Microparticles based on ionic and organosolv lignins for the controlled release of atrazine
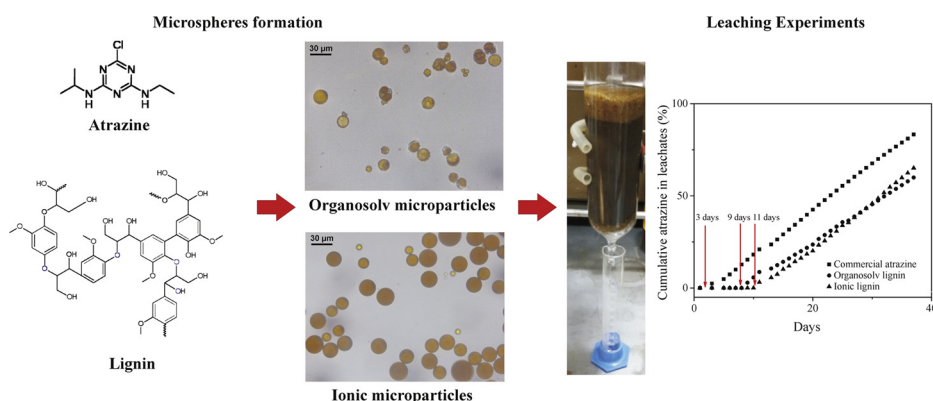
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GRAPHICAL ABSTRACT

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ABSTRACT

Lignins are natural polymers of the lignocellulosic biomass. Nowadays, there is a growing interest in developing value-added products based on lignins due to their renewability, low cost and abundance. In this work, lignin microspheres from organosolv and ionic isolation processes were prepared for the controlled release of atrazine. Microspheres were prepared by the solvent extraction/evaporation technique. The controlled release of atrazine from organosolv and ionic lignins microparticles was studied in water. Mobility experiments were performed in an agricultural soil from Argentina. The results showed that microparticles prepared using dichloromethane as the dispersed phase were spherical, while lignins dispersed in ethyl acetate produce irregular microparticles. Organosolv lignin microparticles presented higher encapsulation efficiency for all herbicide loads. About 98% and 95% of atrazine was released in 24 and 48 h approximately from organosolv and ionic lignin microparticles, respectively. The release profiles of atrazine from both lignin microparticles were not affected by the herbicide load. Atrazine mobility experiments in soil showed that about 80% of free atrazine was leached in 37 days, while 65.0% and 59.7% of the herbicide was leached from ionic and organosolv lignin microparticles, respectively. Thus, atrazine-loaded microparticles could reduce leaching compared to a commercial formulation of free atrazine.

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1. Introduction

Pesticides are important chemicals used in agriculture as crops protection products, and for pest control purposes [1]. However, some of these compounds and their degradation products exhibit persistence and mobility in the environment and may exhibit potential toxic, carcinogenic and reproductive effects on living organisms, including humans beings [1–4].

Triazines are a group of herbicides used in agriculture to remove weeds and to protect crops. In addition, they are used in non-agricultural areas for cereals soil sterilization and road maintenance [5]. Atrazine (2-chloro-4-ethylamine-6-isopropylamine-s-triazine) is a moderately toxic triazine, used as a selective pre- and post-emergence herbicide in various cultivations [6]. It has been estimated that after its application, a large proportion of it remains in the environment [7,8]. This herbicide belongs to the persistent organic pollutants because of its low biodegradability and long half-life (between 30 and 100 days) in water. Moreover, due to its slightly solubility in water ($33\,mg\,L^{-1}$ at $22\,°C$) and relatively low adsorption in soil, atrazine easily migrates towards underground water thus presenting a potential danger for public health as this herbicide and its chlorinated metabolites are considered to be endocrine disruptors [9]. Its widespread use caused concentrations exceeding the permissible limit of water contamination in surface water, rainwater and ground water. As it became a chronic pollutant of water and because of its potential environmental hazard to contaminate drinking water, the commercial use of atrazine has been banned in several countries [10]. Atrazine belongs to the priority list of 76 substances of Water Framework Directive (Directive 2000/60/EC) in Europe.

Although is forbidden in the European Union, atrazine is still detected in EU countries, probably because of its persistence in ground water that may act as a source of surface water and soil contamination. Moreover, some illegal atrazine use cannot be excluded. More importantly, atrazine is extensively applied worldwide in both developed and developing countries [11].

Atrazine can be detected in many environmental media such as soil, surface water, and groundwater at concentrations exceeding its maximum permissible limit [12]. The behavior of pesticides in soils is governed by a variety of complex dynamic physical, chemical and biological processes, including sorption–desorption, volatilization, chemical and biological degradation, uptake by plants, run-off, and leaching. The adsorption of pesticides is influenced by the clay and organic matter content [13], and the environmental risk increases due to the higher pesticide use for different applications. Specifically, the atrazine mobility in soils is moderate due to its relatively low adsorption. Atrazine can be degraded by the action of several microorganisms, however the biological degradation decrease with depth. In Argentina, the persistence of atrazine and its metabolites in soil was investigated [14–16]. It was found that samples with 20 cm of depth contain atrazine for up to 90 days.

