# Stability Constants of Amidoximated Chitosan-*g*-poly(acrylonitrile) Copolymer for Heavy Metal Ions

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**ABSTRACT:** Amidoximated chitosan-*g*-poly(acrylonitrile) (PAN) copolymer was prepared by a reaction between hydroxylamine and cyano group in chitosan-*g*-PAN copolymer prepared by grafting PAN onto crosslinked chitosan with epychlorohydrine. The adsorption and desorption capacities for heavy metal ions were measured under various conditions. The adsorption capacity of amidoximated chitosan-*g*-PAN copolymer increased with increasing pH values, and was increased for $Cu^{2+}$ and $Pb^{2+}$ but a little decreased for $Zn^{2+}$ and $Cd^{2+}$ with increasing PAN grafting percentage in amidoximated chitosan-*g*-PAN copolymer. In addition, desorption capacity for all metal ions was increased with increasing pH values in contrast to the adsorption results. Stability constants of amidoximated chitosan-*g*-PAN copolymer were higher for $Cu^{2+}$ and $Pb^{2+}$ but lower for $Zn^{2+}$ and $Cd^{2+}$ than those of crosslinked chitosan. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 469–476, 1999

**Key words:** amidoximated chitosan-*g*-PAN copolymer; chelate complex; adsorption capacity; desorption capacity; stability constant

## INTRODUCTION

Chitosan [poly[$\beta$-(1→4)-2-amino-2-deoxy-D-glucose]] derived from chitin [poly[$\beta$-(1→4)-2-acetamido-2-deoxy-D-glucose]] by deacetylation is undoubtedly one of the most promising and attracting resources in quantity. Therefore, an extensive utilization study of chitosan has been carried out. Various possibilities have been examined so far, but further basic studies seem to be necessary to elicit its full potential. Among some interesting properties of chitosan, chelating ability arisen from its characteristic structure is especially noteworthy.[1,2] This high adsorption capacity was ascribable primarily to its remarkable hydrophilicity in cooperation with the relatively high amino group content. But difficulties were sometimes encountered in isolating the adsorption products owing to the solubility in waste water with low pH range. Hence, crosslinking would also be effective in preventing dissolution in acidic media. Masri et al. have reported the adsorption capacity of crosslinked chitosan for metal ions under various conditions.[3] From these results, the adsorption capacity of crosslinked chitosan was less decreased than that of chitosan.

Meantime, chelate resins for heavy metal ions adsorption from waste water have been reported.[4–6] Among these polymers containing the amidoxime group derived from poly(acrylonitrile) (PAN) or its copolymer have received much attention and were found to have high adsorption properties for heavy metal ions, such as uranyl ions.[5,6]

In previous articles,[7] we reported the synthesis of amidoximated chitosan-*g*-PAN copolymer by the reaction between hydroxylamine and cyano

group in chitosan-*g*-PAN copolymer prepared by grafting PAN onto chitosan using ceric ammonium nitrate (CAN) as an initiator.

The aims of this present work are to measure the adsorption capacity and desorption capacity of amidoximated chitosan-*g*-PAN copolymer and to obtain the stability constants for metal ions.

## EXPERIMENTAL

### Materials and Reagents

Chitosan was supplied by Tokyo Kasei Co. Acrylonitrile (AN), ethylene diamine tetraacetic acid (EDTA), and CAN were supplied by Shimakyu's Pure Chemical Co. Standard metal ions were supplied by Showa Chemical Co. All other commercially available chemicals were reagent grade and used without further purification.

### Preparation of Amidoximated Chitosan-*g*-PAN Copolymer

### Preparation of Crosslinked Chitosan

Crosslinked chitosan was prepared by the following method. Ten parts of chitosan and 500 mL of 0.5 wt % NaOH solution were charged into a four-necked flask equipped with stirrer, reflux condenser and $N_2$ inlet and then stirred over 2 h. A 0.5 part of epychlohydrine was added to the flask and then maintained at 40°C for 4 h. The reaction mixture was added to excess 5 wt % acetic acid to remove the uncrosslinked chitosan. The precipitated material was filtered and washed over several times with 5 wt % acetic acid. Crosslinked chitosan was obtained by drying in a vacuum oven at 40°C for 24 h.

