



RESEARCH PAPER

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## Removal of heavy metals from aqueous solutions by starch-poly(AN) hydrogels

Mohammad Sadeghi\*, Esmat Mohammadasab, Fatemeh Shafiei, Laleh Mansouri, Mohammad Javad Khodabakhshi

*Department of Chemistry, Science Faculty, Islamic Azad University, Arak Branch, Arak, Iran,*

Article published on April 18, 2014

**Key words:** Starch, polyacrylonitrile, hydrogel, chelating resin, binding capacity.

### Abstract

In this study, to following of synthesis of a superabsorbent hydrogel based on starch (St) and polyacrylonitrile (PAN), the removal of copper(II), zinc(II) and cadmium ions from aqueous solutions by H-St-g-polyAN hydrogel was investigated. The physical mixture of St and PAN was hydrolyzed by NaOH solution to yield St-poly(sodium acrylate-co-acrylamide) superabsorbent hydrogel. The various factors affecting the removal of heavy metal ions, such as treatment time with the solution and initial metal ions concentration were also investigated. The maximum removal of Cu(II) (76.0%) was observed at an optimum pH of 4.8, whereas, the maximum removal of 57.0% for Zn(II) and 49.0% for Cd(II) was observed. It was found that sorption of heavy metals occurs synchronously with the hydrogels swelling. The sorption capacity was high for copper 2.08 mmolg<sup>-1</sup> at pH 6.

\*Corresponding Author: Mohammad Sadeghi ✉ [m-sadeghi@iau-arak.ac.ir](mailto:m-sadeghi@iau-arak.ac.ir)

## Introduction

Loosely crosslinked hydrophilic polymers (hydrogels) being able to absorb and retain hundreds of their own weight of water are known as superabsorbents (Buchholz *et al.* 1997). The swelling properties of these hydrogels have attracted the attention of researchers and technologists, and have found widespread applications in removal of metal ions, drug delivery systems, agriculture, separation processes and many other fields (Hoffman 1996; Pourjavadi *et al.* 2004; Zhang *et al.* 2007). The removal of polluting metal ions from industrial effluents, water supplies and mine waters has received much attention in recent years. Various approaches such as ion exchange, reverse osmosis, and electro dialysis techniques have been developed for the removal and recovery of the metal ions from sewage and industrial waste water. The use of synthetic resins for chelating toxic metal ions in waste water is a possible method for preventing environmental pollution. After the metal ion adsorption processes, the resins that are mostly composed of petroleum based synthetic polymers, are generally discarded in landfills or treated by incineration. Therefore, these processes often result in secondary pollution by contaminating the soil or air. In addition, these synthetic polymers are usually non-renewable and non-biodegradable (Hoffman 1996). However, it by itself could not be satisfactorily applied in chelating or adsorbing heavy metal ions to replace the synthetic chelate resins, because it has inherently no metal-anchoring capability. Hence, many attempts have been made to utilize starch as a metal scavenger, through functionalizing the polysaccharide. In this investigation, we paid attention to investigation of a superabsorbent based on starch and PAN. In finally, the metal ions adsorption of the resin were evaluated.

## Materials and methods

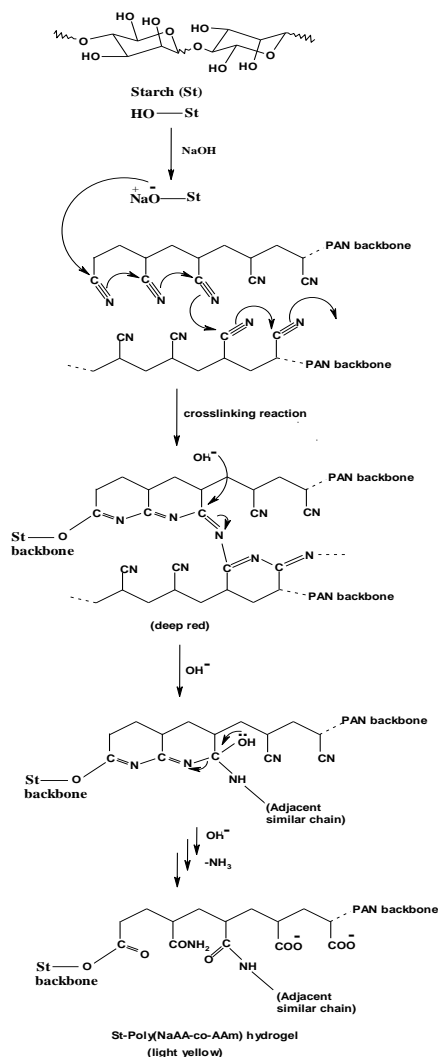
### Materials

Starch (chemical grade, MW 50000) was purchased from Merck Chemical Co. (Germany). The acrylonitrile (PAN) monomer was used after vapour distillation. Metal acetates and other chemicals were

of analytical reagent grade. Double distilled water was used for the hydrogel preparation and swelling measurements.

