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A Gel Which Can Absorb Harmful Heavy Metal Anion

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Aiming at utilizing as an environmental purification materials, heavy-metal-ion absorption feature of dimethylaminoethylmethacrylate quaternised with methyl chloride / acrylamide copolymer gel has been investigated. It has been found, for the first time, that the gel is capable of capturing a hazardous heavy metal anion.

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

1. INTRODUCTION

Comfortable modern life is well known to be supported by many industrial products. However, much attention to the influence of their by-products, waste, on the environment had not been paid before, which caused the environmental pollution issue of the 20th century. However, with a steady effort to solve environmental problems, it is thought that almost of the problems are solved on the toxic waste discharge from industrial facilities nowadays. However, one must not forget the toxic waste that has already been discharged from these facilities in the environment; the polluted area with the stable poisonous waste is thought to be spreading by diffusion rather than being petering out, therefore, it is necessary to take a prompt action to capture them. Especially, the author is paying attention to the harmful heavy metal leakage from the final landfill sites.

The final landfill sites in Japan are classified into three kinds by chemical stability and the degree of toxicity of the stored waste [1]. Least Controlled Landfill Site stores stable industrial wastes from which toxic fluid contaminating the subterranean stream does not percolate through in a usual state such as plastics, rubber, metals, construction scraps, glasses, and earthenware, etc. This final landfill site has the simplest structure among three final landfill sites; wastes are simply buried underground. Controlled Type Sanitary Landfill Sites stores wastes that cause the groundwater contamination by the infiltration of rain water. In order to prevent the groundwater from being polluted by the infiltrated fluid through the wastes, the bottom of this final landfill site is covered with the vinyl and the rubber seat. The water collected in the bottom is led to the sewage treatment plant outside. Strictly Controlled Type Landfill Sites stores the toxic wastes that cannot be made harmless by usual processing; in order to isolate waste from the environments, wastes are enclosed in the building made of concrete.

It is well known that the heavy metals cause the grave social problems. After The Ministry of Health and Welfare in Japan announced, in 1968, that the Itai-Itai Disease seemed to be caused by the cadmium discharged from the Kamioka mine to the upper reaches of the Jintsu River, public attention gathered on the heavy metal pollution and the anxiety about the problem had extended considerably [2,3]. Then, the heavy metal outflow from industrial facilities to the environmental has been severely regulated under such a situation by ordinance and, recently, the situation on the heavy metal pollution becomes improved very much. However, it is thought that the heavy metal that already flows out into the environment doesn't automatically become harmless, and the polluted area has spread rather than decreasing by diffusion [4, 5].

An industrial waste fluid including the heavy metal is provided for specially controlled industrial waste by ordinance [6]. In facilities to treat these wastes, the heavy metal in the waste fluid is collected in the form of the hydroxide precipitation [7], and stored in either of Strictly Controlled Type Landfill Site or Controlled Type Sanitary Landfill Site depending on their toxicities or degrees of chemical stability [6]. The heavy metal waste is safely stored in the above-mentioned final landfill sites with the prescription for which the Ministry of the Environment provided. Though wastes are usually processed without trouble by these processing, they have misgivings about decrease in the shield functionality of the final landfill sites by the influence of acid rain as follows: In the Least Controlled Landfill Site, with the reaction of the wastes and acid rain, it is possible that the fluid which contains the heavy metals oozes out and flows under the final landfill site to contaminate the underground water. In the Controlled Type Sanitary Landfill Site, there is a possibility that the heavy metal waste fluid flows outside through the rip of the shielding sheet. In Strictly Controlled Type Landfill Site, because a concrete wall is easily eroded by acid rain, it is possible that the harmful fluid polluted by the heavy metal flows from the crack of the wall to the outside. In these cases, easy methods not requiring special devices are aspired after to prevent the heavy metal from diffusing in the environment.

Gels show interesting characteristics by the interactions between the network polymer and the solvent [8], which can be utilized as a heavy metal recovery material as described below. One of the famous features of the gels is the volume phase transition. In the case of *N*-isopropylacrylamide (NIPA) hydrogel, 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 changes considerably by introducing an ion-group. *N*-isopropylacrylamide/acrylic acid copolymer gel shows a discontinuous volume change at the transition temperature; the degree of discontinuity increases as the ratio of acrylic acid grows [11,12]. Besides, the introduction of the ion-group also brings the gel ion capturing function. By utilizing this property, Jacson *et al.* developed a metal-ion detector with an interpenetrating network hydrogel composed of poly(vinyl alcohol) and *N*-isopropylacrylamide/acrylic acid [13], however, they did not consider on the ion-adsorption efficiency.