### Preparation of Chitosan-*g*-PAN Copolymer

Chitosan-*g*-PAN copolymer was prepared by the following method. Five parts of crosslinked chitosan, appropriate parts of AN, and 250 mL of 0.5 wt % acetic acid were charged into identical synthesis apparatus for crosslinked chitosan and then stirred over 30 min. CAN solution as an initiator was added to the flask and maintained at 40°C for 2–3 h. The reaction mixture was added to excess dimethyl sulfoxide (DMF)/water cosolvents (volume ratio 7/3) to remove unreacted residue and it was then neutralized by NaOH solution. The precipitated material was filtered and washed over several times with $H_2O$. Chitosan-*g*-

PAN copolymer was obtained by drying in a vacuum oven at 40°C for 24 h. PAN grafting percentage of chitosan-*g*-PAN copolymer was obtained as follows:

grafting %

$$= \frac{\text{weight of chitosan-g-PAN copolymer} - \text{weight of chitosan}}{\text{weight of chitosan}}$$

### Preparation of Amidoximated Chitosan-*g*-PAN Copolymer

The general synthetic procedure for the preparation amidoximated chitosan-*g*-PAN copolymer is summarized here. One part of chitosan-*g*-PAN copolymer (controlled PAN grafting %) and 100 mL of 5% hydroxylamine solution prepared by the mixing of 5.55 wt % $NH_2OH \times HCl$ solution and 3.60 wt % NaOH aqueous solution were charged into identical synthesis apparatus for crosslinked chitosan and then stirred at 75°C for 24 h. The reaction mixture was filtered out and washed several times with $H_2O$. Finally, amidoximated chitosan-*g*-PAN copolymer was obtained by drying in a vacuum oven at 60°C for 48 h.

### Adsorption Capacity of Metal Ions

The adsorption capacity of amidoximated chitosan-*g*-PAN copolymer was determined with various metal ions by the batch method. The exper-



**Figure 1** Experimental apparatus for metal ion adsorption.

**Scheme 1** Reaction mechanism of amidoximated chitosan-*g*-PAN copolymer.

imental apparatus is illustrated in Figure 1. First, 0.1 g of resins were placed in 250 mL round-bottom flasks. To each flask was added 100 mL of 1000 ppm metal ion solution (controlled pH values), and each flask was shaken for 30 h. Then 5 mL of sample was withdrawn at regular intervals. Each withdrawn sample was replaced by 5 mL of fresh medium. The adsorption capacity was obtained by measuring the concentration of withdrawn metal ion solution aliquots with the atomic absorption (AA) spectrometric technique.

### Stability Constant of Metal Ions

The stability constants of amidoximated chitosan-*g*-PAN copolymer (170 grafting %) for metal ions were obtained by using the principal of competitive adsorption between EDTA and amidoxime group in amidoximated chitosan-*g*-

PAN copolymer. The different quantities of amidoximated chitosan-*g*-PAN copolymer and EDTA were placed in 250 mL round-bottom flasks. To each flask was added the metal ion solution. After an equilibration time with shaking for 24 h, the resin was filtered. The quantity of metal ions remaining in the solution was determined by AA spectrometry, and finally, the stability constant was obtained with reference to Loewenschuss's method.[8]



**Figure 2** FT-IR spectra of crosslinked chitosan (A), chitosan-*g*-PAN copolymer (B), and amidoximated chitosan-*g*-PAN copolymer (C).



**Figure 3** $^{13}$C NMR spectra of crosslinked chitosan (A), chitosan-*g*-PAN copolymer (B), and amidoximated chitosan-*g*-PAN copolymer (C).

## Desorption Capacity of Metal Ions

These experiments were performed by the batch equilibration technique as identical method of adsorption capacity. That is, chelate complexes with adsorbed maximum metal ions were shaken for 24 h with buffer solution at a controlled pH value. Finally, the desorption capacity was obtained by the same method as for adsorption capacity.

## Characterization and Analysis

The structure of amidoximated chitosan-*g*-PAN copolymer was confirmed using a Shimadzu DR-8011 Fourier transform infrared (FTIR) spectroscope and a Bruker ARX-300 Carbon ($^{13}$C) nuclear magnetic resonance (NMR) spectroscope. FTIR spectra were obtained from KBr pellets of chitosan, chitosan-*g*-PAN copolymer, and amidoximated chitosan-*g*-PAN copolymer, and $^{13}$C-NMR spectra were measured from solid-state chitosan, chitosan-*g*-PAN copolymer, and amidoximated chitosan-*g*-PAN copolymer. The adsorption capacity and desorption capacity for metal ions were obtained with an Instrument Laboratory AA spectrometer, Model 5501.

