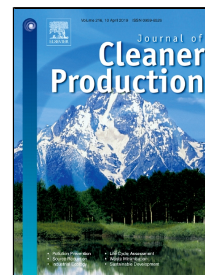


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1 **Technical and environmental assessment of coated urea production with a natural** 2 **polymeric suspension in spouted bed to reduce nitrogen losses**

3
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12
13 Urea is the most used nitrogen fertilizer in the world, but should be supplied to the plants in a
14 controlled way to make it as efficient as possible. Otherwise, nitrogen losses due to
15 volatilization and leaching can reach up to 70 %. The production of coated urea with slow-
16 release polymers can be a good alternative not just to reduce the nitrogen losses but also to
17 avoid the greenhouse gases emissions related to the high consumption of this fertilizer.
18 Therefore, the aim of this study is to evaluate the technical and environmental aspects of coated
19 urea production in a spouted bed to control the nitrogen volatilization. The influence of the
20 operating conditions in the coating performance was evaluated using a central composite
21 rotational design and the environmental performance was determined using a life cycle
22 assessment. The coating performance results showed that coated urea particle growth ranged
23 from 0.8 to 4.4 %, the coating efficiency presented results between 17-47 % and the nitrogen
24 volatilization reduction was significant (11-50 %). The highest nitrogen volatilization reduction
25 was obtained for suspension flow rate equal to 15 mL/min and air temperature equal to 85 °C.
26 The daily volatilized nitrogen release profile and the microscopic analysis showed that the
27 coating film was effective in controlling nitrogen release contained within the particle. The
28 environmental analyses demonstrated that coated urea had a lower impact than uncoated, for
29 most of the impact categories under study, indicating that the coating process is also appropriate
30 to reduce the environmental impacts of urea fertilization.

31 **Keywords:** life cycle assessment, nitrogen volatilization, slow-release, spouted bed, urea
32 coating.

33 **1. Introduction**

34 Income growth and world population growth have resulted in an increase of demand for food
35 and supplies (Gilland, 2002). It is estimated that the human population will reach 8.6 billion in
36 2030 and 9.8 billion in 2050 (UN, 2017), which will reflect an increased demand for food by
37 100 % by 2050 (Eickhout et al., 2006). However, intensifying food production must be done in
38 an environmentally safe manner to be sustainable and the development of more efficient
39 fertilizers plays a significant role to achieve this objective (Reis et al., 2010).

40 Nitrogen is one of the essential elements for plant growth and development (Maheswari et al.,
41 2017). It is the most required nutrient by plants during the crop development stages (Njinga et
42 al., 2013). The world's most commonly used nitrogen fertilizer is urea, i.e. 202 million metric
43 tons in 2018 (IFA, 2018), having the advantage of being a solid with high nitrogen
44 concentration, uncomplicated application, small corrosivity and low costs of manufacture,
45 transportation and storage (Deuner et al., 2008; Glibert et al., 2006; Kiss and Simihaian, 2002).
46 However, the disadvantage of using this fertilizer is related to the high predisposition to
47 nitrogen losses (Huang et al., 2017; Leon and Kohyama, 2017), in which about 70 % of the
48 applied urea is lost to the environment (Kibet et al., 2016; Schlossberg et al., 2018). The losses
49 are associated to volatilization, leaching, decomposition in soil, handling and storage and can
50 contribute to increase the greenhouse gases emissions and for severe environmental
51 contamination (Nascimento et al., 2013; Nielsen, 2006; Serrano-Silva et al., 2011). These
52 factors not only contribute to the environmental pollution but also reduce the urea efficiency,
53 economic cultivation and biomass production (Naz and Sulaiman, 2016).

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1 The nitrogen losses can be reduced by using slow-release fertilizers, which minimize the
2 hydrolysis rate by controlling the water solubility (Afshar et al., 2018; Cao et al., 2006; Saha et
3 al., 2018, 2017). The slow-release by coating can improve the fertilizer efficiency, limit nitrogen
4 losses and reduce environmental pollution (Azeem et al., 2014; Chang-Ai et al., 2016).

5 The conventional spouted bed (CSB), proved to be of interest for particle coating, since it
6 provides good mixing and circulation for particles and produces uniform films as a result of the
7 great transfer of mass and heat inside the bed (Suherman and Anggoro, 2011; Turton, 2008;
8 Tzika et al., 2003). It consists of a cylindrical column with a conical base where spouting air,
9 introduced from the bottom of the base, pass through the particles to be coated and dry the
10 coating suspension over the particle surface (Freitas and Freire, 1998). The control of the
11 operating conditions is the main responsible for the product quality and the process efficiency
12 (Bacelos et al., 2008, 2005; Turton, 2008). Among the operating conditions that affect air-
13 particle contact in CSB are the characteristics of the cylindrical column, spouting air velocity
14 and temperature, load of particles, suspension formulation, flow rate and others (Freitas and
15 Freire, 1998; Link and Schlünder, 1997). Despite the literature on particle coating is heavily
16 based on pharmaceutical applications, with very few reported studies on fertilizers applications
17 (Christodoulou et al., 2018; Rocha et al., 2018), studies identified that the key variables for
18 controlling the urea coating process are the air temperature, the suspension flow rate and the
19 suspension formulation (da Rosa and Rocha, 2010; Rocha et al., 2009).

20 There are a large number of materials that can be used for coating purposes, as sulphur, resin
21 and polymers (Borini et al., 2009; Suherman and Anggoro, 2011). Polymer coating has been
22 used for many different applications, which goes from improving the product aspect to
23 decreasing the release of chemicals (Liu et al., 2018; Rocha et al., 2009). In the fertilizers coated
24 with polymers, the nutrients are released through the polymer film by diffusion, which is the
25 mechanism responsible by controlling the nitrogen volatilization and, consequently, by coated
26 fertilizer quality (Lan et al., 2013).

27 An increasing interest has been observed in the use of natural polymers, since it presents high
28 stability, versatility to chemical modification, biodegradability specific and does not need a
29 toxic organic solvent (Faix et al., 2010; Lan et al., 2013; Suherman and Anggoro, 2011). Starch
30 is one of the most abundant polysaccharides polymer and can be used as a biodegradable
31 polymer (Naz and Sulaiman, 2016). However, the opportunity of using starch to decrease
32 nitrogen loss has been poorly studied (Edmeades, 2015; Khakbazan et al., 2013; Suherman and
33 Anggoro, 2011) and the environmental aspects have been ignored.

34 A holistic technical and environmental approach concerning the production of new fertilizers is
35 extremely important in order to provide support for decision making (Hasler et al., 2015). The
36 potential environmental impacts regarding the production and use of coated urea can be
37 evaluated using life cycle assessment (LCA) methodology. The LCA has been intensively
38 applied to quantify the environmental impacts of chemical fertilizers production (Brockmann et
39 al., 2018; Hanserud et al., 2018; Hayashi et al., 2014; Wang et al., 2017; Zhang et al., 2017), but
40 less attention has been paid to coated urea.

41 Therefore, this work aims to assess the technical and environmental aspects of coated urea
42 production in a CSB using a natural polymeric suspension that offers a slow-release of nitrogen.
43 The steps to achieve this objective include: formulate a coating suspension with polymers from
44 natural sources; determine the optimum operating conditions for urea coating using a central
45 composite rotational design (CCRD); evaluate the nitrogen volatilization reduction and coated
46 urea quality; assess the sustainability of coated urea production using a life cycle assessment.

