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Utilization of magnetic hydrogels in the separation of toxic metal ions from aqueous environments

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ABSTRACT

We report the synthesis of poly(2-acrylamido-2-methyl-1-propansulfonic acid-co-vinylimidazole), p(AMPS-c-VI) hydrogels from various amounts of 2-acrylamido-2-methyl-1-propansulfonic acid (AMPS) and N-vinylimidazole (VI) monomers by photo-polymerization technique. Hydrogel composites with magnetic properties were synthesized *in situ* by incorporating Fe(II) and Fe(III) ions into p(AMPS-c-VI) hydrogels network and then reducing them with alkaline solution. Hydrogels swellings were performed for both bare and magnetic hydrogels. The selective removal capability of toxic metal ions, Cu(II), Cd(II), Fe(II), and Pb(II) by these hydrogels was studied in aqueous medium. Desorption studies were also performed in weakly acidic media to observe whether these hydrogel composites can be utilized as reusable tool for the toxic metal ion removal. The effects of the gel amount, contact time with metal ions, metal species and metal ion concentrations on absorption phenomena were evaluated. The equilibrium removal process of metal ions by the composite hydrogels complies well with the Langmuir adsorption isotherm model.

1. Introduction

Most of the heavy metal ions such as Pb(II), Cu(II) and Cd(II) that are toxic and carcinogenic even at very low concentrations usually cause a serious threat to the environment and to the public health [1–4]. It is well known that heavy metal ions such as Pb(II), Cd (II), Hg(II), Ni(II) and Cu(II) may cause severe health problems in animals and human because they can specifically bind to proteins, nucleic acid and small metabolites in living organisms inhibiting their functions. Heavy metals are detected in industrial waste waters originating from metal plating, mining activities, smelting, battery manufacture [5], petroleum refining [6], paint production [7], pesticides, pigment manufacture, printing and photographic industries. Regarding the removal of these metal ions from wastewaters, a number of methods have been developed so far including cementation, chemical precipitation, ion exchange, liquid–liquid extraction, resins, electrolysis, coagulation, flotation, hyper-filtration, oxidation, biosorption and adsorption [2,3,8,9]. Each method has its own drawback in terms of efficiency, cost, and complexity. For example, electrolysis process often takes higher operational costs and chemical precipitation generates secondary wastes and so on [9,10]. Using low cost biosorbents such as clay materials, biomass, sepiolite, zeolite, active carbon, and ion exchange resins may be alternatives for heavy metal ions removal; however, their absorption capacity, separation rate and design must be improved [11–13]. These adsorbents have some disadvantages in the removal of toxic metal ions from aqueous media. For example, they cannot respond to any change in external parameters such as pH, electrolyte concentrations, salts, and the presence of other solutes, temperature and ionic strength of the media [14–16]. Hydrogels are sometimes referred to as intelligent materials (smart materials) that can exhibit significant volume changes in response to small changes in their environments. The environmental conditions can be received as stimuli are pH, temperature, electric field, solvent, ionic strength, and light and so on [16,17]. Hydrogels also have a wide range of applications in tissue regeneration, as artificial organs in biotechnology, as controlled drug delivery vehicles, sensors, in separation and purification processes, and the recognition of certain molecules, bio-molecules and proteins [18,19]. Hydrogels are water-swollen crosslinked networks of hydrophilic polymers. Due to the hydrophilic groups (–OH, –COOH, $-NH_2$, $-CONH_2$, and $-SO_3H$) in their backbones, they can absorb a large amount of water and swell [19,20]. Hydrophilic functional groups in the hydrogel networks give them the ability to remove toxic metal ions from aqueous media [21]. Furthermore, hydrogels can be modified with new functional groups or prepared as composites to increase their metal absorption capacity and their versatility for practical usage [19,22]. New adsorbents with improved properties for better materials are imperative in the separation processes. Traditional adsorbents show poor recovery of the target metal ions from large volumes of solution due to the low