## RESULTS AND DISCUSSION

### Characteristics of Amidoximated Chitosan-*g*-PAN Copolymer

As we reported previously,[7] chitosan-*g*-PAN copolymer was converted into amidoximated chi-



**Figure 5** Adsorption capacity of amidoximated chitosan-*g*-PAN copolymer according to time.

tosan-*g*-PAN copolymer by the reaction between hydroxylamine and cyano group in chitosan-*g*-PAN copolymer. The synthetic mechanism of amidoximated chitosan-*g*-PAN copolymer is shown briefly in **Scheme 1.** The FTIR spectra and $^{13}$C-NMR spectra of crosslinked chitosan, chitosan-*g*-PAN copolymer, and amidoximated chitosan-*g*-



**Figure 4** Adsorption capacity of amidoximated chitosan-*g*-PAN copolymer according to grafting %.



**Figure 6** Adsorption capacity of amidoximated chitosan-*g*-PAN copolymer according to pH.

**Table I  Equilibrium Measurements for the Cu²⁺–EDTA-Amidoximated Chitosan-*g*-PAN Copolymer System**

| No. | Cu²⁺ (mmol) | EDTA (mmol) | Resin (g) | MR (mmol) | Y (mmol) | MY (mmol) | Rᵃ (mmol) | log ([MR][Y]/[MY]) (mmol) | log [R] (mmol) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.157 | 0.500 | 0.500 | 0.112 | 0.455 | 0.045 | 4.153 | 0.054 | 0.618 |
| 2 | 0.157 | 0.500 | 0.625 | 0.120 | 0.463 | 0.037 | 5.211 | 0.177 | 0.717 |
| 3 | 0.393 | 0.500 | 0.750 | 0.303 | 0.410 | 0.090 | 6.095 | 0.140 | 0.785 |
| 4 | 0.393 | 0.500 | 1.000 | 0.325 | 0.432 | 0.068 | 8.205 | 0.315 | 0.914 |
| 5 | 0.393 | 1.000 | 0.500 | 0.253 | 0.860 | 0.140 | 4.012 | 0.191 | 0.603 |
| 6 | 0.393 | 1.000 | 1.000 | 0.290 | 0.897 | 0.103 | 8.240 | 0.402 | 0.915 |
| 7 | 0.787 | 1.500 | 0.750 | 0.468 | 1.181 | 0.319 | 5.930 | 0.239 | 0.773 |
| 8 | 0.787 | 1.500 | 1.000 | 0.518 | 1.231 | 0.269 | 8.261 | 0.375 | 0.917 |
| 9 | 0.787 | 1.750 | 0.500 | 0.382 | 1.345 | 0.405 | 3.883 | 0.103 | 0.589 |
| 10 | 0.787 | 1.750 | 0.750 | 0.463 | 1.426 | 0.324 | 5.935 | 0.309 | 0.773 |

ᵃ Uncomplexed amidoximated chitosan-*g*-PAN copolymer from the maximum capacity resin (8.53 mmol/g).

PAN copolymer are shown in Figures 2 and 3, respectively. As shown in previous results, a new peak, characterized as the —C≡N stretching vibration at 2200 cm⁻¹, was found in chitosan-*g*-PAN copolymer in Figure 2(B) compared with chitosan in Figure 2(A). After amidoximation of chitosan-*g*-PAN copolymer, the —C≡N peak vanished and a new strong one, attributed to the —C≡N stretching vibration at 1680 cm⁻¹ appeared [Fig. 2(C)]. Also, the ¹³C-NMR spectrum of chitosan-*g*-PAN copolymer [Fig. 3(B)] showed new peaks at 122.5 ppm due to the —C≡N group and 31.7 ppm due to the ethylene group in PAN; that of the amidoximated chitosan-*g*-PAN copolymer [Fig. 3(C)] showed a new peak at 158.1 ppm due to the amidoxime group.

## Adsorption Capacity of Metal Ions

Adsorption capacity of amidoximated chitosan-*g*-PAN copolymer for Cu²⁺, Pb²⁺, Zn²⁺, and Cd²⁺ was measured under various conditions. The results are given in Figures 4–6. As shown in Figure 4, adsorption capacity for Cu²⁺ and Pb²⁺ was increased from 0.35 to 0.42 and from 0.17 to 0.35 (mmol/g), respectively, but that for Zn²⁺ and Cd²⁺ was decreased from 0.28 to 0.24 and from 0.18 to 0.16 (mmol/g), respectively, with increasing PAN grafting % from 0 to 170% in amidoximated chitosan-*g*-PAN copolymer. As shown in Figure 5, the adsorption capacity for all metal ions reached equilibrium state within 10 h. From Figure 6, we see that the adsorption capacity for

