A novel semi-IPN hydrogel: Preparation, swelling properties and adsorption studies of Co (II)

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ABSTRACT

A range of super-absorbent semi-IPN hydrogels—polyvinyl alcohol/poly (acrylic acid-co-acrylic amide) (PVA-P(AA-co-AM)) were synthesized via free radical polymerization method under ultrasound-assisted condition. L_{16} (4^5) orthogonal experiments were designed to optimize the synthesis conditions and the success was characterized by FTIR, SEM and TGA. Swelling capacities were studied in various pH solution and saline solution whose results indicated that pH in solution shows an obvious influence on it and the salt resistance is greater in salt solution of low valence relative to that of high valence. Meanwhile, its swelling behavior was evaluated in water solution, which revealed that the swelling process conformed to the Schott model and the diffusion type was non-Fickian diffusion. Moreover, the adsorption on cobalt (II) from aqueous solutions was also investigated in the paper. The optimum pH value was found close to 4 for the cobalt (II) adsorption and it was discovered that adsorption kinetics and adsorption isotherms for cobalt (II) were in accordance with the pseudo-second-order model and the Freundlich model respectively. Besides, thermodynamic parameters were calculated for the cobalt (II) adsorption and the findings revealed that the adsorption behavior is spontaneous and endothermic.

Introduction

Hydrogels, a novel functional polymer material with three-dimensional network structure, are moderately crosslinked hydrophilic network polymers that can quickly swell in water and conserve it in a certain degree in comparison with general similar materials like cloth, cotton and cellulose fiber and so forth [1]. Polymeric hydrogels contain a large number of strongly hydrophilic groups such as carboxyl groups, sulfonic acid groups and hydroxyl groups and their swelling capacity stems mainly from the hydrophilic groups and space-grid structure. At present, many materials used to prepare the hydrogels are extensively concerned by researchers such as lignin [2], cellulose [3] and chitosan [4] in virtue of their low cost, abundant resources and biodegradability [5]. There are many methods for the synthesis of hydrogel polymers like free-radical solution polymerization [6], electrostatic spinning [7] and reverse phase suspension polymerization [8]. Ultrasound-assisted synthesis with the merits of fast,

simple and convenient operation has been viewed as a significant and effective technique relative to other methods. An increasing number of studies are reported owing to the advantages of ultrasonic-assisted synthetic method [9,10]. So far, hydrogels have been extensively applied in various fields such as hygienic products [11], agriculture [12] and drug delivery system [13,14] as well as waste-water treatment [15,16].

Semi-interpenetrating polymer networks (semi-IPN) are a way of blending two polymers where only one polymer is crosslinked in the presence of another to produce an additional non-covalent interaction between the two polymers [17]. Semi-IPNs have been developed as a convenient method to prepare multi-component polymer materials, which provided a feasible route to modify the properties of natural polymer-based hydrogels [18,19]. The semi-IPN was introduced into the hydrogel structure, which can increase the water absorption of the hydrogel, improve the salt resistance of the hydrogel and enhance the gel strength of the hydrogel. With the continuous development of the application of hydrogels, people's requirement for their performance is getting higher and higher and the semi-IPN technology has also been attracting the attention of scientists, which has a great space for development.

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Nowadays, environmental contamination caused by heavy metals that are potentially toxic at a certain concentrations has raised a great global issue. The distribution and migration of heavy metals are usually affected by human activities. Microorganisms have no ability to decompose heavy metals in creatures and the point is quite different from the organic pollutants that are susceptible to biological degradation. Heavy metals tend to accumulate in living organisms and the producing consequence will lead to severe problems to both human health and wildlife [20–22]. A heavy metal, cobalt, has become an important role in the numerous areas, used extensively in the manufacture of catalysts, alloys and steels [23,24] additionally, cobalt (II) is also the major composition of Vitamin B_{12} and when deprived of cobalt, animals can show the symptoms of retarded growth, loss of appetite and decreased lactation [25] Under normal circumstances, the cobalt concentration is quite low in natural water and it is not harmful to human and creatures at a low concentration but its toxicity will obviously be released when cobalt concentration was accumulated to a certain level in the living body. Cobalt contained in the water has a great impact on the qualities of water like color, smell and taste. Especially on rainbow trout fish, the lethal dose is $250 \, \mu g \, L^{-1}$ [26], but the maximum permissible concentration of cobalt is not strictly specified in drinking water and in the standard of wastewater discharge. Besides, people who have long-term exposure to cobalt dust are likely to suffer from jaundice [27]. Various separation processes were applied for cobalt ions such as adsorption, ion exchange, precipitation, membrane separation, and solvent-extraction methods. Among these [28,29], adsorption has emerged as one of the most promising techniques that is applied for cobalt (II) removal owing to numerous advantages such as various adsorbents, high efficiency, cost effectiveness, capacity to treat very dilute wastewater, recovery and recycling of the adsorbent, and recovery of heavy metals [30–32]. For instance, Fatemeh et al. [33] had prepared the NaAlg-HAp-CNT nanocomposite with the well-done absorption efficiency on cobalt (II) whose adsorption capacity can reach $347.2 \, mg \, g^{-1}$ and Nalan et al. [34] had successfully synthesized the DMAPMAm/IA composites that were used as an adsorbent to adsorb the cobalt (II) from aqueous solutions. However, their application was still limited due to the high cost of their materials. Compared with the two above-mentioned papers, the material cost and synthetic technology have been dramatically improved in the experiment.