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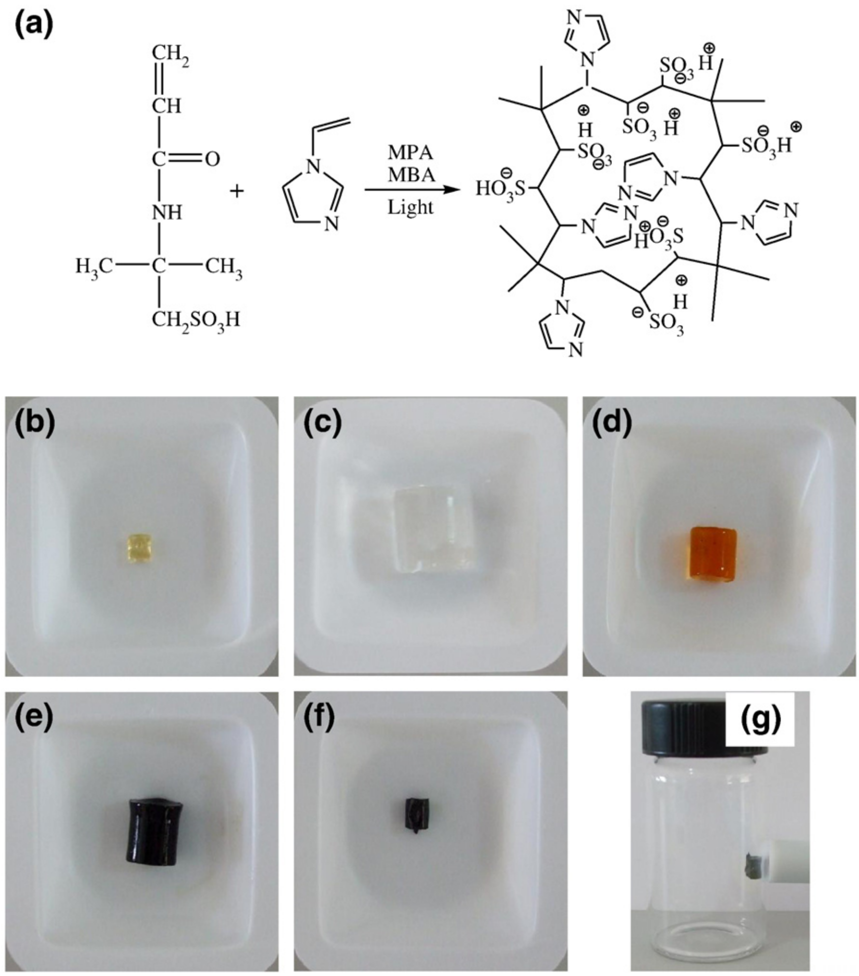

Fig. 1. (a) The schematic representation of the synthesis of p(2-acrylamido-2-methyl propansulfonic acid-c-N-vinylimidazole), p(AMPS-c-VI) hydrogels with different mole ratios. The digital camera images of (b) dry, (c) water-swollen, (d) Fe(II) and Fe(III) ion absorbed, (e) magnetic hydrogels after treatment with alkali solution, and (f) and (g) dried magnetic hydrogel.

binding capacity and lack of active surface sites. It would be greatly beneficial to develop a novel adsorbent that has a high adsorption capacity and fast separation time from large volume of solutions in real applications. Recently, magnetic separation has become a promising method for environmental purification as it produces no contamination and it is easily separated from the medium under applied magnetic field [9,23–25]. Hence, hydrogels with magnetic properties have become a new class of intelligent materials which attract interest as absorbents for the removal of toxic materials from the aquatic media [19]. As hydrogels are extremely porous and have three-dimensional network structure, they can absorb species into their network as well as on their surfaces, unlike solid adsorbent where the adsorption phenomena takes places on the surfaces. Hydrogels uptake species within their three-dimensional networks, and therefore, at the present investigation we will use “absorption” for the intake of metal ions by hydrogels throughout this investigation.

Earlier, we reported the preparation of p(AMPS) hydrogel with magnetic properties for removal of metal ions [19]. In this study, we introduce a new functional group containing monomer (VI) to hydrogel network and still maintain the ability of magnetic particle preparation *in situ*, and used them for separation of different metal ions. A series of p (AMPS-c-VI) hydrogels and their magnetic composites were prepared and utilized as metal ion removal vehicles from aqueous environments. The magnetic responsive behavior was introduced by Fe(II) and Fe(III) ions absorption into hydrogel network followed by the reduction of these ions *in situ* with alkali solution. The swelling behaviors of these materials were investigated in tap, sea and deionized waters and as a function of pH for possible environmental applications. The magnetic hydrogels were used for the selective absorption of metal ions from aquatic environment. The effects of metal ion concentration, the amount of hydrogel, absorption time and metal ion species on the absorption performance were also explored. Desorption studies were performed for the reusability of these hydrogels. Finally, the equilibrium removal performance of the composite gels was analyzed according to the Langmuir and Freundlich isotherm models.

2. Experimental

2.1. Materials

2-acrylamido-2-methyl-1-propansulfonic acid (AMPS) and N-vinylimidazole (VI) as monomers, N,N′-methylenebisacrylamide (MBA) as cross linker, 2,2′-azobis(2-methyl propionamidine) (MPA) dihydrochloride as the photo-initiator were used, and purchased from Sigma-Aldrich and Fluka Chemical Companies. $CuCl_2 \cdot 2H_2O$, (Riedel de Haen Chem. Comp), $CdCl_2$, $PbCl_2$ and $FeSO_4 \cdot 7H_2O$, and $FeCl_3$ (Sigma-Aldrich), and sodium hydroxide (Fluka Chem. Comp.) were used as metal ion sources for the absorption studies and for magnetic particles syntheses, respectively. All the reagents were of analytical grade or highest purity available, and used without further purification. The 18.2 MΩ cm (Millipore Direct-Q3 UV) distilled water was used throughout the absorption experiments. Sartorius Documeter pH meter was used for the pH measurements.