

# Polymer Bearing Amidoxime Groups for Extraction of Arsenic From Aqueous Media

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## Abstract

The chelating ion-exchange resin containing amidoxime functional group was prepared from polyacrylonitrile (PAN) grafted sago starch. The PAN grafted copolymer was obtained by free radical initiating process using ceric ammonium nitrate as an initiator. Conversion of nitrile groups of the PAN grafted copolymers into the amidoxime was carried out by treatment with hydroxylamine under alkaline solution. The identification of amidoxime group was performed by qualitative and FT-IR analysis. The chelating behavior of the poly(amidoxime) resin was investigated using arsenic ( $\text{As}^{3+}$ ) ions. A significant binding properties of  $\text{As}^{3+}$  by the chelating resin was observed and the sorption capacity of  $\text{As}^{3+}$  was maximum  $1.56 \text{ mmol g}^{-1}$  at pH 6. The sorption capacities of  $\text{As}^{3+}$  by the resin were pH dependent and the rate of exchange was rapid i.e.  $t_{1/2} < 9 \text{ min}$ .

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## INTRODUCTION

Metal pollution of the environment possesses unique problems, since metals are not subjected to biodegradation. The chelating resins can be used for extraction of toxic metals in the environment and sewage waters. The possibility of using amidoxime resin to extract metals from sea water is being studied in many countries particularly high number of publications by Egawa et al.<sup>1,2</sup> and Nalan Kabay et al.<sup>3,4</sup> which deal with uranium recovery from sea water. Egawa et al.<sup>5</sup> prepared a macroreticular chelating resin containing amidoxime by reacting acrylonitrile-divinyl benzene copolymer beads with hydroxylamine. Another approach consists of the introduction of amidoxime groups into cellulose by the reaction of cyanoethylcellulose and acrylonitrile grafted cellulose with hydroxylamine.<sup>6</sup> Divinylbenzene cross-linked poly(acryloamidoxime) resins were successfully applied to the determination of trace metals in natural waters.<sup>7,8</sup> Most of the work centralized on the uranium extraction in sea water by poly(amidoxime) resin. There are very few articles published about transition metal uptake by poly(amidoxime) resin. This is may be first approach to the preparation of poly(amidoxime) chelating resin from polyacrylonitrile (PAN) grafted sago starch. In this communication, the PAN grafted copolymer was used as a cheapest starting material for

chelating resin preparation and also examined the binding properties of arsenic ion with the prepared chelating resin.

## **EXPERIMENTAL**

### **Graft copolymerization of acrylonitrile onto sago starch**

To obtain PAN grafted copolymers, about 10.0 g of sago starch and 400 ml distilled water was placed in a 1L three neck flask, which was equipped with a mechanical stirrer, condenser and thermostat water bath. Exactly 8.0 ml diluted sulfuric acid ( $\text{H}_2\text{SO}_4$ :  $\text{H}_2\text{O}$ ; 1:1) and 40 ml of 0.1M of ceric ammonium nitrate solution was added, and 10 min later 24.0 ml of acrylonitrile monomer was added to the mixture. Detailed description of the procedure was presented elsewhere.<sup>9</sup>

### **Preparation of chelating resin containing amidoxime groups**

Exactly 42.1 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) was dissolved in 300 ml methanolic solution (methanol: water; 5:1). The HCl of  $\text{NH}_2\text{OH}$  was neutralized by NaOH solution and the precipitate of NaCl was removed by filtration. The pH of the reaction was adjusted as pH 10 by NaOH solution. About 20.0 g of PAN grafted copolymer was placed in the flask and hydroxylamine solution was added to the flask and the reaction was carried according to the procedure described elsewhere.<sup>10</sup>

### **Resin characterization**

#### **Qualitative test of amidoxime functional groups**

About 0.2 g of wet resin was shaken with vanadium(V) ion in dilute hydrochloric acid solution and the purple colored complex was observed on the resin beads.

#### **FT-IR analysis**

Infrared spectra of PAN grafted copolymer and poly(amidoxime) resin samples with KBr pellets were obtained from FT-IR spectrometer (Perkin-Elmer 1725).