Nowadays, novel delivery systems for herbicides are being investigated in order to reduce their environmental toxicity. In this direction, polymeric micro- and nanoparticles have been studied as potential delivery systems in the agro-industry. In the case of herbicides, these systems offer the following advantages [17]: *i)* reduction of the pesticide required for crops control; *ii)* decrease of environmental contamination risk; *iii)* protection of pesticides from environmental factors, reducing losses due to photolytic, chemical and microbiological degradation; *iv)* reduction of energy consumption; and *v)* improvement of operational efficiency.

Controlled-release systems based on polymers derived from natural sources present several advantages, such as biodegradability, sustainability, low costs, and lack of toxic residues into the environment [18]. Lignins are aromatic biopolymers from biomass, the second most abundant biopolymer after cellulose [19]. The properties of lignins depend on: a) the biomass they come from (hard or soft wood and non-

wood fibers), and b) the employed isolation method. Industrially, lignins are obtained as by-products of cellulose pulp production and alcohol processes, among others [20]. The cellulose pulping process used by the paper industry determines the types of industrially-available lignins. The main cellulose pulp manufacturing processes are: *i)* methods that employ sulphur reagents such as the sulphite and Kraft processes, and *ii)* sulphur-free process such us the soda method [21,22]. In addition, other processes are being developed to obtain sulphur-free cellulose pulp, such as organosolv processes, ionic processes, and steam explosion process [22]. Sulphur-free lignins are considered the closest to the natural product. Isolation of lignins with ionic liquids is an attractive alternative, due to the high lignin yield despite several operating parameters [23]. In addition, ionic liquids are a 'green' recyclable option to the environmentally-harmful organic solvents, since they exhibit a negligible vapor pressure and are non-flammable [24–26]. The main application of lignins is as fuel, but they have also been used as surfactants, adhesives, and polymeric additives [20]. In the last decades, several authors have reported the use of lignin in the agriculture area [20,27–35]. Wilkins [27] has studied the kinetics release of herbicides and insecticides from granules based on Kraft lignin matrices, concluding that the pesticide release occurs through a diffusion mechanism. Studies were conducted with the herbicide 2,4-D, and the lignin granules resulted in a good control of weeds in conifer plantations for 14 months [28]. It has been reported that several factors affect the release kinetics of pesticides from granules, including pesticide load, nature of the polymeric matrix, temperature, size of the granules, and use of additives [29]. Garrido-Herrera et al. [31] evaluated controlled release systems of isoproturon, imidacloprid and cyromazine by mixing the pesticides with Kraft lignin. Recently, Li et al. [20] prepared a new hydrophobic material of sodium lignosulfonate and cetyltrimethylammonium bromide for the encapsulation of avermectin (a photosensitic insecticide). In addition, Costa et al. [33] prepared microcapsules of sugarcane bagasse lignin by nanoemulsion, for encapsulation of neem organic extracts (Azadirachta indica). Flores-Cespedes et al. [35] evaluated Kraft lignin-polyethylene glycol based formulations for the controlled release of chloridazon and metribuzin. The lignin-polyethylene glycol formulations reduced the presence of chloridazon and metribuzin in the leachate compared to technical and commercial products.

Several atrazine delivery systems based on biodegradable polymers have been investigated [17,36–44]. Zhong et al. [36] loaded atrazine into halloysite nanotubes that were then incorporated into poly(vinyl alcohol)/starch films. The composite material allows reducing leaching of atrazine through the soil. Singh et al. [37] prepared atrazine-loaded agar/starch/poly(acrylamide) hydrogels with suitable release profiles for agricultural applications. Oliveira et al. [38] evaluated the post-emergence herbicidal activity of poly(ε-caprolactone) (PLC) nanocapsules containing atrazine, using mustard plants as a target species model. The nanoencapsulation of atrazine enhanced the herbicidal activity in comparison with a commercial atrazine formulation. Li et al. [41] used a carboxymethyl chitosan/bentonite composite gel for reducing the amount of pesticides available for leaching. Grillo et al. [17] encapsulated atrazine into poly(hydroxybutyrate-co-hydroxyvalerate) microspheres prepared by the oil/water emulsion solvent evaporation technique. Lobo et al. [42] studied the importance of evaluating different parameters during the preparation of atrazine delivery systems based on poly(hydroxybutyrate-co-hydroxyvalerate) microspheres. Fernandez-Perez et al. [43] studied alginate-bentonite systems to reduce the mobility of atrazine into greenhouse soil. Dailey et al. [44] reported the preparation of atrazine and metribuzin-loaded microcapsules using cellulose acetate butyrate, ethylcellulose, and poly(methyl methacrylate).

