

## Selective Adsorption of Heavy Metal Cations and Anions from their Aqueous Solution Mixture with Hydrogels

Atsuhiko Nishida, Naofumi Kawamura\*, Tetsuaki Nishida\*,  
Satoru Yoshioka and Kazuhiro Hara

Institute of Environmental Systems, Faculty of Engineering, Kyushu University,  
744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

Fax: 81-92-642-3815, e-mail: haratap@mbox.nc.kyushu-u.ac.jp

\*Department of Biological and Environmental Chemistry,  
School of Humanity-Oriented Science and Engineering, Kinki University,  
11-6 Kayanomori, Iizuka 820-8555

Institute of Environmental Systems, Faculty of Engineering, Kyushu University,  
Fax: 81-948-22-5659, e-mail: nishida@fuk.kindai.ac.jp

Hazardous  $\text{Ni}^{2+}$  and  $\text{Cr}^{6+}$  ions could be selectively adsorbed from the aqueous solution mixture of nickel chloride and chromium trioxide with hydrogels of Acrylamide/sodium acrylate (PAAm/SA) and acrylamide/*N,N*-dimethylaminopropylacrylamide (PAAm/DMAPAA), respectively. The order of adsorption procedure with these gels affected adsorption efficiencies, and the adsorption of  $\text{Ni}^{2+}$  became dominant at intermediate region, while that of  $\text{Cr}^{6+}$  at lower pH region. These results indicate that adsorption of HHM ions could be effectively regulated by changing pH of the solution mixture.

Key words: gel, adsorption, heavy metals, environmental purification

### 1. INTRODUCTION

For the environmental purification and for saving natural resources, it is important to recover hazardous heavy metal (HHM) ions from industrial wastes [1-7]. In chemical laboratories, metal-coating factories, *etc.*, precipitate of HHM hydroxides is dehydrated and transported to a controlled type landfill site [7]. Bottom of controlled type landfill site is covered with a waterproofing vinyl/ rubber sheet in order to prevent the contamination of the groundwater.

The present authors' group has successfully applied polymer gels to the capturing of HHM [8-11]. Chemical interaction of the polymer network with solvent depends on the type of solvent [8-11]. Polymer gel has interesting characteristic features in the physical properties like volume phase transition [12-16]. For example, *N*-isopropylacrylamide (NIPA) hydrogel shows a transition at 36°C due to a hydrophilic-to-hydrophobic transition of isopropyl group. Although NIPA gel originally shows a gradual volume change at the transition temperature, it becomes more distinctly when ionic-groups was introduced into the gel because of a marked increase in the Donan potential [13]. It is known that hydrogel of *N*-isopropylacrylamide/acrylic acid shows a discrete volume change, which becomes more remarkable with an increasing amount of acrylic acid [15,16]. The ion-group introduction into the gel also brings cation- or anion-capturing functionality. Jacson *et al.* invented an "ion sensor" made of an interpenetrating {poly(vinyl alcohol)} and {*N*-isopropylacrylamid/ acrylic acid} hydrogel, which could distinguish several metal ions from each other [17].

By taking account of ion-capturing efficiency, the present authors' group proposed that ionized gel can be

utilized as a heavy-metal recovery agent [8-11]. The advantage of the ionized gel when utilizing as HHM absorbent will be as follows.

- (a) The polymer gel can reduce the transportation cost because the mass ratio of the captured HHM to that of the polymer gel is much larger than that of many inorganic absorbent like zeolite.
- (b) Polymer gel can be prepared and utilized in a wide range of composition, temperature, pressure, pH, *etc.*, we can easily utilize it as an excellent recovery agent.

In our previous papers [8-11], hydro gel of poly (acrylamide/sodium acrylate), hereafter abbreviated as PAAm/SA gel, was successfully utilized HHM capturing agent, as described below. Recently, we found that sodium carboxymethylcellulose, abbreviated as CMC-Na, could be utilized as HHM capturing agent. Because CMC-Na is colorless, odorless, nontoxic and water soluble, it could be used as an additive in detergents, soaps, food products and cosmetics, *etc.* For making CMC-Na gel, the authors' group utilized a  $\gamma$ -ray irradiation effect so that the gel could be made at room temperature without toxic cross-linker [18,19].

This study was carried in order to elucidate the cation- and anion-capturing efficiency of PAAm/SA gel and poly (acrylamide/*N,N*-dimethylaminopropylacrylamide), hereafter abbreviated as PAAm/DMAPAA gel in a HCl-solution mixture (pH=2.4) containing 10 mM  $\text{NiCl}_2$  and 10 mM  $\text{CrO}_3$ . In order to elucidate the cation- and anion-capturing efficiency, PAAm/SA gel and PAAm/DMAPAA gel was immersed into the solution. Two ways of immersion was studied;

1) immersion of PAAm/SA gel into the solution mixture for 24 h and then immersion of PAAm/DMAPAA gel.