The authors found that the ionized gel can be used as a heavy-metal recovery material with the consideration of ion adsorption efficiency. The advantage of the ionized gel as an ion absorbent over other adsorbent is as follows: By utilizing an organic hydrogel, the transportation cost can be greatly suppressed because the gel is composed of light elements (such as H, C, N and O): weight of captured heavy metal per that of the adsorbent can be set far larger than inorganic absorbents like the

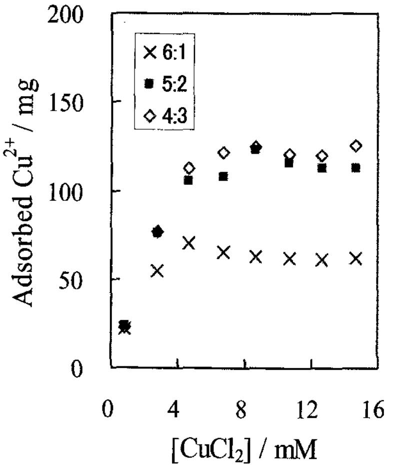

Fig. 1
$CuCl_2$ concentration dependence of the recovered Cu^{2+} weight to 10 g of the PAAm/SA (700 mM) pregel solution [14].
The symbols, ×, ■ and ◇ denote the data of the PAAm/SA gels with molar ratios AAm:SA=6:1, 5:2, 4:3, respectively.

zeolite. Besides, because chemical gels are not easily destroyed in a wide range of temperature, pressure and pH, etc., they can be used as a recovery material in various conditions.

In the authors' investigations, poly(acrylamide/ sodium acrylate) (PAAm/SA) gel was found to have a possibility of being utilized as an environmental purifying material with a high positive-ion-capturing efficiency: As shown in Fig.1 [14], in the investigation, the authors found that Cu^{2+} ion adsorption amount increases with $[CuCl_2]$ up to a certain value and reaches a saturation point then. The maximum captured Cu(II) weight was also found to show an exponential saturation feature with SA. Besides, with the results in the experiment, Cu(II) capturing efficiency was estimated to be ~20wt% of network ingredients, AAm+SA, which is extremely large value as an adsorbent.

The authors also found the similar positive heavy-metal capturing function of sodium carboxymethylcellulose gel [15] made by γ-ray irradiation [16,17], of which the characteristics are non-toxicity, biodegradability and availability at low price. Besides, in the investigation, very interesting and important feature was observed described as follows: the captured Cu(II) weight becomes large with γ-ray dose as well as with the CMC-Na concentration, which is thought to reflect the characteristics of the recovery mechanism of the CMC-Na gel. The key to solve the question is that, in the thick aqueous solution of CMC-Na, the dosage of γ-ray causes increase in the polymer crosslinking degree of CMC-Na [16]. Generally speaking, there seem two mechanisms to capture Cu^{2+} ion: One possible mechanism is that one Cu^{2+} ion is adsorbed by one carboxyl group in CMC-Na. In this case, the captured Cu(II) weight should be in proportion to the CMC-Na concentration, while the adsorbed weight should be irrelevant to the γ-ray dosage, because, in this mechanism, the Cu^{2+} capturing site does not increase by γ-ray irradiation. Another possible one is that plural carboxyl groups participate in capturing one Cu^{2+}, namely Cu^{2+} capturing by the chelation mechanism. In such a case, the captured Cu(II) weight will also increase with the CMC-Na concentration, while a clear difference should appear in the crosslinking degree dependence, namely the γ-ray dosage dependence of the captured Cu(II) weight. Because, in this case, plural carboxyl groups take part to capture one Cu^{2+} ion, the spatial configuration of the carboxyl groups should influence the Cu(II) recovery functionality. By paying attention to the γ-ray dosage dependence of the captured Cu(II) weight, they concluded that the latter mechanism superiorly seemed to occur: the more dose of γ-ray can induce the more steady and adjoining configurations of the CMC-Na network polymers caused by higher crosslinking degree.

In the previous studies, the authors developed the gels which can adsorb positive ions. However, there are many harmful heavy-metal ions with negative polarity in the environment such as $Cr_2O_7^{-2}$ and SeO_4^{2-} described as follows: As for chromium, the chromium metal itself is harmless and most of the tableware is plated with chromium. However, it comes to have toxicity by being oxidized to become the trivalent or hexavalent ion. The natural form of chromium is trivalent and its toxicity is not so high, while the chromium of hexavalent is generated artificially and very harmful. If the skin is stained with the hexavalent chromium, there are fears of becoming not only dermatitis or neoplasm but also cancer. Besides, since the hexavalent chromium is easy to evaporate, it can be absorbed from the digestive organs, lungs, the skin, etc.; the influence on health is serious. As typical hexavalent chromium compounds, there 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 hazardous chromiums exist in the forms of oxoanions in the environment. As for selenium, the metal selenium has semiconductor nature and photoconductivity and used for the sensitization drum of a copy machine. Besides, selenium is an indispensable element below a very-small-quantity level with an anti-oxidization action (required for composition of anti-oxidization enzyme) for a human body. However, when its amount becomes beyond twice the required level, it becomes toxic causing nausea and dermatitis.