47 **2. Materials and methods**

49 The uncoated urea ($\text{CO}(\text{NH}_2)_2$) used in this study, which was obtained in the crystalline form
50 from Yara (Brazil), displayed a chemical purity of 99.6 %. The uncoated urea was physically
51 characterized by density, particle diameter and moisture content measurements. The density was
52 determined in triplicates by Helium pycnometry (Ultrapycc 1200e, Quantachrome, USA) and the
53 particle diameter was determined by liquid pycnometry using glycerol (propane-1,2,3-triol). The
54 uncoated urea under study present density equal to $1.3405 \pm 0.0015 \text{ g/cm}^3$ and particle diameter
55 equal to $3.38 \pm 0.02 \text{ mm}$.

1 The urea moisture content (0.13 ± 0.02 %) was measured by method 920.151 proposed by
2 Association of Official Analytical Chemists (AOAC, 1997) and updated by Alcarde (1992) due
3 to the concomitant elimination of ammonia from the urea at high temperatures. For this reason,
4 the samples were dried at 50 °C for 24 h and not at 105 °C, as the original method. Using the
5 density and the particle diameter, uncoated urea was classified as a group D (spoutable) in
6 Geldart's diagram (Geldart, 1973), which is the reason for choosing the spouted bed for the urea
7 coating.

8 **2.1 Suspension formulation**

10 It was established to produce a suspension composed by polymers from natural sources and low
11 commercial value. The polymeric suspension was composed based on previous studies
12 conducted by Donida (2000) and Rosa and Rocha (2013), replacing the Eudragit® polymer by
13 starch and gelatine. Food grade maize starch and gelatine were chosen because, in addition to
14 being abundant in the world, they present biodegradable properties that are important to
15 promote the gradual release of nitrogen to the plants (Amin et al., 2015; Fabunmi et al., 2007).
16 The coating suspension was formulated according to the composition shown in Table 1. In
17 addition to gelatine and starch, the coating suspension also contains glycerol, distilled water,
18 talc (magnesium silicate hydroxide) and pigment (ColorSeed, RIGRANTEC, Brazil).
19 The maize starch and the gelatine were dissolved in 50 % of the total volume of distilled water.
20 A mechanical stirrer (RW20, IKA, Germany) was used to stir the suspension at 800 rpm. After
21 complete solubilisation, the suspension was heated at 70 °C to achieve the complete
22 gelatinization. The heating was carried out using a heating plate (NI 1337-AL, Nova, Brazil).
23 Once the desired temperature was attained, the known masses of glycerol, talc, pigment and the
24 remaining distilled water were gradually added into the system. The suspension was further
25 reacted at 70 °C for 30 minutes. The final suspension was left to cool at room temperature.
26 The coating suspension was characterized by solid concentration, density, surface tension and
27 dynamic viscosity measurements (Table 1). The solid concentration was gravimetrically
28 determined after drying for 24 h at 105 °C (AOAC, 1997). The density was measured by liquid
29 pycnometry. The surface tension was measured with the help of a tensiometer (EW-59951-20,
30 CSC, EUA) and the dynamic viscosity was determined using an Ostwald viscometer at 20 °C.

31 **2.2 Coating process**

33 Figure 1 presents the experimental system scheme. A spouted bed made in glass, with a
34 cylindrical section at the top and a conical shape at the bottom (4), was selected to conduct the
35 coating experiments. The conical base has an angle of 60°, its height is 60 cm and has 20 cm of
36 diameter. The spout air was supplied by a 5.6 kW blower (1) and the pressure drop was
37 measured by two U-tube mercury manometers (6) connected to an orifice plate (2). The pressure
38 drop in the orifice plate was used to determine the air flow rate. The air was heated by an
39 electrical heater (3) with 18 kW and the air temperature was determined using thermo-
40 hygrometers at the entrance and exit of the bed. The double fluid atomizer, which is situated at
41 the top of the bed, is supplied with air by a 3.7 kW compressor (7) and with coating suspension
42 (9), using a peristaltic pump (8). A cyclone (5) is attached to the bed outlet in order to collect
43 dried powder and elutriated particles dragged by the air.

44 The bed was loaded with a previously fixed mass of particles of 500 g and the atomization time
45 was fixed at 20 min, according to previous studies (da Rosa and Rocha, 2013; Rocha et al.,
46 2009). During the coating process, the atomization pressure was 50 kPa. The minimum spouting
47 velocity was equal to 0.44 m/s and the pressure drop across the bed at the point of minimum
48 spouting velocity was equal to 453 Pa. The operating flow rate for the coating runs was set 20 %
49 superior to the minimum spouting velocity.

50 Different air temperatures and suspension flow rates were tested to analyse their influence on
51 the product quality (coating efficiency, particle growth and nitrogen volatilization reduction).
52 An experimental planning CCRD was performed, since it allows obtaining more predictive
53 second-order models than simple factorial plans (Neto et al., 2001). Table 2 presents the
54 operating conditions and the respective levels used in the experimental design.

1 The coating processes were performed randomly with three replicates at the central point to
 2 provide an estimate of pure error and the statistical significance was assessed through an
 3 analysis of variance (ANOVA).

4 2.3 Characterization of coating performance

5 The coating performance was evaluated according to the particle growth, the coating efficiency,
 6 the nitrogen volatilization reduction, the coating uniformity and structurally.

7 The experimental particle growth (δ_{exp}) was determined as the ratio between the mass of the
 8 coating suspension adhered in the urea surface ($m_{adhered}$) and the initial load of urea added in
 9 the bed (m_0), which in this study was 500 g, according to:

$$10 \delta_{exp} = m_{adhered}/m_0 \quad (1)$$

11 The urea was weighed at the beginning and at the end (m_f) of the coating experiment to
 12 calculate the mass adhered, according to:

$$13 m_{adhered} = m_f - m_0 \quad (2)$$

14 The coating efficiency (η) is defined as the ratio between the mass of the coating suspension
 15 adhered in the urea and the mass of the coating suspension added to the bed (m_{added}) without
 16 losses by elutriation or on the walls of the bed (m_{losses}). The definitions were used by several
 17 authors (da Rosa and Rocha, 2013; Donida, 2000; Martins et al., 2008) and are described
 18 according to:

$$19 \eta = m_{adhered}/m_{added} \quad (3)$$

$$20 m_{added} = W \cdot \rho_s \cdot t \cdot c_s \quad (4)$$

$$21 m_{loss} = m_{added} - m_{adhered} \quad (5)$$

22 where W is the suspension flow rate, ρ_s is the suspension density, t is the process time and c_s is
 23 the suspension solid concentration.

24 The nitrogen volatilization reduction was obtained comparing the nitrogen volatilization of
 25 coated and uncoated urea. The experiments were conducted using a semi-open static collector
 26 during a 14 days' period of exposure, as proposed by Duarte et al. (2007). The urea was
 27 distributed in closed flasks containing 0.10 kg of soil and it was scattered in quantities
 28 corresponding to 100 kg of nitrogen per hectare (Kiss and Simihaian, 2002). The nitrogen
 29 volatilized was collected in the form of ammonia, using paper disks 5 cm above the flasks,
 30 which was treated with 1 mL of sulfuric acid (0.5 mol/L). The remaining acid was titrated with
 31 sodium hydroxide 0.02 mol/L in presence of bromocresol green. The amount of nitrogen
 32 volatilized as ammonia (V_{N-NH_3}) was calculated according to:

$$33 V_{N-NH_3} = 0.28 (V' - V) \quad (6)$$

34 where V' is the volume of sodium hydroxide consumed in the control treatment without the
 35 influence of nitrogen fertilization (zero kg of nitrogen per hectare) and V is the volume of
 36 sodium hydroxide consumed in the sample with urea.

