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Synthesis, characterization and swelling behavior of superabsorbent wheat straw graft copolymers

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ABSTRACT

Swelling behavior is an important characteristic for superabsorbents. A wheat straw-based superabsorbent (WS-SAB) was prepared by graft copolymerization of acrylic acid, acrylic amide and dimethyl diallyl ammonium chloride onto the cellulose of wheat straw, and its swelling and deswelling behavior was investigated. The product had a water absorbency of 133.76 g/g in distilled water and 33.83 g/g in 0.9 wt.% NaCl solution. Fourier transform infrared spectroscopy and scanning electron microscopy indicated that the monomers were successfully grafted onto the wheat straw. The largest swelling capacity was at pH 6. The effect of ions on the swelling was in the order: $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$ and $Cl^- > SO_4^{2-}$. The swelling capacity did not change after several times of water absorption and release.

1. Introduction

Superabsorbent hydrogels are three-dimensional crosslinked hydrophilic polymers with the ability to absorb large quantities of water, saline or physiological saline solutions compared to ordinary absorbing materials (Chang et al., 2010). With excellent hydrophilic properties and high swelling ratio, they are used in agriculture, hygienic products, waste-water treatment, drug-delivery and coal dewatering (Xie et al., 2011; Kosemund et al., 2009; Paulino et al., 2006; Guilherme et al., 2007; Wang et al., 2009; Yu et al., 2005). Many kinds of materials are used for preparing superabsorbents, but most of those materials are acrylic acid and acrylamide-based products. However, these types of superabsorbent are expensive and can be hazardous to the environment (Kiatkamjornwong et al., 2002). A low absorption rate at high concentrations of electrolytes and undesirable water-keeping capacity also restrict the application and development of superabsorbents.

Some natural resources such as polysaccharides and inorganic clay minerals have also been used to produce polymer hydrogels (Li et al., 2007; Liu et al., 2008). Cellulose is often used in the biomedical field, and cellulose-based superabsorbents have been prepared using radiation-induced and chemical crosslinking (Chang et al., 2010). Wheat straw contains a high content of cellulose, so it could be chemically modified and used as backbone material for superabsorbents (Rémond et al., 2010).

Superabsorbents using wheat straw have been synthesized (Liang et al., 2009; Xie et al., 2011; Guo et al., 2006), but most of the products were single-ion superabsorbents. In some cases, the product was synthesized indirectly through the introduction of carboxymethyl cellulose. On the basis of the previous work (Ma et al., 2011), a new amphoteric superabsorbent was prepared and the swelling and deswelling behaviors of the new wheat straw-based superabsorbent (WS-SAB) in water and saline solution were studied. The WS-SAB was produced directly through graft copolymerization of the monomers (acrylic acid (AA), acrylic amide (AM) and dimethyl diallyl ammonium chloride (DMDAAC)) into the network of the cellulose in wheat straw.

2. Experimental

2.1. Materials

Wheat straw was obtained from Liaocheng, Shandong Province (China). Acrylic acid (AA, analytical reagent), acrylic amide (AM, chemically pure), dimethyl diallyl ammonium chloride (DMDAAC, chemically pure) and N,N′-methylenebisacrylamide (MBA, analytical reagent) were dissolved in distilled water before use. Other agents were of analytical grade and all solutions were prepared with distilled water.

2.2. Preparation of the wheat straw-based superabsorbent (WS-SAB)

Dried wheat straw was ground in an electromagnetic mill and sifted through an 80-mesh sieve. The particles were submerged

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in 10% ammonia at a mass ratio of 1:12 for 48 h, washed with the distilled water and filtered through a qualitative filter paper in sand-core funnel (pore size is 10–15 μm) under vacuum. The filtered residue was mixed with 1 mol/L nitric acid at a mass ratio of 1:12, and heated at 100 °C for 45 min. Finally, the mixture was filtered through a qualitative filter paper in sand-core funnel under vacuum pump, washed with distilled water and dried at 105 °C for 24 h to obtain pretreated wheat straw (PTWS).

The PTWS (1.0 g) was transferred into a three-necked flask equipped with a stirring apparatus. $K_2S_2O_8$ (20 mg/L) and $(NH_4)_2Ce(NO_3)_6$ (10 mg/L) were added into the flask to initiate graft polymerization. The solution was heated by a water bath for 15 min at 50 °C under nitrogen atmosphere. Na_2SO_3 (2.3 mL at a concentration of 10 mg/L), 4 mL of AA after neutralization with KOH, 4.46 mL of AM (40%) and 1.6 mL of DMDAAC (60%) were added. After1 h, the cross-linker, MBA, was added. Finally, after 4 h at 50 °C, the resultant product was dried to a constant weight at 70 °C. The dried product was soaked in distilled water and washed several times until the water became colorless. The purified product was dried in an oven at 70 °C, milled by the electromagnetic mill and sifted through 20-mesh and 40-mesh sieves. Based on the previous study (Ma et al., 2011), the optimal synthesis conditions of the WS-SAB were as follows: the temperature was 50 °C for 5 h, mass ratio of m(PTWS);m(AA);m(AM);m(DMDAAC) of 1:4:2:1, weight rate of the initiator and the cross-linker of were 1% and 0.2% (w/w), and the neutralization degree of AA of 85%.

