

Effect of Terminal-Group Substitution 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 / absorbent material) weight ratio. In the present study, it has been demonstrated that the terminal group substitution in a heavy-metal-anion capturing gel has a dominant effect on its efficiency.

Key words: gel, heavy metal anion, capture, environment, terminal group

1. INTRODUCTION

It is famous that some heavy metal causes a serious social problem. The public attention gathered about the heavy metal pollution after a view was announced from the Japanese Ministry of Health and Welfare that the Itai-Itai Disease seemed to be caused by the cadmium which was discharged from Kamioka Mine to the upper reaches of Jintsu River in 1968; and an anxiety about this problem got quickly abroad [1,2]. In this situation, the heavy metal waste from industrial facilities to the environment was strictly regulated by statutes, therefore, the conditions on the heavy metal pollution have been improved very much recently. However, the heavy metals which have already flowed out in environment will not become harmless automatically and the polluted areas will spread out by the diffusion of the heavy metals [3,4]. Therefore, it is necessary to take quick measures to recover them before their diffusion.

The authors have been paying attention to the harmful heavy metal leakage from final landfill sites [5]. According to ordinance, industrial waste fluid containing heavy metals are treated as specially controlled industrial wastes [6]. The heavy metals in the waste fluid are usually recovered in the form of hydroxide precipitations [7], which are stored in either of Strictly Controlled Type Landfill Site or Controlled Type Sanitary Landfill Site depending on their toxicities and degrees of chemical stability [5,6].

Though the wastes are usually processed without trouble in conformity with the prescription provided by the Ministry of the Environment, there are fears for the decrease in the shield functionality of the final landfill sites by acid rain. In the Least Controlled Landfill Site, the fluid containing the heavy metals may soak through the ground and pollute the underground water. In the

Controlled Type Sanitary Landfill Site, the heavy metal waste fluid may flow outside through the shielding sheet rip. In Strictly Controlled Type Landfill Site, the polluted fluid may flow out from the crack of the concrete wall which is easily eroded by acid rain.

In such a case, prompt recovery treatments should be performed in order to prevent the heavy metal diffusion into the environment. Therefore, it is necessary that the recovering apparatus should be transportable and easy to handle without requiring special devices. The authors have been considered that several functional gels are promising for such an application and they have been investigating the heavy metal recovery functionality of several gels as mentioned below. The gels show unique properties with the interactions between network polymer and solvent [8] and some of them can be utilized for the heavy metal recovery. Among them, the volume phase transition is one of the famous phenomena suitable for the waste recovery functionality.

Let us introduce some features of the volume phase transition. In the case of *N*-isopropylacrylamide (NIPA) hydrogel, the volume phase transition occurs by changing temperature: a continuous transition is observed around 36°C due to the metastasis of the isopropyl group from hydrophilic to hydrophobic nature with increasing temperature [9,10]. The transition feature of the NIPA gel changes considerably by introducing an ion-group: *N*-isopropylacrylamide/acrylic acid (NIPA/AAc) gel shows a discontinuous volume change, of which the degree increases with the ratio of acrylic acid [11,12]. Besides, the ionized gel also shows an ion capturing functionality; 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 [13], however, they did not consider the efficiency of the ion adsorption

which is important for the purpose in the present study.

Due to a high efficiency of the ion-adsorption, the authors have considered that the ionized gel can be used as a heavy-metal recovery material. The advantages of the ionized gel over other adsorbents are as follows:

- (1) Because organic gels, which we have adopted as adsorbents, are usually composed of light elements (such as H, C, N and O), the weight ratio of captured heavy metal to the adsorbent is much larger than those of the inorganic adsorbents like the zeolite, by which the transporting expenses from recovery fields to treatment facilities can be suppressed so much.
- (2) Because network of chemical gels are not easily broken in wide temperature, pressure and pH ranges, they can be used in various conditions.

From the viewpoint of the ion-capturing efficiency measured in the previous study, poly(acrylamide/sodium acrylate) (PAAm/SA) gel is adequately fit for practical use as an environmental purifying material: the capturing efficiency was estimated ~20wt% of network polymer, namely total weight of AAm and SA, which is very large value as an adsorbent [14].

The positive heavy-metal capturing property was also investigated for sodium carboxymethylcellulose (CMC-Na) gel in the previous study [14], which was made by γ -ray irradiation [15,16]. The characteristics of the CMC-Na gel in the practical usage are non-toxicity, biodegradability and availability at low price. It was found that the CMC-Na gel can adsorb almost the same amount of cupric ion with the PAAm/SA gel in the investigation of the ion-capturing property of the CMC-Na gel made by γ -ray irradiation [14]. This feature indicates the possibility of a biodegradable heavy-metal adsorbent made by CMC-Na gel. As shown in Fig.1, in the case of the CMC-Na gel, an interesting feature was observed: the captured-ion weight increases with γ -ray dosage [14], which may reflect the recovery mechanism of the CMC-Na gel. In order to explain this feature, the authors were concluded that two or more carboxyl groups can take part in the Cu^{2+} recovery, such as chelation, based on the fact that the dosage of γ -ray causes increase in the polymer crosslinking degree of CMC-Na in the thick aqueous solution of CMC-Na [15].

