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Preparation and properties of the magnetic absorbent polymer via the chemical transformation process

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ABSTRACT

Magnetic polyacrylic acid sodium polymer (MPAAS) was prepared by chemical transformation method. Key parameters were investigated in the synthesis process of the magnetic polymer and an optimum preparation condition was gained. The structure of the magnetic polymer was characterized by X-ray diffraction (XRD), Fourier transform infrared spectrosocopy (FTIR) and scanning electron microscope (SEM). Magnetic property of the magnetic polymer was measured by the magnet and superconducting quantum interference device (SQUID). Both the swelling ratio and kinetics and the water retention ratio and kinetics were investigated. Based on the results, it can be gained that both swelling rate and equilibrium swelling rate were lowered after magnetization while the water retention ability of the magnetic polymer is stronger than that of the polymer.

1. Introduction

Recently, many kinds of polymer material with the response to the external stimuli such as temperature, pH and magnetic field were prepared [1–3]. Among these functional materials, the magnetic polymer material was prepared and separated by magnetic field with the additional advantages of instant action and contactless control. The sensitivity of the magnetic polymer to magnetic field was obtained by the magnetic particles in the polymer [4,6]. Therefore, the magnetoresponsive polymer benefits from the combination of features inherent to both their components: magnetic particles and polymer.

Magnetic polymer materials are applied for a wide range of areas such as separation and protein purification [7–11], magnetic targeting [12], and controlled drug release [13,14]. Three-dimensional structure was formed in the magnetic polymer due to a certain degree of crosslink. Strong mechanical strength and resistance of acid and alkaline was also ensured by the crosslink.

Magnetic polymeric material is a new type of functional polymer material, which can be prepared by these methods such as embedding method, monomer polymerization and chemical transformation [15–17]. Hazem et al. prepared magnetic iron oxide particles by the oxidation-precipitation method and then these magnetic particles were encapsulated in polymer matrices composed of poly (acrylamide-styrene sulfonic acid sodium salt) via in situ inverse mini-emulsion polymerization process [18]. Ozgur et al. prepared the magnetic hydrogels and the magnetic hydrogels can be effectively utilized in the removal of toxic metal ions in the water [19]. Alexandre et al. synthesized the magnetic biomaterial with a potential device of a chitosan-based hydrogel by one-pot synthesis [20]. The study indicates that the magnetic hydrogel exhibits a different crystalline structure to that without magnetic properties and an excellent dispersion throughout the hydrogel is gained. However, in the practical application there are some special requirements including narrow size distribution, superparamagnetic behavior, high colloidal stability and high and uniform magnetic content.

Absorbent polymers can absorb a large amount of water and swell in their sizes due to high molecular weight, crosslinked hydrophilic polymers, and afterward their individual particle structures are still retained [21–23]. Superabsorbent polymers were employed to draw the water from the fine coal and the water content in the fine coal was decreased from high level of 29.4% to 12–14% within a contact time of 4 h [24]. The water exclusion of other fine mineral tailings was investigated by using superabsorbent polymer [25]. Farkish and Fall investigated the feasibility of using absorbent polymers for the dewatering and densification of the mature fine tailings of oil sand [26]. In the dewatering process, absorbent polymers were obliged to be regenerated for the reutilization due to high cost and diminishing losses. In the past, research on absorbent polymers focused on absorption capacity, swelling ratios and improving salt resistance [21,26]. Little information is available about water swelling ratio &

Abbreviations: PAAS, polyacrylic acid sodium; XRD, X-ray diffraction; FTIR, Fourier transform infrared spectrosocopy; SEM, scanning electron microscope; SQUID, superconducting quantum interference device; AA, Acrylic acid; MBA, N, N′-methylene-bis-acrylamide; PPS, potassium persulfate

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kinetics and retention ratio and kinetics of absorbent polymers. In fact, water retention ratio and kinetics is as important as water swelling ratio and kinetics in the dewatering process of fine minerals or fine mineral tailings by using absorbent polymers.

In this paper, the magnetic absorbent polymer was expected as a multifunctional absorbent polymer by introducing magnetic particles into the polymer and was prepared by chemical transformation method. As a result, the obtained magnetic adsorbent polymers can be separated under a magnetic field and their features provide an effective approach via magnetic separation. The effects of impregnation time, impregnation temperature, iron ion concentration and molar ratio of ferric ion to ferrous ion were investigated. And thus an optimum operating conditions was obtained. The structure of the magnetic polymer was characterized by XRD and IR. Magnetic property of the magnetic polymer was measured by the magnet and superconducting quantum interference device (SQUID). Swelling ratio and kinetics and water retention ratio and kinetics were also discussed.

