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Preparation of wheat straw based superabsorbent resins and their applications as adsorbents for ammonium and phosphate removal

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HIGHLIGHTS

- A wheat straw cellulose based semi-IPNs SAR is prepared by graft polymerization.
- The SARs behave as good adsorbents for the removal of NH_4^+ and PO_4^{3-}.
- The SARs can serve as N and P controlled-release fertilizer in agriculture.
- Equilibrium, kinetics and thermodynamic study of the adsorption is achieved.
- The desorption and reusability of SARs is assessed.

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ABSTRACT

A novel wheat straw cellulose-g-poly (potassium acrylate)/polyvinyl alcohol (WSC-g-PKA/PVA) semi-interpenetrating polymer networks (semi-IPNs) superabsorbent resin (SAR) was prepared by graft copolymerization. The structure and performance of the WSC-g-PKA/PVA semi-IPNs SAR was studied and compared with those of wheat straw cellulose-g-poly (potassium acrylate) (WSC-g-PKA) SAR. The effects of various experimental parameters such as solution pH, concentration, contact time and ion strength on NH_4^+ and PO_4^{3-} removal from solutions were investigated. Equilibrium isotherm data of adsorption of both NH_4^+ and PO_4^{3-} were well fitted to the Freundlich model. Kinetic analysis showed that the pseudo-second-order kinetic model was more suitable for describing the whole adsorption process of NH_4^+ and PO_4^{3-} on SARs. Overall, WSC-g-PKA/PVA semi-IPNs SAR showed better properties in comparison with WSC-g-PKA SAR and it could be considered as one efficient material for the removal and recovery of nitrogen and phosphorus with the agronomic reuse as a fertilizer.

1. Introduction

Nitrogen and phosphorus compounds, which are widely used in agriculture as fertilizers, are very essential elements for the growth of living organisms. Meanwhile, N and P are considered as nonrenewable and irreplaceable resources that will be scarce in the future (Biswas et al., 2008). However, excessive ammonium nitrogen (NH_4^+) and phosphate phosphorus (PO_4^{3-}) in water may cause eutrophication of coastal seas, lakes and rivers. Eutrophication can result in excessive growth of algae and other microorganisms, as well as in increased dissolved oxygen depletion and fish toxicity (Huang et al., 2010). Therefore, it is necessary to remove and collect NH_4^+ and PO_4^{3-} nutrients before the disposal of wastewater.

For the treatment of NH_4^+ or PO_4^{3-} contained wastewater, a variety of techniques have been implemented to purify the wastewater. Typical methods for NH_4^+ removal consist of biological treatment (Andalib et al., 2012), microwave radiation (Lin et al., 2009), ion exchange (Karadag et al., 2008) and adsorption (Onyango et al., 2007). Several methods have been applied to remove PO_4^{3-}, including precipitation–microfiltration (Lu and Liu, 2010), reverse osmosis (Kumar et al., 2007), coagulation (Zhao et al., 2011) and adsorption (Köse and Kıvanç, 2011). Adsorption is one of the most efficient processes to remove NH_4^+ and PO_4^{3-} from wastewater, which provides an alternative treatment, especially if the adsorbent is cheap and widely available. Adsorption with various adsorption materials, such as activated carbon and fiber (Nethaji et al., 2013; Mirmohseni et al., 2012) have been studied extensively. However, because of the lower adsorption capacity, high costs and lower regenerability, the use of these materials has been limited. So, there is a practical need to find new adsorbents to remove NH_4^+ and PO_4^{3-} from wastewater.

Superabsorbent resin (SAR) is loosely cross-linked hydrophilic polymers with network structure, which has the ability to absorb and retain large amounts of aqueous fluids, and the absorbed solution cannot be released even under certain pressure. Semi-interpenetrating polymer networks (semi-IPNs) are

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characterized by the penetration on a molecular scale of networks by some of the linear or branched macromolecules (Sperling, 1984). Semi-IPN systems usually exhibit surprising properties superior to either of the two single polymer alone (Myung et al., 2008). Superabsorbents of semi-IPNs, which are composed of crosslinked and linear polymers can be used to enhance the performance of polymer composites. Recently, due to the abundant resources and enormous potential to reduce production cost, cellulose grafted SAR with eco-friendly property and biodegradability are found increasing interest in the academic and industrial field (Lionetto et al., 2005).

Wheat straw (WS) is one of the best-known fiber crops, whose industrial potential is now being intensively reconsidered. For the reason that a large amount of easily available hydroxyl groups exists in the cellulose, hemicelluloses and lignin of WS which can easily actuate a series of chemical reactions, such as esterification, etherification and copolymerization, WS presents a suitable chemical composition in comparison with other agricultural residues and indicates a broad potential for application to SAR production (Ma et al., 2011a).