This study aimed to prepare an excellent PVA-P (AA-co-AM) semi-IPN hydrogel through making full use of outstanding performances of the PVA. The PVA-P (AA-co-AM) semi-IPN hydrogel was synthesized via free radical polymerization method under ultrasound-assisted condition and the synthetic conditions were optimized by orthogonal design. Swelling properties of PVA-P (AA-co-AM) semi-IPN hydrogel were discussed including pH sensitivity, resistance to various salt solutions and water-retention rate. Besides, in order to expand the field of application, it was also studied that PVA-P (AA-co-AM) semi-IPN hydrogel as an adsorbent adsorbed the cobalt (II) from aqueous solutions and the effect of adsorption was evaluated as a function of the contact time, solution pH, and initial concentration.

Experimental

Materials

Polyvinyl alcohol (PVA, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was dissolved at 90 °C with magnetic stirring. Acrylic acid (AA, Shanghai Macklin Biochemical Co., Ltd.) and Acrylic amide (AM, Aladdin Industrial Corporation) were as polymeric monomers. Ammonium persulfate (APS, Shanghai Suran Chemical Reagent Co., Ltd.) and N′,N-methylenebisacrylamide (NMBA, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were as an initiator and a cross-linking agent, respectively. The other agents in the experiment were purchased from Nanjing Chemical reagent Co., Ltd., such as sodium hydroxide, ethanol and cobaltous nitrate hexahydrate. All aqueous solutions used for polymerization reactions, swelling and adsorption study were prepared with deionized water.

Preparation of the PVA-P (AA-co-AM) semi-IPN hydrogels

A series of semi-IPN hydrogels PVA-P (AA-co-AM) was prepared by free radical polymerization under ultrasound-assisted condition with following procedures. 5 mL AA in a beaker placed in an ice-water bath was partially neutralized by adding dropwise NaOH solution while stirring with a glass rod. Later, other reactants such as AM, PVA and NMBA as well as APS were with stirring continually added into the mixed solution sequentially. Then, the above-mentioned solution was moved to a KQ-2200 CNC ultrasonic-cleaner and kept at 70 °C for 3 h to accomplish this system. In the end, the resulting hydrogel was soaked for 24 h with absolute ethyl alcohol to remove unreacted monomers. The sample was dried in vacuum oven at 80 °C to a constant weight and the dry sample was thoroughly smashed to attain article size in the range of 40–60 mesh. The amount of reagents above was arranged according to the following orthogonal Table 1.

Table 1
Arrangements of the 5-variable 4-level orthogonal experiment.

$L_{16} \, (4^5)$	(A) PVA/g	(B) Initiator/g	(C) Cross-linker/g	(D) Neutralization degree/%	(E) AM/AA/%
1	A_1 0.1	B_1 0.0087	C_1 0.0011	D_1 65	E_1 4
2	A_1 0.1	B_2 0.0145	C_2 0.0017	D_2 70	E_2 6
3	A_1 0.1	B_3 0.0203	C_3 0.0023	D_3 75	E_3 8
4	A_1 0.1	B_4 0.0261	C_4 0.0029	D_4 80	E_4 10
5	A_2 0.2	B_1 0.0087	C_2 0.0017	D_3 75	E_4 10
6	A_2 0.2	B_2 0.0145	C_1 0.0011	D_4 80	E_3 8
7	A_2 0.2	B_3 0.0203	C_4 0.0029	D_1 65	E_2 6
8	A_2 0.2	B_4 0.0261	C_3 0.0023	D_2 70	E_1 4
9	A_3 0.3	B_1 0.0087	C_3 0.0023	D_4 80	E_2 6
10	A_3 0.3	B_2 0.0145	C_4 0.0029	D_3 75	E_1 4
11	A_3 0.3	B_3 0.0203	C_1 0.0011	D_2 70	E_4 10
12	A_3 0.3	B_4 0.0261	C_2 0.0017	D_1 65	E_3 8
13	A_4 0.4	B_1 0.0087	C_4 0.0029	D_2 70	E_3 8
14	A_4 0.4	B_2 0.0145	C_3 0.0023	D_1 65	E_4 10
15	A_4 0.4	B_3 0.0203	C_2 0.0017	D_4 80	E_1 4
16	A_4 0.4	B_4 0.0261	C_1 0.0011	D_3 75	E_2 6