



## Metal sorption behavior of poly(*N*-vinyl-2-pyrrolidone)/(acrylic acid-co-styrene) hydrogels synthesized by gamma radiation

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### ABSTRACT

pH-sensitive hydrogels based on Poly (*N*-vinyl-2-pyrrolidon) (PVP), acrylic acid (AAc) and styrene (Sty) were prepared by gamma irradiation. PVP/(AAc-co-Sty) hydrogels were modified to use as adsorbent materials for removal of heavy metal ions from aqueous solution. Effect of functionalization of hydrogels by sulfonation (Sf), partial hydrolysis with alkaline solution (NaOH) and treated with the two processes (NaOH/Sf) on metal ion uptake has been studied, and it results in appreciable uptake of Co<sup>2+</sup>, Cu<sup>2+</sup> and Fe<sup>3+</sup> ions from aqueous solution. The degree of swelling and gel content increase with increasing AAc ratio in the initial feed solutions. The structure of hydrogels was characterized by FT-IR and <sup>1</sup>H NMR spectral data and the results were consistent with the expected structures. It was characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The capacity of the hydrogels to bind various metal ions was tested under a range of uptake conditions, with varying uptake time, pH, temperature and initial feed concentration. The metal ion uptake efficiency of PVP/(AAc-co-Sty) hydrogel is in the order: hydrogel treated with NaOH/Sf > hydrogel treated with NaOH > hydrogel treated with Sf > untreated hydrogel. The highest metal ion uptake was observed for Fe<sup>3+</sup> and the lowest was observed for Cu<sup>2+</sup>. It was observed that the specific interaction between metal ions and ionic moieties on the polymeric chains can affect the metal binding capacity of the hydrogel. These results are of interest for the development of hydrogel-based technologies for water purification and metal ions separation and enrichment.

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### Introduction

Hydrogels are crosslinked three-dimensional network structure of hydrophilic homopolymers or copolymers. In the previous two decades, special attention has been given to hydrogel adsorbents [1–3]. Due to the super-hydrophilicity characteristics and porous structure networks, they can swell quickly in the aqueous solution, which is beneficial for shortening the time to reach the adsorption equilibrium [4]. Hydrogels can be prepared with different functional groups such as carboxylic acid, amine, hydroxyl, amidoxime and sulfonic acid groups. The presence of these functional groups, not only improves water uptake capacity of the hydrogels, but these also act as efficient *anchors* for active molecular species and metal ions. The capacity of the hydrogels for metal uptake increases many folds with post functionalization by simple polymer analogous reactions. As hydrogels possess ionic functional groups, they can absorb and trap metal ions or ionic

dyes from wastewater [5,6]. Therefore, a great deal of interest has been observed in relation to the applicability of hydrogels as adsorbents for the removal and separation of metal ions from heavy metal contaminated water [5–8], and the recovery and preconcentration of precious metal ions from different media [9]. Compared with conventional solid adsorbents like ion exchange and chelating resins, main advantages of such materials are easy loading and, in most cases, stripping of cations with simple chemicals, reusability and the possibility of semi-continuous operation. In addition, high wettability and high swelling of hydrogels also might be beneficial for improving adsorption of target metals [9].

Pollution caused by the presence of metal ions is assuming dangerous proportions as toxic metal ions are present in most of the water discharged from industries, mining effluents and municipal wastes [10–13]. They are not biodegradable and can accumulate in living organisms [14]. Therefore, these heavy metals can be considered as one of the most important pollutants for waters and waste waters [15–17]. As industry expands, heavy metal ion contamination is exacerbated. When heavy metal ions are assimilated into living organisms, they accumulate in living bodies, causing serious diseases even at very low concentrations

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[18,19]. Therefore, many separation methods have been developed for removing heavy metal ions from aqueous solutions, including reduction and precipitation, coagulation, reverse osmosis, electro-dialysis, and adsorption [20–23]. Among these technologies, adsorption of heavy metal ions using chelating resins is highly popular because they are reusable, easy to handle and have higher adsorption efficiencies and selectivity. Poly acrylic acid polymer is choice as a hydrogel material, it shows a very high hydrophilicity and its pendant carboxylic group acts as efficient anchor for the polar and ionic species. Also, these hydrogels are highly susceptible to variation in pH and ionic nature of the medium, this enables it to use as ion exchangers [24]. With regard to the degree of functionalization, the transformation of poly styrene into cation exchange polymer can be accomplished by several methods. This gives rise to an aromatic electrophilic substitution reaction and sulfonic acid groups are incorporated to the aromatic rings. The degree of sulfonation, and hence the exchange capacity, is an important feature of cation exchange of polymer because in exchange and catalytic operations their performance depends on this parameter [25]. Hegazy et al. used radiation synthesized and well characterized poly(*N*-vinyl-2-pyrrolidone/acrylic acid) and poly(*N*-vinyl-2-pyrrolidone/acrylamide) hydrogels for the separation and extraction of some heavy-metal ions from waste water [26].