**Table II  Equilibrium Measurements for the Pb²⁺–EDTA-Amidoximated Chitosan-*g*-PAN Copolymer System**

| No. | Pb²⁺ (mmol) | EDTA (mmol) | Resin (g) | MR (mmol) | Y (mmol) | MY (mmol) | Rᵃ (mmol) | log ([MR][Y]/[MY]) (mmol) | log [R] (mmol) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.157 | 0.500 | 0.500 | 0.079 | 0.422 | 0.078 | 4.186 | −0.369 | 0.622 |
| 2 | 0.157 | 0.500 | 0.625 | 0.082 | 0.425 | 0.075 | 5.249 | −0.328 | 0.720 |
| 3 | 0.393 | 0.500 | 0.750 | 0.241 | 0.348 | 0.152 | 60157 | −0.258 | 0.789 |
| 4 | 0.393 | 0.500 | 1.000 | 0.253 | 0.360 | 0.140 | 8.277 | −0.186 | 0.918 |
| 5 | 0.393 | 1.000 | 0.500 | 0.124 | 0.731 | 0.269 | 4.141 | −0.472 | 0.617 |
| 6 | 0.393 | 1.000 | 1.000 | 0.193 | 0.800 | 0.200 | 8.337 | −0.153 | 0.921 |
| 7 | 0.787 | 1.500 | 0.750 | 0.282 | 0.995 | 0.505 | 6.116 | −0.255 | 0.786 |
| 8 | 0.787 | 1.500 | 1.000 | 0.336 | 1.049 | 0.451 | 8.194 | −0.107 | 0.913 |
| 9 | 0.787 | 1.750 | 0.500 | 0.200 | 1.163 | 0.587 | 4.065 | −0.387 | 0.607 |
| 10 | 0.787 | 1.750 | 0.750 | 0.277 | 1.240 | 0.510 | 6.121 | −0.172 | 0.787 |

**Table III  Equilibrium Measurements for the $Zn^{2+}$–EDTA-Amidoximated Chitosan-*g*-PAN Copolymer System**

| No. | $Zn^{2+}$ (mmol) | EDTA (mmol) | Resin (g) | $MR$ (mmol) | $Y$ (mmol) | $MY$ (mmol) | $R^a$ (mmol) | log ([$MR$][$Y$]/[$MY$]) (mmol) | log [$R$] (mmol) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.157 | 0.500 | 0.500 | 0.023 | 0.366 | 0.134 | 4.242 | −1.202 | 0.628 |
| 2 | 0.157 | 0.500 | 0.625 | 0.029 | 0.372 | 0.128 | 5.302 | −1.074 | 0.724 |
| 3 | 0.393 | 0.500 | 0.750 | 0.112 | 0.219 | 0.281 | 6.286 | −1.059 | 0.798 |
| 4 | 0.393 | 0.500 | 1.000 | 0.127 | 0.234 | 0.266 | 8.403 | −0.952 | 0.924 |
| 5 | 0.393 | 1.000 | 0.500 | 0.051 | 0.658 | 0.342 | 4.214 | −1.008 | 0.625 |
| 6 | 0.393 | 1.000 | 1.000 | 0.063 | 0.670 | 0.330 | 8.467 | −0.893 | 0.928 |
| 7 | 0.787 | 1.500 | 0.750 | 0.097 | 0.810 | 0.690 | 6.301 | −0.944 | 0.799 |
| 8 | 0.787 | 1.500 | 1.000 | 0.105 | 0.818 | 0.682 | 8.425 | −0.900 | 0.926 |
| 9 | 0.787 | 1.750 | 0.500 | 0.068 | 1.031 | 0.719 | 4.197 | −1.011 | 0.622 |
| 10 | 0.787 | 1.750 | 0.750 | 0.085 | 1.048 | 0.702 | 6.313 | −0.896 | 0.800 |

all metal ions increased as the pH values of the buffer solution increased. $H^+$ in buffer solution is supposed to prevent the chelate complex from forming between metal ion and amidoximated chitosan-*g*-PAN copolymer.

