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Lignin-based multifunctional fertilizer for immobilization of Pb (II) in contaminated soil

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ABSTRACT

Excessive application of fertilizers and their losses have exerted a great threat on soil environment. Slow- or controlled-release fertilizers have been widely produced to alleviate the problem. However, most of them can not remedy contaminated soil environment, and even make it worse. To improve nutrient use efficiency and reduce soil environmental pollution, lignin, an extensive biomass source, was used to synthesize a lignin-based superabsorbent (LPA), which was then introduced into the fertilizer as an outer coating material to obtain lignin-based multifunctional fertilizer (LMF). Results showed that the introduction of LPA can improve water-holding and water-retention capacity of soil and nutrients release behavior of fertilizers. The cumulative release rates of nitrogen, phosphorus and zinc were 79.5%, 46.7% and 60.1% after 25 days, respectively. Additionally, LMF can efficiently immobilize and restrict the migration of bivalent lead (Pb(II)) by complexation with lignin. About 91.7% of Pb(II) was immobilized after soil-sand mixture with $Pb(NO_3)_2$ was treated by LMF. The pot experiments indicated that the LMF exhibited a positive effect on the growing of corn in Pb(II)-contaminated soil. Therefore, this work provides a promising fertilizer to improve the utilization efficiency of water, sustained release of nutrients, and immobilization of Pb (II) in contaminated soil.

1. Introduction

As the constant growth of world population, it is necessary to have a sufficient food supply which directly points to the improvement and optimization of agricultural production. Soil fertility is critical to improve crop production within a certain range, and the fertility can only be ensured by an adequate fertilizer supply [1]. At present, large amounts of fertilizers are used to achieve any substantial increase in the production of foodstuffs [2]. However, the overuse of fertilizers will directly result in nutrient loss, soil fertility degeneration and soil environmental deterioration [3]. To alleviate these side effects, slow- or controlled-release fertilizers (S/CRFs) have been widely produced to enhance effective nutrient uptake and fertilizer utilization efficiency in modern agriculture. In fact, many inorganic or organic raw materials have already been used to produce S/CRFs, such as hydroxides [4], attapulgite [5], hydroxyapatite [6], alginate [7], konjac glucomannan [8], κ-carrageenan [2], cellulose [9,10], starch [11,12], chitosan [13] and so on. Although these S/CRFs can effectively reduce nutrient loss, increase nutrient utilization efficiency and improve water retention capacity, most of them can not remedy contaminated soil environment, and even make it more worse.

Nowadays, soil pollution has severely influenced on the growth of plants and productivity of crops. Moreover, the fertilizer over-application, the drainage of industrial wastewater, the over-application of pesticide, and the disposal of chemical pollutants have historically impacted on food safety, which represents an important threat to human health [14,15]. Substantial increase in heavy metal pollution of agricultural soils has already become a global concern accompanied with rapid population expansion, industrial development and insufficiency of pollution controls. Therefore, a great deal of attention has been diverted toward the productions of cheaper, more convenient and environment-friendly agricultural soil remediation materials from natural polymers. Natural polymers have great advantages including abundance, low cost, nontoxic, biodegradability and biocompatibility [16]. However, compared to other natural polymers, lignin has received little attention and only approximately 2% of lignin available from the pulp and paper industry is used commercially with the remainder burned as a low value fuel [17,18].

Lignin, the second most abundant natural polymer on earth, is an extensive biomass source with renewable, non-toxic and low-

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priced characters [19]. Based on these features, lignin has great potential for various applications in the field of fertilizer, adsorbent and carrier material. For example, pine kraft lignin was used as coatings to prepare fertilizer, which can retard the dissolution of urea in water and slow release [20]. Sipponen et al. [21] developed a slow release urea formulation from lignin as the binder component, which demonstrated a simple and affordable fertilizer system. Li et al. [22] presented kraft lignin nanocapsule was prepared utilizing a totally green process, which required only a solvent of ethanol and water. Two types of adsorption gels from wood powder (PA−lignin and EN−lignin) were found to be effective for the adsorption of Au(III), Pd(II), and Pt(IV) in hydrochloric acid condition [23]. A new type of lignin microsphere was produced by an inverse suspension copolymerization method and it showed a fast response rate and a high adsorption capacity to Pb(II) in water [24]. However, there are several problems brought by the application of lignin-based materials as absorbents for heavy metals, such as low adsorption efficiency, negative effects on nutrients release and repeated pollution to contaminated soil. Therefore, the development of multi-functional fertilizers, which can simultaneously provide soil remediation and nutrients sustained release are desired.

In this study, a lignin-based superabsorbent was prepared and used as the outer coating to develop a novel and multi-functional fertilizer, and Its water-holding and water-retention, nutrients release characters and immobilization of Pb(II) in contaminated soil were investigated.