#### **Cation exchange capacity**

About 5.0 g of the resin was completely converted to the  $\text{H}^+$  form by treatment with liberal excess of methanolic solution of 0.1 M HCl in a conical flask by batch equilibration. The resin was then washed with metanol-water to remove sorbed HCl, until the washing solution became free of Cl and the resin was dried at 50°C to constant weight. Exactly 0.2000 g of  $\text{H}^+$  form resin was weight into a 250 ml Erlenmeyer flask and 25 ml of standard 0.1M NaOH solution was added to the flask with stopper and shaking for 4 h. After shaking, 10 ml aliquots of the supernatant solution back titrated to the phenolphthalein end point with standard 0.1M HCl solution.<sup>11</sup>

#### **Sorption of arsenic by batch technique**

Arsenic ( $\text{As}^{3+}$ ) ion binding was measured by batch equilibration technique with varying pH

solution (pH 2-6). Exactly 0.2000 g of dry resin was placed in a 100 ml volume polyethylene bottle and the resin was allowed to equilibrate with 10 ml distilled water. Then 10 ml of 0.1M sodium acetate buffer at various pH and 10 ml of 0.1M  $\text{As}^{3+}$  solution was added to bottle. The mixture was shaking for 24 h and after equilibration completed, then 5 ml supernatant solution was collected for  $\text{As}^{3+}$  ion determination. The initial and final concentration of  $\text{As}^{3+}$  ion was determined by AAS (GBC-903).

### Kinetic exchange

The rate of exchange of  $\text{As}^{3+}$  in acetate buffer at pH 4 was determined by contacting of 0.1500 g of resin beads with 10 ml of 0.1 M  $\text{As}^{3+}$  ion solution for various time intervals and  $\text{As}^{3+}$  ion determined as described above. The time required for 50% exchange ( $t_{1/2}$ ) was calculated from the plot of  $\text{As}^{3+}$  capacity ( $\text{mmol g}^{-1}$ ) vs time.<sup>12</sup>

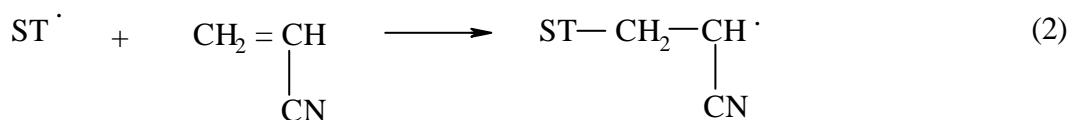
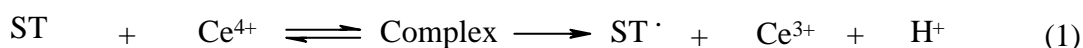
## RESULTS AND DISCUSSION

### Polyacrylonitrile grafted copolymer

The polyacrylonitrile (PAN) grafted sago starch was obtained from acrylonitrile monomer with sago starch and grafting reaction was carried out by free radical initiating process.<sup>9</sup> The optimum yield of PAN grafted copolymer was obtained at the concentration of ceric ammonium nitrate, acrylonitrile, sago starch (expressed as anhydroglucose unit) and sulfuric acid of  $9.52 \times 10^{-3}$ , 0.506, 0.146, 0.190  $\text{molL}^{-1}$ , respectively. The optimum reaction temperature and period were 50°C and 90 min, respectively.

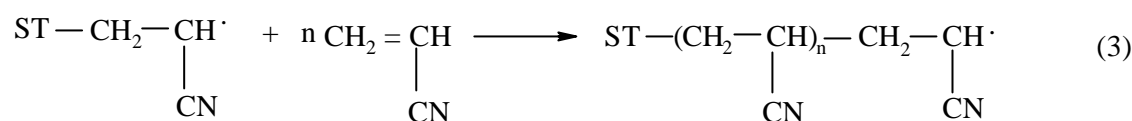
The mechanism of graft copolymerization of the vinyl monomer onto starch macromolecules was proposed by Ceresa.<sup>13</sup> Here, the reaction of acrylonitrile monomer with sago starch initiated by ceric ion followed in the three steps as follows:

Initiation:

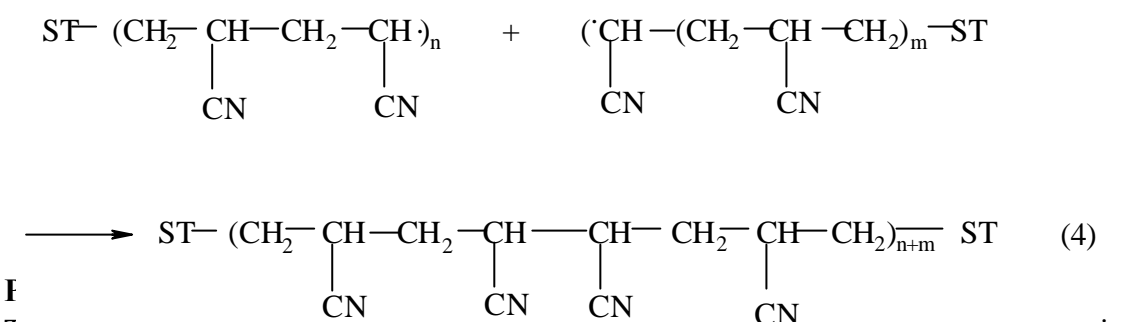


where ST and  $\text{ST}^{\cdot}$  is the sago starch and free radical of sago starch respectively. The structure of sago starch molecule (anhydroglucose unit) was presented elsewhere.<sup>9</sup>

Propagation:



Termination:



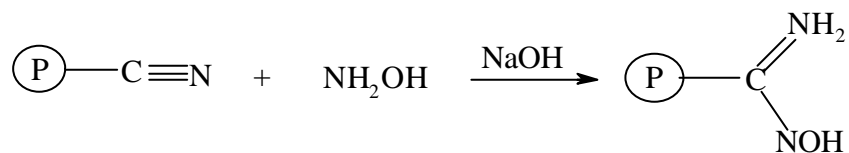
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(PAN grafted sago starch)

methanol-water ratio, 5:1; pH, 10 of the reaction medium were determined.<sup>10</sup>

According to Egawa et al.<sup>2</sup> the reaction mechanism of polyacrylonitrile with hydroxylamine to convert poly(amidoxime) is shown in Scheme 1.



where P is the backbone polymer.

Poly(amidoxime)

*Scheme 1.*

### Qualitative test of amidoxime functional groups

There are several methods have been employed for confirmation of amidoxime groups in the resin.<sup>8</sup> Many metal ions bind with amidoxime to produce visual color in the resin bead. Therefore, the presence of amidoxime groups in the resin was confirmed by vanadium ion test in the formation of a purple complex.

### Analysis of FT-IR spectra

To the study of FT-IR spectra of sago starch, the characteristic absorption bands of starch were found at  $3402 \text{ cm}^{-1}$  and  $1639 \text{ cm}^{-1}$  due to O-H stretching and bending modes, respectively (Figure 1.a). In addition, absorption bands of starch appeared at  $2930 \text{ cm}^{-1}$  and

1024  $\text{cm}^{-1}$  due to C-H stretching and bending modes, respectively. FT-IR spectra of polyacrylonitrile grafted sago starch are presented in Figure 1.(b). The characteristic absorption of polyacrylonitrile at 2245  $\text{cm}^{-1}$  due to  $\text{C}\equiv\text{N}$  stretching modes in addition of same absorption bands of sago starch. After amidoxime group preparation, the  $\text{C}\equiv\text{N}$  band of 2245  $\text{cm}^{-1}$  was disappeared and formed a new band of amidoxime at 1652  $\text{cm}^{-1}$ , and amide II band of N-H at 1568  $\text{cm}^{-1}$ , respectively (Figure 1.c).