In the present study, lignin-based microparticles were prepared for the controlled release of atrazine, reducing its potential leaching in soil. Lignin was selected as polymeric matrix because of its low cost, free availability, non-toxicity and biodegradation. Two lignins obtained

from organosolv and ionic isolation processes were evaluated for the preparation of atrazine-loaded microparticles. Organosolv and ionic lignins were derived from bagasse and spruce sources, respectively. Microparticles were prepared by the solvent extraction/evaporation technique. The effect of experimental conditions and lignin type on microparticles characteristics was investigated. Particle size and morphology of the microparticles were analyzed by optical microscopy and the encapsulation efficiency was measured by High Performance Liquid Chromatography (HPLC). The *in vitro* release of atrazine from the different lignin microparticles was evaluated in water. In addition, atrazine mobility in an agricultural soil was investigated.

2. Experimental work

2.1. Materials

Ionic lignin from spruce, obtained though a patented procedure that employs ionic imines. It was kindly provide to us by Dr. Stefan Saur and Prof. Dr. Willi Kantlehner from Hochschule Aalen (Aalen, Germany). Organosolv lignin from sugar bagasse was provided by the Pulp and Paper Group of the National University of Misiones (PROCyP, Argentina). Atrazine commercial formulation ($\geq 90\%$, SYNGENTA) was used for soil mobility test. For the other analysis, atrazine standard (98%, Chem Service Inc., USA) was used. The following chemical reagents were used as received: potassium bromide (Cicarelli), sodium nitrate (Anedra), polyvinyl alcohol (PVA; 205 kDa; 87.7% hydrolyzed; Sigma Aldrich), dichloromethane (DCM; Anedra), tetrahydrofuran (THF, Cicarelli), ethyl acetate (EA; Cicarelli), acetonitrile (HPLC grade, Sintorgan), glacial acetic acid (analytical reagent, Anedra). Ultrapure water (0.055 μS/cm) was used for all dilutions. This water was obtained from an OSMOION purification equipment.

2.2. Characterization of lignins

2.2.1. Moisture, ash content and elemental composition

To determine moisture content, 1–1.5 g of lignin were weighed in crucibles, and dried at 105 °C until constant weight. The ash content was measured by calcifying 2–5 g of lignin for three hours at 575 °C in a furnace according to the methodology proposed by El Mansouri et al. [45].

The content of C, H, S and N was quantified in a Perkin Elmer CHNSO SerieII elemental analyzer with EA Data Manager 2400 software.

2.2.2. Polymer molar mass distributions

The molar mass distributions (MMD) of the employed lignins were determined by size exclusion chromatography (SEC). To this effect, lignins were dissolved in 0.25 mL of THF (0.4% w/v). The injection volumes were 50 μL. The Liquid Chromatograph was a Waters 1525 fit with an automatic injector (Water 717), two Styragel Columns (HR 1 and HR4), and a differential refractive index detector (Waters 2414). The calibration was carried out with a set of 12 standards from PPS Polymer Standards Service GmbH, consisting of 9 lower molar mass standards of poly(ethylene glycol) (PEG) and 5 higher molar mass standards of poly(ethylene oxide) (PEO).

2.3. Preparation of lignin microparticles by the solvent extraction/ evaporation technique

The following procedure was employed: *a)* approximately 30 mg of organosolv or ionic lignin was dispersed in 3 mL of organic solvent (DCM, EA or THF); *b)* the suspension was then filtered though a 0.45 μm nylon microfiltration membrane (Microclar, Argentina) to remove the undissolved lignin; *c)* atrazine standard was added to the solution at a concentration of 10, 15 or 20% w/w with respect to the polymer, and the dispersion was sonicated for 3 min; *d)* the solution

obtained was slowly dropped onto the aqueous phase (17 mL of 1 or 2% w/v PVA solution) under continuous stirring by a homogenizer (Kinematica Polytron PT 2500e, Switzerland); *e)* the emulsion was stirred for 5 min; *f)* 70 mL of 0.3% w/v PVA solution was added to the emulsion and the stirring was continued for 30 min; *g)* the organic solvent was evaporated under vacuum on a rotary evaporator (Büchi EL 130, Germany) for 2 h at room temperature; *h)* solid microparticles were washed twice with deionized water and collected by centrifugation using a Hettich Universal 16 centrifuge (Germany) at 2000 rpm for 2 min; and *i)* microspheres were lyophilized using a Telstar Cryodos 80 lyophilizer (Spain) and stored until further analysis. Different batches of unloaded microspheres were prepared in order to study the effect of the following experimental conditions on microspheres features (see Table 3): *i)* type of organic solvent (DCM, EA and THF); *ii)* PVA concentration (1 and 2% w/v); and *iii)* homogenization rate (500, 1000 and 3000 rpm).

2.4. Particle size measurements

The dry microparticles were resuspended in distilled water and observed in an optical microscope (DM 2500 M, Leica, Germany) coupled with a camera (DFC 290 HD, Leica). The mean particle diameter was determined using image processing software, after analyzing approximately 300 particles per sample.

