

## Harmful-Heavy-Metal-Anion Adsorbing Property of Acrylamide/Dimethylaminoethylacrylatemethylchloride Gel

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The authors have been investigating heavy-metal-adsorption property of several gels in order to put them into practical use as environmental purification materials; in the investigations, they have been demonstrating the gels' large heavy-metal adsorbing capabilities. In the present study, the authors have measured the heavy-metal-anion capturing amounts of acrylamide/dimethylaminoethylacrylatemethylchloride gel and have compared with those of the acrylamide/dimethylaminoethylmethacrylatemethylchloride gel reported in the previous study. From the experimental results observed in the present study, it has been verified how the structural change affects the ion-capturing efficiency even though the structural alteration occurs far from the positions of the functional groups where the adsorption process is taken place.

Key words: gel, heavy metal, environment, anion, dimethylaminoethylacrylatemethylchloride

### 1. INTRODUCTION

Some heavy metals are notorious for their serious damage to health; by their toxicity, triggered were the environmental issues in Japan. In 1968, after The Ministry of Health and Welfare in Japan announced that the cadmium discharged from the Kamioka mine to the upper reaches of the Jintsu River might cause the *Itai-Itai Disease*, the heavy-metal problems attracted public attention and the misgivings about the environmental pollution had been expressed [1,2]. In response, the industrial facilities have been severely regulated not to discharge the hazardous heavy-metal to the environment; by such measures, the heavy-metal pollution has been reduced appreciably in these days. However, we have to remember that the heavy-metals that have already flown out into the environment don't become harmless spontaneously, therefore one could say that the polluted area can spread by diffusion [3,4]. Among such environmental pollutions, the authors especially have paid attention to the waste-fluids diffidence from the final landfill sites as mentioned below:

Industrial waste fluids which contain the heavy metals are defined as specially controlled industrial wastes by ordinance [5]. The heavy-metals dissolved in the waste fluids are solidified in the form of hydroxide precipitates [6], which are then stored in either of Strictly Controlled Type Landfill Site or Controlled Type Sanitary Landfill Site depending on their toxicity and chemical stability [5]. Usually, in accordance with the prescription of the Ministry of the Environment, the heavy-metal wastes have been securely disposed in the final landfill sites; however, they have felt insecurity about the shield-capability depress of the final landfill

sites by the acid rain. As for the Least Controlled Landfill Site, because the heavy-metal-waste fluid may ooze out by the reaction with the acid rain, they are worried about the contamination of the underground water by the heavy-metal waste-fluid seeping underground of the final landfill site. In the case of Controlled Type Sanitary Landfill Site, they also feel apprehensive about the pollution of the underground water by the heavy-metal waste-fluid flowing outside through the rip of the shielding sheet. In the case of Strictly Controlled Type Landfill Site, they are anxious about the effluence the harmful heavy-metal fluid from the crack of the wall eroded by acid rain. In these situations, in order to prevent the heavy-metal from spreading in a wide area, quick, easy and inexpensive methods have been coveted for regardless of the final-landfill-site type. In these circumstances, the authors have been seeking for such solution in order to reduce the environmental pollution effectively and have proposed the utilization of some hydrogels.

By the interaction changes between the network polymer and the solvent, several gels show interesting phenomena [7]. Among them, the volume phase transition is the most famous feature demonstrating such a property change in the gels. For illustration, let us describe on the volume phase transition of the *N*-isopropylacrylamide (NIPA) hydrogel. In the NIPA gel, a continuous volume change is observed around 36°C due to the metastasis of the isopropyl group from hydrophilicity to hydrophobicity with increasing temperature [8,9]. Meanwhile, the volume change becomes discontinuously by introducing ion-groups in the gel; the degree of discontinuity becomes clear with the ratio of acrylic acid [10,11]. In addition to the change in the

volume-change feature, the installation of the ion-groups appends an additional property, ion-capturing function. Utilizing such a functionality, a metal-ion detector made by an interpenetrating network hydrogel made of poly(vinyl alcohol) and *N*-isopropylacrylamide/acrylic acid have been developed by Jacson *et al* [12]. However, they did not notice the efficiency of the ion-recovery.

The authors have been considering that some gels are practicable for recovering the hazardous heavy-metal from the effluent waste fluid in view of the high ion adsorption efficiency which are demonstrated by the authors' previous [13-16] and present studies. The gels which the authors have dealt with are some organic hydrogels formed by the chemical cross-linkage and with the ionized pendants in the side-chain. Because the above-mentioned gels are composed of the light elements (such as hydrogen, carbon, nitrogen and oxygen), the weight ratio of the adsorbed heavy metal to the adsorbent becomes much larger than the inorganic adsorbents composed of heavy elements such as zeolite. Therefore, the transportation cost can be greatly suppressed compared with the inorganic adsorbents. Besides, compared with the polymer flocculants, the ionized chemical hydrogels are utilizable in more various conditions because chemical gels are not easily disassembled in a wide range of the environmental conditions. In order to verify the possibility of the utilization of some hydrogels as a high-efficiency environmental purifying material, the authors have implemented a series of the investigations quantitating their adsorption amounts of the hazardous heavy metals [13-16].

