

Side-Chain Structural Effect of a Harmful-Heavy-Metal-Anion Adsorbing Gel

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The authors have been investigating harmful-heavy-metal adsorption property of several gels aiming at utilizing as environmental purification materials. In our previous investigations, their hazardous-heavy-metal capturing capability was revealed with an advantage in the large (captured ions/adsorbent material) weight ratio. In the present study, the authors have investigated Cr(VI) capturing feature of *N,N*-dimethylaminopropylacrylamide/acrylamide gel and demonstrated how the change in the side-chain's alkylene-group number affects the heavy-metal-ion capturing efficiency.

Key words: heavy metal anion, capture, environment, *N,N*-dimethylaminopropylacrylamide/acrylamide gel

1. INTRODUCTION

It is well known that some heavy metals cause a serious health hazards. The public attention has focused on the heavy metal pollution after an official view was revealed from the Japanese Ministry of Health and Welfare in 1968 that the Itai-Itai Disease is estimated to be caused by the cadmium eluted off to the upstream of Jintsu River from Kamioka Mine. Then an apprehensiveness on the environmental pollution got into circulation [1,2]. In response to this, the government toughly directed the industrial facilities not to discharge the heavy metal waste to the environment. With the effort, the situation on the environmental issue has been improved so much recently. However, it should be remembered that the heavy metals already flown out to environment will not become harmless without detoxification treatments but, in a sense, the polluted areas may become wider by diffusion [3,4]. Therefore, it is indispensable to take quick and effective measures in order to prevent their spread.

Especially, the authors have been concerned about the harmful heavy metal leaked out from final landfill sites [5]. The industrial-waste fluids containing the heavy metals are treated as specially controlled industrial wastes [6]. In order to separate the heavy metals from the waste fluid, they are usually precipitated in the form of hydroxides [7] and final-disposed in either of Strictly Controlled Type Landfill Site or Controlled Type Sanitary Landfill Site according to their degrees of chemical stability and toxicities and danger to public health [5,6]. Though the wastes are usually processed without trouble in conformity with the prescription provided by the Ministry of the Environment, by acid rain, there is threat against the shield-functionality decrease of the final landfill sites. Also in the Least

Controlled Landfill Site, there is a fear that the waste-fluid polluted by the heavy metals may permeate the ground and may contaminate groundwater. As for the Controlled Type Sanitary Landfill Site, it is concerned that the heavy metal waste fluid may flow outside through the shielding sheet rip. In Strictly Controlled Type Landfill Site, there is also a threat that the acid rain may erode the concrete wall of the storage and the polluted fluid may flow out from the crack on the wall. In such an accident, a prompt and effective recovery measurement should be taken in order to head off the heavy metal diffusion into the environment. Therefore, the essential qualifications for the recovering apparatus for such an application should be portability and ease of operation without requiring special devices. Under these circumstances, the authors have estimated that several gels are promising as an environmental purifying material and have been investigating their heavy metal recovery functionality as mentioned below.

The authors found that the ionized gels show high efficiencies of the heavy-metal-ion adsorption as mentioned in the following sections. The advantages of the ionized gel over other adsorbents are as follows: Because, as adsorbents, the authors have adopted organic chemical gels composed of light elements (such as H, C, N and O), the weight ratio of captured heavy metal to the adsorbent material can be set much larger than those of the inorganic adsorbents such as the zeolite, by which the transporting expenses from recovery fields to treatment facilities can be suppressed so much. Besides, because their network is not easily broken in wide temperature-, pressure- and pH-range, they can be used in various conditions.

In the present study, in these circumstances, the authors have investigated hazardous Cr(VI) (in the form

of the oxoanions CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$) capturing functionality of *N,N*-dimethylaminopropylacrylamide (DMPAA) / acrylamide (AAm) gel and have compared with those of the previously-studied heavy-metal-oxoanion capturing gels.

2. EXPERIMENTALS AND RESULTS

Because the hexavalent chromium oxoanions CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ occur without any treatment, an aqueous solution of chromium trioxide is adopted as a model fluid which contains heavy-metal anion in the same way as the previous studies [8,9]. As for the adsorbent, DMPAA/AAm copolymer gels have been adopted.

