

A Possibility of Hydrogels as Environment Purifying Materials

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A possibility of full-scale applications of the some hydrogels as environmental purifying materials has been examined by measuring the capturing amount of the heavy metals. The experimental results indicate that the hydrogels can be fully useful for such applications with an advantage in the quantity of the captured ion per the absorbent weight over other adsorbents.

Key words: hydrogel, heavy metal, capture, environment

1. INTRODUCTION

Modern life in these days is supported by a number of industrial products; the industry plants discharge a lot of wastes in proportion to the amount of the industrial product. However, because less attention to the waste influence on the environment had not been paid before, the environmental pollution issue had broken out in those situations in the 20th century. By the occurrence of many environmental problems, the effective pollution-control measures had been carried out and, in these days, many environmental problems are settled on the toxic waste discharge from industrial facilities. However, it should be always reminded that the stable toxic-wastes that have been already discharged in the environment from the industrial facilities do not disappear by themselves and the polluted area can be spreading by diffusion. Therefore, in order to hold the damage to a minimum, a prompt action to capture them should be taken. As an effective method for that purpose, the authors have proposed to utilize hydrogels.

Among the hazardous wastes, almost all of the heavy metals cause serious environmental problems in spite of their functionality usable for many applications. The entrances of heavy metals to the human body may occur through food, water, air, or by the skin contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. The toxicities of heavy metals are expressed when they remain and accumulate in the body [1]. In the United States, the Agency for Toxic Substances and Disease Registry (ATSDR, a part of the U.S. Department of Health and Human Services) has been publishing a Priority List every two years from 1997, in which the heavy metals, such as arsenic, lead, mercury, cadmium, and chromium, rank among the "Top 20 Hazardous Substances" [2]. In the list, there are heavy metals in the form of the positive ion in the environment, for example,

lead and cadmium, therefore, it is necessary to develop the adsorbent which can capture the positive ion. Therefore, in the first stage of this study [3], the authors have developed the positive-ion-capturing gels. However, there are many harmful heavy-metal ions with negative polarity in the environment such as $\text{Cr}_2\text{O}_7^{2-}$ and SeO_4^{2-} described as follows: As for chromium, the chromium metal itself is harmless. However, it comes to have toxicity by being oxidized to become the hexavalent ion. 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 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.

In 1968, public attention had gathered on the heavy metal pollution because The Ministry of Health and Welfare in Japan announced 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 [4,5]. Since then, the discharge of heavy metals from industrial plants to the environment has been strictly controlled by the environmental ordinances and the waste water disposal equipments have been set up to the industry plants. With these efforts, the situation on the heavy metal pollution becomes much improved recently. However, almost of the heavy metals that have already flown out to the environment doesn't become harmless by themselves, therefore the polluted area can

spread by diffusion [6, 7].

In addition to the threat of heavy metals left in the environment, it is said that there is a fear that the heavy metals in final disposal sites may flow out by the facility damage caused by the acid rain. The industrial waste fluids containing heavy metal are provided for specially controlled industrial wastes by ordinance [8]. In the facilities to treat these wastes, the heavy metals in the waste fluid are collected in the form of the hydroxide precipitation [9], 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 [8]. Ordinarily, 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 treatments, there are possibilities of the shield functionality decrease of the final landfill sites caused by the acid-rain influence as mentioned below:

- With the reaction between the acid rain and the wastes in the Least Controlled Landfill Site, the fluid which contains the heavy metals can infiltrate in a deep region of the final landfill site to contaminate the underground water.
- In the Controlled Type Sanitary Landfill Site, the heavy metal waste fluid can flow outside through the rip of the shielding sheet.
- In Strictly Controlled Type Landfill Site, because a concrete wall is easily eroded by acid rain, the harmful fluid polluted by the heavy metal can flow outside from the crack of the wall.

In order to cope with these cases, quick and easy methods which do not require special devices are awaited for preventing the heavy metals from diffusing in the environment.

