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Structure and property of polyvinyl alcohol/precipitated silica composite hydrogels for microorganism immobilization

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ABSTRACT

Polyvinyl alcohol (PVA) hydrogel filled with precipitated silica (PSi) was prepared by chemical crosslinking in the saturated boric acid solution. The structure and property of the composite hydrogel was studied. It was found that PSi could accelerate the crosslinking reaction of PVA, and the intermolecular bonding of PVA/PSi composite was confirmed. Effect of PSi on reactive kinetics of PVA hydrogel was investigated. The tensile strength of PVA hydrogel increased with PSi content. Proper content of PSi could also enhance the permeability and swelling property, resulting in the improvement of the capillary water absorption capacity of PVA hydrogel. By addition of PSi, many large pores formed in the hydrogel so as to provide channels for microbial metabolites. When being applied in waste water treatment, the value of oxygen uptake rate (OUR) and COD removal rate of the PVA composite hydrogel immobilized with activated sludge increased significantly, indicating that the microbial activity of PVA immobilized beads could be enhanced.

1. Introduction

Polyvinyl alcohol (PVA) hydrogels are hydrophilic three-dimensional polymeric networks, which are insoluble in water due to the presence of chemical or physical crosslinks [1–4], and have good biocompatibility, high elastic modulus, excellent physicochemical and bio-tribological properties [5–8]. Thus, PVA hydrogels have gained wide biomedical applications in articular cartilage replacement as a pharmaceutical release agent, reconstructive (vocal cord) surgery, drug-delivery matrices, microorganism immobilization, etc. [9–16].

PVA composite hydrogels filled with inorganic fillers have been widely studied. Sirousazar et al. [17] prepared PVA/mineral kaolinite clay nanocomposite hydrogels via freezing/thaw cyclic method. It was demonstrated that addition of kaolinite could improve mechanical property of PVA hydrogel matrix. Sirousazar et al. [18] synthesized PVA/montmorillonite (PVA/MONT) nanocomposite hydrogels by freeze/thaw method. It was found that the swelling characteristics of the nanocomposite hydrogels including the equilibrium degree of weight and volume swelling and the equilibrium water content decreased by increasing the quantity of MONT incorporated into the hydrogel. Sinha et al. [19] prepared PVA/nano-hydroxyapatite (PVA/nano-HA) gel composites by in situ synthesis of nano-HA particles in PVA solution and being accompanied by freeze/thaw method. It was found that nano-HA particles reinforced PVA gel composites endow composites with bioactive properties and excellent mechanical properties. Tong et al. [20] reported that PVA nano-composite hydrogels, containing carbon nanotube, could enhance mechanical and swelling properties of PVA hydrogel.

Precipitated silica (PSi) with high specific surface area, is one of the reinforcing fillers widely used in many compounds [21,22]. The surface of PSi consists of a combination of different types of hydroxyl (i.e. silanol) groups and siloxane bridges [23–27]. In this work, PVA hydrogel filled with PSi was prepared by chemical crosslinking in the saturated boric acid solution [10]. The interface interaction between PVA and PSi was studied. Effect of PSi on reactive kinetics of PVA hydrogel was investigated. The improvement of mechanical property, permeability and swelling property of PVA hydrogel would be expected. And its microbial activity in the wastewater treatment process was investigated.

2. Experimental

2.1. Materials

PVA with an average molecular weight (M_n) of 74800 g/mol was supplied by Sichuan Vinylon Co. (China). Sodium alginate was purchased from Kelong Chemical Co. (Chengdu, China). Boric acid was purchased from Bodi Chemical Co. (Tianjin, China). PSi was purchased from Chengdu Jinzhong organic silicone materials Co. (Chengdu, China). Other chemical agents were all of analytically

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purity and used as received. Activated sludge was taken from Chengdu Sewage Treatment Plant.

2.2. Preparation of PVA hydrogel beads

PVA, sodium alginate, PSi were dissolved in distilled water, and then dropped into the saturated boric acid and $CaCl_2$ solution, and kept for 1 h to form spherical beads. The formed beads were finally washed with distilled water, and stored for further use.

2.3. Measurements

2.3.1. Fourier transform infrared (FTIR) analysis

The samples of PVA and PVA/PSi composite hydrogel were first dried and analyzed with a Nicolet-560 FTIR spectrometer (Madison of WO, USA). The pellet sample was prepared by pressing the mixture of the samples and KBr powder. The scanning rate is 20 min^{-1}, and the differentiate rate is 4 cm^{-1}.

2.3.2. Mechanical property

The tensile property of the samples of PVA hydrogel was measured with a 4302 material testing machine from Instron Co. (USA) according to GB/T 528-1998. The tensile speed and temperature were 20 mm/min and 23 °C, respectively.

