

An Attempt to Utilize Polymer Gels for Environmental Purification

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The utilizing possibility of polymer gel as an environmental purifying material has been investigated by examining hazardous-ion-capturing functionality of the PAAm/SA and CMC-Na gels. The experimental results reveal that they can be good candidates for such a usage with an advantage in the quantity of captured ion per the absorbent weight.

Key words: gel, heavy metal, capture, environment

1. INTRODUCTION

It is well-known that our convenient life is supported by a lot of industrial products. However, much attention had not been paid to their by-product, wastes, some of which are very hazardous and threatened our safety life. With increase in the concern about the environmental problems and with steady efforts for solving them, many ways out of such problems have been found as to the hazardous-waste emission from the industrial facilities. However, one should not forget that some stable wastes which are already discharged from these facilities will keep existing in the environment; the polluted area can spread by diffusion rather than disappear. In such a case related to the hazardous wastes, a prompt action to capture them should be done at once; the authors are especially paying attention to the hazardous heavy-metal leakage from the final landfill sites.

According to the degree of toxicity and chemical stability of stored wastes, the final landfill sites in Japan are classified into three kinds: Least Controlled Landfill Site, Controlled Type Sanitary Landfill Site and Strictly Controlled Type Landfill Site [1]. Least Controlled Landfill Sites store stable industrial wastes such as plastics, rubber, metal, construction scrap wood, glass, and pottery, from which no toxic substances are estimated to exude in usual conditions; the wastes are simply buried in the soil. Controlled Type Sanitary Landfill Sites store the wastes which will cause the groundwater contamination by rain water penetration. Bottoms of these landfill sites are covered with waterproofing vinyl or rubber sheets to prevent the groundwater from being contaminated by the permeated fluid, which is led to the sewage treatment plants outside the reservoir. Strictly Controlled Type Landfill Sites store toxic wastes which cannot be harmless with any usual treatments; in order to isolate these wastes from the environment, they are confined in concrete buildings.

As is well-known, heavy metals cause serious social problems. Since the Ministry of Health and Welfare in Japan announced in 1968 that the *Itai-Itai Disease* was suspected to be caused by the leaked cadmium from Kamioka mine to the Jintsu River upstream, the heavy metal contamination problems gained public attention [2] and the worry about the heavy metal environmental pollution considerably spread [3]. Under these circumstances, the heavy-metal outflow from industrial facilities to the environment has been severely restricted and the situation of the heavy metal pollution becomes much improved nowadays. However, as described above, though the effluent-control regulations seems to solve the heavy-metal environmental problems, the fact should be reminded that heavy metals which have already been leaked in the environment will not become harmless automatically; the contaminated areas can rather spread by diffusion than diminish [4, 5].

The industrial fluid waste containing heavy metals is provided for a specially controlled industrial waste by regulations [6]. In the facilities for treating these wastes, the heavy metals in the waste fluid are collected in the form of hydroxide precipitation [7] and finally disposed to either the Strictly Controlled Type Landfill Site or the Controlled Type Sanitary Landfill Site depending on their degree of toxicity and chemical stability [6]. In usual conditions, the heavy-metal wastes are safely stored in the above-mentioned final landfill sites by the method according to the prescription of the Ministry of the Environment. However, although these treatments are usually proceeded successfully, they are afraid of the decline in the shielding ability of the final landfill sites by acid rain: At the Least Controlled Landfill Site, the waste, which is thought to be stable, can release the heavy metals in a reaction with the acid rain and the contaminated fluid can flow outside of the landfill site. At the Controlled Type Sanitary Landfill Site, the heavy metals can also flow out through rips in the water

shielding sheet. At the Strictly Controlled Type Landfill Site, because the concrete wall is easily eroded by the acid rain, the fluid contaminated by hazardous heavy metals can easily flow out through the cracks which occur in the eroded part of the shielding wall. Under such circumstances, quick and easy recovery systems are anxious for in order to prevent the heavy metals from permeating into the environment; the characteristics demanded as the recovery material can be easy handling and simple treatment process without any special equipment. Besides, it should be better that carbon dioxide and detrimental gases are not emitted in the separating process of heavy metals from the recovery material.