37 The surface of uncoated urea and the coating film uniformity of coated urea were assessed
 38 through micrographs obtained by scanning electron microscope (SEM) (s-440i, LEO, England).
 39 The structural characterization of uncoated and coated urea was performed by X-ray diffraction
 40 (XRD) using a diffractometer (Miniflex II, Rigaku, EUA) with $CuK\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$).
 41 The diffractometer reflections were taken at room temperature, operating in the Bragg-Brentano
 42 geometry in a 2θ range of $10-80^\circ$ at a scan step of 0.05° . The possible crystal structure was
 43 obtained comparing XRD patterns with standard data sets of possible types of compounds
 44 (JCPDS, 1999).

45 2.4 Environmental performance

46 A cradle-to-grave LCA was used to compare the environmental impacts of uncoated urea and
 47 coated urea that presented the best coating performance. Same methodological choices and
 48 assumptions (functional unit, system boundaries and impact assessment method) were
 49 considered, in order to allow a direct and reliable comparison of urea production systems.
 50 The functional unit (FU) is the nitrogen fertilization, in the form of urea, of 1 hectare with
 51 uncoated/coated urea. The nitrogen amount fertilized effectively available to the plants, after
 52
 53

1 disregarding volatilization losses, was considered equal to 100 kg per hectare, according a study
2 performed by Kiss and Simihaian (2013). The urea was transported from the regional
3 storehouse to the landfarming over a distance of 50 km and scattered in the soil previously
4 prepared by hand hoeing. The transport distance to the landfarming was based on distances of
5 existing regional storehouse units in Brazil. The urea application was made using a broadcaster
6 with a capacity of 500 L. The diesel consumed by the broadcaster during scattering and the
7 related emissions to air were taken from Ecoinvent v3.5 (Ecoinvent, 2017). The system
8 boundaries also include the production of urea from ammonia and carbon dioxide, as well as the
9 transport of intermediate products. The production of the machinery used to perform the
10 operations and the transport of workers were not included.

11 In the production of coated urea, the raw materials used to produce the coating suspension
12 (gelatine, starch, glycerol, talc, pigment and water) are included in the system boundary, as well
13 as the electricity consumed during the suspension processing (heating and mixing), during
14 suspension atomization (compressor and peristaltic pump) and during the coating process (air
15 blower and air heater).

16 The Ecoinvent database (Ecoinvent, 2017) was used for the background processes for which the
17 production has no specific influence or information (e.g., raw material production and
18 electricity). Moreover, it should be noted that the specific data concerning the foreground
19 processes to produce coated urea was obtained from experimental tests. Table 3 presents the
20 inventory data for the fertilization with uncoated and coated urea.

21 The calculation procedures follow the recommendations of the International Organization for
22 Standardization included in ISO 14044 (ISO, 2006). The impact evaluation method used was
23 ReCiPe 2016 (H) midpoint (Huijbregts et al., 2016). The impact categories chosen for the
24 environmental evaluation were those which presented available inventory data, for instance,
25 global warming (GW), particulate matter formation (PMF), ozone formation (OF), terrestrial
26 acidification (AC), marine eutrophication (ME), marine ecotoxicity (MEC), human carcinogenic
27 toxicity (HTOX), mineral resource scarcity (MS), fossil resource scarcity (FS) and water
28 consumption (WCON).

30 **3. Results and discussion**

31 Figure 2 presents the daily nitrogen volatilization rate over a period of 14 days for coated and
32 uncoated urea and the soil pH profile.

33 Regardless of the formulation, the highest volatilization rates were observed near the 3rd day
34 after application. Some studies also observed a high nitrogen volatilization in the early days
35 after urea application in soil (Raymond et al., 2016; Rech et al., 2017; Soares Filho et al., 2015).
36 The reason for this phenomenon is the rapid urea hydrolysis, which depends on the physical and
37 chemical properties of the soil, as well as the amount of fertilizer applied in excess of that
38 utilized by plants (Sigurdarson et al., 2018; Vahed et al., 2011).

39 The urea is hydrolysed by the action of urease, an enzyme produced by fungi, bacteria and
40 actinomycetes (Konieczna et al., 2012; Mora and Arioli, 2014). In wet soils, with adequate
41 temperatures, urea is converted into ammonium (NH_4^+). In addition to the formation of NH_4^+ ,
42 there is the release of hydroxide (OH^-), which sharply increases the soil pH (Fageria et al., 2010;
43 Ghaly and Ramakrishnan, 2013). The increase in soil pH (Figure 2) can be observed near the
44 3rd day after urea application.

45 The NH_4^+ formed can be absorbed by plants, or transformed into ammonia (NH_3) together with
46 OH^- from the soil, resulting in a high nitrogen loss from the system soil:plant due to
47 volatilization (Choi et al., 2007; Pereira et al., 2009). The NH_3 volatilization will be greater
48 under alkaline soil conditions (Rochette et al., 2013). However, the soil pH increase is
49 temporary, as nitrification occurs, the soil pH decreases rapidly (Tarre and Green, 2004; Ying et
50 al., 2017). This behaviour was observed in Figure 2, near the 7th day after urea application.

51 In nitrification, NH_4^+ is converted into nitrite (NO_2^-) and then into nitrate (NO_3^-) by the
52 mediation of two distinct groups of bacteria: bacteria that convert ammonia to nitrites
53 (*Nitrosomonas*, *Nitrosococcus*, *Nitrospira* and *Nitrosolobus*) and that convert nitrites to
54 nitrates (*Nitrobacter*, *Nitrococcus* and *Nitrospina*) (Ghaly and Ramakrishnan, 2013; Tarre and
55 Green, 2004). The hydrogen cation (H^+), resulted from the nitrification process, contributes to

1 soil acidification (Tarre and Green, 2004; Ying et al., 2017). The NH_4^+ nitrification is clearly
2 affected by the soil pH, considering that the bacteria development decreases if the pH is not near
3 neutrality (Keen and Prosser, 1987).

4 In the 3rd day after urea application, the nitrogen volatilization of uncoated urea was equal to
5 6.61 mg of NH_3 . Coated urea presented lower nitrogen losses, demonstrating that the coating
6 film was effective in controlling the nitrogen volatilization. The fertilizers with highest loss
7 peaks in this initial period were, in decreasing order: uncoated urea, coated urea 7 (operating
8 conditions of 75 °C and 7.8 mL/min) and coated urea 1 (operating conditions of 65 °C and 9
9 mL/min), which also presented the highest accumulated nitrogen losses throughout the test
10 period. The lowest peaks of volatilization were observed in coated urea, where the following
11 stood out positively: coated urea 8 (operating conditions of 75 °C and 16.2 mL/min) and coated
12 urea 4 (operating conditions of 85 °C and 15 mL/min). However, all formulations were more
13 efficient in controlling nitrogen volatilization than uncoated urea.

14 Table 4 shows the coating performance according to the particle growth, process efficiency and
15 nitrogen volatilization reduction.

16 It can be observed that the particle growth ranged from 1.0 to 4.4 %, for an experimental coating
17 of 20 min. According to Donida (2000), the polymer coating is characterized by a particle
18 growth between 2-8 % and most of the scenarios evaluated are among the expected range.
19 However, some scenarios are below the range that provides a good coating, especially those
20 scenarios that have low inlet air temperature.

21 It was also seen that the coating efficiency presented results between 17-47 % and is
22 interconnected with the particles growth, since both are related to the mass of solids added to
23 the bed. The coating film provided a satisfactory reduction in the nitrogen volatilization for all
24 operating conditions under study and the results are between 11-50 %. The results presented
25 adequate reproducibility verified by the three replicates at the central point.

26 Figure 3 presents the influence of the operating conditions (air temperature and suspension flow
27 rate) on the coating performance (particle growth, coating efficiency and nitrogen volatilization
28 reduction).