### Stability Constant of Metal Ions

The stability of the chelate complex formed between metal ions and amidoximated chitosan-*g*-PAN copolymer is determined by calculating its stability constant. Generally, the methods applied to study the stability constant are the ligand competition method,[8] the metal competition method,[9] and the pH of the decomplexing method.[10] In this investigation, we used the ligand competition method to calculate the stability con-

stant of amidoximated chitosan-*g*-PAN copolymer for $Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$, and $Cd^{2+}$. In this system, two competing complexation reactions occur:

$$M + Y \leftrightarrows MY \quad K_{MY} = \frac{[MY]}{[M][Y]} \qquad (1)$$

and

$$M + R \leftrightarrows MR \quad K_{MR} = \frac{[MR]}{[M][R]} \qquad (2)$$

where $Y$ and $R$ are competing ligands (i.e., EDTA and amioximated chitosan-*g*-PAN copolymer; grafting % 170). $MY$ and $MR$ are chelate complex, formed between metal ion and EDTA or amidoxi-

**Table IV  Equilibrium Measurements for the $Cd^{2+}$–EDTA-Amidoximated Chitosan-*g*-PAN Copolymer System**

| No. | $Cd^{2+}$ (mmol) | EDTA (mmol) | Resin (g) | $MR$ (mmol) | $Y$ (mmol) | $MY$ (mmol) | $R^a$ (mmol) | log ([$MR$][$Y$]/[$MY$]) (mmol) | log [$R$] (mmol) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.157 | 0.500 | 0.500 | 0.005 | 0.348 | 0.152 | 4.260 | −1.941 | 0.629 |
| 2 | 0.157 | 0.500 | 0.625 | 0.007 | 0.350 | 0.150 | 5.324 | −1.787 | 0.726 |
| 3 | 0.393 | 0.500 | 0.750 | 0.045 | 0.152 | 0.348 | 6.353 | −1.707 | 0.803 |
| 4 | 0.393 | 0.500 | 1.000 | 0.053 | 0.160 | 0.340 | 8.477 | −1.603 | 0.928 |
| 5 | 0.393 | 1.000 | 0.500 | 0.008 | 0.615 | 0.385 | 4.257 | −1.893 | 0.629 |
| 6 | 0.393 | 1.000 | 1.000 | 0.014 | 0.621 | 0.379 | 8.516 | −1.639 | 0.930 |
| 7 | 0.787 | 1.500 | 0.750 | 0.020 | 0.733 | 0.767 | 6.378 | −1.719 | 0.804 |
| 8 | 0.787 | 1.500 | 1.000 | 0.025 | 0.738 | 0.762 | 8.505 | −1.616 | 0.930 |
| 9 | 0.787 | 1.750 | 0.500 | 0.011 | 0.974 | 0.776 | 4.254 | −1.860 | 0.629 |
| 10 | 0.787 | 1.750 | 0.750 | 0.016 | 0.979 | 0.771 | 6.382 | −1.692 | 0.805 |

**Table V  Stability Constant of EDTA**

| | Metal Ion | | | |
|---|---|---|---|---|
| Resin | $Cu^{2+}$ | $Pb^{2+}$ | $Zn^{2+}$ | $Cd^{2+}$ |
| EDTA | 18.80 | 18.04 | 16.50 | 16.46 |

mated chitosan-*g*-PAN copolymer. The overall reaction is

$$MY + R \leftrightharpoons MR + Y \qquad (3)$$

$$K_{MR} = \frac{[MR][Y]}{[MY][R]} \qquad (4)$$

$$K_{overall} = \frac{K_{MR}}{K_{MR}} \qquad (5)$$

and, if both sides have logarithm, as

$$\log \frac{[MR][Y]}{[MY]} = \log[R] + \log K_{overall} \qquad (6)$$

and

$$\log K_{MR} = K_{overall} + \log K_{MY} \qquad (7)$$



**Fig. 7**  Typical plots of amidoximated chitosan-g-PAN copolymer between log [R] and log ([MR][Y]/[MY]).

**Table VI  Log $K_{overall}$ of Amidoximated Chitosan-*g*-PAN Copolymer**

| | Metal ion | | | |
|---|---|---|---|---|
| Resin | $Cu^{2+}$ | $Pb^{2+}$ | $Zn^{2+}$ | $Cd^{2+}$ |
| Log $K_{overall}$ | −1.00 | −1.50 | −2.25 | −3.00 |

Grafting % = 170.