### Preparation of chelating resin

A facile one step preparative method was used for synthesis of St-poly(sodium acrylate-co-acrylamide) hydrogel. A general procedure for alkaline hydrolysis of St-PAN mixture was conducted as follows. Starch (0.50-1.33 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 50-500 rpm), including 35 mL doubly distilled water. The reactor was immersed in a thermostated water bath. After complete dissolution of starch to form a homogeneous solution, certain weight percent of sodium hydroxide (2.0-20.0 wt %) was added to the starch solution at desired temperature (alkalization temperature, 50-90 °C). The mixture was allowed to stir for certain times (alkalization times, 30-360 min). The various amount of polyacrylonitrile (0.50-1.50 g) was dispersed in the reaction mixture to saponify for certain times and temperatures (alkaline time and temperature). During the saponification NH<sub>3</sub> gas was evolved and a color change from red to light yellow. This discoloration was an indication of the reaction completion. The pasty mixture was allowed to cool to room temperature and neutralized to pH 8.0 by addition of 10 wt % aqueous acetic acid solution. Then the gelled product was scissored to small pieces and poured in ethanol (200 mL) to dewater for 5 h. The hardened particles were filtered and dried in oven (50°C, 10h). After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat and light. The Proposed mechanism to produce the St-poly (NaAA-co-AAm) hydrogel is shown in Scheme 1.



**Scheme 1** Proposed mechanism for crosslinking during the hydrolysis of nitrile groups of the St-PAN mixture to produce the St-poly(NaAA-co-AAm) resin hydrogel.

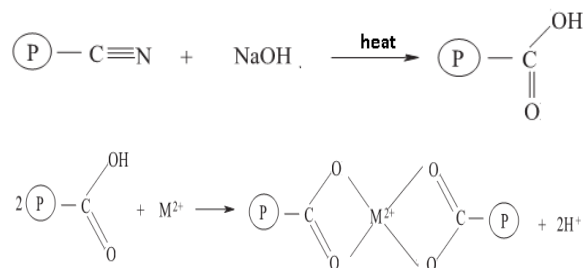
### 2.2 Swelling study of the resin

Exactly 0.5 g of dry resin was soaked in distilled water for 12 h and filtered under slightly reduced pressure. The filtration was continued for exactly 0.5 min after the disappearance of the surface water. The swollen resin was then pressed lightly between filter papers to remove surface water and the resin was rapidly weighed (Fanta.1973).The equilibrated swelling (ES) was measured twice using the following equation:

$$ES(g/g) = \frac{\text{Weight of swollen gel} - \text{Weight of dried gel}}{\text{Weight of dried gel}} \quad (1)$$

### 1.1. Cation exchange capacity

A sample (about 5.0 g) of the ion exchanger was completely converted to the H<sup>+</sup> form by treatment with excess ethanolic solution of 0.1 M HCl in a conical flask by batch equilibration. The resin was then washed with ethanol-water to remove sorbed HCl, until the washing solution became free of Cl<sup>-</sup> and the resin was dried at 50 C to a constant weight. Exactly 0.2 g of the H<sup>+</sup> form of resin was weighed into a 250 ml Erlenmeyer flask and 25 ml of standard 0.1M NaOH solution was added to a flask with a stopper and was shaken for about 12 h. After shaking, 10 ml aliquots of the supernatant solution was back-titrated to the phenolphthalein end point with standard 0.1 M HCl solution (Peppas.1990; Kost .1995; Zhang *et al.*2007). A possible chelation mechanism of carboxylic acid with bivalent metal ion for the complexation is shown in Scheme 2.



