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Synthesis and adsorption properties of superabsorbent hydrogel and peanut hull composite

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ABSTRACT

The cellulose was extracted from peanut hull by methanoic acid and hydrogen peroxide, then superabsorbent hydrogel composite was synthesized by aqueous solution polymerization, using peanut hull cellulose, acrylic acid (AA), acrylic amide (AM), 2-acrylamide-2-methyl-1-propanesulfonic acid (AMPS) as raw materials, *N*,*N*′-methylene bisacrylamide (MBA) as cross-linker, and $K_2S_2O_8$ as initiator. The structure and morphologies of the superabsorbents were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscope (SEM). The kinetic studies for Pb(II) adsorption onto hydrogel composite showed that the pseudo-second-order adsorption mechanism was predominant. The adsorption isotherm data were found to be well described by Freundlich model.

Introduction

Superabsorbent hydrogels (SAH), particularly those based on natural polymers, can absorb and retain large amounts of water, saline solutions or physiological solutions as high as hundreds to thousands of times their own weight due to considerable hydrophilic groups with three-dimensional network structures [1–7]. Hydrogels have received increasing attention of researchers due to their significance both in theory and application. They have been widely used in fields such as personal health products, civil construction, industrial, agricultural production, medical materials, baby diapers, soil for agriculture and horticulture, absorbent pads, etc. [2,4,5,8–10]. Hydrogels were also used in environmental applications for the removal of undesired heavy metal ions [2,11–13] and dyes [14–16]. SAH properties depend strongly on the degree of polymer crosslinking, chemical composition of the polymer chains, and interactions of the network. The hydrophilicity of hydrogels can be enhanced by the presence of hydrophilic groups, such as hydroxide radical, carboxyl, and amido [17,18].

Commodity crops such as peanuts generate considerable quantities of hulls each year which have little or no value. Peanut hulls were low in density and high in volume. China ranked first in peanut production, which represented a potential of 4500 thousand tons of peanut hulls produced each year and this material had shown to be an excellent source of high quality and low cost [19]. However, as agricultural by-products, most of the peanut hulls were either sludged for forage and fuel or abandoned, resulting in an enormous waste of natural resources [20]. In order to make the best of the peanut hulls, several reports that peanut hulls had been used as adsorbents applied to adsorb various metal ions [19,21,22] and dyes [23,24]. To the best of our knowledge, peanut hull powder became secondary pollutants due to the difficulty of recovery after adsorbing metal ions or dyes.

For the sake of solving the problem and improving the properties of the superabsorbent hydrogels, in recent years, there have been many reports about superabsorbent composites, especially, natural materials and superabsorbent hydrogel composites have been attracted much attention [1,9,18,25]. Hence, this study was aimed to use the peanut hull to synthesize superabsorbent hydrogel composite. The peanut hull was handled to extract the cellulose, which owning abundance of hydroxyl groups and oxygen atoms was the most potential natural materials. It was also able to form an extensive network of intra- and intermolecular hydrogen bonds, which confers remarkable chemical stability and makes the direct utilization of cellulose a challenge [26,27]. Herein, the peanut hull cellulose and superabsorbent hydrogel composite was investigated in the present work, which not only solve the direct utilization of cellulose, but also improve the properties of the superabsorbent hydrogel, such as chemical stability, biodegradability, adsorption behavior and so on. This paper described the synthesis of hydrogel composite and the adsorption properties were also researched.

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Experimental

Materials

Peanut hull (PNH, obtained from local plant in Qinhuangdao, China) used as raw material was smashed and handled with methanoic acid and hydrogen peroxide. All chemicals used in this experiment were purchased in analytical purity and used directly without any further purification. All stock solutions were prepared in deionized water.