2.3.3. Swelling ratio

The preweighed dry samples of PVA hydrogel were immersed into the distilled water at room temperature until they swelled to equilibrium. After excessive surface water was removed with filter paper, the samples were weighed. The swelling ratio can be determined as a function of time [28,29]:

$$\text{Swelling ratio } (\%) = (W_t - W_0)/W_0 \times 100\%$$

where W_0 was the dried weight of hydrogel, and W_t was the weight of hydrogel in swollen state.

2.3.4. Permeability

PVA gel beads were immersed into the diluted ink, kept for three hours at room temperature. The UV transmission rate of ink solution at band 450–700 nm was measured with U3010 UV–visible spectrophotometer (Japan), which was used to characterize the permeability of the gel beads.

2.3.5. Scanning electron microscope (SEM) analysis

The fractured surface morphology of PVA hydrogel beads was observed with a JEOL JSM-5900LV scanning electron microscope (SEM) (Japan) with an acceleration voltage of 20 KV. The PVA hydrogel beads were freezing dried and cryogenically fractured in liquid nitrogen. Then the samples were sputter-coated with gold for 2–3 min.

2.3.6. Oxygen uptake rate (OUR) analysis

About 100 ml distilled water was put into a flask, and aerated to make the dissolved oxygen saturated by air pump. Stop aeration and 5 g of PVA hydrogel beads immobilized with sludge was added. The concentration of the dissolved oxygen (DO) variation with time was measured with AZ 8403 DO meter (China).

2.3.7. Chemical oxygen demand (COD) removal rate

The wastewater solution with different concentrations was prepared, the UV absorbance of the solution at 254 nm was measured with U3010 UV–visible spectrophotometer (Japanese), and the standard curve of UV absorbance–wastewater concentration was obtained. The absorbance at 254 nm of the sample was measured, and the corresponding wastewater concentration can be obtained by the standard curve [30–32]. The COD removal rate was then calculated with the following equation:

$$\text{COD removal rate } (\%) = (C_t - C_0)/C_t \times 100\%$$

where C_0 was the original wastewater concentration before treatment, and C_t was the wastewater concentration after treatment.

3. Results and discussion

3.1. Intermolecular bonding of PVA/PSi composite hydrogels

The FT-IR spectra of PSi, PVA and PVA/PSi were shown in Fig. 1. The pure PSi sample showed a characteristic band at 800 cm^{-1} and 1080–1220 cm^{-1}, attributed to the symmetric and asymmetric Si–O–Si stretching vibration, respectively. The characteristic band at 972 cm^{-1} was attributed to Si–OH stretching absorption, and the characteristic band at 3438 cm^{-1} was attributed to –OH stretching absorption [33,34]. For the sample of pure PVA, the wide absorption band at 3298 cm^{-1} was attributed to the presence of –OH, while the absorption band at 2938 and 1420 cm^{-1} was attributed to dissymmetrical stretching vibration and the symmetry bending vibration of $-CH_2$, respectively. The absorption band at 1090 cm^{-1} was attributed to the presence of C–O bond, while the absorption band at 848 cm^{-1} was attributed to stretching vibration of C–C bond [35]. For the sample of PVA/PSi composites, a new peak appeared at about 835 cm^{-1}, which was the characteristic absorption peak of Si–O–C [36]. The Si–O–C linkage might be formed by the dehydration and condensation reaction of the hydroxyl groups of PVA with hydroxyl groups on the surface of PSi particles. Furthermore, compared with the absorption peak of hydroxyl groups of PVA, the absorption peak of hydroxyl groups of PVA/PSi composite shifted toward higher wave number at about 3427 cm^{-1} due to intramolecular hydrogen bonding of PVA weakened by incorporation of PSi.

3.2. Effect of PSi on the crosslinking reaction kinetics of PVA hydrogel

During the crosslinking reaction of PVA/PSi system by using boric acid as the crosslinking agent, both the hydroxyl groups on the molecule of PVA and the surface of PSi may react with boric acid. Therefore, the effect of PSi on the crosslinking reaction kinetics of PVA hydrogel was investigated. Fig. 3 illustrated the molar concentration of boric acid versus crosslinking time of PVA composite hydrogels with different content of PSi. It can be seen that in the first 20 min of reaction, the molar concentration of boric acid

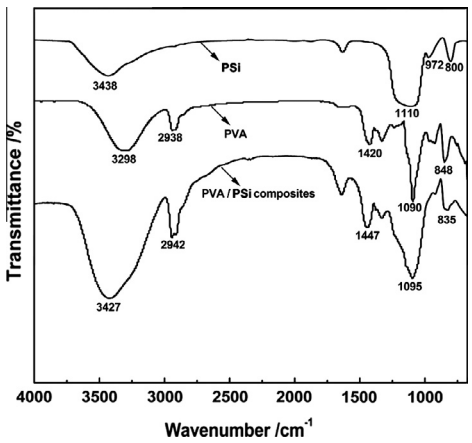

Fig. 1. FTIR spectra of PSi, PVA and PVA/PSi composites.