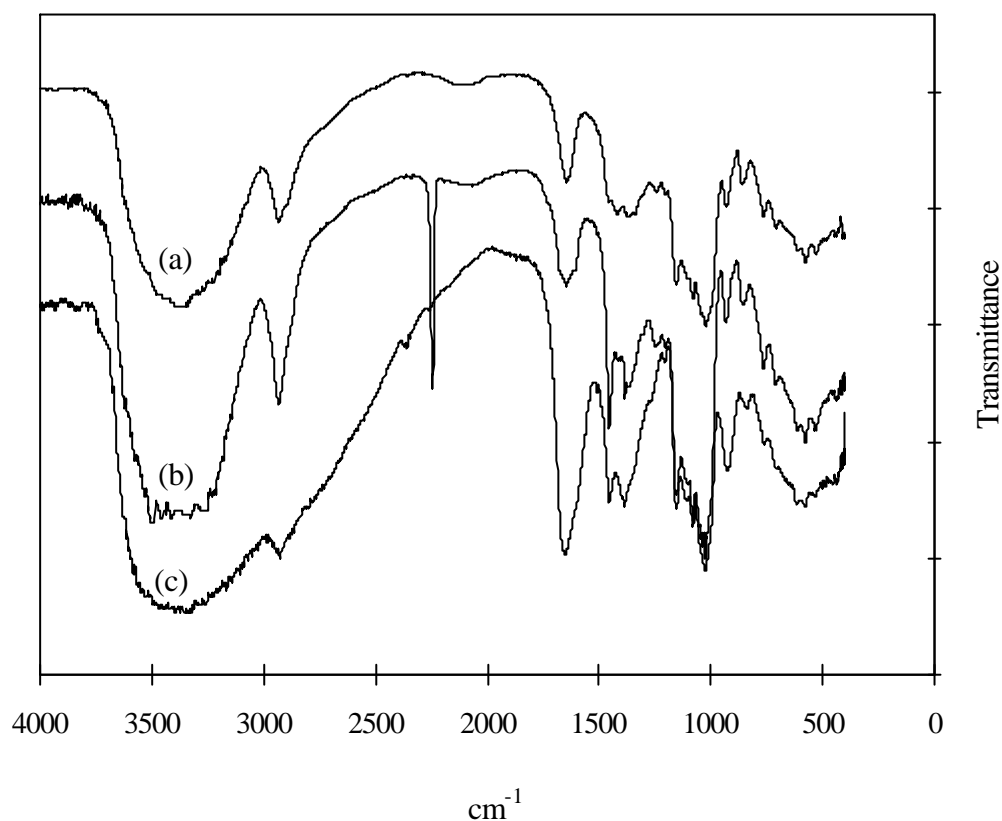


Figure 1: FT-IR spectra of (a) sago starch, (b) polyacrylonitrile grafted sago starch and (c) poly(amidoxime) resin.

#### Sorption of arsenic ion by batch method

The binding property of arsenic ion with poly(amidoxime) resin was carried out into buffer at pH 2 -6. It was found that  $\text{As}^{3+}$  ion uptake by resin was increased with increasing pH up to 6 (Figure 2). The  $\text{As}^{3+}$  capacity was observed maximum 1.56  $\text{mmol g}^{-1}$  at pH 6. Sorption capacity of  $\text{As}^{3+}$  ion by the resin was pH dependent.