Extraction of cellulose

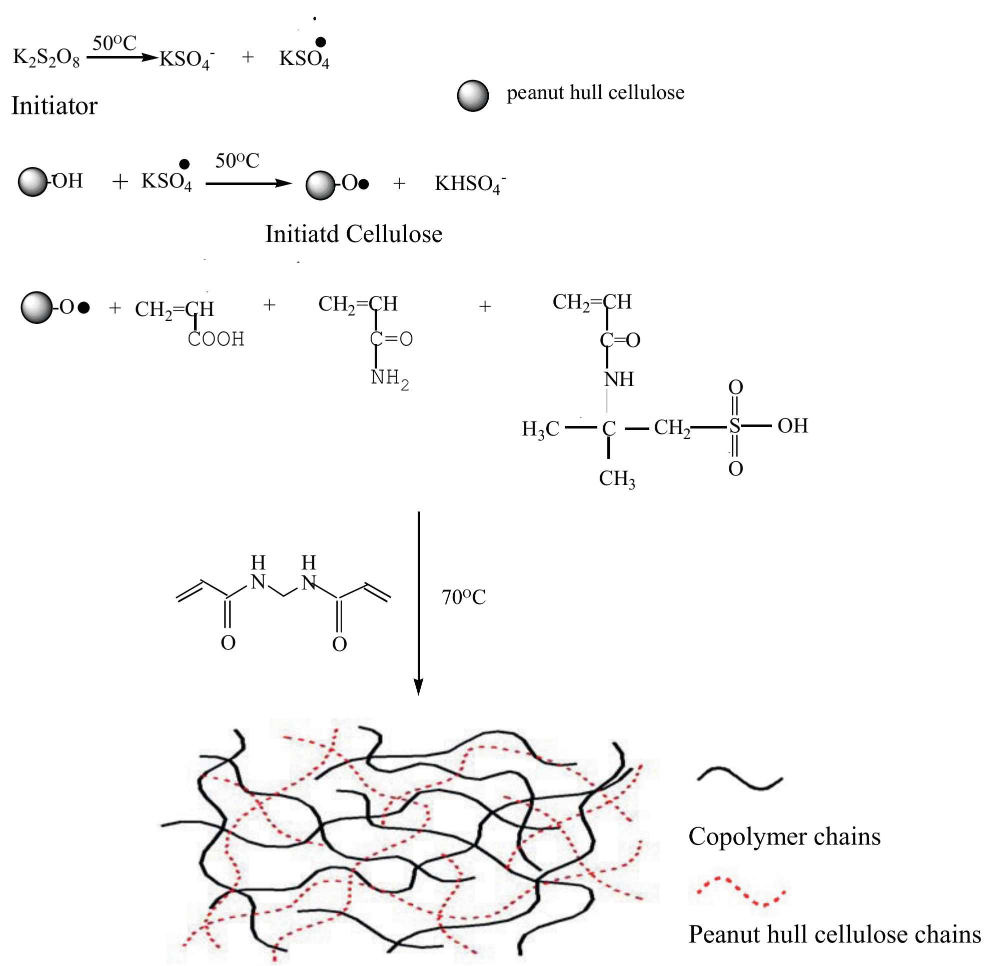
The cellulose was extracted from peanut hull by methanoic acid and hydrogen peroxide. The peanut hull powder (10 g), methanoic acid (80 mL) and hydrogen peroxide (14 mL) were added to a three-necked round-bottom flask equipped with a magnetic stirrer, then the mixture was soaked for 1 h under water bath with the temperature increased to 80 °C. The reaction was stirred magnetically for 2.5 h at 80 °C, and sustained for 2.5 h at 95 °C. Afterwards, the mixture of the reaction was filtered and the filter cake was put into the flask again and added methanoic acid and hydrogen peroxide equaling to the above-mentioned with stirred 2.5 h at 80 °C. At last, the mixture was filtered and the filter cake was washed with deionized water many times until the pH of filtrate was 7, then dried at 75 °C for 12 h, the as-prepared peanut hull cellulose was obtained.

Synthesis of superabsorbent hydrogel and peanut hull composite (SAH–PNH)

An appropriate amount of peanut hull cellulose was added to a beaker with a certain amount of $K_2S_2O_8$ under water bath at 50 °C for 15 min, to induce graft copolymerization. 20 g AA was partially neutralized with sodium hydroxide solution, in order to achieve a required neutralization degree. Then, the mixed solutions of AA, AM (6 g), and AMPS (4 g) were gradually added into the above solution with stirring. After about 1 h of reaction, crosslinking agent (*N*,*N*′-methylenebisacrylamide) was put into the reaction solution. Afterwards, the reaction was kept at 70 °C for 1 h to complete the polymerization. Finally, the resulting product was cut into small pieces and then vacuum-dried at 80 °C to a constant weigh. The dried product was crushed, sieved into particles by a 100 mesh stainless steel sieve, and stored in a desiccator. The proposed mechanism of the grafting and chemically crosslinking reaction was outlined in Scheme 1.

Characterization

Scanning electron microscopy (SEM) images were performed at Hitachi-3400N scanning microscope. The accelerating voltage was 15.00 kV and the scanning was performed in situ on a sample powder. The presence of functional groups in samples were determined from FT-IR (Nicolet is 10) spectra using KBr disks in the rang from 4000 to 500 cm^{-1}. The themogravimetry (TG) and



Scheme 1. Proposed reaction mechanism for synthesis of superabsorbent hydrogel and peanut hull composite.