Taking these conditions into consideration, the authors expect that gel can be utilized as a heavy-metal recovery material because the gel shows interesting properties through changes in the interaction between network polymer and solvent [8]. One of the famous features is the volume phase transition [9, 10] of *N*-isopropylacrylamide (NIPA) hydrogel observed around 36°C due to a hydrophilic-to-hydrophobic transition in the nature of the isopropyl group. Originally, the NIPA gel shows continuous volume change at the transition temperature; the feature changes considerably by bringing ionic-groups into the gel due to the effect of Donan potential [9]. To be more concrete, an *N*-isopropylacrylamide/acrylic acid hydrogel shows a discrete volume change [11, 12], of which the degree increases with the ratio of the acrylic acid. The ion-group introduction also brings the gel an ion capturing functionality. By noticing the function, Jacson *et al.* invented an ion sensor made of an interpenetrating {poly(vinyl alcohol)} and {*N*-isopropylacrylamid/ acrylic acid} hydrogel, which can distinguish several metal ions [13], however they did not consider the capturing efficiency.

By taking the ion-capturing efficiency into consideration, the authors have found that the ionized gel can be utilized as a heavy-metal recovery agent as described in this paper. The advantage of the ionized gel as an ion absorbent at actual use are as follows: (a) The organic hydrogel can reduce the transportation cost because the weight ratio of the captured heavy metal to that of the gel can be set much larger than that of many inorganic absorbent like zeolite. (b) Because the chemical gel is not easy to collapse in a wide condition range of temperature, pressure, pH and so on, it is possible to utilize the gel as a recovery agent in a variety of places and conditions.

As the first example for examining possibility of utilizing the ionized hydrogel as an environmental purification agent, the authors adopted the poly(acrylamide /sodium acrylate) gel (abbreviated as PAAm/SA gel) and found an enough heavy-metal recovering capability as described below. The experimental results on the heavy-metal recovery of the PAAm/SA gel is described in the first half of this paper. In addition to the ion-capturing functionality, the burden on the environment of the post-process after the ion-recovery should be also an important problem on the material selection in practical use. As one of the criteria of such selection, the authors adopted the

biodegradability of the material and were surveying bio-related and biodegradable polymers neither toxic nor expensive in addition to the heavy-metal recovery function. Recently, they have found that sodium carboxymethylcellulose (abbreviated as CMC-Na), a derivative of cellulose, can be usable for this purpose. Because the CMC-Na is colorless, odorless, nontoxic and water soluble, it is used in various scenes as an additive in detergents, soaps, food products and cosmetics and so on. In the process making the CMC-Na gel, the authors utilized γ -ray irradiation because the gel can be made without toxic cross-linker and without heating energy by this method [14-15]. The heavy-metal recovery property of the γ -ray irradiated CMC-Na gel is described in the second half of this paper.

As a model cation adopted is Cu^{2+} ion for the heavy-metal recovery amount evaluation in the present investigations of both the PAAm/SA and CMC-Na gels, and amount of captured Cu^{2+} ion was estimated by the atomic absorption spectrometry method.

2. EXPERIMENTALS AND DISCUSSIONS

In order to examine ion-capturing functionality of several PAAm/SA gel with different ingredient ratios, 700 mM pregel solutions of which the [AAm]:[SA] molar ratio = 6:1, 5:2 and 4:3 were prepared and, for initiating the gelation, 0.133 wt% of *N,N'*-methylenebis-acrylamide, 0.04 wt% of ammonium persulfate and 0.24 wt% of *N,N,N',N'*-tetramethylethylenediamine were added to the solutions. The gelation process was conducted at room temperature for 24 hrs. After then, cubic portions were cut out and immersed in pure water for 24 hrs to wash out unreacted ingredients.

To make the gel capture the cupric ion, for 24 hrs, the purified gel cubes were immersed in the cells filled with aqueous CuCl_2 solutions with different concentrations from 1 to 15 mM, then, the gel blocks were taken out from the cells. After these procedure, Cu(II) concentrations and volumes of the remainder solutions were measured; the captured Cu(II) amounts were estimated by subtracting the concentrations multiplied by the volumes from those in the preparation.