In order to examine the heavy-metal-anion-capturing functionality of the DMPAA/AAm copolymer gel, prepared were pregel solutions of which the molar ratios in a range from [DMPAA]:[AAm]=1:6 to 6:1, and the total polymer concentrations, from 0.7M to 2.1M. Also, as a crosslinker, 0.133 wt% of *N,N*-methylenebisacrylamide (BIS) was added to each the pregel solution. In order to initiate the gelation, 0.04wt% of ammonium persulfate was put into each the pregel solution with BIS, which was left intact for 24 hrs at room temperature. After the solution solidified, cubic portions of 0.3g were cut out and immersed in pure water for 24 hrs in order to wash out unreacted ingredients.

In the experiments of examining the DMPAA/AAm gel's hexavalent-chromium-oxoanion capturing functionality, each the purified gel cube was immersed in a cell filled with aqueous CrO_3 solution of 10mM at room temperature for 24 hrs, then, the gel cubes were carefully taken out from the cells. After these procedure, Cr(VI) concentration and volume of each the remainder solution in the cell was measured. The Cr(VI) concentration of the remainder solution was measured by an atomic absorption spectrometer (Shimadzu, AA-6500F). The amount of captured Cr(VI) by each the gel was derived by subtracting the measured (concentration \times volume) from the ingredient weight in the pregel solution.

Figure 1 shows DMPAA fraction dependence of the recovered Cr(VI) weight at 10 g of the pregel solutions with different total concentrations. In the same manner as the previous studies [8,9], the authors adopted this description to express definitely the amount of the DMPAA and AAm in the respective gels because the DMPAA/AAm gel expands in a different degree with the composition ratio of AAm to DMPAA in the washing procedure in pure water. As can be seen from Fig.1, these experimental results demonstrate that the DMPAA can adequately work as a heavy-metal anion capturer in polymer network of the DMPAA/AAm copolymer gel. As for the capturing feature, roughly speaking, the captured Cr(VI) amount increases with DMPAA fraction and also with the total concentration of the DMAEA/AAm gel. However, having a good look at the molar ratio and concentration dependences, the amount of adsorbed Cr(VI) increases with molar ratio of DMPAA in the lower range, while that, in the higher molar ratio region, almost the flat dependence. Similar behavior is also estimated in the ingredient's concentration dependence from the crowded arrangement of the data points in the higher

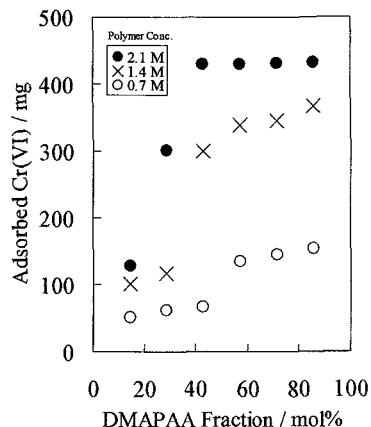


Fig. 1
Adsorbed Cr(VI) amount change with the DMPAA molar fraction and with total concentration of DMPAA/AAm gel to 10 g of the pregel solution.

concentration region.

3. DISCUSSIONS

The gels show interesting properties by the interactions between network polymer and solvent [10], and some of them can be utilized for the heavy metal recovery. Among them, one of the most famous phenomena is the volume phase transition, which can be applicable for the waste recovery. Let us explore some characteristic aspects of the volume phase transition. In the case of *N*-isopropylacrylamide (NIPA) hydrogel, the volume phase transition occurs with changing temperature. The transition feature alters from the second order to the first order by introducing the ionized group in the side-chain: In pure NIPA gel, a continuous transition is observed around 36°C due to the metastasis of the isopropyl group from hydrophilic to hydrophobic nature with increasing temperature [11,12]. By introducing an ion-group, namely in the case of the ionized NIPA gel such as *N*-isopropylacrylamide/acrylic acid (NIPA/AAc) gel, the transition becomes discontinuous and the degree of the discontinuity increases with the ratio of the ionized part (acrylic acid) [13,14].

In addition to the transition-feature change, the introduction of the ionized part develops the ion-capturing functionality which is very important for the present purpose. By utilizing this property, Jacson *et al.* developed a metal-ion detector by utilizing an interpenetrating network hydrogel composed of poly(vinyl alcohol) and NIPA/AAc [15], however, they did not consider the efficiency of the ion adsorption which is important for the purpose in the present study. As for the cupric-ion capturing-efficiency, poly(acrylamide/sodium acrylate) (PAAm/SA) gel is amply applicable for practical use as an environmental purifying material from the results measured in the previous study [16]: the capturing efficiency was estimated ~20wt% of network polymer, which is very large value as an adsorbent [16].