To describe more fully, as mentioned above, in order to prevent damage from the toxicity of heavy-metal ions, it should be necessary to develop the adsorbents capturing positive and negative ions. Therefore, the authors have developed the gels which can capture the positive and negative heavy-metal ions in the present study. Gels show specific properties through the interactions between polymer network and solvent [10], which will be useful for a heavy metal recovery. One of the unique features of the gels related to the heavy-metal-recovery applications can be the property change by introducing ionized groups into hydrogels. *N*-isopropylacrylamide (NIPA) hydrogel shows a continuous volume transition around 36°C due to the change in the isopropyl group nature from hydrophilic to hydrophobic with increasing temperature [11,12]. The transition feature changes considerably by introducing an ion-group: ionized NIPA hydrogels, *N*-isopropylacrylamide/acrylic acid and *N*-isopropylacrylamide/sodium acrylate gel show a discontinuous volume change at the transition temperature; the degree of discontinuity increases with the ratio of acrylic acid and sodium acrylate [13,14]. Besides, the introduction of the ion-group also gives the ion capturing function to the hydrogels. 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 [15], 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 as mentioned below. The advantages of the ionized gel as an ion absorbent over other adsorbent and treatments are 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 adsorbents like zeolites.
- 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.
- The heavy-metal-recovery treatment with the hydrogels can be done easily without any complicated equipments.
- In the ordinal treatments, the heavy metals in the waste fluid are collected in the form of the hydroxide precipitation, which produce an enormous amount of hydroxide sludge, while the recovery-method by utilizing the hydrogels does not produce any by-product.

2. EXPERIMENTALS

Positive-ion-capturing gel

As a typical positive-ion capturing gel, the authors adopted *poly*-(acrylamide/sodium acrylate) (PAAm/SA) gel and have examined its ion-capturing amount with changing ingredient ratio. Pregel solutions (total concentration 700 mM) with [AAm]/[SA] (in molar ratio) = 6/1, 5/2 and 4/3 were prepared. At the beginning of the gelation, *N,N'*-methylenebisacrylamide (0.133 wt%), ammonium persulfate (0.04 wt%) and of *N,N,N',N'*-tetramethylethylenediamine (0.24 wt%) were added to the pregel solutions. The gelation process was conducted at room temperature for 24 hrs. After completion of the gelation, 0.3g of cubic portions were cut out and immersed in pure water for 24 hrs to wash out unreacted ingredients. Each of the purified gel cubes was immersed in a cell filled with aqueous CuCl₂ solution with a different concentration from 1 to 15 mM for 24 hrs. Then, the gel cubes were taken out from the cells. After this procedure, Cu(II) concentration and volume of the remainder solutions were measured. The Cu(II) concentration of the remainder solution was measured with a high sensitivity by the atomic absorption spectrometry. The captured Cu(II) amounts were estimated by subtracting the concentrations multiplied by the volumes from those in the preparation.

Negative-ion-capturing gel

As for a negative-ion capturing gel, dimethylaminoethylacrylatemethylchloride/acrylamide (DMAEA-MeCl/AAm) gel have been adopted and its ion-capturing amount has been examined with changing ingredient

ratio. In this experiment, an aqueous solution of chromium trioxide is adopted as a model fluid which contains hexavalent chromium oxoanions CrO_4^{2-} and

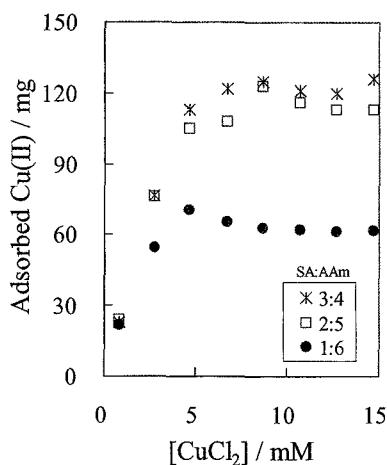


Fig. 1

The recovered Cu(II) weight by several PAAm/SA gels at different CuCl_2 concentration per 10 g of the 700 mM pregel solutions.

The symbols, ●, □ and * denote the data of the PAAm/SA gels with molar ratios SA:AAm=1:6, 2:5, 3:4, respectively.