2) immersion of PAAm/DMAPAA gel into the solution mixture for 24 h and then immersion of PAAm/SA gel

## 2. EXPERIMENTAL

PAAm/SA gel with different ratios was prepared from 700 mM pregel solution having an [AAm]:[SA] molar ratio of 1:6, 2:5 and 4:3. For initiating the gelation, 0.133 wt% of *N,N'*-methylenebisacrylamide, 0.04 wt% of ammonium persulfate and 0.24 wt% of *N,N,N',N'*-tetramethylethylenediamine were added to the solution. The gelation process was conducted for 24 h at room temperature. Each gel was cut into a cube of 1x1x1 cm<sup>3</sup>, which was immersed in pure water for 24 h in order to wash out unreacted ingredients. PAAm/DMAPAA gel was prepared similarly from acrylamide and *N,N*-dimethylaminopropylacrylamide so that the [AAm]:[DMAPAA] molar ratio be 1:6, 2:5 and 4:3. Determination of Ni<sup>2+</sup> and Cr<sup>6+</sup> adsorbed by gel (1x1x1 cm<sup>3</sup>) was made by subtracting the initial Ni<sup>2+</sup> or Cr<sup>6+</sup> content of the solution mixture by the final content of these ions after each adsorption procedure. Determination of HHM ions was made by the atomic absorption spectrometry.

## 3. RESULTS AND DISCUSSION

Adsorption of Ni<sup>2+</sup> and Cr<sup>6+</sup> with PAAm/SA and PAAm/DMAPAA gels is illustrated in Fig. 1. Each number given in Fig. 1 reflects the composition of gel and the order of adsorption. Numbers ① and ② show the results obtained with PAAm/SA (1:6) and PAAm/DMAPAA gels (1:6), respectively. Numbers ③ and ④ show the results obtained for PAAm/SA (2:5) and PAAm/DMAPAA gels (2:5), respectively, and numbers ⑤ and ⑥ for PAAm/SA (4:3) and PAAm/DMAPAA gels (4:3), respectively.

Figure 1 shows that Ni<sup>2+</sup> and Cr<sup>6+</sup> are effectively adsorbed in the order of ① ≥ ③ > ⑤, and ② > ④ > ⑥. These results indicate that the amount of HHM ions adsorbed by PAAm/SA or PAAm/DMAPAA gel is increased with an increasing amount of SA and DMAPAA that play a role of cation- and anion-capturing sites, respectively.

It is understood from Fig. 1 that the adsorption efficiency, i.e., cation- or anion-capturing efficiency depends on the adsorption procedure, i.e., in a group of ①, ③ and ⑤, PAAm/SA gel was first put into the solution mixture containing Ni<sup>2+</sup> and Cr<sup>6+</sup>, and then was put PAAm/DMAPAA gel. By contrast, in a group of ②, ④ and ⑥, PAAm/DMAPAA gel was first put into the solution mixture, and then PAAm/SA gel. It is noted that in the procedure ①, pH of the solution mixture changed from 2.4 to 4.5 when PAAm/SA gel (1:6) was put into the solution mixture as a 1st step. The value of pH changed from 4.5 to 6.6 when PAAm/DMAPAA gels (1:6) was put into the solution mixture as a 2nd step. In the procedure ②, pH of the solution was changed from 2.4 to 5.4 when PAAm/DMAPAA gels (1:6)

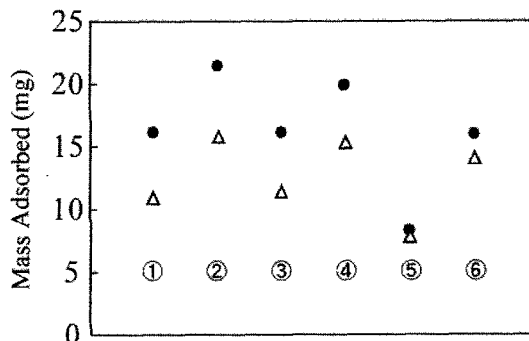


Fig. 1. Adsorption of Ni<sup>2+</sup> and Cr<sup>6+</sup> with PAAm/SA and PAAm/DMAPAA gel; ●: Ni<sup>2+</sup>, Δ: Cr<sup>6+</sup>

