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Radiation crosslinked poly (vinyl alcohol)/acrylic acid copolymer for removal of heavy metal ions from aqueous solutions

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ABSTRACT

Poly(vinyl alcohol) and acrylic acid (AAc) were copolymerized in different compositions using gamma irradiation. Swelling characteristics of the obtained polymeric hydrogels (PVA/AAc) were evaluated and showed reasonable sensitivity to both pH and temperature. The diffusion of water within the hydrogel was found to be of Fickian character, the water molecules may simply diffuse through the polymer network by diffusion processes. The adsorption of Zn^{2+}, Co^{2+} and Mn^{2+} ions onto (PVA/AAc) has been investigated. The parameters studied including; the effects of pH, contact time and the initial metal ion concentrations by batch method. It was found that the adsorption of Zn^{2+}, Co^{2+} and Mn^{2+} ions by PVA/AAc hydrogel is pH-dependent and the maximum sorption of Zn^{2+}, Co^{2+} and Mn^{2+} was found to be 388, 245 and 152 mg/g, respectively, at pH 5. The adsorption studies are fitted in various adsorption models such as Langmuir and Freundlich. The kinetic data was tested using pseudo-first-order, pseudo-second-order kinetic models and an intraparticle diffusion model. The correlation results suggested that the pseudo-second-order model was the best choice among all the kinetic models to describe the adsorption behavior.

1. Introduction

Toxicities of water sources due to the discharge of industrial effluents, is a world-wide environmental problem. Industrial waters and even natural waters are often contaminated by toxic or sometimes carcinogenic impurities causing ecological disequilibrium and severe public health problem. For instance, heavy metal contamination in water is a serious problem due to toxicity, long persistence, bioaccumulation, and biomagnifications in food chain of heavy metals (Gurgel, Freitas, & Gil, 2008). In the past decades, several techniques,

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such as chemical precipitation (Harja, Buema, Sutiman, & Cretescu, 2013) solvent extraction (Djedidi et al., 2009) ultrafiltration (Trivunac & Stevanovic, 2006) organic and inorganic ion exchange (Rafati, Mahvi, Asgari, & Hosseini, 2010) have been employed for the removal of heavy metal ions from aqueous solutions. Most of these techniques suffered from technical, economic, environmental and health problems related to low efficiency, long time of processing, high energy consumption and the large quantity of hazardous materials used. However, adsorption is an attractive method because of its high efficiency and the availability of different adsorbents (Guo, Su, & Wu, 2009). Many researches concentrated on the metal ion recovery using chelating polymers because they are reusable, easy handing and have higher adsorption capacities, efficiencies as well as high selectivity to some metal ions (Mahmoud & Mohamed, 2012).

Hydrogels are hydrophilic polymer networks that are capable of imbibing large amounts of water, yet are insoluble because of the presence of physical or chemical crosslinks, entanglements, or crystalline regions. The absorption of water by hydrogel is one of the most important factors that determine its properties and applications. Swollen hydrogels contain liquid-filled cavities able to absorb a large amount of the electrolyte. The behavior of swollen is a function of the network characteristics density of crosslinking, which are closely related to the chemical structure of the hydrogel (Chen & Chen, 2004). Because of the presence of certain functional groups along the polymer chains, hydrogels are often sensitive to the conditions of the surrounding environment.

Gamma irradiation is found to be a very effective method for constructing three-dimensional polymeric networks. It offers advantages over conventional physical or chemical methods of network formation: mild reaction conditions, negligible by-product formation, fast gelation and no need of catalysts (Nikolic, Krkljes, Popovic, Lausevic, & Miljanic, 2007). It is possible to control the physical properties of hydrogels by the adjustment of the radiation dosage and the polymer composition (Yang, Sua, Leu, & LandYang, 2004). The hydrogels which contains ionizable groups such as carboxylic when they are ionized produce fixed ions that repel one another, and this repulsion leads to greatly enhanced swelling of the network (Yu, Xu, Chen, Hao, & Jing, 2006). The swelling of the ionized hydrogel at equilibrium increases with an increase in the incorporation of functional ionizable groups of the network.

Several research groups have focused their studies on the PVA/AAc hydrogels (Hegazy et al., 2004). In this work, the hydrogels, obtained by radiation-induced crosslinking of poly(vinyl alcohol) (PVA) and acrylic acid (AAc) was synthesized by γ-irradiation and used for the removal of Zn^{2+}, Co^{2+} and Mn^{2+} ions from aqueous solutions. The swelling kinetics of the hydrogels has been carried out to evaluate the swelling mechanism. The influences of experimental parameters such as pH, contact time and initial metal ions concentration on adsorption were studied. The adsorption kinetics and isotherms of the hydrogel toward the investigated metal ions were also discussed. Desorption studies were conducted by suitable agents to regenerate the spend adsorbent.

2. Materials and methods

2.1. Materials

Poly(vinyl alcohol) (PVA; *Mw* 15,000) was purchased from Aldrich Co. and acrylic acid (AAc), obtained from (Merck, Germany)were used as received. All other chemicals used namely metal chlorides, the components of the citrate and phosphate buffers were reagent grade and purchased from El-Nasr Co. for Chemical Industries (Egypt) and used as purchased without further purification. Distilled water was used in all experiments.

2.2. Preparation of PVA/AAc copolymer

The PVA/AAc copolymers were synthesized by the free radical polymerization. An aqueous solution of 10% PVA (w/v) was used; the determined quantity of PVA was dissolved at 80 °C in water bath with constant stirring for 6 h. After cooling down to room temperature, 20% aqueous solution of AAc mixed with PVA solution, where, the mixing ratios of AAc in the solution were ranged from 2 to 10%.The resulting solutions were poured into glass Petri dishes, and then they were irradiated with a ^{60}Co source at radiation dose 20 kGy. After polymerization, films of PVA/AAc hydrogels of about 1 mm thick were formed. They were soaked and washed repeatedly with distilled water to ensure removing any unreacted chemicals.

2.3. Gel content

The irradiated hydrogel samples were vacuum-dried at 40 °C to a constant weight. The dried samples were soaked in distilled water for 24 h at 80 °C, then, they were taken out and washed with hot water to remove the soluble part, dried to a constant weight. The gel content was calculated gravimetrically with the following formula:-

$$\text{Gel content}(\%) = \frac{W_d}{W_0} \times 100 \quad (1)$$

where W_d and W_0 are the dried sample masses after and before extraction, respectively.

2.4. The swelling measurements

The clean, dried, film of preweight was soaked in bidistilled water at room temperature for different intervals time durations. The film was removed and the excess water on the surface was removed by blotting quickly with filter paper and weighed. The swelling ratio was calculated as follows:

$$\text{Swelling ratio} = \frac{W_s - W_d}{W_d} \quad (2)$$

Where W_d and W_s are the masses of dry and wet film, respectively.

To investigate the swelling behavior at various pH's, the samples were swollen in several buffer solutions at room temperature in the same way as mentioned above. In the case of temperature-dependent swelling behavior, the swelling