2.3. Method of characterization

2.3.1. FTIR spectroscopy

FTIR spectra were obtained on a NEXUS-470 series FTIR spectrometer (Thermo Nicolet, NEXUS). The samples were taken in KBr pellets.

2.3.2. SEM analysis

The surface morphology of the gels was examined using scanning electron microscopy (SEM, JSM-5600LV, JEOL, Ltd. Japan). Samples were mounted on aluminum stubs and coated with a thin layer of palladium gold alloy.

2.3.3. Macroscopic analysis

In order to understand the shape change of the WS-SAB before and after absorption, the WS-SAB samples before swelling and after swelling were photographed with a digital camera (IXUS105, 12 million pixels, Canon, Japan) to characterize the shape changes of WA-SAB in swelling process.

2.4. Study of properties

2.4.1. Swelling and deswelling study

The WS-SAB particles were soaked in excess distilled water or salt solution to reach the swelling equilibrium. The swollen sample was separated by filtration through a 200-mesh cloth. The swelling capacity of the WS-SAB was calculated by the following equation:

$$Q_{eq} = \frac{(m_2 - m_1)}{m_1}$$

where m_1 and m_2 are the mass of the dried and swollen sample, respectively. The Q_{eq} value was calculated as grams of water per gram of sample.

For the swelling study, the dry WS-SAB was allowed to adsorbed water and reach the swelling equilibrium. The swollen samples were transferred to Erlenmeyer flask containing a 0.9% NaCl solution (about 150 mmol/L), and the water retention of the samples was calculated as follows:

$$Waterretention(\%) == \frac{m_3}{m_4} \times 100$$

where m_3 is the weight of the swollen sample. And m_4 is the weight of the sample which has deswollen in the salt solution.

2.4.2. Swelling kinetics

The WS-SAB samples (0.50 g) were contacted with distilled water in 50 mL Erlenmeyer flask for different times, and the swollen WS-SAB was filtered through a filter cloth. After weighing, the swelling capacity of the WS-SAB at a given moment was calculated according to Eq. (1). Five grams of swollen sample was added into the 0.9% NaCl solutions and water retention was determined at various times. In order to identify the effect of temperature on swelling capacity, swelling kinetics studies were undertaken at 10, 25 and 40 °C.

2.4.3. Swelling at various pHs

A series of solutions with different pHs were prepared by diluting NaOH or HCl. The solutions had an ionic strength of 0.1 M, achieved by adding NaCl. Then 0.50 g of WS-SAB was used for the swelling capacity measurements according to Eq. (1).

2.4.4. Swelling and deswelling in salt solutions

The swelling capacities of the superabsorbent were determined in 10 mM NaCl, KCl, $CaCl_2$, $MgCl_2$ and Na_2SO_4 and in 5, 10, 50, 100 and 150 mM NaCl, respectively, as described in Section **2.4.1**. The deswelling of the WS-SAB in 5, 10, 50, 100 and 150 mM NaCl solution was also determined.

2.4.5. Effect of particle size on swelling

The WS-SAB samples were sieved through sieves of 10, 20 and 40 mesh to obtain different particle sizes. Swelling and deswelling capacity of the superabsorbent hydrogels with different particle sizes were determined as described in Section **2.4.1**.

2.4.6. Reswelling capability

Samples were immersed in 50 mL distilled water until they reached swelling equilibrium. The swollen samples were filtered through a 100-mesh filtering cloth and weighed to calculate the swelling capacity for the first swelling process. Then the swollen WS-SABs were placed in an oven at 105 °C to dry. Fifty mL of distilled water was added for the second swelling process. The same procedures were repeated five times in distilled water and 0.9% (wt) NaCl solution.

3. Result and discussions

3.1. Mechanism of hydrogel formation

The WS-SAB was prepared by graft copolymerization of AA, AM and DMDAAC onto cellulose of pretreated wheat straw in the presence of initiator and crosslinking agents. The proposed mechanism for the grafting and chemically crosslinking reactions is shown in Fig. 1. The pretreatment is assumed to have removed compounds such as the pectin which might have enveloped cellulose and prevented its reaction (Li et al., 2006). The $K_2S_2O_8$, $(NH_4)_2Ce(NO_3)_6$ and Na_2SO_3 initiator system reacted with the cellulose chain in the wheat straw, breaking the ring structure of β-D-glucose in the cellulose, resulting in the formation of some more active groups such as the alkoxy radicals (Lanthong et al., 2006).The monomer molecules, AA, AM and DMDAAC, reacted with these groups. The reaction among the monomers, groups and chain caused the graft chain to grow (Wang and Wang, 2010). The polymer chains reacted with the end vinyl groups of the cross-linker, MBA, during chain