As mentioned above, the toxicity of some negative heavy-metal ions seems more serious than that of the positive ions. In these circumstances, the authors have developed the gel which can capture the negative heavy-metal ion in the present study for the first time.

2. EXPERIMENTALS

In the present experiment, an aqueous solution of chromium trioxide is adopted as a model fluid which contains heavy-metal anion because, in the solution, hexavalent chromium oxoanions CrO_4^{2-} and $Cr_2O_7^{-2}$ occur without any treatment. Besides, in the present experiment, the authors have adopted a polymer (molecular weight ~300×10^4) of dimethylamino-ethylmethacrylate quaternised with methyl chloride (DMAEMA-MeCl) for capturing the heavymetal anion.

In order to examine ion-capturing functionality of the gel containing the DMAEMA-MeCl, the authors prepared pregel solutions of which the molar ratio [poly(DMAEMA-MeCl)]:[AAm] was in a range from 1:41 to 7:7, and the total concentration, from 1.4M to 4.2M. For conducting gelation, γ-ray from ^{60}Co (~50 kGy) was irradiated to the pregel solutions at Koka Research Institute of the Japan Radioisotope Association. After the solution became solid gels, 0.3g of cubic portions were cut out and immersed in pure water for 24 hrs to wash out unreacted ingredients.

To make the gel capture the hexavalent chromium oxoanions, each the purified gel cube was immersed in a cell filled with 10mM of aqueous CrO_3 solution for 24 hrs, then, the gel blocks were carefully taken out from the experimental cells. After these procedure, Cr(VI) concentrations and volumes of the remainder solutions in the cells were measured, respectively. The Cr(VI) concentration of the remainder 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.

3. RESULTS AND DISCUSSIONS

Figure 2 shows [poly(DMAEMA-MeCl)]:[AAm] molar ratio dependence and ingredient's concentration dependence of the recovered Cr(VI) weight to 10 g of each the pregel solution. The authors adopted this description to express definitely amount of the poly(DMAEMA-MeCl) and AAm in the recovery experiments because the poly(DMAEMA-MeCl)/AAm gel expands in a different degree with the composition ratio of AAm to poly(DMAEMA-MeCl) in the washing in pure water.

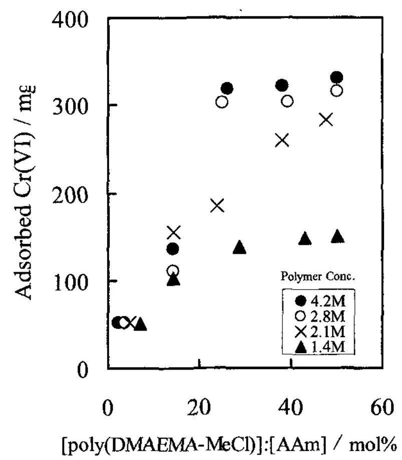

Fig. 2
Adsorbed Cr(VI) amount change with the [poly(DMAEMAMeCl)]:[AAm] molar ratio and ingredient's concentration of poly(DMAEMA--MeCl)/AAm copolymer gel to 10 g of the pregel solution.

The experimental results shown in Fig.2 demonstrate that the poly(DMAEMA-MeCl)/AAm copolymer gel fully works as a heavy-metal anion capturer. However, having a good look at the molar ratio and concentration dependences, one can notice that the amount of adsorbed Cr(VI) increases with molar ratio of poly(DMAEMA-MeCl) 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 indicates that there occurs a structural change which inactivates the ion-capturing functionality.

In the present investigation, the possibility of the utilization of the gel for capturing a heavy-metal anion has been clearly demonstrated for the first time. Besides, from the experimental results as shown in Figs. 1 and 2, the degree of heavy-metal capturing ability have been revealed to be almost the same amount, which is also much larger than that by other adsorbents such as zeolite or ion-exchange resins.

The characteristics of the gels are flexibility of the structure and properties. As is demonstrated in the present and previous studies, by simply changing the ion-group of the side chain, the polarity of captured ions can be easily switched to the opposite one, which indicates a potential ability being utilized for a variety of purposes.

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