2.5. ANOVA test

The mean particle size was statistically compared by analysis of variance (ANOVA) at a level of 95% confidence using free software (R program version 2.3.3.3). Multifactorial design was proposed, where factors correspond to PVA concentration, homogenization rate and organic solvent employed. The suitability of the models (independent residues normally distributed and homoscedasticity with mean zero and variance for all factor levels) was verified.

2.6. In vitro release assays in water

Approximately 4 mg of atrazine-loaded microparticles were dispersed in 25 mL of ultrapure water. The vials were incubated at 25 °C. At different times, 2 mL of samples were taken and replaced with an equal volume of fresh medium. Experiments were performed in duplicate. Atrazine quantification was performed by HPLC employing an HPLC-UV/Visible Waters chromatograph equipped with an YMC-Triart C18 column (5 μm particle size, 4.6 × 250; inner diameter x length) and a Waters 2489 UV–vis detector. Atrazine retention time was 5.32 min. The mobile phase consisted of an acetonitrile/water mixture (70:30 v/v) acidified with acetic acid at a flow rate of 1.0 mL min^{-1}. The column temperature and the detection wavelength were 25 °C and 221 nm, respectively. A calibration curve was performed in the 0–100 mg L^{-1} range. Five atrazine standards were used for calibration (1, 5, 30, 60, 100 mg L^{-1}). The Limit of Detection was 0.3 mg L^{-1} and the Limit of Quantification was 1 mg L^{-1}. LOD and LOQ were determined according to Miller and Miller [46].

2.7. Atrazine mobility in soil

2.7.1. Soil characterization

The soil was obtained from a field in the north of Santa Fe province, Argentina (29° 42′ 59″ S and 60° 5′ 35″ W) with over 20 years of continuous soybean cultivation. The kind of soil according to its taxonomy is acuic Argiudoll. The soil textural class was determined from the granulometric properties yielding a silty clay loam. The soil characteristics are shown in Table 1. The following methods were used: Bouyocus for the gravimetric analysis, organic matter and carbon by the Walkley-Black method, phosphorus by Bray-Kurtz method, density by pycnometer method, ash by gravimetric analysis, cations by atomic

Table 1
Soil characterization.

Parameter	Soil
Granulometry (%)	Sand 6.4; Silt 66.6; Clay 27.0
C dry base (%)	1.97
Organic matter (%)	3.40
P dry base (mg kg^{-1})	0.023
Actual density dry base (g cm^{-3})	2.67
Porosity (%)	70.7
pH (1:2.5)	5.96
Ashes (%)	94.83
K (mg kg^{-1} soil)	462.71
Ca (mg kg^{-1} soil)	184.88
Mg (mg kg^{-1} soil)	84.36
Na (mg kg^{-1} soil)	10.39
N (%)	0.153
C/N Ratio	12.9

absorption spectroscopy and nitrogen by Kjeldahl method.

2.7.2. Leaching experiment

The mobility of atrazine in soil was investigated using glass columns (length 30 cm, internal diameter 4.6 cm) filled with air-dried soil. In order to avoid losses of soil, glass-wool and sand (1 cm) were placed at the columns bottom. The columns were hand-packed with 200 g of soil and sand was added at the top. The columns were saturated with water and allowed to drain for 24 h, and then the average pore volume was estimated gravimetrically. Initially, 0.7 mg of atrazine commercial formulation (free atrazine) or a mass of microparticles containing approximately 0.7 mg of encapsulated atrazine were dispersed in 10 mL of water and added into the columns, to emulate an application rate of 2 kg ha^{-1}. For leachates sampling, 20 mL of water were added daily to the columns during 37 days. Leachates were collected daily in glass vials and stored at 4 °C. The samples were filtered and atrazine was quantified by HPLC as described in Section 2.6. Experiments were performed in duplicate.

3. Results and discussion

3.1. Characteristics of the base lignins

The main characteristics of the employed lignins are presented in Table 2.

The moisture content of organosolv lignin is similar to that reported by El Mansouri et al. [45]. The ash content of organosolv lignin was higher than that reported by Vallejos et al. [47] and lower than ionic lignin. The ash content of ionic lignin is similar to that reported by Espinoza-Acosta et al. [48].

Regarding elemental composition, both lignins exhibit similar results and they are in agreement with the results reported by several authors [45,49,50]. Note that the sulfur content in lignins isolated from

Table 2
Characteristics of the employed lignins.

		Organosolv lignin	Ionic lignin
% Moisture		3.66	23.34
% Ash (dry basis)		0.05	0.6
Composition			
Elemental composition	C	65.34	66.26
%	H	7.99	8.17
	N	0.26	0.26
	S	0.72	0.71
Molecular properties			
$\overline{M}_n$ (g mol^{-1})		842	768
$\overline{M}_w$ (g mol^{-1})		2122	3718
Dispersity		2.12	4.84

Table 3
Experimental conditions and mean diameters of the resulting lignin microparticles.