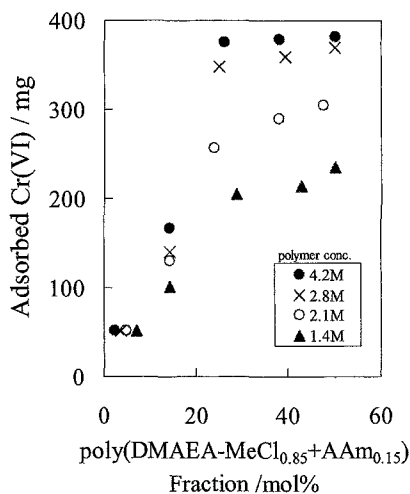


Fig. 2

Adsorbed Cr(VI) amount change with $(\text{poly}(\text{DMAEA-MeCl}_{0.85}+\text{AAm}_{0.15})) / (\text{AAm})$ molar ratio and total concentration per 10 g of the pregel solution.

$\text{Cr}_2\text{O}_7^{2-}$. A linear polymer of DMAEA-MeCl_{0.85}AAm_{0.15} with the polymerization degree of $\sim 500 \times 10^4$ (supplied by Toagosei) was used as a start material and ~ 20 pregel solutions with different molar ratio of (DMAEA-MeCl_{0.85}AAm_{0.15} polymer)/(AAm) in a range from 1/41 to 7/7 and total concentration from 1.4M to 4.2M in order to examine the negative-ion-capturing amount of the DMAEA-MeCl/AAm gel. For conducting gelation, ^{60}Co γ -ray irradiation (~ 50 kGy) to the pregel solutions was performed at Koka Research Institute of the Japan Radioisotope Association; after the γ -ray irradiation, the solution became solid gels. Then, 0.3g of cubic portions were cut out from the lump of the DMAEA-MeCl/AAm gel and immersed in pure water for 24 hrs to wash out unreacted ingredients. In order to capture the hexavalent chromium oxoanions, each the purified gel cube was immersed in a cell filled with aqueous CrO_3 solution (10mM) for 24 hrs. After the ion-capturing procedure, the gel cubes were picked out from the experimental cells. Then, Cr(VI) concentration and volume of the solutions in the cells were measured. The Cr(VI) concentration of the remainder solution was also measured 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 in the same manner with the previous experiment.

3. RESULTS AND DISCUSSIONS

The CuCl_2 -concentration dependence of the captured Cu(II) weight per 10 g of each the pregel solution are shown in Fig.1. As is shown in the figure, the Cu(II) adsorption increases with the concentration in the lower concentration region, however the value becomes almost constant over a certain concentration. Figure 2 shows $(\text{poly}(\text{DMAEA-MeCl}_{0.85}+\text{AAm}_{0.15})) / (\text{AAm})$ molar ratio and total concentration dependences of the adsorbed Cr(VI) weight also per 10 g of the pregel solutions. The amount of adsorbed Cr(VI) increases with fraction of $\text{poly}(\text{DMAEA-MeCl}_{0.85}+\text{AAm}_{0.15})$ in the lower value region, while the value becomes almost constant over a certain ratio. Such a tendency in the total concentration dependence can be also estimated from the crowded data configuration in the higher concentration region.

Let us examine the amount of captured Cu(II). In the present experiment, the (AAm+SA) weight of the (10 g, 700 mM and $[\text{AAm}]/[\text{SA}]=4/3$) PAAm/SA gel is ~ 0.58 g, while the captured Cu(II) weight can be estimated as ~ 0.12 g in the constant region in Fig.1. Therefore, the captured Cu(II) amount can be $\sim 20\text{wt}\%$ of the weight of (AAm+SA), which is extremely large value as an adsorbent compared with zeolite or ion-exchange resins. Besides, as can be easily seen by comparing Figs. 1 and 2, Cr(VI) capturing amount of the DMAEA-MeCl/AAm gel is much larger than that of the PAAm/SA gel.

In the present investigation, the possibility of the utilization of the gels for capturing a heavy-metal cation and anion has been clearly demonstrated. The experimental results shown in Figs. 1 and 2 demonstrate that these gels can be fully used as heavy-metal cation and anion capturers.

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