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Lignin based controlled release coatings

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ABSTRACT

Urea is a commonly used fertilizer. Due to its high water-solubility, misuse easily leads to excess nitrogen levels in the soil. The aim of this research was to develop an economically feasible and biodegradable slow-release coating for urea. For this purpose, lignin was selected as coating material. From four commercially available lignins, two lignosulfonates (Wafex P and Borresperce), a softwood kraft (Indulin AT) and soda flax lignin (Bioplast), the latter showed the best potential with respect to film forming properties.

Bioplast dispersions up to a dry matter content of 50% are processable. However, high losses during processing resulted in thin coating layers on the urea granules. To reduce urea release, hydrophobic compounds and crosslinkers were added to the Bioplast dispersions. Addition of alkenyl succinic anhydride (ASA) significantly decreased the release of urea in water. However, complete release of urea still occurred within one hour, which can be explained by a low reactivity of the selected compounds towards lignin, too low percentages of applied coating or negative effects of the selected compounds on the film forming process. In addition, urea partly dissolves in the aqueous lignin dispersions due to its high water-solubility. This causes incorporation of urea in the lignin layer, which results in coatings with a low water resistance. This was improved by application of an inner coating layer with high dry matter content.

In conclusion, lignin shows high potential as coating material. For industrial application, more insight in the film forming properties is desired.

1. Introduction

Fertilizers are in general classified in two groups, i.e. natural organic products and synthetic chemical products. Urea belongs to the synthetic group of fertilizers. Since urea is very water-soluble, the most common method to obtain controlled release of fertilizer is to control the solubility of the fertilizer itself (Ramírez et al., 1997; Ramírez-Cano et al., 2001). A review was written concerning slow-release of nitrogen fertilizers in vegetable production (Guertal, 2009). In case of urea, slow-release products are typically made by reacting urea with various aldehydes to reduce the solubility of the material. For example, isobutylidene diurea (IBDU) is a condensation product of urea and isobutyraldehyde. It contains about 31% nitrogen of which 90% is water insoluble. Urea can also react with formaldehyde giving methylene urea polymers, varying in chain length and degree of crosslinking. Nitrogen is released from the insoluble portion of these materials by microbial degradation. As with the production of IBDU, the urea actually takes part in the reaction to form urea formaldehydes.

Another method of regulating plant nutrient release is the application of a coating. Several release mechanisms are possible depending on the type of applied coating. When a hydrophobic coating without pores is used, release only takes places after partly degradation of coating by e.g. micro-organisms. Water-soluble coatings usually only slow down fertilizer release. After a certain uptake of water, the coating becomes porous or even breaks and burst release of fertilizer takes place. Controlled or slow release coatings should on one hand be sufficiently hydrophilic to take up water, and thus make fertilizer transport possible, and on the other hand be sufficiently hydrophobic to prevent disruption of the coating wall. When damage occurs to a controlled release coating, the product loses its controlled release properties completely or in part, since coating holes, cracks or thin spots allow for rapid access of water in which the fertilizer is soluble. Controlled release coatings based on lactic acid homo- and co-polymers solutions showed that the amount of cracks and pin holes, which is dependent on the type of polymer and molecular weight, plays an important role in urea release (Jintakanon et al., 2008).

Lignin is one of the most abundant renewable materials. Until now, only a small part of the total available amount is being exploited, mainly in the pulp and paper industry (Gosselink et al., 2004). Based on its interesting functional properties, lignin has good potential for various applications. Lignin is amorphous and, in comparison with other biopolymers, a relatively hydropho-

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bic material. The film forming properties in combination with its hydrophobic character make lignin an interesting group of materials for the development of slow-release coatings for fertilizers. Lignin can be derived from a kraft, sulfite or soda pulping process, resulting in lignins with different chemical and physical properties. The combination of urea and lignin is well known in literature, and a number of patents are covering the area of lignin-based adhesive formulations.

Several matrix systems including fertilizer and lignin have been described. A reversible lignin gel is described for the sustained release of pesticides (DelliColli et al., 1981). The gel was used as a carrier for an organic pesticide. Lignin was crosslinked with formaldehyde or formaldehyde-forming material, such as paraformaldehyde, glyoxal, glutaraldehyde, and combinations of glutaraldehyde and epichlorohydrin. A hydrolyzed lignosulfonate-acrylonitrile graft copolymer matrix providing slow release solubility to urea fertilizer is described (Detroit, 1988). The method provided matrix systems in which the urea was entrapped in a lignosulfonate-polyacrylic acid matrix. In this way, the solubility of urea was decreased and a slow release formulation was obtained. Several technical lignins were subjected to oxidative ammoniation (ammoxidation) for producing slow-release nitrogen fertilizers (Meier et al., 1997). A range of polyelectrolyte polymers that can be ionically crosslinked may be used to bind lignin. Alginic acid, and a number of alginate formulations of pesticides have been described, but release is rapid unless a sorptive phase (e.g. kaolin, charcoal, lauric acid, linseed oil) is included (Wilkins, 1999; Pepperman and Kuan, 1995). Lignosulfonates have been used in combination with fertilizer materials as hardening agents or to impart anti-caking or anti-dusting properties (Sanford and Davis, 1991). The modified lignosulfonate is soluble in the molten urea and solidifies with the fertilizer when cooled in the air-cooling tower, thereby homogeneously distributing the lignin in the urea. Particles can also be covered with a sulfur overcoat (Gullett and Simmons, 1987). Also, combinations of lignin and ethylcellulose are described as controlled release formulations of urea (Fernández-Pérez et al., 2008).