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 trivalent and hexavalent ions are very toxic. In the environment, the natural form of chromium is trivalent and almost harmless, while the artificially generated hexavalent chromium is very harmful. If the skin is stained with the hexavalent chromium, there are possibilities of not only dermatitis or neoplasm but also cancer. Besides, the volatile hexavalent chromium can be easily absorbed from the digestive organs, lungs, the skin, and so on, therefore the effect on the health must be considered seriously. As typical hexavalent chromium compounds, there are chromium acid potassium and dichromic acid potassium, which are used for an oxidizer, plating, etc., therefore,

almost of the hazardous chromium compounds exist in the forms of oxoanions. As for selenium, the raw selenium is a semiconductor and has a photoconductive functionality, which is utilized for the photosensitive drum surface of a copy machine. In addition, in a very small amount, selenium is an indispensable element by its anti-oxidization action which is required for composition of enzyme in a human body, while it becomes toxic and causes nausea and dermatitis beyond twice the indispensable level.

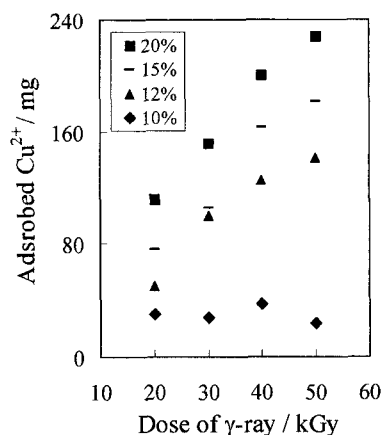


Fig. 1 Cu^{2+} recovery of CMC-Na gel made by γ -ray irradiation. In the figure, γ -ray dose dependence of adsorbed Cu^{2+} amount to 10 g of CMC-Na gels is depicted at several CMC-Na concentrations [14].

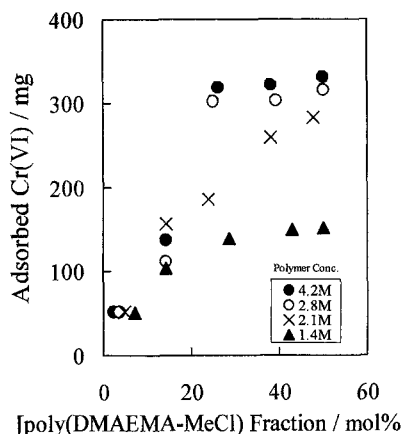


Fig. 2 Adsorbed Cr(VI) amount change with the [poly(DMAEMAMeCl)]:[AAm] molar ratio and ingredient's concentration of poly(DMAEMA-MeCl)/AAm copolymer gel to 10 g of the pregel solution [17].

In these circumstances, the authors have been also developing the negative heavy-metal ion capturing gels. In the previous study [17], the heavy-metal-anion absorption feature of dimethylaminoethylmethacrylate quaternised with methyl chloride (DMAEMAMeCl) / acrylamide (AAm) copolymer gel was investigated as a first trial. And the possibility of the utilization of the gel for capturing a heavy-metal anion has been clearly demonstrated for the first time. Besides, by comparing the amounts of the captured heavy-metal ions by the DMAEMAMeCl/AAm [17], PAAm/SA [14] and CMC-Na [14] gels, their ion-capturing functionalities 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, there is only one data on the negative heavy-metal ion adsorption gel, therefore more investigations of such a gel is indispensable for achieving higher efficiency.

In these circumstances, in the present study, the authors have investigated how the anion-capturing functionality changes by substituting DMAEMAMeCl with *N,N*-Dimethylaminoethylacrylate (DMAEA) of which the structure is almost identical with DMAEMAMeCl except for the polarizing terminal group. The authors have been convinced that such an investigation should be very important for searching for the most effective ion-capturing gel.

2. EXPERIMENTALS

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 study [17]. As for the adsorbent, DMAEA/AAm copolymer gels have been adopted in the present experiment by the reason mentioned above.

In order to examine the anion-capturing functionality of the DMAEA/AAm copolymer gel, prepared were pregel solutions of which the molar ratios in a range from $[\text{DMAEA}]:[\text{AAm}]=1:6$ 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 DMAEA/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 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.