29 The Pareto chart (A.1) shows that both operating conditions under study have significant effects
30 on the particle growth, since they are located at the right size of the significance level ($p \leq 0.05$),
31 as well as the interaction between them. The most pronounced effect was the suspension flow
32 rate, which had a positive influence on the particle growth. The highest particle growth (coated
33 urea 8), shown in Table 4, was obtained for the highest suspension flow (16.2 mL/min), despite
34 the influence of temperature. The air temperature effect was less pronounced but was also
35 positive, indicating that the particle growth is proportional to the flow rate and air temperature,
36 since the increase of one of these parameters induces the increase on particle growth and the
37 decrease causes the opposite effect.

38 It can also be verified, through the response curve (A.2), that the region that maximizes particle
39 growth is close to the +1 level of suspension flow, where the flow is high ($>15\text{mL/min}$). This
40 result was expected, since the coating suspension forms successive films on the urea surface
41 while the coating suspension is added to the bed, which was also confirmed by other authors (da
42 Rosa and Rocha, 2010; Donida and Rocha, 2002). For air temperature, both levels (+1 and -1)
43 demonstrated an appropriate particle growth. However, other studies show that high
44 temperatures can have negative effects on coating performance, since the suspension can be
45 dried before reaching the particle surface (da Rosa and Rocha, 2010), but this effect was not
46 noted in the present study.

47 For coating efficiency, the Pareto chart (B.1) shows that both operating conditions under study
48 have significant effects for a significance level of $p \leq 0.05$. The linear and quadratic effects of the
49 suspension flow were the most pronounced and the influence was positive, which means that
50 increasing the suspension flow will also increase the coating efficiency. The highest coating
51 efficiency was observed for coated urea 8 (Table 4), obtained for a high suspension flow
52 (16.2 mL/min), as expected. Martins et al. (2008) also observed a positive effect on efficiency
53 during enteric coating of gelatine capsules in a spouted bed, as well as Donida (2000) in a study
54 of urea coating with polymeric film in a two-dimensional spouted bed. However, Rosa (2010)
55 verified that the influence of the suspension flow was negative on the coating efficiency, which

1 means that increasing the suspension flow there is a decrease in coating efficiency. The study
2 was conducted with suspension flows between 7 and 13 mL/min and it was observed that the
3 highest efficiency was obtained near the central point (10 mL/min).
4 The effect of the air temperature also demonstrated a significant and positive influence on
5 coating efficiency, since the coating suspension is better dried on the urea particle in high
6 temperatures, increasing the coating efficiency. At low temperatures, higher suspension losses
7 were observed in the wall of the spouted bed.
8 The significant influence of the air temperature on the coating efficiency was also observed by
9 other authors (da Rosa and Rocha, 2013; Donida, 2000). However, da Rosa and Rocha (2013),
10 were not able to claim if the influence was positive or negative, since the quadratic effect was
11 negative and the linear effect was positive. During the experiments, the authors observed that
12 high air temperature appears to be the reason for lower coating efficiency, since it was detected
13 coating suspension losses due to the elutriation phenomenon. However, very low temperatures
14 can also lead into losses due to a greater adhesion of the particles in the walls. On the other
15 hand, Donida (2000) found that air temperatures between 50 and 70 °C negatively influence the
16 coating efficiency.
17 According to the response curve (B.2) it is observed that the region that maximizes the coating
18 efficiency is close to the positive levels, where the temperature and flow rates are higher. It is
19 also possible to obtain high efficiencies near the +1 level of the air temperature and -1 of the
20 suspension flows, since there is lower moisture content present in the bed and the suspension
21 can adhere to the wall more easily.
22 For nitrogen volatilization reduction, the Pareto chart (C.1) shows that the linear effect of
23 suspension flow is the most pronounced, for a significance level of $p \leq 0.05$, followed by the
24 linear effect of air temperature. Both effects had a positive influence on the response, indicating
25 that the reduction of the volatilization is proportional to the flow rate and temperature. It can
26 also be observed, through the response curve (C.2), where nitrogen volatilization reduction is
27 higher near the +1 level of suspension flow, whereas the temperature showed less pronounced
28 effect. The highest nitrogen volatilization reduction was obtained for coated urea 4 (Table 4)
29 and the operating conditions were as follows: suspension flow rate equal to 15 mL/min and air
30 temperature equal to 85 °C.
31 Second-order polynomial models were obtained to estimate the coating performance (particle
32 growth, coating efficiency and nitrogen volatilization reduction), as a function of the operating
33 conditions statistically significant (Figure 3). The statistical significance of the models was
34 verified through the F-test (ANOVA) and is presented in Table 5. The regression can be
35 considered significant when the F_{value} is higher than the F_{tabled} and for all models tested this
36 criterion was fulfilled. The determination coefficient for the particle growth model
37 ($R^2=99.74\%$), coating efficiency model ($R^2=93.06\%$) and nitrogen volatilization reduction
38 model ($R^2=87.03\%$) were considered predictive, considering the inherent variability of the
39 coating process.
40 The coating film uniformity was analysed through micrographs obtained by SEM at
41 magnification of 40X, 200X and 1000X (Figure 4), comparing uncoated and the coated urea
42 with the highest nitrogen volatilization reduction (coated urea 4).
43 The SEM micrographs showed that the uncoated urea surface (A) was almost equal to the one
44 that received a polymeric coating (B), for a magnification of 40X and 200X. However, an
45 asymmetric structure and porosity is clearly observed for uncoated urea at the magnification of
46 1000X. Uncoated urea does not have a homogeneous surface and many fine openings were
47 observed in the micrographs, which can allow the free circulation of water between the interior
48 and exterior of the particle, so as to dissolve the urea granule.
49 However, a seemingly decrease in membrane porosity was noticed for coated urea, which
50 appeared much smoother, denser and with less microspores. It indicates that, the suspension
51 under study appears to be a suitable sealant to coat the urea and decrease the penetration of
52 water into the granule. The slower the penetration time the longer it will take the urea to
53 dissolve and subsequently volatilize to the atmosphere (Uzoh et al., 2019; Yang et al., 2012).
54 This characteristic is desirable to decrease the nitrogen losses in coated urea.

1 In order to investigate any changes that might have occurred in the crystal structure of coated
2 urea (run 4) compared to uncoated urea, XRD analysis is employed and the patterns are depicted
3 in Figure 5.

4 Through XRD analysis, it can be seen that urea crystals are definitely present in both materials.
5 Uncoated urea exhibited typical X-ray diffraction pattern with major peaks at diffraction angles
6 of $2\theta = 22.20^\circ$ ($d = 4.001$), 24.55° ($d = 3.623$) and 29.25° ($d = 3.051$) and showed consistent
7 signature peak distribution with previous published studies (Karas, 2005).

8 Coated urea contains all the diffraction peaks of uncoated urea. This indicates that the crystal
9 structure of the urea does not change during the whole processing of coating and drying.

10 Moreover, it was noticed that the main diffraction peaks were broadened as compared to
11 uncoated urea. For example, in coated urea diffraction patterns, the main diffraction peak at
12 $2\theta = 22.25^\circ$ is much higher than the diffraction peak at the same position of uncoated urea.
13 The increased crystallinity of coated urea is attributable to the drying process, which occurs
14 simultaneously with the coating process. As the inlet air flows in co-current with the urea
15 particles and the temperature inside the bed increased, the water molecules present in the urea is
16 subjected to drying release moisture due to forced convection effects at the particle surface. This
17 made the molecular chains more orderly and resulted in a higher crystallinity.