In one of the previous studies, the author found that the poly(acrylamide/sodium acrylate) (PAAm/SA) gels can effectively capture the positive heavy-metal ions [13]. (In a series of the investigations,  $\text{Cu}^{2+}$  ion was used as a model heavy-metal cation.) Up to a certain  $\text{Cu}^{2+}$  concentration, the captured  $\text{Cu(II)}$  amount increases, while, above that concentration, the captured amount becomes almost constant. A similar behavior has been observed in the gel-network-polymer concentration dependence of the captured  $\text{Cu(II)}$  amount. Beside, from the experimental results, it has been demonstrated that the weight ratios of the captured  $\text{Cu(II)}$  to the gels' ingredients, AAm+SA, are estimated to be ~20wt%, which is extremely large value as an adsorbent compared with the inorganic adsorbents and ion-exchange resins.

Though the heavy-metal capturing property of the PAAm/SA gel has proven the gels' usefulness as an environmental purifying material, there is another problem to be solved: the PAAm monomer is known to be toxic. Therefore, in order to solve this problem, the authors searched for non-toxic substances with which the positive-heavy-metal-adsorbing gel can be brought forth and found that sodium carboxymethylcellulose (CMC-Na) can be a candidate for the purpose in the present study. As well as the non-toxicity, the CMC-Na shows biodegradability and it is available at low price, which are favorable for the raw material of the environmental purifying gel. In the following part, let us describe the positive-ion capturing property of the

CMC-Na gel. In the previous study [14], the authors examined the positive heavy-metal capturing property of the CMC-Na gel made by  $\gamma$ -ray irradiation [17,18], and verified that the  $\text{Cu(II)}$ -capturing efficiency is almost equal to that of the PAAm/SA gel. Besides, it has been found that the captured  $\text{Cu(II)}$  weight becomes large with  $\gamma$ -ray dose as well as with the CMC-Na concentration. The feature may reflect the positive-heavy-metal-ion recovery-mechanism of the CMC-Na gel which is related to the formation mechanism of the gel. Because, in the thick CMC-Na aqueous solution, the  $\gamma$ -ray dosage is reported to increase the polymer cross-linking degree of CMC-Na [17], therefore, it may be natural to consider the relation between the number of the cross-linking points and the  $\text{Cu(II)}$  capturing amount. An ion-capturing mechanism inferred from the above-mentioned relation may be as follows: Roughly speaking, one may imagine the two mechanisms by which the  $\text{Cu}^{2+}$  ions can be captured. One of the two mechanisms may be that one  $\text{Cu}^{2+}$  ion is adsorbed by one carboxyl group of CMC-Na. If this mechanism predominates another one, the captured  $\text{Cu(II)}$  weight may be irrelevant to the number of the cross-link points and, therefore, the  $\gamma$ -ray dosage. Another possible ion-capturing mechanism can be that one  $\text{Cu}^{2+}$  ion is adsorbed by plural carboxyl groups, namely by the chelation mechanism. If the mechanism is dominant over the previous one, the captured  $\text{Cu(II)}$  amount can increase with the cross-linking degree and the  $\gamma$ -ray dosage because, in this mechanism, the  $\text{Cu(II)}$  recovery amount can be much influenced by the spatial configuration of the plural carboxyl groups and the increase in the cross-linking points can lead to multiply the  $\text{Cu}^{2+}$  ion capturing sites. With these discussion, the authors concluded that the chelation mechanism can dominantly occur by taking the experimental results on the  $\gamma$ -ray dosage dependence of the captured  $\text{Cu(II)}$  weight into consideration.

In addition to the positive ions, there are many harmful negative-heavy-metal ions in the environment

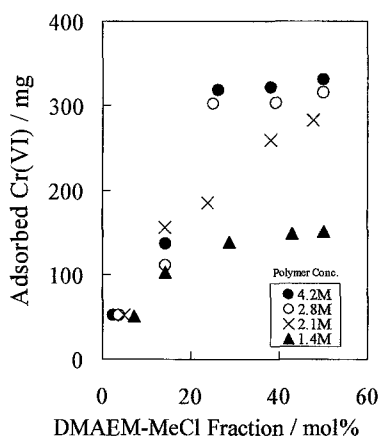


Fig. 1 Adsorbed  $\text{Cr(VI)}$  amount change with DMAEM-MeCl fraction and total polymer concentration of DMAEM-MeCl /AAm gel reduced to 10 g of the pregel solution [15].