3. RESULTS AND DISCUSSIONS

Figure 3 shows DMAEA 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 study [17], the authors adopted this description to express definitely the amount of the DMAEA and AAm in the respective gels because the DMAEA/AAm gel expands in a different degree with the composition ratio of AAm to DMAEA in the washing procedure in pure water.

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 demonstrate 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. Though the detailed quantitative analyses on this feature are in progress, it can be qualitatively said that the polarization intensity of the side-chain terminal-groups can affect the ion-capture functionality so much because the terminal groups of DMAEMA-MeCl and DMAEA are the quaternary ammonium and the tertiary amine, respectively.

In the present investigation, the possibility of the utilization of the gel for capturing a heavy-metal anion has been also confirmed as well as the previous study [17] though the degree of the ion-capturing functionality of the DMAEA/AAm gel is somewhat less than that of DMAEMA-MeCl/AAm gel; however it is still much larger than that of other adsorbents such as zeolite or ion-exchange resins, etc.

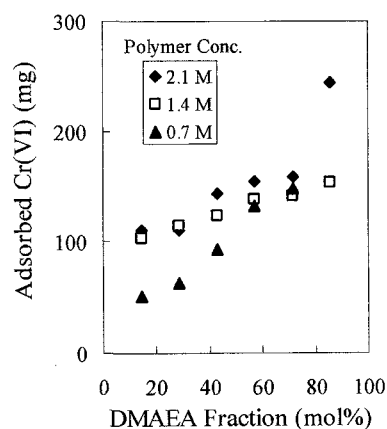


Fig. 3 Adsorbed Cr(VI) amount change with the DMAEA molar fraction and with total concentration of DMAEA/AAm gel to 10 g of the pregel solution.

REFERENCES

- [1] Preventative Measures Against Water Pollution, Jinzu River, Toyama Prefecture (in the Home Page of International Center for Environmental Technology Transfer (ICETT)), http://www.icett.or.jp/lpca_jp.nsf/Jinzu%20River,%20Toyama%20Prefecture?OpenView.
- [2] Jun Ui (Ed.), *Industrial pollution in Japan (The Japanese Experience Series)*, United Nations University Press, Tokyo, 1992. (<http://www.unu.edu/unupress/unupbooks/uu35ie/uu35ie00.htm>)
- [3] F. M. D'Itri, in W. P. Cunningham, T. H. Cooper, E. Gorham and M. T. Hepworth (Eds.), *Heavy metals and heavy metal poisoning in Environmental Encyclopedia (Second edition)*, Gale Research, Detroit, 1998, pp.511-513.
- [4] J. S. Thayer, in R. A. Meyers (Ed.), *Encyclopedia of Environmental Analysis and Remediation, Vol.4*, Wiley, New York, 1998, pp. 2126-2139.
- [5] The ministerial ordinance by which the technical standard concerning the final landfill site of municipal wastes and that of industrial wastes are provided (Prime Minister's Office and Welfare Ministerial Ordinance No.1 enacted on March 14, 1977, and lastly revised by the Environmental Ministerial Ordinance No.7 on March 29, 2002.)
- [6] The Ministry of Health and Welfare Bulletin, No. 194 in 1992.
- [7] G. L. Rorrer, in R. A. Meyers (Ed.), *Encyclopedia of Environmental Analysis and Remediation, Vol.4*, Wiley, New York, 1998, pp. 2102-2125.
- [8] T. Tanaka; *Sci. Am.* 244, 124 (1981).
- [9] T. Tanaka, *Phys. Rev. Lett.*, 45, 1636 (1980).
- [10] T. Tanaka, *Phys. Rev. Lett.*, 40, 820 (1978).
- [11] S. Hirotsu, Y. Hirokawa, and T. Tanaka, *J. Chem. Phys.*, 87, 1392 (1987).
- [12] S. Hirotsu, *Phase Transitions*, 47, 183 (1994).
- [13] D.K. Jackson, S.B. Leeb, A. Mitwalli, D. Fusco, C. Wang, and T. Tanaka, *J. Intell. Mater. Syst. Struct.*, 8, 184, (1997).
- [14] K. Hara, M. Yoshigai and T. Nishida, *Trans. Mater. Res. Soc. Jpn.*, 30, 823, (2005).
- [15] B. Fei, R. A. Wach, Jackson, H. Mitomo, F. Yoshii, and T. Kume, *J. Appl. Polym. Sci.*, 78, 278, (2000).
- [16] K. Terao, H. Nishida, S. Kondo, T. Dobashi, F. Yishii, T. Hashimoto, and S. Yagihara, *Trans. Mat. Res. Soc. Jpn.*, 27, 593 (2003).
- [17] K. Hara, M. Yoshigai, and N. Nishida, *Trans. Mat. Res. Soc. Jpn.*, 31, 815 (2006).

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