To obtain the stability constant, first, log $K_{overall}$ was obtained from the intercept with the *y*-axis of the graph, plotted between log $R$ against log $[MR][Y]/[MY]$. Then, the stability constant, log $K_{MR}$, can be obtained by substituting log $K_{overall}$ in eq. (7). The equilibrium measurements for the metal ion–EDTA-amidoximated chitosan-*g*-PAN copolymer system are shown in Tables I–IV. log $K_{MY}$ for $Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$, and $Cd^{2+}$ is given in Table V.[11] Typical plots for obtaining the log $K_{overall}$ of amidoximated chitosan-*g*-PAN copolymer for metal ions are shown in Figure 7. In Figure 7, the intercept of each line with *y*-axis is log $K_{overall}$. The log $K_{overall}$ for $Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$, and $Cd^{2+}$, obtained from Figure 7, are given in Table VI. Finally, stability constants of amidoximated chitosan-*g*-PAN copolymer, log $K_{MR}$ for $Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$, and $Cd^{2+}$ was obtained from Tables V and VI using eq. (7); the results are given in Table VII. As shown in Table VII, the stability constant of amidoximated chitosan-*g*-PAN copolymer was 17.80 for $Cu^{2+}$, 16.54 for $Pb^{2+}$, 14.25 for $Zn^{2+}$, and 13.46 for $Cd^{2+}$. Also, stability constants of amidoximated chitosan-*g*-PAN copolymer were higher for $Cu^{2+}$ and $Pb^{2+}$ but lower for $Zn^{2+}$ and $Cd^{2+}$ than those of crosslinked chitosan.

**Table VII  Stability Constant of Crosslinked Chitosan and Amidoximated Chitosan-*g*-PAN Copolymer**

| | Metal Ion | | | |
|---|---|---|---|---|
| Resin | $Cu^{2+}$ | $Pb^{2+}$ | $Zn^{2+}$ | $Cd^{2+}$ |
| Crosslinked chitosan | 17.24 | 16.22 | 15.20 | 15.20 |
| Amidoximated chitosan-*g*-PAN copolymer | 17.80 | 16.54 | 14.25 | 13.46 |

Grafting % = 170.

**Table VIII   Desorption Capacity and Recovery % of Amidoximated Chitosan-*g*-PAN Copolymer**

| Metal ion | Maximum adsorption capacity (mmol/g) | Desorption capacity (mmol/g) | | | Recovery % |
|---|---|---|---|---|---|
| | | pH 7 | pH 4 | pH 1 | pH 1 |
| $Cu^{2+}$ | 0.42 | 0.23 | 0.30 | 0.33 | 78.57 |
| $Pb^{2+}$ | 0.35 | 0.20 | 0.26 | 0.28 | 80.00 |
| $Zn^{2+}$ | 0.24 | 0.14 | 0.18 | 0.20 | 83.33 |
| $Cd^{2+}$ | 0.14 | 0.08 | 0.11 | 0.12 | 85.71 |

Grafting % = 170.

### Desorption Capacity of Metal Ions

The desorption capacity of amidoximated chitosan-*g*-PAN copolymer was measured at various pH values. The results are given in Table VIII. As shown in Table VIII, desorption capacities for all metal ions decreased with increasing of pH values in contrast to results of adsorption capacity. These were supposed to be results that the chelate complex, formed between metal ion and amidoximated chitosan-*g*-PAN copolymer is more stable in high pH values than low pH values. Also, recovery % for $Cd^{2+}$ at pH 1 was about 85.71%, 83.33% for $Zn^{2+}$, 80.00% for $Pb^{2+}$, and 78.57% for $Cu^{2+}$.

### CONCLUSION

Amidoximated chitosan-*g*-PAN copolymer was prepared by the reaction of hydroxylamine and cyano group in chitosan-*g*-PAN copolymer. The adsorption capacity of amidoximated chitosan-*g*-PAN copolymer with increasing of pH values was increased from 0.35 to 0.42 for $Cu^{2+}$ and from 0.17 to 0.35 (mmol/g) for $Pb^{2+}$, but decreased from 0.28 to 0.24 for $Zn^{2+}$ and from 0.18 to 0.16 (mmol/g) for $Cd^{2+}$ with increasing PAN grafting % from 0 to 170% in amidoximated chitosan-*g*-PAN copolymer. Stability constants of amidoximated chitosan-*g*-PAN copolymer (170 grafting %) were 17.80 for $Cu^{2+}$, 16.54 for $Pb^{2+}$, 14.25 for $Zn^{2+}$, and 13.46 for $Cd^{2+}$. The desorption capacity for all metal ions was increased with increasing pH values. These results indicate that amidoximated chitosan-*g*-PAN copolymer could be a good adsorbent in the recycling of metal ions through withdrawal from sea water or waste water.

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