18 Crystallinity is a major factor that influences the mechanical and dimensional properties of
19 materials (Chivers and Moore, 1994; Talbott et al., 1987). In addition, compared with uncoated
20 urea, the thermal stability of coated urea was improved after coating process.

21 The environmental performance was analysed comparing the impacts of uncoated and coated
22 urea (run 4), using the life cycle assessment methodology. Figure 6 shows the relative
23 contribution of each stage to the total impact.

24 Regarding uncoated urea, its production represents 95 % of the total impact in the global
25 warming category due to the high carbon dioxide (CO_2) and methane (CH_4) emissions during
26 the production of ammonia. In the particulate matter formation, the nitrogen volatilization is
27 responsible for a large part of the total impact (97 %), mainly due to the ammonia emissions.
28 For ozone formation, the stage with the largest contribution for the total impact was the
29 production of urea (70.4 %), followed by the fertilization (23 %). The main contribution in this
30 category is associated with the emissions of nitrogen oxides (NO_x) due to fuel combustion
31 during the heating process to produce ammonia and by the broadcaster. In the acidification, the
32 impacts related to this category come mostly from the nitrogen emissions during urea
33 volatilization (98 % of the total impact). In the marine eutrophication, the emission of NH_4^+ to
34 water contributed to about 99 % of the total impact. In the marine ecotoxicity, the urea
35 production is responsible for 97 % of the total impact, mainly due to vanadium emissions to the
36 air and zinc emissions to the water. The production of urea is also responsible for impacts in the
37 human carcinogenic toxicity (98 % of the total impact), mainly due to chromium VI emissions
38 to the water and nickel emissions to the air. In the mineral resource scarcity, the stage with the
39 largest contribution for the total impact is also the production of urea (99 %), due to the
40 consumption of nickel. In the fossil resource scarcity, the urea production is the stage that
41 contributed most to the total impact (about 96 %), due to the consumption of natural gas. The
42 production of urea is also responsible for 99 % of the total impact in water consumption
43 category.

44 Regarding coated urea, the production of urea represents 68 % of the total impact in the global
45 warming category, followed by the electricity consumed by the air heater (18 %). In the
46 particulate matter formation, the nitrogen volatilization is the main responsible for the total
47 impact (92 %), as well as in uncoated urea. In the ozone formation, the urea production
48 represents 54 % of the total impact, the fertilization represents 17 % and the electricity
49 consumed by the air heater represents 16 %. In the acidification, the main responsible for the
50 total impact is the nitrogen volatilization (97 %), as well as in uncoated urea. In the marine
51 eutrophication, the production of urea represents 50.4 % of the total impact, followed by the raw
52 materials consumed in the coating suspension (39 % of the total impact). In the marine
53 ecotoxicity, the impacts are due to the production of urea (56 % of the total impact) and the
54 electricity consumed by the air heater (26 % of the total impact). In the human carcinogenic
55 toxicity, the urea production represents 38 % of the total impact, the electricity consumed by the

1 air heater represents 37 % and the electricity consumed by the air blower represents 12 %. In the
2 mineral resource scarcity, the stage with the largest contribution for the total impact is the
3 production of urea (48 % of the total impact), followed by the raw materials consumed in the
4 coating suspension (47 % of the total impact). In the fossil resource scarcity, the urea production
5 represents 79 % of the total impact and the electricity consumed by the air heater represents
6 11 % of the total impact. Urea production accounts for most of the water consumption (61 % of
7 the total impact), followed by the electricity consumed by the air heater (24 % of the total
8 impact).

9 Table 6 presents the total impact obtained for the nitrogen fertilization of 1 ha with uncoated
10 and coated urea. Figure 7 shows the relative reduction in the environmental impact.

11 It was observed that the environmental impacts of coated urea are lower than the impacts related
12 to uncoated urea, for most of the impact categories under study, indicating that the coating
13 process for reducing the nitrogen losses is also an appropriate alternative for minimizing the
14 environmental impacts.

15 In the global warming, the fertilization with coated urea instead of uncoated urea can reduce the
16 environmental impacts by 35 %, avoiding 346 kg of CO₂ equivalent per hectare. In the
17 particulate matter formation, the environmental impact reduction achieved 75 %, avoiding about
18 43.2 kg of particulate matter less than 2.5 μm (PM_{2.5}) equivalent per hectare. In the ozone
19 formation, the use of coated urea achieved a reduction of about 37 %, avoiding nearly 0.56 kg of
20 NO_x equivalent per hectare. In the acidification, the environmental impact reduction is about
21 76 %, avoiding 350 kg of sulphur dioxide (SO₂) equivalent per hectare. In the marine
22 eutrophication, the reduction achieved 8 % and the nitrogen equivalent per hectare avoided was
23 equal to 2.4 g. In the marine ecotoxicity, 20 % of the environmental impacts were reduced using
24 coated urea and the 1,4 dichlorobenzene (1,4-DCB) equivalent avoided was equal to 1.08 kg. In
25 the human carcinogenic toxicity, the fertilization with coated urea increased the environmental
26 impacts in about 18 %. The reason for this singularity is the high consumption of electricity by
27 the air heater. Electricity production generates emissions of many metals, including chromium
28 VI, that is the main responsible for the impacts in this category. The addition of 1,4-DCB
29 equivalent due to the use of coated urea was equal to 0.70 kg. In the mineral resource scarcity,
30 the environmental impact reduction is small (3 %), avoiding only 10.4 g of copper (Cu)
31 equivalent per hectare. In the fossil resource scarcity, the environmental impact reduction
32 achieved 43 %, avoiding about 176 kg of oil equivalent per hectare. In addition, the fertilization
33 with coated urea instead of uncoated urea can reduce the water consumption in 25 %, avoiding
34 about 15 m³ of water per hectare.

36 4. Conclusions

37 The research findings depict that natural polymers (starch and gelatine) are potential coating
38 materials that can be exploited to develop slow-release urea with higher efficiency and less
39 environmental hazard. Coated urea exhibited nitrogen controlled-release in soil, and the release
40 is highly dependent of the coating operating conditions (air temperature and suspension
41 flowrate) in the spouted bed.

42 In addition, the results showed that coated urea presented lower nitrogen losses compared to
43 uncoated urea, with reductions between 11-50 %, demonstrating that the coating film was
44 effective in controlling the nitrogen volatilization. The highest nitrogen volatilization reduction
45 was obtained for suspension flow rate equal to 15 mL/min and air temperature equal to 85 °C.
46 Coated urea particle growth ranged from 0.8 to 4.4 %, while the coating efficiency presented
47 results between 17-47 %.

48 Regarding the coating quality, the SEM micrographs showed that the surface of uncoated urea
49 presented an asymmetric structure and many fine openings, which increase the nitrogen losses,
50 while coated urea presented a seemingly decrease in membrane porosity, indicating that the
51 coating suspension is a suitable sealant for the urea. The XRD analysis showed that coated urea
52 contains all the diffraction peaks of uncoated urea, demonstrating that the urea crystal structure
53 does not change during the coating process. However, the main diffraction peaks were
54 broadened due to convection effects during the drying process, which vaporize the water present
55 in coated urea surface, making molecular chains more orderly and crystalline.

1 The environmental assessment of coated urea production through LCA methodology showed
 2 environmental savings compared to uncoated urea, for most of the impact categories under
 3 study, indicating that the coating process for reducing the nitrogen losses is also an appropriate
 4 alternative for minimizing the environmental impacts. The maximum reduction achieved was
 5 76 % in the acidification impact category, which represents 350 kg of SO₂ equivalent per
 6 hectare avoided.

