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# Synthesis composite hydrogels from inorganic-organic hybrids based on leftover rice for environment-friendly controlled-release urea fertilizers

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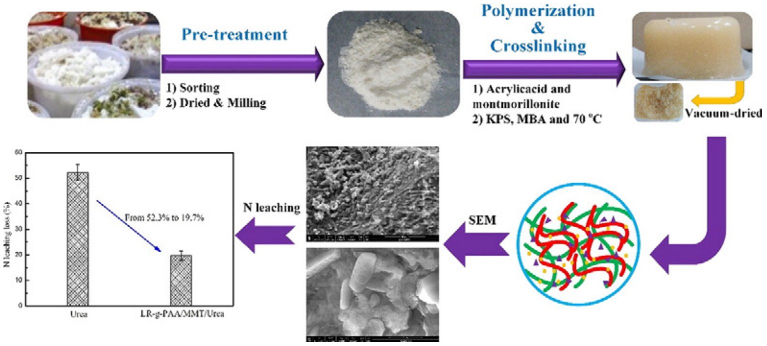
## HIGHLIGHTS

- A novel slow-release nitrogen fertilizer was developed based on leftover rice.
- The sample had the potential to carry the necessary N.
- Mechanism of LR-AA/MMT/Urea formation was elucidated.
- The developed fertilizer could be applicable in agriculture and horticulture.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nearly 1.3 billion tons of food are discarded annually in the production process. In this study, a novel slow-release nitrogen fertilizer with water absorbency was developed using leftover rice and crosslinking methods. Urea was incorporated as the nitrogen source in a leftover rice-g-poly(acrylic acid)/montmorillonite (LR-g-PAA/MMT) network, and then the leftover rice-g-poly(acrylic acid)/montmorillonite/Urea (LR-g-PAA/MMT/Urea) retained in the soil, and used as the loss control agent for water and nutrients. Variables including concentrations of acrylic acid, montmorillonite, N,N′-methylenebis acrylamide (MBA), and potassium persulfate (KPS) were investigated. Samples were with a water absorbency of 102.6 g/g in distilled water and 25.1 g/g in 1.0 wt% NaCl solution under optimized conditions. Swelling measurements and water-retention indicated that higher-covalent cations would aggregate the hydrogels and decrease swelling. Investigating leaching behavior showed that these samples have the potential to carry the necessary nitrogen (N). The results demonstrated that the LR-g-PAA/MMT/Urea had a low leaching losses of N (19.7%) compared with pure urea (52.3%). Therefore, the developed fertilizer may be widely applicable in agriculture and horticulture, and could provide a new platform for reusing leftover rice.

## 1. Introduction

Fertilizer and water are two fundamental factors for crops that limit agricultural production. Exponential population growth and diminishing arable land have motivated society to utilize larger quantities of nutrients, especially nitrogen (N), phosphorus (P), and potassium (K) to enhance crop yields (Azeem et al., 2014; Wen et al., 2016). In

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addition to increasing fertilizer demand, lower fertilizer use efficiency has been a serious issue worldwide (Zhang et al., 2016). This is especially true for nitrogen (N), which is the most widely applied plant nutrient and a key contributor to agricultural productivity (González et al., 2015; Schneider Teixeira et al., 2016). Among N fertilizers, urea is used widely due to its high N content, low cost, and easy application. However, urea has low thermal stability, high solubility, and small molecular weight, and tends to migrate into the air and aquatic systems through volatilization, runoff, and leaching. These impacts cause large economic losses and major environmental concerns, including soil, freshwater, and ocean contamination and decreasing farmland biodiversity (Mangiafico et al., 2009; Rojas et al., 2013; Xiang et al., 2008; Zhang et al., 2016). Therefore, controlling fertilizer loss, maximizing nutrient retention in soil, improving utilization efficiency, and reducing environmental pollution risk are the main focuses of improving fertilizers. One promising mechanism for reducing the high costs associated with intensive application while minimizing environmental impacts is to use controlled, or slow-release fertilizers (Jin et al., 2010; Min et al., 2005).

Various types of controlled/slow-release fertilizers have been developed using hydratable polymers, nitrification inhibitors, urea formaldehyde, and other reactants over the past 20 years (Gullett et al., 1991; Li et al., 2007; Ni et al., 2011). Although these products effectively increase nutrient-use efficiency, most do not possess a high water retention capacity. Now that large swaths of farmland suffer from water resource shortages, especially in arid and semiarid regions, efficient water usage would be significant. In this context, superabsorbent polymers are the subject of significant focus because of their excellent water absorption and retention capacities as controlled/slow-release fertilizers in agriculture applications (Ni et al., 2011; Zhou et al., 2015). Compared with traditional superabsorbent polymers, biomass-based polymers are superior because they are biocompatible, biodegradable, and inexpensive (Abdel-Halim and Al-Deyab, 2014; Bai et al., 2015). Food waste generated from cafeteria operations has high organic matter content and biodegradability, and is regarded as a green resource with abundant nutrient elements (Levis and Barlaz, 2011). Leftover rice (LR), the main composition of food waste, contains various functional groups, such as hydroxyl, carboxyl, phosphate, and amino groups, and can be employed in the preparation of water-absorbent polymers. Recycling LR into water-absorbent polymers could reduce production costs, improve biodegradation properties, and promote plant growth, contributing to the development of sustainable and environment-friendly agriculture.