Organosolv lignin				
Solvent	Homogenization rate (rpm)	PVA concentration (% w/v)	Mean diameter	Standard deviation
DCM	500	1	17.47	3.88
DCM	1000	1	9.81	2.36
DCM	3000	1	5.61	2.09
DCM	500	2	12.24	3.52
EA	500	1	21.89	8.50
EA	500	2	16.76	7.48
Ionic lignin				
DCM	500	1	25.34	6.74
DCM	3000	1	4.94	1.11
EA	500	1	21.48	8.19
EA	500	2	13.65	4.21

organosolv and ionic processes is lower than the values reported for other isolation processes, such as Kraft and sulphite [45,51]. A lower sulfur content in lignins is highly desirable since it is very harmful to the environment. Ionic lignin exhibited higher weight-average molar mass and dispersity than organosolv lignin and these values are in accordance with those reported in the literature [48].

Pesticides are predicted as being compatible with lignin in a matrix formulation if they have a solubility parameter close to lignin. Several works describe the interaction between polymeric matrices and pesticides based on the Hansen solubility parameter [31,51]. The values reported of Hansen solubility parameter are similar for lignins (20-33.3 MPa$^{1/2}$) and for atrazine (20.9 MPa$^{1/2}$) [52–54], indicating good compatibility [31].

3.2. Characteristics of the unloaded microparticles

Table 3 shows the mean size of microparticles prepared from ionic and organosolv lignins using different experimental conditions.

Considering the effect of the organic solvent used during preparation, microparticles were not obtained using THF solvent because: *a)* its high solubility in water produces irregular agglomerates, and *b)* solubility of lignins in this solvent is low. The effects of EA and DCM on microparticles morphology were similar for both lignins. When dispersed in EA, the produced microparticles showed irregular shapes (Fig. 1a–c). In contrast, spherical microparticles were obtained with DCM as solvent. This result is associated to the higher solubility of EA in water (8.3 g/100 mL) compared to DCM (1.2 g/100 mL) [55].

ANOVA results are presented in Table 4. As it can been seen, the effects of experimental factors (organic solvent, homogenization rate and PVA content) on particle mean size are statistically significant. In addition, interactions between solvent and PVA content were detected (p > 0.05).

Fig. 2 shows organosolv lignin microparticles prepared at homogenization rates of 500 and 3000 rpm. As expected, the mean diameter of microparticles decreases at higher homogenization rates. Similar results were observed for ionic lignin (see Table 3).

Surfactants play an important role in the formulation of microspheres and in their resulting shapes and sizes. The main role of the surfactant is to prevent the emulsion droplets from coalescing. Fig. 3 shows the effect of surfactant concentration on the microparticles size. The mean particle size decreases when the surfactant concentration in the aqueous phase was increased. This behaviour is related to the reduction of droplets surface tension mediated by the surfactant and the stabilization of the droplets during the homogenization process.

Based on the different experimental conditions affecting microparticles features, DCM was adopted as the organic solvent since spherical microparticles with a narrow distribution were obtained
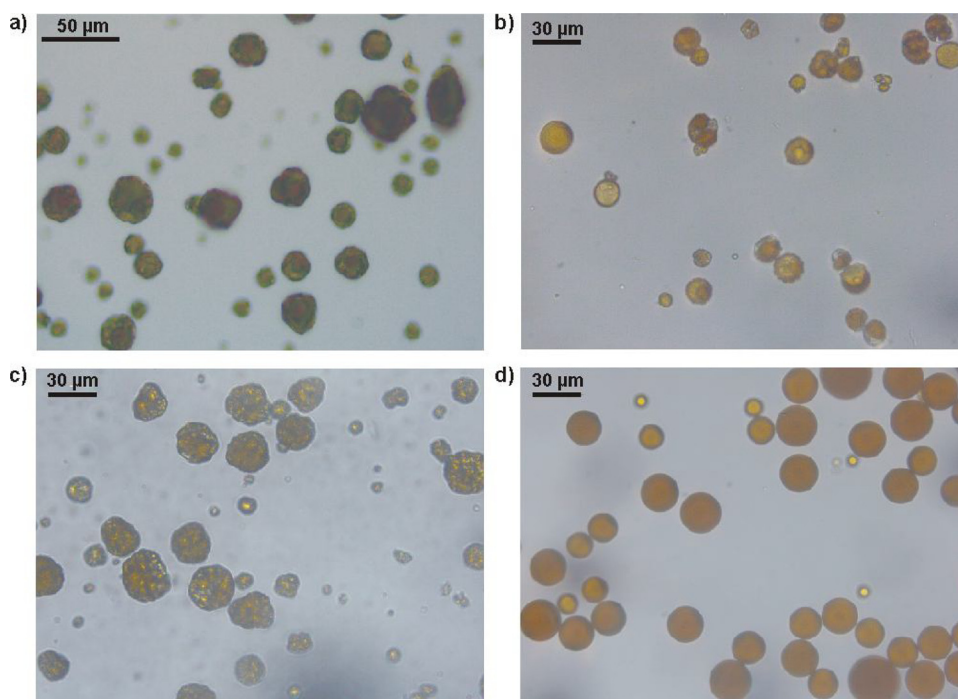
Fig. 1. Optical images of: organosolv lignin microparticles prepared with: EA (a) and DCM (b); and ionic lignin microparticles prepared with: EA (c), and DCM (d). The homogenization rate was 500 rpm.