The $[\text{CuCl}_2]$ dependences of the captured Cu(II) weight at 10 g of the PAAm/SA gel before washing are shown in Fig.1: the authors compared the ion-capturing functionality in this way because the PAAm/SA gel expands in different degrees with the fraction of SA in the washing process. As can be seen from the figure, the Cu(II) adsorption increases with $[\text{CuCl}_2]$, then reaches a saturation point, which can be noticed by the arrangement of crowded data in the figure. Such dependence can be explained by a chemical equilibrium composed of carboxyl group and Cu^{2+} . The average of captured Cu(II) weight in the saturation range also shows an exponential saturation feature with SA as shown in Fig.2. In the present experiment, the [AAm+SA] weight of the [10 g, 700 mM and AAm:SA =4:3] PAAm/SA gel is ~0.58 g, while the captured Cu(II) weight is ~0.12 g in the saturation region. From this estimation, the captured Cu(II) amount is ~20wt% of (AAm+SA), which is extremely large value as an adsorbent.

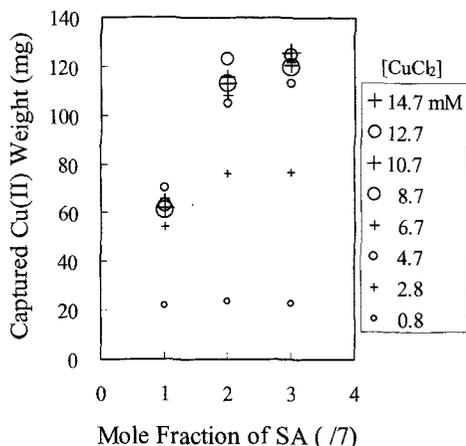


Fig. 1
Change in the captured Cu(II) weight with CuCl₂ concentration by the PAAm/SA gel of 700 mM at 10 g before washing.
Size of the data points correspond to [CuCl₂]. See also text.

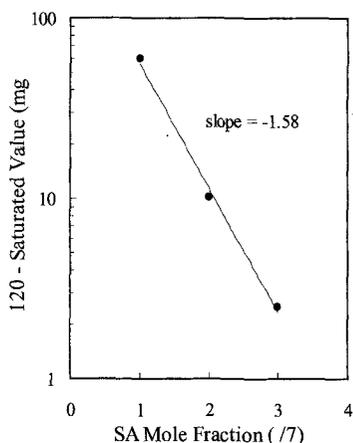


Fig. 2
Exponential saturation behavior in the average value of the captured Cu(II) weight in the saturation range of the [CuCl₂] dependence shown in Fig.1.

See also text.

Let us move to the research of the heavy metal ion adsorption of the biodegradable CMC-Na gel. The aqueous solutions of several concentrations (1~20 wt%) were made by dissolving different amounts of CMC-Na (Wako Pure Chemical Industries, D=0.7~0.8, n=460~500) in distilled water. Then γ -ray from ⁶⁰Co (~20 kGy) was irradiated to the CMC-Na aqueous solution at Koka Research Institute of the Japan Radioisotope Association. By the γ -ray irradiation, there occurred interesting features in the specimens as described below. From 1 to 6 wt% of CMC-Na concentration, γ -ray irradiation seemed no effect on the solution. In the more concentrated range of [CMC-Na] from 7 to 8 wt%, though several fluffs appeared in the solution, the

specimen kept fluidity. A remarkable change occurred in the [CMC-Na] range from 10 to 20 wt%: the specimen solidified by γ -ray irradiation, namely, the specimen became a gel indicating that the γ -ray-induced polymerization rate surpasses decomposition rate above 10wt% by a thick population of CMC-Na polymer chains [14]. Taking these feature into consideration, examined were the heavy-metal recovery functionality of the specimens with the concentrations from 10 to 20 wt% in the following experiment. The specimens for the heavy-metal recovery experiments were also formed by the ⁶⁰Co γ -ray irradiation with several doses (from 20 to 50 kGy) to the aqueous solutions (40 g) of the several CMC-Na concentrations (10 to 20 wt%) at Koka Research Institute of the Japan Radioisotope Association. Then, for ~10 hrs, the solidified parts taken out from each the specimen were immersed in distilled water to wash out unreacted ingredients. After then, weight of some of the specimens were measured before and after drying at 100 °C, by which the solidified portion fraction of the specimens were revealed to be almost same irrespective of the γ -ray dose, while, to depend on the CMC-Na concentration showing increase in a low concentration range and saturation above a certain value.