8 Nomenclature

c_s	solids concentration (g/g)
δ_{exp}	particles growth (%)
η	coating efficiency (%)
m_0	initial load of urea (g)
m_{added}	mass of the coating suspension added to the bed (g)
$m_{adhered}$	mass of the coating suspension adhered in the urea (g)
m_f	final load of urea (g)
m_{losses}	mass of the coating suspension lost (g)
ρ_s	suspension density (g/cm ³)
T	air temperature (°C)
t	process time (min)
V	volume of sodium hydroxide consumed in the sample with urea (mL)
V'	volume of sodium hydroxide consumed in the blank sample (mL)
V_{N-NH_3}	nitrogen volatilized as ammonia (mg)
W	suspension flow rate (mL/min)

9

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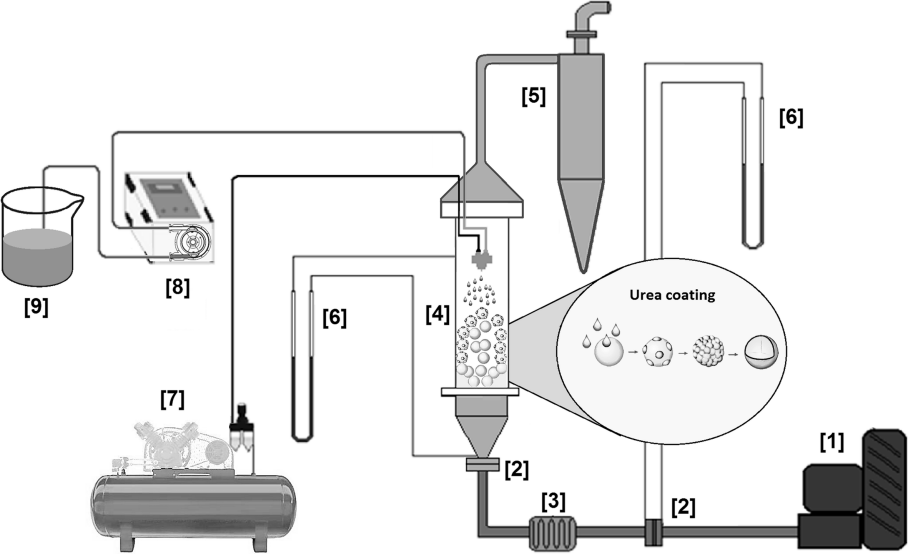
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55 Figure Captions

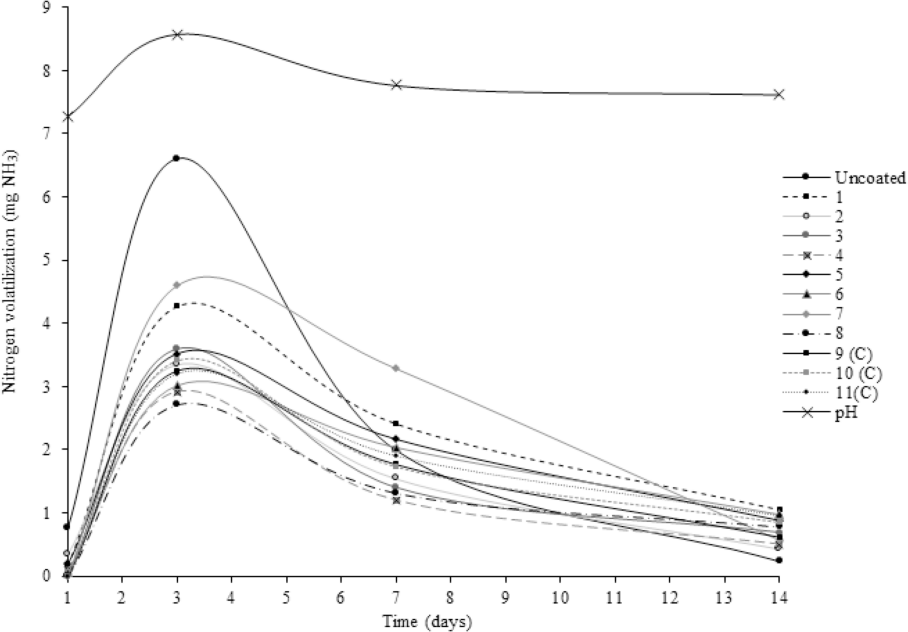
- 1 Figure 1. Experimental system of coating of urea in a spouted bed.
2 Figure 2. Nitrogen volatilization daily profile for urea with and without coating over a period of
3 14 days and the soil pH profile.
4 Figure 3. Pareto charts and response curves of the estimated effects on the coating performance
5 (particle growth, coating efficiency and nitrogen volatilization reduction) as a function of the
6 operating conditions (air temperature and suspension flow rate).
7 Figure 4. Micrographs of coating film uniformity of uncoated (A) and coated urea (B) obtained
8 by SEM at magnification of 40X, 200X and 1000X.
9 Figure 5. X-ray diffraction patterns of uncoated and coated urea.
10 Figure 6. Hotspot analysis showing the relative contribution of each stage to the total impact for
11 uncoated and coated urea.
12 Figure 7. Relative reduction in the environmental impact of coated urea with respect to uncoated
13 urea.
14
15 **Tables**
16 Table 1. Coating suspension composition and characterization.
17 Table 2. Independent variables of operating conditions and experimental design levels.
18 Table 3. Inventory data of the fertilization with uncoated and coated urea per FU (1 ha).
19 Table 4. Experimental results for particle growth, coating efficiency and nitrogen volatilization
20 reduction.
21 Table 5. Variance analysis.
22 Table 6. Environmental impacts of nitrogen fertilization with uncoated and coated urea per FU
23 (1 ha).

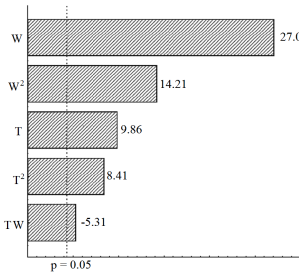
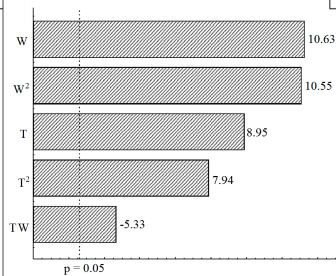
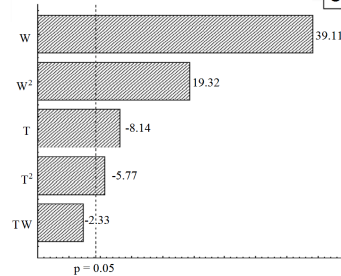
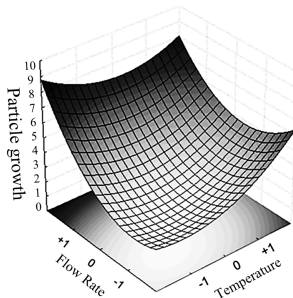


- ① blower
- ② orifice plate (30 mm diameter)
- ③ electrical heater

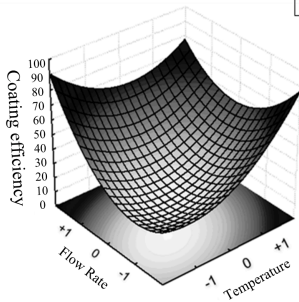
- ④ spouted bed
- ⑤ cyclone
- ⑥ U-tube manometer