Superabsorbent polymers have been mostly used in the form of gel beads, which have weak mechanical strength to resist external forces (Wen et al., 2016). Some innovative methods have been developed to solve these problems, including composite materials comprised of inorganic-organic hybrids (CM-IOH). These materials have attracted considerable attention due to their excellent combination of the organic and inorganic characteristics within a single molecular-scale composite. The organic constituents of the hybrids possess toughness, good elasticity, low density, and formability, while the inorganic components are stiff, hard, and thermally stable. Therefore, the hybrid materials are employed in a wide range of applications based on a combination of their organic and inorganic properties (Likhitha et al., 2014). Montmorillonite (MMT), with a structural unit consisting of two tetrahedral layers (Si—O) separated by an octahedral layer (Al-O-OH), is a good substrate for superabsorbent polymers with reactive –OH groups on the surface, high surface area, swelling capacity, and valuable cation exchange capacity (Chen et al., 2015; Zhansheng et al., 2006). Furthermore, MMT is environment-friendly and readily available in large quantities at low cost. Notably, the eco-friendly and economically viable CM-IOH, which uses a high-proportion of biomass and clays, is now regarded as a strategic research area due to their low production cost and good biodegradability (Peng et al., 2016; Wu et al., 2016).

Several approaches have focused on developing superabsorbent polymers, such as microwave irradiation (MW), ultraviolet irradiation, ultrasound, and chemical initiation (Dholakia et al., 2012; Enomoto et al., 2014; Khan et al., 2004). Among these methods, the chemical initiation method has been extensively used for organic synthesis due to its practicality and high polymerization yields (Azad and Sandros, 2016; Bozaci et al., 2015; Cao et al., 2015). Furthermore, the optimized combination of superabsorbent polymers and slow-release fertilizers improve the water-holding capacity and nutrient retention of soils, increase fertilizer use efficiency, lower irrigation frequency, and mitigate environmental problems, compared with conventional fertilizers (Rashidzadeh and Olad, 2014).

In the present work, a CM-IOH network (LR-g-PAA/MMT/Urea) with water absorbency were synthesized based on LR via chemical initiator initiation, in which urea was used as the N source. The structure and properties of samples were characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). In addition, the mechanical properties of LR-g-PAA/MMT/Urea were tested with extruding experiments. Water absorbency, water-retention capacity, leaching behavior, and swelling kinetics of the sample were also systematically investigated. Furthermore, the mechanism for LR-g-PAA/MMT/Urea formation was elucidated.

## 2. Materials and methods

### 2.1. Materials

LR was obtained from a student canteen at Tongji University, Shanghai, China. Raw materials were dried to a constant weight at 70 °C, ground to a powder with a planetary ball mill machine (QM-1SP4), and passed through 100 mesh sieves. Acrylic acid monomer (AA), urea, sodium hydroxide, potassium persulfate (KPS), and N,N′-methylenebis acrylamide (MBA) were obtained from commercial vendors for this study. All reagents were of analytical grade and all solutions were prepared with distilled water. AA was distilled under reduced pressure before usage to remove the polymerization inhibitor and then stored in a brown reagent bottle. Potassium persulfate (KPS) was used as an initiator for grafting polymerization. The MMT samples were collected from the Aladdin deposits in Shanghai, China.

### 2.2. Preparation of LR-g-PAA/MMT/Urea

LR-g-PAA/MMT/Urea hydrogels were prepared from mixing the LR, AA, MMT, and urea with different weight proportions. For instance, 5.0 g of AA, 0.05 g of MBA, and 4 mmol/L KPS were introduced to 50 mL of mixed water solution containing 1.0 g of MMT, 10.0 g of urea, and 1.0 g of LR in a 100 mL beaker. The concentration of KPS (4 mmol/L) was calculated based on the ratio of the reaction mixture (50 mL). Then the beaker was transferred to a thermostat water bath magnetic stirrer with 70 °C for 30 min under constant stirring until a paste formed. Finally, the mixture stiffened, creating a whitish material after complete polymerization for the next 60 min without stirring. All procedures were performed in a nitrogen atmosphere. Subsequently, the gel products were cooled to room temperature. The free homopolymers and copolymers, and the traces of KPS, AA, and MMT were removed through washing with deionized water and ethanol. LR-g-PAA/MMT/Urea hydrogels were dried at 60 °C in a vacuum oven to constant weight and then ground with mortar to fine particles for future use.

### 2.3. Characterization

Fourier transform infrared spectroscopy (FT-IR) (Nicolet 5700 FT-IR Spectrometer) was used to qualify the chemical bonds between functional groups of the raw materials and hydrogel samples. The samples were subjected to wave numbers within the range of 500–4000 $cm^{-1}$ at a resolution of 4 $cm^{-1}$. Scanning electron microscopy (SEM) (FEI Nova Nano SEM 450) was used to study the surface morphology of the hydrogel. X-ray diffraction (XRD) measurements were conducted using an X-ray diffractometer (XRD, D8 Advance). The patterns with