Table 4
p-value from ANOVA test.

Mean particle size	
Factor	**p-value**
Solvent	0.0371
Homogenization rate	0.0005
PVA content	0.0174
Solvent:homogenization rate	< 0.05
Solvent:PVA content	0.97
Homogenization rate:PVA content	< 0.05

compared to EA. A PVA concentration of 1% w/v and a homogenization rate of 500 rpm were adopted in order to obtain microparticles with a larger particle size, which allows extending the release period of the herbicide.

The studied system exhibits low environmental impact because lignins are polymers derived from renewable bioresources. Lignin degradation is related to the nature of vegetation and land-use, but also to the weather and soil characteristics. Lignin degradation is caused by certain fungi as well as several bacterial species [56]. Fungi are more efficient in the breakdown of lignin than bacteria, in which delignification is slower and more limited.

On the other hand, PVA is recognized as one of the very few vinyl polymers soluble in water also susceptible of ultimate biodegradation in the presence of suitably acclimated microorganisms. During the preparation of microparticles most of PVA is removed through the washing steps. It is possible that a small amount of PVA molecules remains adsorbed on the surface of microparticles, however it can be considered negligible.

In addition, the slightly solubility of DCM in water and the low boiling point of the solvent (39.6 °C) allow its complete removal from microparticles through extraction in water and evaporation under vacuum on the rotary evaporator. In addition, it is reported that residual solvent in microparticles results in particle coalescence and aggregation, eventually leading to polymeric film formation after the drying step [57]. This behaviour was not observed in the preparation of lignin microparticles since they are easily dispersed in water.

3.3. Encapsulation and release of atrazine

For the encapsulation and release experiments, the following experimental conditions were adopted for the preparation of
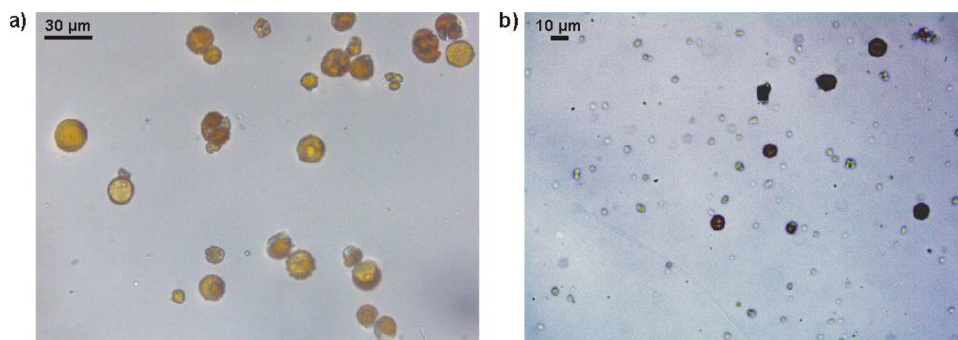

Fig. 2. Optical images of organosolv lignin microparticles prepared at different homogenization rates with DCM: (a) 500 rpm, and (b) 3000 rpm.
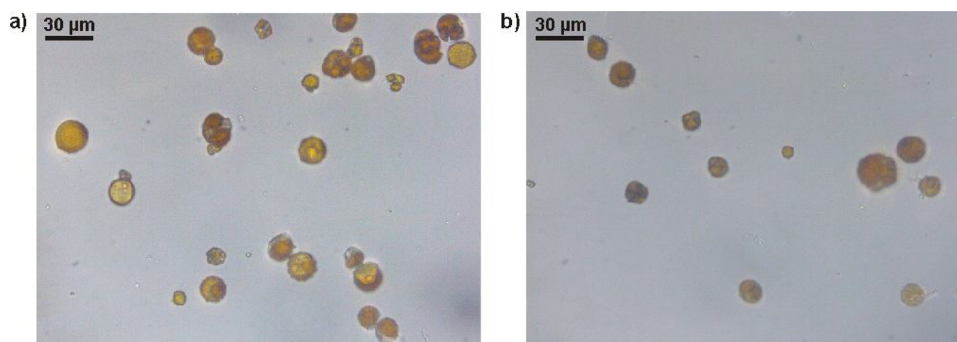
Fig. 3. Optical images of organosolv lignin microparticles prepared using different PVA concentrations: (a) 1% w/v and (b) 2% w/v.

microparticles: *a)* the use of DCM as solvent of the dispersed phase, *b)* 1% w/v PVA, and *c)* homogenization rate of 500 rpm. For these conditions, microparticles were spherical and their mean particle diameters were 17.4 ± 3.9 and 25.3 ± 6.7 μm for organosolv and ionic lignins, respectively (see Table 3).