2. Materials and methods

2.1. Material

Lignin (Alkaline, L) was obtained from TCI (Shanghai) Development Co., Ltd., Acrylic acid (AA, CP, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China) and acrylamide (AM, CP, Xilong Scientific Co., Ltd., Guangzhou, China) were used as monomer. N,N'-methylene bis (acrylamide) (MBA, AR, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was used as a crosslinker. Natural attapulgite (APT, supplied by Gansu Haozhou APT Co., Ltd., Gansu, China) was milled and sieved through a 200-mesh screen before use. Cellulose acetate butyrate (CAB, Mn-12,000, 30–35 mol% butyrate) and liquid paraffin (LP, CP) were obtained from Aladdin Reagent Co., Ltd. All other reagents were analytical reagent grade and used as received. The soil used in this study is a representative sample of Lanzhou, which lies in the northwest of China and is a semiarid region.

2.2. Preparation of ammonium zinc phosphate (NH_4ZnPO_4)

The ammonium zinc phosphate was prepared according to the literature [25]. Briefly, zinc sulfate solution (0.3 mol/L) was added to diammonium phosphate solution (0.3 mol/L) by dripping slowly at room temperature under vigorous stirring. Then, ammonia (25–28 wt%) was added into the mixed solution to adjust the pH value to 9.0. After aging for 2 h, the suspension was filtered and dried under vacuum to constant weight.

2.3. Preparation of lignin-based superabsorbent (LPA)

Firstly, 0.5 g lignin was dissolved in 50 mL NaOH solution (1 M) and lignin solution was obtained. Then, 3.0 g acrylic acid, 3.0 g acrylamide and 0.26 g MBA were added into 25 mL deionized water. The mixed solution and 0.8 g attapulgite were added into the lignin solution under magnetic stirring at room temperature. The pH value of the mixture was adjusted to 4–5 by adding HCl solution (0.1 M) before 0.065 g potassium persulfate (KPS) was added, and the reaction was carried out at 66 °C for 1 h, 75 °C for 1 h and 85 °C for 1 h, respectively, under magnetic stirring in nitrogen atmosphere. The obtained hydrogel was immersed in 200 mL 0.1 M NaOH solution for 5 min and washed for three times with deionized water. Finally, lignin graft poly(acrylic acid-*co*-acrylamide)/attapulgite superabsorbent (LPA) was obtained after drying at 55 °C for 48 h. For comparison, poly(acrylic acid-*co*-acrylamide)/attapulgite (PA) absorbent was prepared without lignin as the above method.

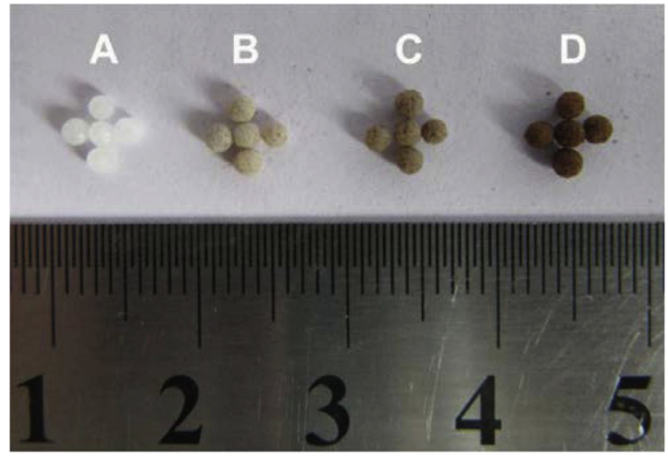

Fig. 1. The morphology of urea granule (A), fertilizer core (B), fertilizer coated with CAB (C), and LMF (D).

2.4. Preparation of lignin-based multifunctional fertilizer (LMF)

Firstly, an amount of NH_4ZnPO_4 and lignin (1:1 wt%) were ground to powder and mixed well. Then, the mixture was gradually feed into a rotating disk with urea granules (12–18 mesh) in batches. The fertilizer cores were obtained by adhered mixture under 85% alcohol atomization. Subsequently, CAB and LP were dissolved at the ratio of 2:1 (w/w) in ethyl acetate and the solution (5%, w v^{-1}) was obtained. Then, the solution was sprayed on the fertilizer cores to form the inner coating of the fertilizer granules. LPA superabsorbent powder (below 110 mesh), as the outer water absorbing and holding material, was coated on the surface of the inner coating fertilizer granule under rotation and 75% alcohol atomization. Finally, the coated granule lignin-based multi-functional fertilizer (LMF) was obtained after drying at 50 °C and screened.

2.5. Instrumental analysis

Fourier transforms infrared (FTIR, NEXUS 670 FTIR Spectrometer, Nicolet USA) spectra of samples were performed with a KBr pellet in the range of 400–4000 cm^{-1}. Scanning electron microscopy (SEM, JSM-5600LV, JLPAn) was used to observe the surface morphology of the samples. Before SEM observation, the surface of samples was coated with gold. Thermal analysis was performed by differential scanning calorimeter (DSC, Sapphire DSC, PerkinElmer instruments) and thermogravimetric (TG, STAPT1600, Linseis Inc.) The content of nitrogen in original and residual fertilizer was determined by an elemental analysis instrument (Model 1106, Germany Elemental Vario EL Corp.) and the content of zinc and phosphorus was determined by an IRIS advantage ER/S inductively-coupled plasma atomic-emission spectrometry (ICP, TJA Inc., USA).