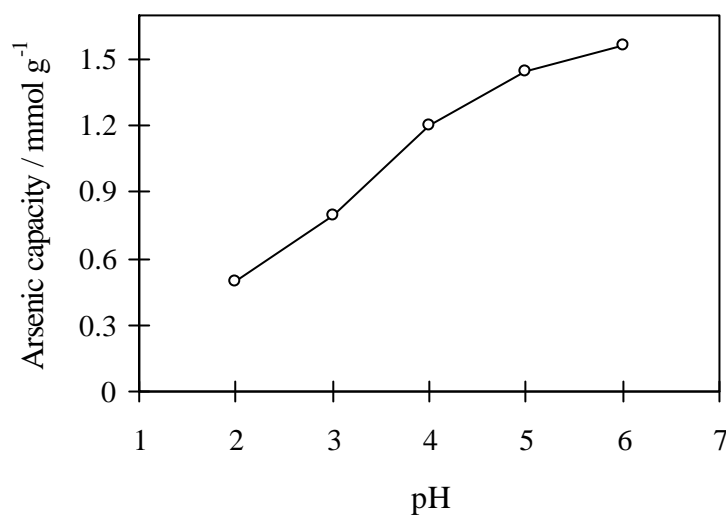
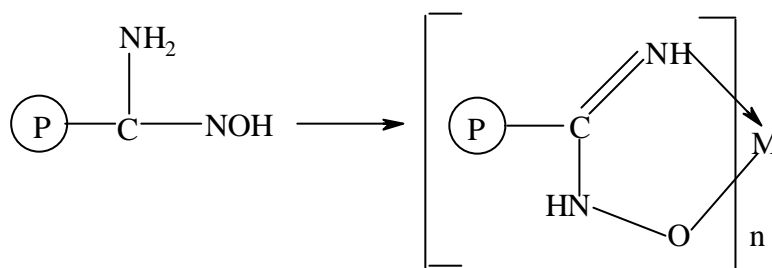


Figure 2: Sorption capacity of arsenic ion with poly(amidoxime) resin as a function of pH.

The chelate complex by amidoxime ligand with metal ion is presented in Scheme 2.



where p is the backbone polymer and n is the oxidation state of metal (M).

***Scheme 2.***

The time required for 50% arsenic exchange was calculated from the plot of  $\text{As}^{3+}$  capacity expressed as  $\text{mmol g}^{-1}$  as a function of time. The rate of sorption was rapid,  $t_{1/2} < 9$  min, based on the rate of  $\text{As}^{3+}$  sorption at pH 4 is presented in Figure 3.

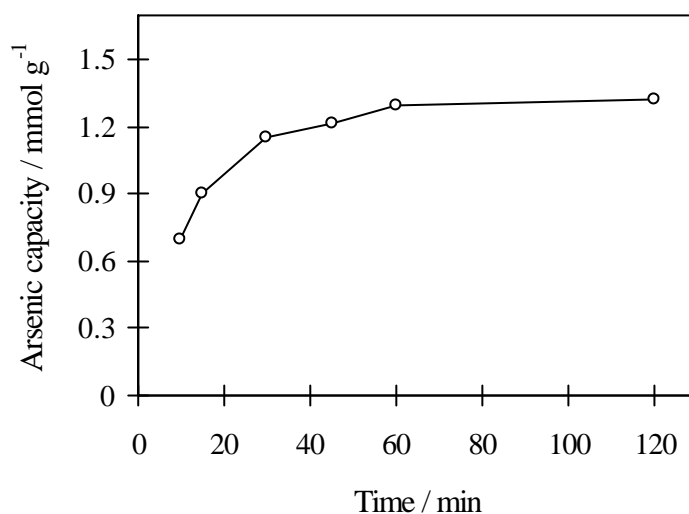


Figure 3: Rate of sorption of arsenic ion with poly(amidoxime) resin.

Cation exchange capacity of the amidoxime resin was determined based on the amount of sodium hydroxide reacted with H<sup>+</sup> form resin. The resin was reacted with specific amount of 0.1M NaOH solution and the amount sodium hydroxide was measured by back titration to the phenolphthalein end point with standard HCl solution.<sup>11</sup> The physical and chemical properties of the resin are listed in Table 1.

Table 1: Physical and chemical properties of the poly(amidoxime) chelating resin.

Physical or chemical properties	Parameters
% of Grafting	82
Polyacrylonitrile concentration, %	45
Sago starch concentration, %	55
Particle size / $\mu\text{m}$	100-200
Cation exchange capacity / $\text{mmol g}^{-1}$	4.21
Exchange rate / $t_{1/2}$ , min	< 9

## CONCLUSION

The binding capacity of As<sup>3+</sup> ion by the poly(amidoxime) resin was carried out by batch technique and the sorption capacity of As<sup>3+</sup> ion with resin was excellent. The proposed resin has the advantage of faster rate of equilibrium probably due to the new backbone polymer. In future our work will be extended to the extraction of arsenic ion from environmental source.

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