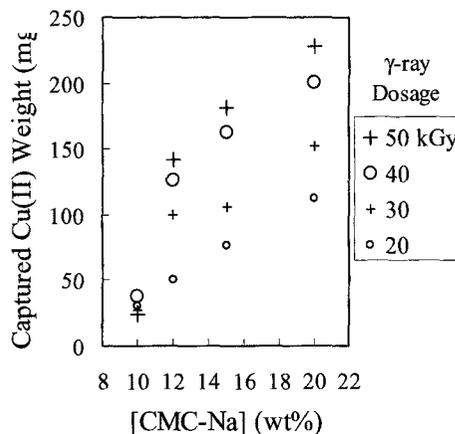


Fig. 3
Change in captured Cu(II) weight by the CMC-Na gel (at 10 g before washing) formed by γ -ray irradiation with the dose and polymer concentration.

Size of the data points correspond to γ -ray dosage. See also text.

As in the case of the PAAm/SA gel, in order to examine the heavy-metal capturing functionality of the CMC-Na gel, first, each the gel was immersed in 100 ml of 10 mM aqueous CuCl₂ solution for 120 hrs, then secondly, after taking out the Cu(II)-adsorbed gel from the experimental cell, measured were volume and Cu(II) concentration of the remainder solution in the cell. Thirdly, Cu(II) weight in each the remainder solution was also calculated by multiplying the measured volume and concentration together. Finally, captured Cu(II) weight was derived by subtracting the estimated weight in the remainder solution from that in the initial solution

mentioned above. With these procedure, the γ -ray dose dependences of the captured Cu(II) weight at 10 g of the CMC-Na gels with several concentrations were estimated as shown in Fig.3, which revealed that the captured Cu(II) weight becomes large with the CMC-Na concentration and with γ -ray dose except for the 10wt% CMC-Na gel. The facts that the captured Cu(II) weight increases with the γ -ray dosage is thought to reflect the characteristics in the Cu(II) recovery mechanism of the CMC-Na gel, which can be important in utilizing the gel for the environmental purification, however, there are almost no reports on that point of view. In the present thick aqueous solution of CMC-Na, the dosage of γ -ray causes increase in the polymer crosslinking degree of CMC-Na. The Cu(II) capturing mechanism can be clarified by considering this fact as a key to solve the problem. Seemingly, hit on are two possible mechanisms which bring about the Cu(II) capturing of the CMC-Na gel. One possible mechanism is thought to be that one copper ion is adsorbed by one carboxyl group. In that case, the captured Cu(II) weight is in proportion to the CMC-Na concentration, while the adsorbed weight should be irrelevant to the γ -ray dosage. Another possible case is thought that plural carboxyl groups participate in capturing one Cu(II), namely the chelation mechanism. In such a case, the captured Cu(II) weight will also increase with the CMC-Na concentration, namely with the carboxyl-group number, on the other hand, a clear difference with the previous case 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(II), 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, it can be presumed that which of the abovementioned two mechanisms has superiorly happened. From the present experimental results as shown in Fig.3, it seems probable that the latter mechanism superiorly occurs: 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, which is advantageous to capture Cu(II) in the mechanism like chelation with plural carboxyl groups. From the practical-use viewpoint, it should be noted that the CMC-Na gel crosslinked by the γ -ray irradiation has a Cu(II) capturing functionality, of which the extent is almost the same amount with the chemically cross-linked PAAM/SA gel (Fig.1). And also it should be recalled, that no toxic ingredients, such as AAm and *N,N*-methylenebisacrylamide, are not contained in the CMC-Na gel formed by γ -ray irradiation. In addition, the biodegradable CMC-Na gel can be disposed by a method other than incineration. Taking these merits into consideration, the CMC-Na gel can be a promising environmental purifying material which can be usable in various scenes in daily life.

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