less porosity of the tablets compared to the granules.

The release data of nitrate in water and in simulated soil solution were analyzed by applying the empirical equation proposed by Ritger and Peppas (Ritger and Peppas, 1987):

$$M_t / M_0 = Kt^n \quad (1)$$

where M_t/M_0 is the percentage of active ingredient released at time t , K is a constant that incorporates characteristics of the macromolecular network system and the active ingredient, and n is a diffusional parameter which is indicative of the transport mechanism.

The values of K and n obtained from initial 90% of nitrate released in water and simulated soil solution are presented in Tables 1 and 2, respectively. There was a good correlation of the release profiles of the nitrate systems prepared with the empirical equation, the correlation coefficient (r) being higher than 0.96.

The averages values of n ranged from 0.02 and 0.19 for the granule system in simulated soil solution and decarbonated water, respectively, to 0.04 and 0.61 for the tablet system, in simulated soil solution and decarbonated water, also respectively.

Values of n close to 0.43 are indicative of Fickian diffusion in spherical monolithic matrices (Ritger and Peppas, 1987). The complexity of the granular systems, with a high heterogeneity, could explain the higher deviation from the n value above indicated.

The time period for 50% release of nitrate (T_{50}) was calculated for the granules and tablets using the constants from Tables 1 and 2. The average values ranged from 8.7×10^{-4} h and 12.3 h for the granule system in simulated soil solution and decarbonated water respectively, up to 17.6 and 54.5 h for the tablet system, in simulated soil solution and decarbonated water, also respectively. The release of nitrate is faster in the simulated soil solution medium than in decarbonated water medium as expected; this fact might be explained taking into account the strong specificity of LDH for the ions present in the soil solution.

It seems clear from the data commented that the key factor in controlling the release of nitrate from the systems studied is the shape of the systems. Tablets are much more effective than the granules in retarding the release of nitrate, being no relevant the size of the granules neither the addition of HPMC to the tablets in LDH/HPMC

Table 2
Kinetics data for simulated soil solution.

	System	K (h ⁻ⁿ)	n	r	T ₅₀ (h)
Granules	LDH/HPMC 5/1 (0.2 mm)	0.72	0.06	0.9593	$2.6 \cdot 10^{-3}$
	LDH/HPMC 5/1 (0.5 mm)	0.64	0.02	0.9686	$9.10 \cdot 10^{-6}$
	LDH/HPMC 5/1 (1 mm)	0.62	0.02	0.9769	$9.10 \cdot 10^{-6}$
Tablets	LDH/HPMC 5/1	0.08	0.55	0.9882	24.20
	LDH/HPMC 5/0.5	0.08	0.53	0.9961	28.60
	LDH/HPMC 5/0.25	0.83	0.04	0.9851	$3.10 \cdot 10^{-6}$

proportions higher than 5/0.5 So, the LDH/HPMC 5/0.5 system seems to be the most adequate in order to be used as a nitrate controlled release formulation as this system shows the slower release kinetic. This system is also more efficient than those studied by other authors. So, the value of T_{50} obtained in water solution to study the controlled release of nitrogen using urea and ammonium nitrate from ethylcellulose coated formulations was much lower than that corresponding to our LDH/HPMC 5/0.5 system (9.47 and 35.7 h vs. 96.1 h, respectively) (Fernández-Pérez et al., 2008; Pérez-García et al., 2007).

4. Conclusions

A synthesized hydrotalcite containing nitrate as interlayer anion has been modified with HPMC in different proportions and two types of systems have been prepared: tablets and granules, the latter with a proportion LDH/HPMC equal to 5/1 having three different sizes of 200 μm, 500 μm and 1 mm. The nitrate release results showed that, on the one hand, the addition of HPMC to both systems clearly diminishes the percentage of nitrate released in comparison with the unmodified LDH, being this percentage in general, lightly higher when the experiment was carried out in a simulated soil solution than for the decarbonated water medium. On the other hand, no effects of the granules size on the rate of nitrate release have been observed, at least in the experimental conditions studied.

Moreover, the comparison of the results obtained for the LDH/HPMC formulation tablets with those corresponding to the LDH/HPMC formulation granules showed that the tablet systems exhibit the lower nitrate release rate, probably due to their higher homogeneity and less porosity. In addition, the influence of HPMC percentage in these systems appears clearly defined and so, the tablet system with the LDH/HPMC 5/0.5 proportion is the most appropriate to delay the release rate of nitrate as evidenced by the higher value of the parameter T_{50} , obtained from the fit of the release kinetic data to the Ritger and Peppas equation. This fact could be useful for designing systems which control the nitrogen release, according to the plant requirements.

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Table 1
Kinetics data for decarbonated water.

	System	K (h ⁻ⁿ)	n	r	T ₅₀ (h)
Granules	LDH/HPMC 5/1 (0.2 mm)	0.39	0.17	0.9675	4.03
	LDH/HPMC 5/1 (0.5 mm)	0.30	0.19	0.9940	15.06
	LDH/HPMC 5/1 (1 mm)	0.30	0.18	0.9657	17.88
Tablets	LDH/HPMC 5/1	0.04	0.61	0.9774	61.24
	LDH/HPMC 5/0.5	0.03	0.59	0.9908	96.10
	LDH/HPMC 5/0.25	0.32	0.24	0.9747	6.32

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