The encapsulation efficiencies of organosolv and ionic lignins microparticles with nominal herbicide loads of 10, 15 and 20% w/w were 52.8 and 39.0, 74.4 and 40.1, 77.5 and 47.4%, respectively. The organosolv lignin presented higher encapsulation efficiency for all herbicide loads, probably due to differences in the solidification rate of microparticles. The lower solubility of the organosolv lignin in DCM determines a lower viscosity of the dispersed phase. This phenomenon increases the solvent diffusion rate into the external aqueous phase and polymer precipitation, preventing the diffusion of atrazine into the aqueous phase and resulting in higher entrapment efficiency [58]. In addition, higher encapsulation efficiency was observed for a nominal herbicide load of 20% w/w.

Figs. 4 and 5 show the *in vitro* release profiles of atrazine in water from microparticles loaded with 10, 15 and 20% w/w atrazine prepared using organosolv and ionic lignins, respectively. The atrazine release profiles from organosolv lignin microparticles (Fig. 4) showed that approximately 98% of atrazine was released in less than 2 days. As it can be seen in Fig. 5, the release profiles of atrazine from ionic lignin

microparticles are little affected by the herbicide load and approximately 95% of atrazine was released in 2 days. The faster release of atrazine from organosolv lignin microparticles compared to ionic lignin microparticles can be explained from the differences in their mean particle sizes and average molar masses. Organosolv lignin microparticles exhibit a smaller mean particle size and the release rate increases as a consequence of the higher surface/volume ratio. In addition, the ionic lignin exhibits a higher weight-average molar mass than organosolv lignin reducing the herbicide diffusion coefficient [58].

A comparison between the present work and others reported in the literature about atrazine delivery systems is presented in Table 5.

Several atrazine delivery systems were studied, including nanocapsules, microparticles, films, hydrogels and beads. In all cases, both natural and synthetic biodegradable polymers were used. The controlled release period of atrazine from the different systems varies from 5 h to 5 days approximately. Compared to the present work, lignin microparticles showed similar results.

3.4. Mobility of atrazine in soil

Fig. 6 shows the cumulative breakthrough profiles in soil of free atrazine and of atrazine encapsulated in lignin microparticles. Different behaviors are observed in the leaching patterns of atrazine. The pore
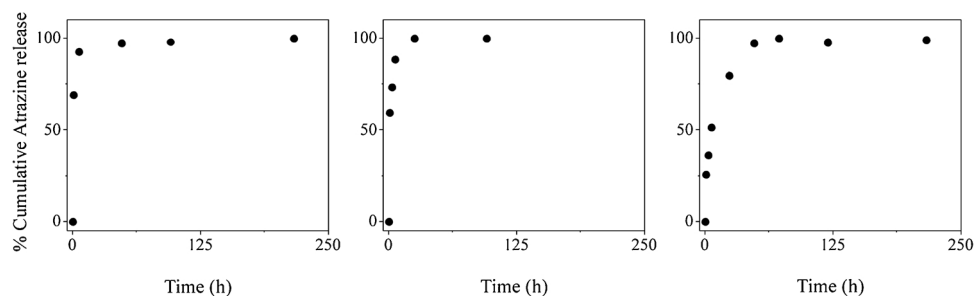

Fig. 4. Cumulative release of atrazine in water from organosolv lignin microparticles with different herbicide loads: a) 10, b) 15, c) 20% w/w. The experiments were performed in duplicate.
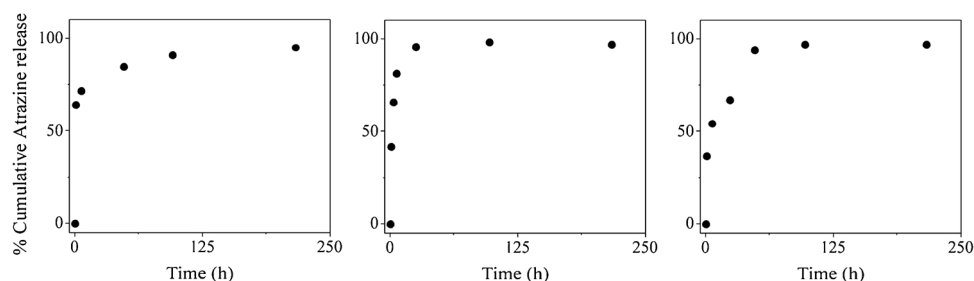

Fig. 5. Cumulative release of atrazine in water from ionic lignin microparticles with different herbicide loads: a) 10, b) 15, c) 20% w/w. The analyses were performed in duplicate.