2. Experimental section

2.1. Materials

$FeCl_2{\cdot}4H_2O$, $FeCl_3{\cdot}6H_2O$ and sodium hydroxide (NaOH) were purchased from Tianjin Baishi Chemical Reagent Co. Ltd, China. Acrylic acid (AA, chemically pure, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was distilled under nitrogen and reduced pressure prior to polymerization. N,N′-methylene-bis-acrylamide (MBA, analytical grade, Sinopharm Chemical Reagent Co., Ltd, China) and potassium persulfate (PPS, analytical grade, Xi'an Chemical Reagent Factory, China) were used as received without further purification. Distilled water was used throughout the preparation process.

2.2. Synthesis of magnetic absorbent polymer

Acrylic acid (AA, 6.1 g) was added in 120 mL of distilled water, and then NaOH solution (2 mol L^{-1}, 34 mL) was dropwised at the room temperature with the constant stirring for 1 h. N, N′-methylene-bis-acrylamide (MBA, 0.015 g) and potassium persulfate (PPS, 0.01 g) were added and the reaction proceeded with the stirring of 100 rpm in nitrogen at 70 °C for 2 h and then the obtained sample was remained at 70 °C for 12 h. The final product was washed several times with distilled water and then was dried for 24 h at 40 °C in vaccum oven. The obtained product was denoted as PAAS polymer.

PAAS polymer was impregnated in the solution by adding $FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ at the given temperature, and thus Fe^{3+} and Fe^{2+} were impregnated into the structure of polymer. Magnetic nanoparticles were prepared according to a reported procedure [27–29]. Under the total same amount of Fe, Fe^{3+}/Fe^{2+} ratio and Fe^{2+} concentration were changed in the given range. The aqueous NaOH (2 mol L^{-1}) was dropped in the above solution and Fe^{3+} and Fe^{2+} inside the polymer were changed into Fe_3O_4 by the method of chemical reaction. As a result, Fe_3O_4 was evenly distributed in the polymer, and then the magnetic polymer was prepared. Polyacrylic acid sodium polymer and magnetic polyacrylic acid sodium polymer are denoted as PAAS and MPAAS, respectively.

2.3. Instrumentation

The X-ray diffraction (XRD) pattern was collected on a Rigaku instrument with Cu-K_α radiation at 40 kV and 40 mA. FTIR spectra were recorded at ambient temperature using a Nicolet 380 spectrometer in the frequency range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1} on thin wafers of the samples. The morphology of PAAS and MPAAS was characterized using a scanning electron microscope (SEM, Hitachi SU8010, Japan). Magnetic property of the samples was measured at 300 K using a superconducting quantum interference device magnetometer (SQUID) (Quantum design MPMS-XL7, USA). In this paper, the characterization results of XRD, IR, SEM and magnetic property were given based on the obtained MPAAS at these operating conditions as following: impregnation time 60 min, impregnation temperature 70 °C, molar ratio of ferric ion to ferrous ion 2 and ferrous ion concentration 0.4 mol L^{-1}.

2.4. Determination of Fe_3O_4 content

The content of Fe_3O_4 was determined after the magnetic polymer was roasted in the presence of air at 800 °C for 3 h in the muffle roaster. The polymer was completely burn down and Fe_3O_4 was changed into Fe_2O_3 with oxygen. According to the amount of Fe atom in the Fe_2O_3, the Fe_3O_4 content of the magnetic polymer was obtained.

2.5. Swelling ratio and kinetics

At room temperature, the obtained samples were put into the distilled water. The initial sample mass, the mass of sample absorbing water and the swelling time were denoted as m_0, m_t, and t, respectively. And then the Swelling Ratio (SR) was calculated as follow:

$$SR_t = \left(m_t - m_o\right)/m_0 \tag{1}$$

The swelling kinetics was investigated by the change of the swelling capacity F with the impregnation time. The mass of sample absorbing water and the mass of saturated sample absorbing water were denoted as m_t and m_∞, respectively. And then the swelling capacity was calculated as follow:

$$F = m_t/m_\infty = Kt^n \tag{2}$$

Deduction available:

$$\ln F = n \ln t + \ln k \tag{3}$$

Based on the Eq. (3), the values of K and n are calculated and then the swelling kinetic model is established according the value of n.

2.6. Water retention ratio and kinetics

At room temperature, the polymer was put into the distilled water until saturated. The obtained sample was weighed and the mass was denoted as m_∞, and then was dried at temperature T for time t and the mass was denoted as m_t. Thus the water retention ratio ($R_{T,\ t}$) was calculated as following:

$$R_{T,t} = m_t/m_\infty \times 100\% \tag{4}$$

Water retention kinetics was investigated according to the equation from four to seven. Water retention ratio was calculated from Eq. (4) and the reaction order of water retention (n) was determined according to Eq. (5)

$$r = dR_{T,t}/d_t = kR^n_{T,t} \tag{5}$$

Where r is the reaction rate, h^{-1}; k is the reaction constant.

According to Arrhenius Eq. (6):

$$k = A \exp(-E_a/RT) \tag{6}$$

Eq. (7) was derived from Eqs. (5) and (6):

$$\lg k = -E_a/2.303RT + \lg A \tag{7}$$

where E_a is apparent activation energy, J/mol, A is pre-exponential factor.