Apart from the above described matrix systems, coating systems comprised of fertilizer and lignin have been described. Urea and phosphate fertilizers were coated by spraying a mixture of rosins and kraft lignins in a rotating drum (Garcia et al., 1996, 1997). To apply an abrasion resistant coating, urea granules were first coated with a sulfonated terpolymer SEPDM (Chen and Geiger, 1997). These particles were subsequently covered with a lignosulfonate solution to wet the particles, and dusted with a finely divided mineral filler such as talc (hydrous magnesium silicate) and mixing until the filler is distributed over the surface of the particles.

Several studies described the chemical and physical modification of lignin to improve coating properties, such as water sensitivity. The use of phenol oxidizing enzymes for lignin crosslinking has been widely reported (Bolle, 2000; Crestini et al., 2000; Kharazipour et al., 1990). Examples of suitable phenol oxidizing enzymes are catechol oxidases, laccases, bilirubin oxidases, monophenol monooxygenases and peroxidases.

Slow release of urea can be achieved by applying a semipermeable coating, such as a polyolefin or polyurethane, on urea beads. The synthesis and use of a block copolymer of poly[N-isopropyl acrylamide]-co-polyurethane was reported (Mathews and Narine, 2010). Also, double-coated release coatings based on poly(acrylic acid) and polystyrene were described (Liang and Liu, 2006). Since these materials are relatively expensive and maybe slow to biodegrade, in this study research is carried out on lignin, an inexpensive and renewable material.

2. Materials and methods

2.1. Materials

Wafex P (spruce lignosulfonate) and Borresperce 3A (modified spruce lignosulfonate) were supplied by Borregaard/lignotech, Sweden. Indulin AT (a softwood kraft lignin) was provided by Mead Westvaco, USA and Bioplast (a sulfur-free soda lignin from flax) was given by Granit, Switzerland.

Urea beads were obtained from Agrium, Canada.

Glycerol, Lupranol, Acronal, Styronal, sorbitol, PEG400, PEG2000 or PEG6000 were purchased from BASF, Netherlands and used as plasticizers. To improve the water resistance of lignin coatings, formaldehyde (BASF, Netherlands), alkenyl succinic anhydride (Hercules, Netherlands), 2-2′-phosphinicobis-butanedioic acid (Bayer, Germany) were used.

For lignin analysis, chemicals of high purity were used (Gosselink et al., 2004).

2.2. Dry matter content

The dry matter content of lignin was gravimetrically determined after drying of the lignin for 24 h at 105 °C until constant weight.

2.3. Chemical composition

The nitrogen and sulfur content of lignin was determined by elemental analysis.

2.4. Molecular weight distribution

The molecular weight distribution was determined by High Performance Size Exclusion Chromatography (HPSEC) with DMF/LiCl as solvent. Lignin was dissolved in DMF with addition of 0.2 mol l^{-1} LiCl at room temperature at a concentration of 0.1% (w/w) by gently shaking the solution for 1–2 min every 8–12 h. After 24 h, the lignin solution was injected on the size exclusion columns, styragel HR columns, HR0.5, HR2 and HR4, 7.8 mm I.D. × 300 mm, 5 μm particles and a precolumn (Waters, Etten-Leur, The Netherlands). Size exclusion was performed at 80 °C with DMF and 0.2 mol l^{-1} LiCl, a flow rate of 1 ml/min and UV detection at 280 nm. Calibration was performed with polystyrene standards ranging from 580 Da to 1200 kDa (Gosselink et al., 2004).

2.5. Functional group analysis

The amount of phenolic hydroxyl and carboxylic groups was determined by a non-aqueous potentiometric titration with 0.1 N tetra-n-butylammonium hydroxide (TnBAH). 0.15 g lignin on dry mass and 0.02 g p-hydroxybenzoic acid as internal standard were dissolved in 60 ml DMF and stirred under nitrogen for 15 min to ensure complete dissolution. The solution was titrated after addition of 1 ml water and 0.1 ml concentrated hydrochloric acid.

2.6. Solubility in water or alkaline solution at pH 12

A 10% (w/w) lignin solution was prepared by adding lignin to a 0.5 M sodium hydroxide solution. The pH was adjusted to 12 by adding concentrated sodium hydroxide. The lignin solubility was visually judged.

2.7. Viscosity

Lignin was dissolved as described above (2.6) in 0.5 M NaOH and the pH was adjusted to 12 with concentrated NaOH. The Brookfield