Table 5
Comparison of atrazine delivery systems.

| Polymeric or composite matrix	Delivery system	Performance	Reference
Ionic and organosolv lignins	Microparticles	About 95% of atrazine release occurs in 48 h. In the soil mobility assay, 80% of free atrazine was leached in 37 days, while 65.0% and 59.7% of the herbicide were leached from ionic and organosolv lignin microparticles, respectively.	In this work
Poly(vinyl alcohol)/starch /halloysite nanotubes	Films containing nanotubes	Atrazine release from the composite system resulted in 61% after 96 h, while this value reached 97% in films without halloysite nanotubes. The leaching of atrazine is retarded.	[36]
Agar/starch/poly(acrylamide)	Hydrogels	50% of atrazine release occurred in 34 h.	[37]
Poly(ε-capractolone)	Nanocapsules	An effective tool in the post-emergence control of weeds was reported.	[38]
Poly(ε-caprolactone)/ chitosan-coating	Nanocapsules	All formulations showed slower release rates compared to free atrazine. About 80% of the encapsulated atrazine was release in 4 days, while 100% of free atrazine was released in this time.	[39]
Carboxymethyl chitosan/bentonite	Gel	90% of atrazine release occurs in 360 h for the different systems. The composite carrier reduces the potential leaching of pesticides.	[40]
Poly(ε-caprolactone)	Nanocapsules	Over 5 days of experiment, approximately 73% of atrazine was release from the nanocapsules.	[41]
Poly(hydroxybutyrate-co-hydroxyvalerate)	Microparticles	Total release of atrazine occurs in 5 h.	[42]
Poly(hydroxybutyrate-co-hydroxyvalerate)	Microparticles	75% of atrazine was released in 25 h.	[17]
Sodium alginate/bentonite	Beads	The mobility of atrazine in soils was reduced. After 50 days, 9.79% of atrazine was leached in soil.	[43]
Cellulose acetate butyrate Ethylcellulose	Microcapsules	Approximately 50% of atrazine was leached in soil after 32 weeks.	[44]
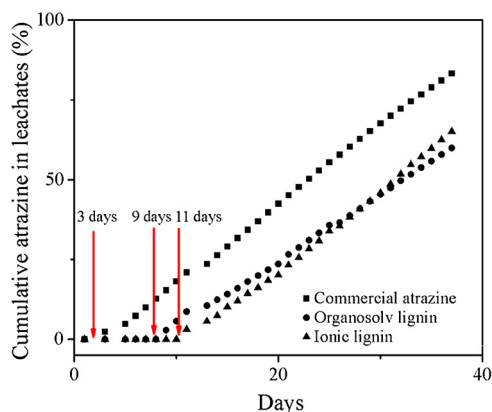
Fig. 6. Breakthrough profiles in soil of free atrazine and atrazine encapsulated in organosolv and ionic lignin microparticles.

volume was 79.7 ± 5.01 mL for the investigated soil. Breakthrough experiments with free atrazine (commercial formulation) show the presence of the herbicide in leachates after day 3. However, when the herbicide was applied in the form of controlled-release formulations, a delay in the appearance of atrazine in leachates was observed (9 days for organosolv lignin microparticles and 11 days for ionic lignin microparticles). Ionic lignin microparticles exhibited a higher delay compared with organosolv lignin microparticles. As it can be seen in Fig. 6, about 80% of free atrazine was leached in 37 days, while 65.0% and 59.7% of the herbicide were leached from ionic and organosolv lignin microparticles, respectively. The total water volume added to the column corresponds to approximately 9 pore volumes of the investigated soil. The atrazine mobility in soils is moderate due to its relatively low adsorption. However, Wang et al. [59] studied the interaction between atrazine and dissolved organic matter in soil, indicating that dissolved organic matter enhanced the adsorption efficiency of atrazine by soil. Through leaching effect, atrazine can be transported from contaminated soils to the water environment. This demonstrates that the application of the herbicide in the form of a controlled-release formulation could reduce leaching of atrazine and the herbicide remains available for a longer period.

According to the results of different atrazine systems presented in Table 5, the leaching behavior of the herbicide in soil showed different results, probably due to differences in soil composition and experimental conditions. Natural polymers are preferred instead of synthetic ones due to its lower cost, free availability and non-toxicity. In this direction, the use of lignins for microparticles preparation appears as an interesting option for the valorization of this abundant natural resource in agricultural applications.

4. Conclusions

Atrazine-loaded microparticles based on organosolv and ionic lignins were prepared. The influence of the organic solvent used during preparation on microparticles morphology was investigated. Lignins dispersed in EA produce with irregular shaped microparticles, but spherical microparticles were obtained with DCM for both lignins. The mean particle sizes were 17.4 ± 3.9 and 25.3 ± 6.7 μm, respectively. The organosolv lignin presented higher encapsulation efficiency for the applied herbicide loads, probably due to differences in the solidification rate of microparticles. The release profiles of atrazine in water showed a higher release rate of the herbicide from organosolv lignin microparticles compared to ionic lignin microparticles, due to differences in the mean particle size and the average molar masses of the base lignins. Leaching experiments performed in soil demonstrate that microparticles-based formulations reduce the presence of atrazine in leachates compared to free atrazine. In addition, ionic lignin microparticles exhibited the higher delay of leaching. Therefore, lignin microparticles allow increasing the dosing time and reduce the leaching of atrazine in soil. The investigated systems constitute an attractive alternative for the utilization of lignins in high-value-added products with low environmental impact.

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