In addition to the positive heavy-metal ion, there are many harmful heavy-metal ions with negative polarity in the environment such as AsO_4^{3-} , $\text{Cr}_2\text{O}_7^{2-}$ and SeO_4^{2-} . As for chromium, though the chromium metal itself is harmless and most of the tableware is plated with chromium, its oxidized hexavalent ions are very toxic. In the environment, the natural form of chromium is trivalent and almost harmless, while the hexavalent chromium is artificially generated and very harmful: if the skin is stained with the hexavalent chromium, there are possibilities of cancer as well as dermatitis and neoplasm. Besides, because the hexavalent chromium is volatile, it can be absorbed from the digestive organs, lungs, the skin, and so on. As typical hexavalent chromium compounds, the chromium acid potassium and dichromic acid potassium are used in a variety of industrial procedures, therefore, almost of the hazardous chromium compounds in the environment are in the forms of oxoanions. In these circumstances, the authors have been also developing the negative heavy-metal ion capturing gels [8,9].

As the first examination of the heavy-metal-anion absorption-efficiency of hydrogels, dimethylaminoethylmethacrylate quaternised with methyl chloride (DMAEMAMeCl)/acrylamide (AAm) copolymer gels were investigated in the previous study [8]; and the experimental results clearly demonstrated the utilization-possibility as an environmental purifying material which captures heavy-metal anions (Fig.2) [8]. Besides, by comparing the amounts of the captured heavy-metal ions by DMAEMAMeCl /AAm [8], PAAm/SA [16] and CMC-Na [16] gels, their ion-capturing efficiencies were revealed to be almost the same level, and needless to say, much higher than other adsorbents such as zeolite, ion-exchange resins and so on. However, the more systematic investigations of such gels were indispensable for achieving the higher efficiency. In these circumstances, in the previous study [9], the authors investigated how the anion-capturing functionality changes by substituting DMAEMA-MeCl with *N,N*-dimethylaminoethylacrylate (DMAEA) of which the structure is almost identical with DMAEMAMeCl except for the polarizing terminal group. Figure 3 shows DMAEA fraction dependence of the recovered Cr(VI) weight at 10 g of the pregel solutions with different total concentrations. As can be seen from Fig.3, the captured Cr(VI) amount increases with DMAEA fraction and also with the total concentration of the DMAEA/AAm copolymer gel. These experimental results demonstrated that the DMAEA can work as a heavy-metal anion capturer in polymer network of the DMAEA/AAm copolymer gel. However, by comparing Figs. 2 and 3, one may also notice that the amount of adsorbed Cr(VI) becomes around 2/3 by substituting DMAEMA-MeCl with DMAEA, which indicates that the polarization intensity of the side-chain terminal-groups can affect the ion-capture functionality so much. However, though the degree of the ion-capturing functionality of the DMAEA/AAm gel is somewhat less than that of DMAEMA-MeCl/AAm gel, it is still much larger than that of other adsorbents such as zeolite or ion-exchange resins, etc.

Along this line, in order to carry on the systematic investigations, the authors have examined the heavy-

metal-oxoanion capturing property of the DMAPAA /AAm gel in the present study, and, as depicted in Fig. 1, the DMAPAA/AAm gel has shown the largest Cr(VI)-capturing-amount among the heavy metal-ion-capturing gels which the authors investigated (Figs. 1-3); these experimental features may indicate that there are at least two factors governing the ion capturing functionality: the polarization intensity of the terminal-group at the end of the side-chain and the number of alkylene groups between the main chain and the terminal group. The effect of the polarization intensity of the side-chain terminal-groups can be examined by comparing the adsorption efficiencies of DMAEMA-MeCl/AAm and DMAEA/AAm gels (Figs. 2 and 3) because their structures are almost identical except for the functional