**Scheme 2.** Proposed mechanism for chelation of carboxylic acid with bivalent metal ions.

### Sorption of metal ions by batch technique

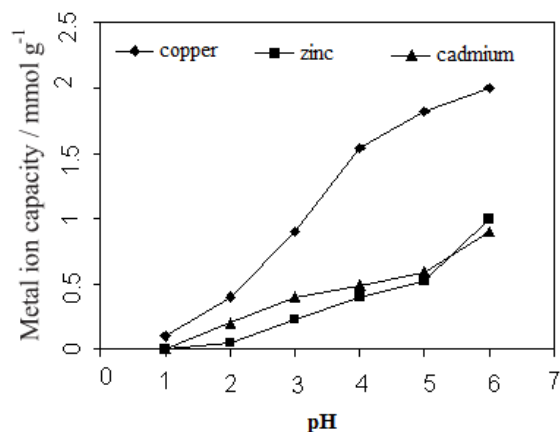
Metal ion binding capacity was measured by the batch equilibration technique with varying pH solutions (pH 1–6). For the batch technique, the resin (100–200µm size) was dried at 60 °C to a constant weight. Exactly 0.2 g of dry resin was placed into a series of 100 ml clean polyethylene bottles, and the resins were allowed to equilibrate with 25 ml distilled water for at least 15 min. After adding 25 ml of 0.1 M sodium acetate buffer at various pHs, 15 ml of 0.1M metal ion solution was added to each bottle 10 min later. The mixture was shaken for about 24 h by a rotary shaker(Hua *et al.*2007; Wang *et al.*2007). After equilibration was completed, 5 ml supernatant solution was collected for metal ion determination.

The initial and final amounts of metal ion concentration was determined by AAS.

**Results and discussion**

*Studies on sorption of metal ions*

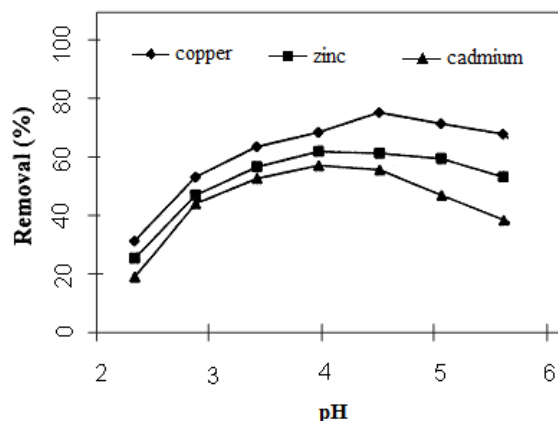
The cation exchange capacity of the chelating resin was firstly measured to be 16.8 mmol /g. Metal ion binding capacities of the resin were measured by the batch equilibrium technique with varying pH solutions (pH 1–6). Thus, the binding properties of a series of bivalent metal ions, i.e., copper, zinc and cadmium, with the H-St-g-polyAN resin were determined in buffer at acidic pHs. Since the metal cations were converted to insoluble/semi-soluble species in alkaline media, higher pH values were not investigated (Zheng *et al.*2009). It was found that metal ion uptake by the resin was pH-dependant, so that it was increased with increasing pH up to 6 (Fig. 1). The copper sorption capacity was observed to be a maximum of 2.08 mmol/g at pH 6. The sorption capacities of zinc and cadmium was measured 1.10 and 0.94 mmol /g, respectively, at pH 6 (Chen *et al.*2009). Therefore, the adsorption capacities at pH 6 were found to be in order Cu 2+ > Zn2+ > Cd2+.



**Fig 1.** The pH-dependent behavior the H-St-g-polyAN resins for sorption of the copper, zinc and cadmium ions.

In order to examine the effect of pH on metal uptake, experiments were conducted using an initial concentration of 35mg/l (Fig. 2). The percentage removal of metal ions by H-St-g-polyAN resins increased with increase in pH upto a certain value

and then decreased with further increase in pH. The maximum removal of Cu(II) (76.0%) was observed at an optimum pH of 4.8, whereas, the maximum removal of 57.0% for Zn(II) and 49.0% for Cd(II) was observed. Below and above this pH, a decreasing trend in removal was observed (Wang *et al.*2010).



**Fig 2.** Effect of pH on the removal of metals by H-St-g-polyAN resins.

**Conclusion**

The H-St-poly (NaAA-co-AAm) ion exchange resin was synthesized from polyacrylonitrile grafted onto starch. The results of the removal of Cu (II), Zn (II) and Cd (II) heavy metals from individual, mixed solutions and natural water by means of hydrogels sorption are provided. It was found that sorption of heavy metals occurs synchronously with the hydrogels swelling. The sorption capacity was high for copper 2.08 mmolg<sup>-1</sup> at pH 6.

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