such as selenite and dichromate ions. As for chromium, the chromium metal and Cr(III) is not so high, however it becomes toxic on being transformed into the hexavalent Cr(VI) with the fears for cancer. Besides, the volatile Cr(VI) is easy to be absorbed from the digestive organs, lungs, the skin, etc. The typical Cr(VI) compounds are chromium acid potassium ( $K_2CrO_4$ ) and dichromic acid potassium ( $K_2Cr_2O_7$ ), which are used for an oxidizer, plating, etc.; therefore, the most of the hazardous Cr(VI) exist in the forms of oxoanions in the environment. The selenium is a semiconductor and shows photoconductivity, which is used for the sensitization drum of copy machines. Besides, the selenium with a very low concentration is an indispensable element for an anti-oxidization action of a human body. However, it also turns into being toxic and causes nausea and dermatitis, when the absorbed amount becomes above a certain level.

Because the toxicity of some negative heavy-metal ions seems as serious as that of the positive ions as mentioned above, the authors have developed the gels which can effectively capture the negative heavy-metal ions [15,16] by leveraging the wide selectability of functional ingredients. For example, by simply changing the ion-group of the side-chain pendant, the polarity of sorbable ion can be easily switched to the opposite one as verified in the previous studies [13-16]. In one of the previous studies [15], the authors examined the Cr(VI) adsorptive capacity of the copolymer gels made of acrylamide (AAM) and dimethylaminoethylmethacrylate quaternised with methyl chloride (AAM/DMAEM-MeCl). The experiment demonstrated that the AAM/DMAEM-MeCl gels fully work as a heavy-metal anion capturer. Figure 1 shows the captured Cr(VI) amounts by the AAM/DMAEM-MeCl gels synthesized with different DMAEM-MeCl molar ratios and with the network concentrations. As can be seen in Fig.1, the amount of the adsorbed Cr(VI) increases with DMAEM-MeCl molar ratio in the lower-ratio range while almost the flat dependence in the higher region. The similar trend is implicated in the polymer concentration dependence of the captured Cr(VI) from the crowded arrangement of the data points in the higher concentration region. Besides, it was also found that the degree of heavy-metal capturing ability has been revealed to be almost the same amount of Cu(II) by the PAAm [13] and CMC-Na gels [14], which is much larger than that by other adsorbents such as zeolite or ion-exchange resins.

Along this line, in these days, the authors have been investigating the ion-capturing properties of the anion-adsorbing gel with a systematic approach. In the present investigation, they examined the ion-capturing feature of a new anion-capturing gel of which the side-chain group in the opposite side of the functional group across the main chain is different from that of the AAM/DMAEM-MeCl gels. Concretely speaking, in the present study, the authors have adopted dimethylaminoethylacrylate quaternised with methyl chloride (DMAEA-MeCl) as the functional unit in the network sequence of the hazardous-heavy-metal-anion adsorbing gel. By measuring the capturing Cr(VI) amounts of the AAM/DMAEA-MeCl gels and by comparing them with those of the AAM/DMAEM-MeCl gels measured in the

previous study [16], they have examined the side-chain substitution effect on the Cr(VI) oxoanion capturing functionality of the isomorphous gels.

## 2. EXPERIMENTALS

In order to measure the captured Cr(VI) amount by the AAM/DMAEA-MeCl gels, the authors prepared aqueous pregel solutions of DMAEA-MeCl<sub>0.85</sub>/AAM<sub>0.15</sub> polymer (molecular weight  $\sim 500 \times 10^4$ ) and AAM: the DMAEA-MeCl<sub>0.85</sub>/AAM<sub>0.15</sub>:AAM molar ratio was in a range from 1:41 to 7:7, and the total concentration was in a range from 1.4M to 4.2M. For conducting gelation,  $\gamma$ -ray from  $^{60}Co$  ( $\sim 50$  kGy) was irradiated to the pregel solutions at Koka Research Institute of the Japan Radioisotope Association, which was the same method that was performed for preparing AAM/DMAEM-MeCl gels in the previous study [15]. After the solution became solid gels by the  $\gamma$ -ray irradiation, cubic portions were cut out and immersed in pure water for 24 hrs to wash out unreacted ingredients.