In view of the above, we have attempted to develop hydrogels with incorporated polyelectrolytes by graft copolymerization of acrylic acid, styrene onto poly(*N*-vinyl-2-pyrrolidone) via radiation to act as polymeric adsorbents for metal ions such as  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  from aqueous solution.

## Experimental

Acrylic acid, styrene, and poly(*N*-vinyl-2-pyrrolidone) of purity 99%, supplied from Merck, Germany, and used as received without further purification. Analytical grade cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), cupric chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) and ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), in addition to other chemicals, such as citric acid, tri-sodium citrate, sodium di-hydrogen phosphate, di-sodium hydrogen phosphate buffer analytical reagents were purchased from El-Nasr Co. for Chemical Industries, Egypt and used without further purification.

## Method

### Preparation of PVP/(AAc-co-Sty) hydrogels

Poly (*N*-vinyl-2-pyrrolidone) and acrylic acid were separately dissolved in water whereas styrene was dissolved in ethanol/water mixture. AAc and Sty were mixed together with different AAc:Sty compositions at room temperature. PVP (50 wt%) was mixed with different AAc:Sty compositions and then irradiated with  $^{60}\text{Co}$  gamma rays at dose rate 6.13 kGy/h. The obtained hydrogel was washed with ethanol/water mixture for removal of unreacted monomers component and then dried in vacuum oven at 40 °C.

### Alkaline treatment of hydrogels

Treatment of tested PVP/(AAc-co-Sty) hydrogels was carried out by immersing it in 3 wt% aqueous solution of NaOH for 6 h, then the hydrogel is washed with hot deionized water to remove occluded NaOH and dried in an oven at 40–50 °C.

### Sulfonation of hydrogels

In order to introduce ion exchange character, styrene copolymers requires sulfonation. The PVP/(AAc-co-Sty) hydrogels were immersed in a dichloromethane solution  $\text{CH}_2\text{Cl}_2$  and 5% sulfuric acid (95–98%), silver sulfate is used as a catalyst for 2 h. After slow

drying at ambient temperature, the hydrogel is washed with de-ionized water and finally dried in an oven at 60 °C [27].

### Gel determination

Dried hydrogels were extracted with distilled water for 24 h at 100 °C to extract the insoluble parts of the hydrogel. The insoluble or gelled parts were taken out and washed with hot distilled water for the removal of the soluble parts and then were dried and weighed. This extraction cycle was repeated until the weight become constant. The gel yield of hydrogel was determined as follows:

$$\text{Gel (\%)} = \left( \frac{W_e}{W_d} \right) \times 100 \quad (1)$$

where  $W_d$  and  $W_e$  represent the weights of the dry hydrogel and the gelled part after extraction, respectively.

### Swelling determination

Dried hydrogel discs (0.3–0.4 mm thickness, 4-mm diameter) were left to swell in distilled water or phosphate buffer solutions of desired pH. Swollen gel removed from the swelling medium at regular time intervals and superficially dried with filter paper, then, it was weighed and placed in the same bath. The measurements were continued until a constant weight was reached, the swelling of hydrogel was determined as follows:

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

where  $W_s$  and  $W_d$  represent the weights of swollen and dry samples, respectively.

### Metal uptake measurement

The fixed weight of the prepared hydrogel was immersed in metal feed solutions, Fe(III), Co(II), and Cu(II) of a definite concentration. The concentrations of metal ions remaining in the solution were detected by ultraviolet spectroscopy (UV) and used for the calibration process. The pH and temperature of the metal feed solutions were adjusted before it applied for treatment processes. The adsorption amount ( $E$ ) was calculated as follows:

$$E \text{ (mg/g)} = \frac{V(C_i - C_r)}{W} \quad (3)$$

where  $V$  is the volume of solution [1],  $W$  is the weight of the hydrogel (g), whereas,  $C_i$ , and  $C_r$  are the concentrations of metal ions in mg/L before and after the adsorption, respectively.

### FT-IR spectroscopy

The dry hydrogels were grounded and pressed with KBr and then measured with FT-IR spectroscopy (Mattson 1000, Unicam, England) in the range of 400–4000  $\text{cm}^{-1}$ .

### Ultraviolet spectroscopy (UV)

Determination of the metal ion concentration before and after treatment was carried out using Perkin-Elmer, Lambda1 UV-vis spectrophotometer in the range of 190–900 nm.

### Thermal gravimetric analysis (TGA)

Shimadzu TGA-50 system in nitrogen atmosphere (20 mL/min) was used. The temperature range was from the ambient temperature to 600 °C at heating rate of 10 °C/min.

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