- ⑦ compressor
- ⑧ peristaltic pump
- ⑨ coating suspension

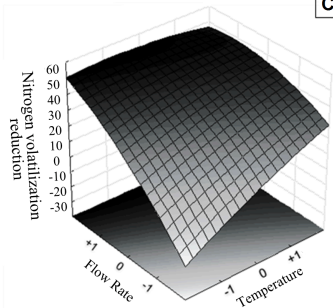


A.1**B.1****C.1****A.2**

$$Y = 1.71 + 0.35T + 0.36T^2 + 0.96W + 0.61W^2 - 0.27TW$$

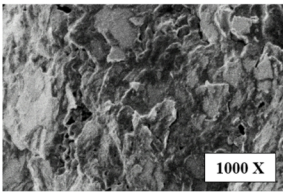
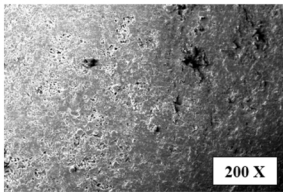
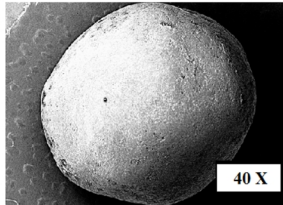
B.2

$$Y = 25.40 + 4.85T + 5.13T^2 + 5.74W + 6.81W^2 - 4.07TW$$

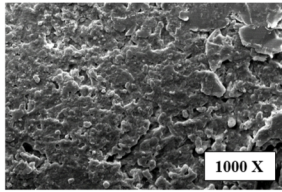
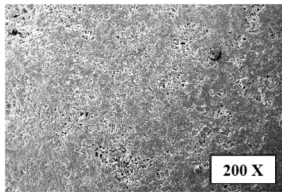
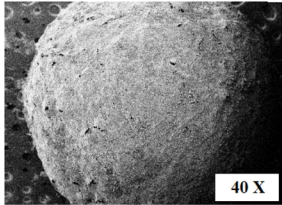
C.2

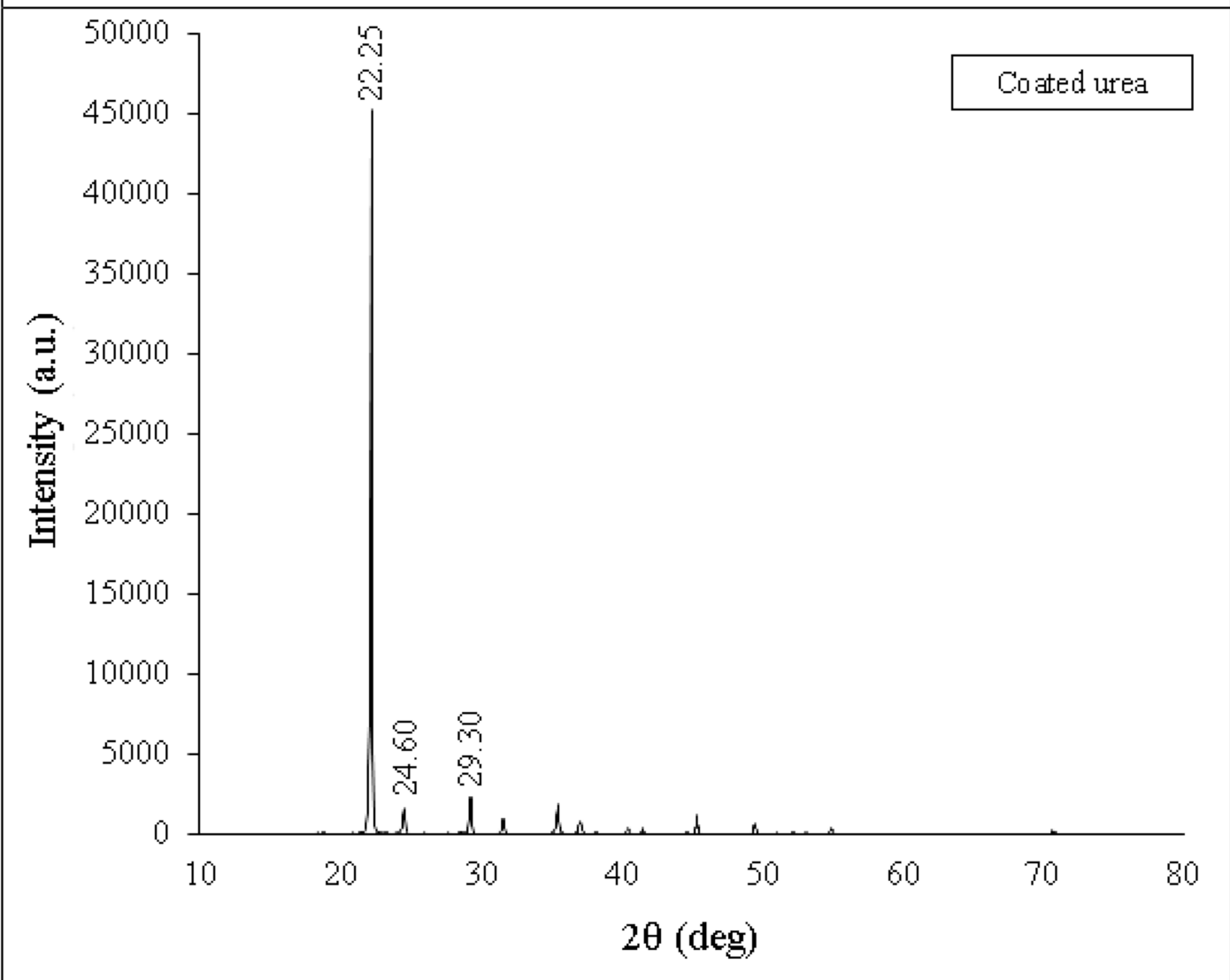
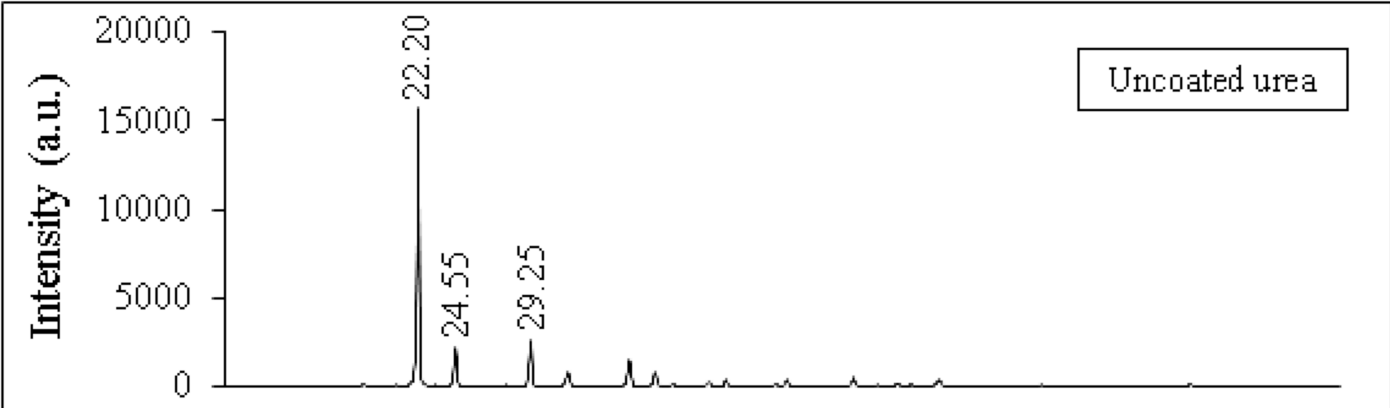
$$Y = 36.74 + 5.38T + 10.91W + 1.70W^2 - 3.21TW$$

[A]