In the previous and present studies, an aqueous solution of chromium trioxide ( $CrO_3$ ) have been adopted as a model fluid which contains hazardous heavy-metal anions; because, by only dissolving  $CrO_3$  in water, produced are typical hexavalent chromium (Cr(VI)) oxoanions, chromate ( $CrO_4^{2-}$ ) and dichromate ( $Cr_2O_7^{2-}$ ) ions. After the preparation of the AAM/DMAEA-MeCl gels, each the purified gel cube was immersed in a cell filled with 10mM of aqueous  $CrO_3$  solution for 24 hrs in order to make the gel capture the Cr(VI) oxoanions. Then, the gel blocks were carefully taken out from the experimental cells to measure the Cr(VI) concentration and volume of the Cr(VI) solution left in each the cell. The Cr(VI) concentration of the solution was measured with a high sensitivity by the atomic absorption spectrometry. The captured Cr(VI) amount of each the gel was estimated by subtracting the measured concentration multiplied by the measured volume from the ingredient weight in the pregel solution.

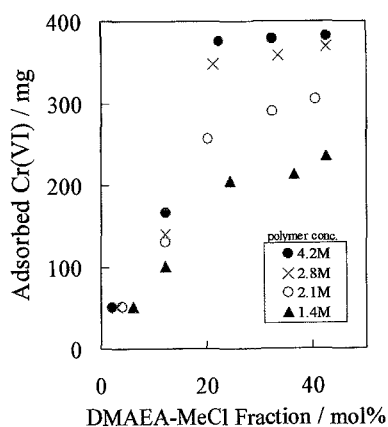


Fig. 2 Adsorbed Cr(VI) amount change with the DMAEA-MeCl fraction and total polymer concentration of DMAEA-MeCl/AAM gel reduced to 10 g of the pregel solution.

### 3. RESULTS AND DISCUSSIONS

The increase in the Cr(VI) capturing amount with the DMAEM-MeCl-fraction suggests that the Cr(VI) can be captured in the form of the oxoanions by taking into consideration of the functional-group polarity of the AAm/DMAEM-MeCl gels. Such a mechanism seems to be natural because the chromium trioxide is known to produce  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  in the aqueous solution.

Figure 2 shows the Cr(VI) weights recovered by the AAm/DMAEA-MeCl gels with different DMAEA-MeCl molar ratios and the total network concentrations; the data values are converted to the adsorbed Cr(VI) weight per 10 g of the pregel solution. The authors have adopted this description to express definitely amount of the DMAEA-MeCl and AAm in the recovery experiments because the AAm/DMAEA-MeCl gel expands in a different degree with the composition ratio of DMAEA-MeCl to AAm in the washing in pure water: the weight ratio after to before washing is ~62 in the DMAEA-MeCl<sub>0.85</sub>/AAm<sub>0.15</sub>:AAm = 7 : 7 gel, while ~4 in the 1 : 41 gel.

As can be easily seen in Fig.2, the experimental results in the present study have proven that the AAm/DMAEA-MeCl copolymer gel can be fully used as a heavy-metal anion adsorbing material. The Cr(VI) recovering efficiencies clearly surpass those of the AAm/DMAEM-MeCl gels studied in the previous study [15]. The Cr(VI) capturing behaviors with changing the functional-part ratio and total network concentration is similar to those of the AAm/DMAEM-MeCl gels; the recovered Cr(VI) amount increases with DMAEA-MeCl molar ratio in the lower ratio range while the fashion becomes saturated in the higher ratio region, besides the similar trends can be also confirmed in the total network concentration dependences. With these experimental results, the Cr(VI) recovering mechanism of both the AAm/DMAEM-MeCl and AAm/DMAEA-MeCl gels are presumable to be the same one.

From the experimental results in the present study, the usefulness of the AAm/DMAEA-MeCl gels for recovering a heavy-metal anion has been clearly verified. Besides, by comparing the Cr(VI) recovering efficiencies of the AAm/DMAEM-MeCl and AAm/DMAEA-MeCl gels estimated by the experimental data shown in Figs. 1 and 2, it has been demonstrated how the structure of the gel affects the ion-capturing efficiency in spite that the structural differences exist in an area far from the functional group.

For the practical use of the ion-recovering gels, it may be necessary to emphasize again that the heavy-metal capturing capacity of the DMAEA-MeCl gel have been verified to be much larger than those of other adsorbents such as zeolite or ion-exchange resins, which was also demonstrated for the isomorphous gels in the previous studies reported by the authors [13-16]. The characteristics of the gels are flexibility of the structure and properties. As is demonstrated in the present and previous studies [13-16], the structure of the gels can be easily changed by simply altering the parts of the polymer network, which induces a potential ability being utilized for a variety of purposes.

In the present study, the AAm/DMAEM-MeCl gels

have been formed by the  $\gamma$ -ray irradiation method which is a promising technique to make gels without usually hazardous cross-linker. While the dosage amount has been fixed to 50 kGy in the present study, the  $\gamma$ -ray dosage dependence of the Cr(VI) adsorption amount can reveal a capturing mechanism in the same way as in the previous study on the Cu(II) adsorption change of the CMC-Na gels made with different  $\gamma$ -ray dosages [14].

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