Research on SAR materials prepared from cellulose has been reported in previous work, but there is little information concerning the semi-IPNs SAR prepared from wheat straw used for nitrogen and phosphorus removal in the agricultural water in order to reduce the nitrogen and phosphorus release in the process of agricultural fertilization. So in the present work, a new superabsorbent wheat straw cellulose-g-poly (potassium acrylate)/polyvinyl alcohol (WSC-g-PKA/PVA) semi-IPNs SAR was synthesized by a graft copolymerization method using wheat straw cellulose (WSC) as a basic macromolecular skeletal material, potassium acrylate (KA) as a monomer, and polyvinyl alcohol (PVA) as a semi-IPNs polymer. The aim of this study is to determine and compare the efficacy of WSC-g-PKA/PVA semi-IPNs SAR and common WSC based SAR (WSC-g-PKA SAR) as adsorbents for removal of NH_4^+ and PO_4^{3-} from aqueous solution by adsorption method. The factors which would influence the NH_4^+ and PO_4^{3-} removal performance of the two adsorbents, such as pH value, concentration, contact time and ion strength were evaluated. Batch isotherm and kinetic experiments were performed and modeled by different isotherm equations and kinetic equations. Due to the low cost, high efficiency and simplicity of application, the use of wheat straw based SAR for the removal of NH_4^+ and PO_4^{3-} is considered to be an effective and competitive treatment method. Furthermore, the WSC-g-PKA/PVA semi-IPNs SAR can be used as a fertilizer controlled release agent in farmland to reduce the nitrogen and phosphorus release in the process of agricultural fertilization, improve soil fertility and increase crop yields.

2. Methods

2.1. Materials

Wheat straw was collected from Liaocheng, Shandong Province (China). Acrylic acid (AA), N,N′-methylenebisacrylamide (MBA) and polyvinyl alcohol (PVA) with the molecular weight of 1.8 hundred thousand were all of analytical grade. All solutions were prepared with distilled water. The concentration of initiators and MBA were 2.0 g/100 mL dist. water. The working solutions containing different concentrations of ammonium chloride (NH_4Cl) and potassium dihydrogen phosphate (KH_2PO_4) were prepared by stepwise dilution of the stock solutions.

2.2. Preparation and characterization of SARs

The washed and dried wheat straw was smashed and sifted through a 100-mesh sieve. Then the wheat straw powder was soaked in 10% ammonia at the mass ratio of 1:12 for 48 h, and the mixture was washed with distilled water and filtered by a vacuum filter. The filtered residue was dipped in 1 mol/L nitric acid at a mass ratio of 1:12, and heated at 100 °C for 45 min. Then the mixture was washed and filtered by the same way. Finally, it dried at 70 °C to obtain WSC.

The WSC-g-PKA/PVA semi-IPNs SAR was prepared by AA, WSC and PVA in aqueous solution. They were synthesized by graft copolymerization and semi-IPNs technology. 1.0 g WSC was transferred in a three-neck flask equipped with a stirrer. The water bath was heated and maintained at 50 °C. Stock solutions of 10 ml $K_2S_2O_8$ and 2 ml (NH_4)2Ce(NO3)6 were added into the flask. After 15 min, 3.3 ml Na_2SO_3 and 10.0 g AA with neutralization degree of 65% were successively added. After 15 min graft copolymerization reaction between AA and WSC, 2.0 g PVA was put in. Then, 2 ml of MBA was added after 45 min. The solution was stirred at 50 °C for 4 h to complete the polymerization reaction.

WSC-g-PKA SAR was prepared by the same method without added PVA. After that, the formed SARs were oven dried at 70 °C until to reach constant weight. The products used during the absorption process were milled through a 20–40 mesh screen.

The Fourier Transformation Infrared Spectra (FTIR) for WSC-g-PKA/PVA semi-IPNs SAR and WSC-g-PKA SAR were recorded (KBr) on a FTIR-20SX Model Fourier Transform Infrared Spectrometer to confirm the modification.

2.3. Swelling measurements

0.05 g samples were immersed in excess NaCl aqueous solutions with different concentrations. The swollen SARs were filtered using a 100-mesh gauze at different intervals. After weighing, the swelling capacity of SAR at a certain moment was calculated as follows:

$$Q_{eq} = (M_2 - M_1/M_1) \tag{1}$$

where M_1 (g) and M_2 (g) are the weights of the dry and swollen sample, respectively. Q_{eq} (g/g) was calculated as grams of water per gram of sample. All samples were carried out three times repeatedly and the averages were reported in this paper.

2.4. Adsorption experiments

The adsorption experiments were carried out by using a sample with 0.05 g of WSC-g-PKA/PVA semi-IPNs SAR or WSC-g-PKA SAR and 50 mL of NH_4Cl or KH_2PO_4 solution in 250 mL sealed flasks and shaking on a horizontal shaker, respectively. The concentrations of NH_4^+ and PO_4^{3-} were determined by the atomic absorption spectrophotometer.

2.4.1. Effect of pH on adsorption

The influences of different pH on NH_4^+ and PO_4^{3-} adsorption onto WSC-g-PKA/PVA semi-IPNs SAR and WSC-g-PKA SAR were studied at pH range from 2.0 to 12.0. The pH values of solutions were adjusted with 1 mol/L HCl and NaOH. The initial concentrations of NH_4^+ and PO_4^{3-} were both 50 mg/L. 0.05 g SARs were immerged in 50 ml solutions with various pH values and stirred at 20 °C for 4 h. The adsorption capacities of SARs for NH_4^+ and PO_4^{3-} were calculated according to the following equation:

$$q = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where C_0 and C_e (mg/L) are the initial and final concentrations of NH_4^+ or PO_4^{3-} in solution, respectively; V (ml) is the volume of solution; m (g) is the dry weight of SAR used; q (mg/g) is the adsorption capacity.