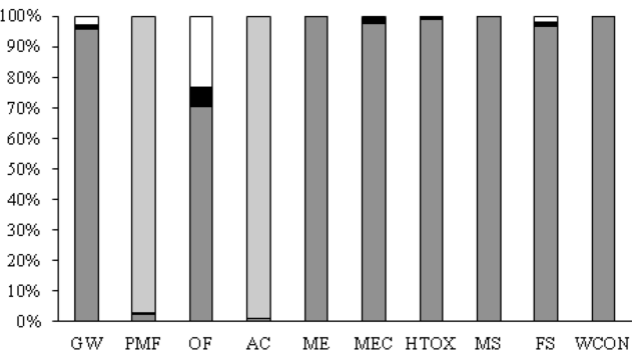
[B]



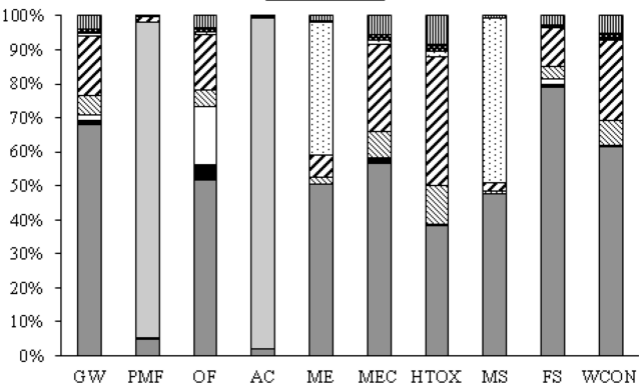


Uncoated urea		Coated urea		d-values from	
2θ-value (deg)	observed d-values	2θ-value (deg)	observed d-values	JCPDS data card	{h k l}
22.20	4.001	22.25	3.992	3.994 (37-1464)	{110} Urea
24.55	3.623	24.60	3.616	3.617 (31-1979)	{101} Urea
29.25	3.051	29.30	3.046	3.048 (31-1979)	{111} Urea

Uncoated urea



Coated urea



- Urea production
- Transport
- Fertilization (broadcaster)
- Nitrogen volatilization
- ▨ Air blower
- ▨ Air heater
- Suspension raw material
- ▨ Suspension processing
- ▨ Suspension atomization

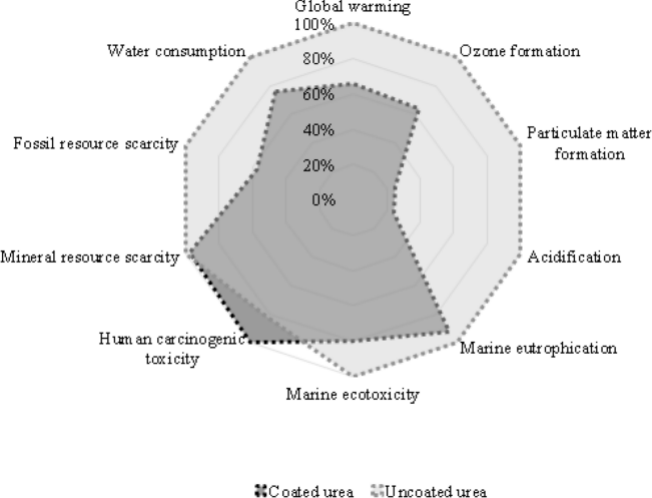


Table 1. Coating suspension composition and characterization.

Reagents	(% weight)
Gelatin	0.5
Starch	0.5
Pigment	2
Glycerol	3
Talc	9
Water	85
Characterization	Average/deviation
Solid concentration (%)	14.667 ± 0.432
Density (g/cm ³)	1.0535 ± 0.0001
Surface tension (N/m)	0.068 ± 0.002
Dynamic viscosity (Pa.s)	0.036 ± 0.004

Table 2. Independent variables of operating conditions and experimental design levels.

Independent variables		
Runs	T (level)	W (level)
1	-1	-1
2	-1	1
3	1	-1
4	1	1
5	-1.41	0
6	1.41	0
7	0	-1.41
8	0	1.41
9 (C)	0	0
10 (C)	0	0
11(C)	0	0
Levels	T (°C)	W (mL/min)
-1.41	60.9	7.8
-1	65	9
0	75	12
1	85	15
1.41	89.1	16.2

(C) Central point

Table 3. Inventory data of the fertilization with uncoated and coated urea per FU (1 ha).

	Uncoated urea	Coated urea
Inputs:		
Urea (t)	0.740	0.345
Gelatine (kg)		1.03
Starch (kg)		1.03
Pigment (kg)		4.14
Glycerol (kg)		6.21
Talc (kg)		18.6
Water (m ³)		0.176
Electricity (kWh)		656
Diesel (L)	9.21	4.29
Product		
Fertilized area (ha)	1.00	1.00
Emissions to air		
NH ₃ (kg)	233	55.4
CO ₂ (kg)	24.4	11.4
CO (kg)	0.0311	0.0145
CH ₄ (g)	1.01	0.471
NO _x (kg)	0.342	0.159
N ₂ O (g)	0.940	0.438
NM VOC (g)	21.7	9.87
PM _{2.5} (g)	30.8	14.3
SO ₂ (g)	7.89	3.68
Cr (mg)	0.392	0.183
Cu (g)	0.0133	0.00621
Ni (mg)	0.548	0.255
Zn (mg)	7.83	3.65
Emissions to soil		
Zn (g)	1.33	0.619

Table 4. Experimental results for particle growth, coating efficiency and nitrogen volatilization reduction.

Runs	m_{added} (g)	$m_{adhered}$ (g)	m_{loss} (g)	δ_{exp} (%)	η (%)	V_{N-NH_3} reduction (%)
1	28.7	4.94	23.7	0.987	17.2	17.8
2	41.1	17.3	23.8	3.46	42.0	40.9
3	28.7	9.70	19.0	1.94	33.8	40.7
4	41.1	17.4	23.7	3.48	42.3	50.9
5	32.7	10.3	22.4	2.06	31.4	29.5
6	32.7	15.3	17.4	3.06	46.9	36.7
7	24.8	9.43	15.4	1.89	38.0	11.8
8	46.9	22.0	24.9	4.41	46.9	49.8
9 (C)	32.7	7.78	24.9	1.56	23.8	38.3
10 (C)	32.7	8.38	24.3	1.68	25.6	37.3
11(C)	32.7	8.77	23.9	1.75	26.8	36.8

Table 5. Variance analysis.

		Sum of squares	Degrees of freedom	Mean of square	F _{value}	F _{tabled}
Particle growth	Regression	11.5	5	11.5	61.5	5.05
	Residual	0.550	5	0.190		
	Lack of fit	0.531	3	0.180		
	Pure error	0.0200	2	0.0100		
	Total	11.5	10			
Coating efficiency	Regression	928	5	928	17.4	5.04
	Residual	157	5	53.7		
	Lack of fit	152	3	50.9		
	Pure error	4.67	2	2.34		
	Total	997	10			
Nitrogen volatilization reduction	Regression	1242	4	1242	26.7	4.53
	Residual	185	6	46.6		
	Lack of fit	184	4	45.9		
	Pure error	1.24	2	0.620		
	Total	1427	10			

Table 6. Environmental impacts of nitrogen fertilization with uncoated and coated urea per FU (1 ha).

Impact category	Unit	Uncoated urea	Coated urea
GW	kg CO ₂ eq	1010	664
OF	kg NO _x eq	1.50	0.962
PMF	kg PM _{2.5} eq	57.6	14.3
AC	kg SO ₂ eq	462	112
ME	kg N eq	0.0312	0.0289
MEC	kg 1,4-DCB	5.45	4.36
HTOX	kg 1,4-DCB	3.31	4.01
MS	kg Cu eq	0.416	0.405
FS	kg oil eq	413	236
WCON	m ³	61.8	46.8