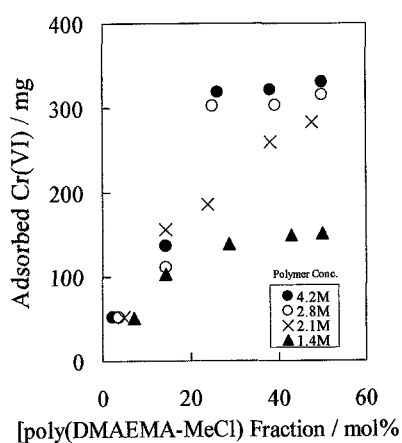


Fig. 2 Adsorbed Cr(VI) amount change with the [poly(DMAEMA-MeCl)];[AAm] molar ratio and ingredient's concentration of poly(DMAEMA-MeCl)/AAm copolymer gel to 10 g of the pregel solution [8].

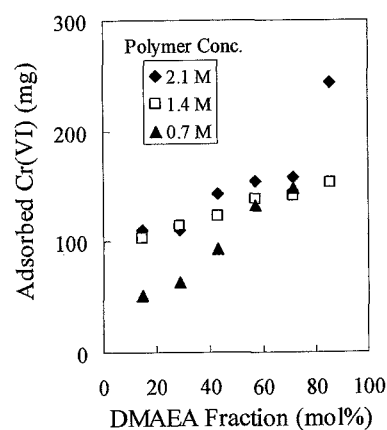


Fig. 3 Adsorbed Cr(VI) amount change with the DMAEA molar fraction and with total concentration of DMAEA/AAm gel to 10 g of the pregel solution [9].

terminal groups: those of DMAEMA-MeCl/AAm gel are intensely-polarized quaternary ammonium groups, while, DMAEA/AAm gel, weakly-charged tertiary amine groups. Actually, the Cr(VI)-oxoanion capturing efficiency of DMAEMA-MeCl/AAm gel is higher than that of DMAEA/AAm gel in accordance with the polarization intensities of the terminal groups. The effect of the number of alkylene groups between the main chain and the terminal group can be extrapolated by comparing the adsorption efficiencies of DMAEA/AAm and DMAPAA/AAm gels (Figs. 1 and 3) because their structures are almost the same except for the number of the number of alkylene groups between the main chain and the terminal group: there are 3 alkylene groups in DMAPAA/AAm gel, while 2 alkylene groups in DMAEA/AAm gel. As can be seen from Figs. 2 and 3, the Cr(VI) adsorbing efficiency is pushed up with increasing the number of the alkylene groups.

As for the capturing feature observed in the present study, roughly speaking, the captured Cr(VI) amount increases with DMAPAA fraction and also with the total concentration of the DMAEA/AAm gel. However, having a good look at the molar ratio and concentration dependences, the amount of adsorbed Cr(VI) increases with molar ratio of DMAPAA in the lower range, while that, in the higher molar ratio region, almost the flat dependence. Similar behavior is also estimated in the ingredient's concentration dependence from the crowded arrangement of the data points in the higher concentration region. Such a feature was commonly observed in the previous studies as shown in Fig.2 [8,16], except for the case of the DMAEA/AAm gel [9] (Fig.3). Though the observed adsorption behaviors may be controlled by several factors and their mechanism may not be so simple, some features can be roughly discussed: The flat adsorption-dependence in the higher functional-group fraction region can correspond to the maximum capturing capabilities of the respective gels, which may be related to the structure of the gel network. The authors have guessed a mechanism in order to explain the flat functional-group-fraction dependence of the capturing amount as follows: Though the more polarized groups are necessary for increasing the captured amount of the heavy-metal oxoanions, the number increment of the polarized groups can also increase the swelling force of the gel network which can keep the polarized terminal-groups away from each other, and, consequently, may hinder the formation of the chelation. Consequently, the polarized groups connected to the freely movable network which are located away from the crosslink point cannot take part in the chelation, which can be mainly formed by the immovable polarized groups around the crosslink point. Therefore, because the number of the polarized group around the crosslink point may governed by the number of the crosslink points, the adsorption amount can be independent of the number of the polarized groups estimated by the preparation amount of the ingredients.

In the present investigation, the possibility of the utilization of the gel for capturing a heavy-metal anion has been fully confirmed as well as the previous studies [8,9,16]. However, the examinations has been carried out in somewhat simple conditions, therefore, the investigations in more realistic conditions are desired for

the practical use in the environmental purification, some of which are in progress by the authors.

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