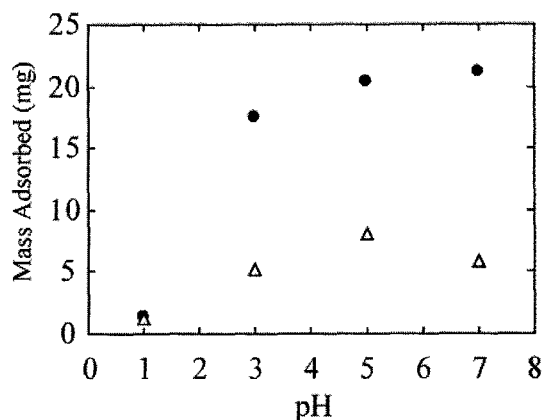


Fig. 2. Mass of metal ions adsorbed by PAAm/SA gel; ●: Ni<sup>2+</sup>, Δ: Cr<sup>6+</sup>

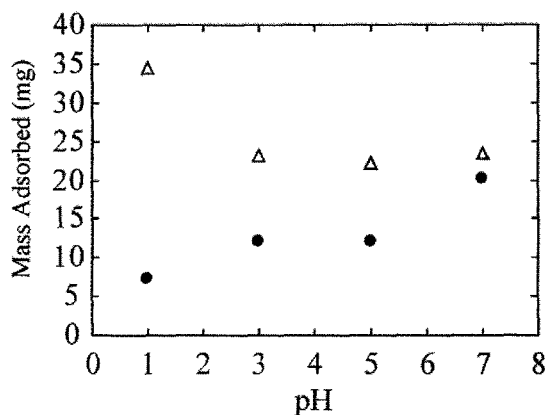


Fig. 3. Mass of metal ions adsorbed by PAAm/DMAPAA gel; ●: Ni<sup>2+</sup>, Δ: Cr<sup>6+</sup>

was first put into the solution mixture (1st step), and then it became 6.5 when PAAm/SA gel (1:6) was put (2nd step). These experimental results suggest that pH of the solution is closely related to the adsorption efficiency of PAAm/SA and PAAm/DMPAA gels.

Effect of pH on the adsorption efficiency of  $\text{Ni}^{2+}$  and  $\text{Cr}^{6+}$  was investigated in 0.10 mM  $\text{NiCl}_2\text{-HCl}$  and 0.10 mM  $\text{CrO}_3\text{-HCl}$  solutions, as illustrated in Figs. 2 and 3, respectively. In these experiments, pH of the solution was changed from 1.0 to 7.0 with an aqueous solution of 1M-NaOH. It is understood from Fig. 2 that  $\text{Ni}^{2+}$  is effectively adsorbed by PAAm/SA gel along with an increasing value of pH. It is noted that small amounts of  $\text{Cr}^{6+}$  ions could be adsorbed by PAAm/SA gel, probably because some of  $\text{Cr}^{6+}$  ions were present as a positively-charged ion like  $\text{Cr}^{6+}(\text{H}_2\text{O})_n$ , not as a negatively charged  $\text{CrO}_4^{2-}$ .

Figure 3 indicates that a large amount of  $\text{Cr}^{6+}$ , mostly in the form of  $\text{CrO}_4^{2-}$ , is effectively adsorbed by PAAm/DMPAA gel along with a decreasing value of pH. This result proves that lower pH of the solution mixture is favorable for the  $\text{Cr}^{6+}$  adsorption, while higher (intermediate) pH for the  $\text{Ni}^{2+}$  adsorption. It is noted that in the procedure ①, pH of the solution mixture was changed from 2.4 to 4.5 when PAAm/SA gel (1:6) was first immersed, while it changed from 2.4 to 5.4 when PAAm/DMPAA gel (1:6) was first put in the procedure ②, as described. Taking account of the experimental results illustrated in Figs. 2 and 3, we can conclude that procedure ② is more favorable for the effective adsorption of both  $\text{Ni}^{2+}$  and  $\text{Cr}^{6+}$ , since pH 5.4 is more favorable condition for the  $\text{Ni}^{2+}$  adsorption than pH 4.5.

#### 4. SUMMARY

$\text{Ni}^{2+}$  and  $\text{Cr}^{6+}$  could be successfully adsorbed with hydrogels of PAAm/SA and PAAm/ DMAPAA. A marked difference in the adsorption efficiency was observed, depending on the pH of solution mixture;  $\text{Ni}^{2+}$  was more effectively adsorbed from the neutral solution, while  $\text{Cr}^{6+}$  was effectively adsorbed from the acidic solution. It is concluded that effective adsorption of HHM ions can be regulated by changing the pH of the solution. The present method will be effective for the solution of environmental pollution, especially when combined with a technique for recovering HHM ions from the adsorbed gel.

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