

## Utilization of Gels for the Environmental Purification

Kazuhiro Hara, Misako Yoshigai\* and Tetsuaki Nishida\*

Institute of Environmental Systems, Faculty of Engineering, Kyushu University,  
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581 Japan

Fax: 81-92-642-3815, e-mail: haratap@mbox.nc.kyushu-u.ac.jp

\*Department of Biological and Environmental Chemistry,  
School of Humanity-Oriented Science and Engineering, Kinki University,  
11-6 Kayanomori, Iizuka 820-8555 Japan

Fax: 81-948-22-5659, e-mail: nishida@fuk.kindai.ac.jp

In order to examine possibilities of gels as a kind of environmental purifying materials, the authors have investigated ion-capturing properties of several gels. From the experimental results, it has been found that gels can be candidates for such a usage with an advantage in the {captured ion/absorbent} weight ratio.

Key words: ion capture, gels, environmental, purification

### 1. INTRODUCTION

Utilizing manufactured goods, we can live in comfort. However, an attention should be paid to the fact that the industries also give rise to a lot of wastes at the same time. In these days, remarkable increase in the wastes, which are finally stored in final landfill sites, becomes a social problem. There are three types of final landfill sites in Japan, which store wastes classified by characters such as toxicity and chemical stability, as described below [1]:

1. *Least controlled landfill site*  
stores wastes, such as stable industrial wastes such as waste plastics, rubber, metal, construction scrap wood, glass, and pottery, from which no toxic substances are estimated to exude. The wastes are simply buried in the soil.
2. *Strictly controlled type landfill site*  
stores wastes which are apt to exude toxic ingredients such as combustion residue, fly ash, sludge and slag. In order to isolate these wastes from the environment, they are confined in concrete buildings.
3. *Controlled type sanitary landfill site*  
stores less hazardous wastes than those in the strictly controlled type landfill site. Bottom of this type of landfill site is covered with waterproofing vinyl or rubber sheets not to exude the waste fluid, which is extracted from the storage and treated by a purification facility, then discharged to the environment.

Among the wastes, heavy metals cause one of the most serious social problems. Since the Ministry of Health and Welfare in Japan announced in 1968 that the discharged cadmium from Kamioka mine to the Jintsu River upstream was suspected to cause the Itai-itai disease, the heavy metal contamination became a focus of public attention in Japan [2] and the concern for heavy metal environmental pollution has been greatly

increased [3]. Under the circumstances, the effluence of heavy metals to the environment has been severely regulated and the heavy-metal-related situation has been much improved. However, though it seems that the heavy-metal effluence problem has been solved by the discharge regulations, it should be reminded that heavy metals which have already been in the environment will not disappear without any treatments [4, 5]. It can be rather said that the contaminated areas are spreading with time.

The fluid wastes containing heavy metals are classified as specially controlled industrial wastes [6], which are periodically transported to special waste fluid processing institutions from cumulus places. In the institutions, the heavy metals are precipitated as metal hydroxides [7], which are remitted to the strictly controlled type landfill site or the controlled type sanitary landfill site according to their influences on the environment [6]. Although these treatments are performed with the prescripts of the Ministry of the Environment, they are afraid that there occur damages to shielding ability of the final landfill sites by the acid rain: At the least controlled landfill site, stable heavy-metal compounds can react to the acid rain, dissolve and flow out of the landfill site. At the strictly controlled type landfill site, the heavy metals can also flow out through cracks in the concrete wall caused by reaction to the acid rain. At the controlled type sanitary landfill site, there is a possibility that a detrimental heavy metals can flow out through tears of the waterproofing sheet.

In order to stop the heavy metal diffusion in the environment, recovery and fixation systems should be necessary. In the case of the heavy metal waste recovery, the utilized agents should be easily handled and the recovery process should be conducted without any special equipment. Besides, the captured heavy metals should be easily transported to post-process institutions. Furthermore, it should not generate carbon dioxide and

detrimental gas in the process separating heavy metals from the recovery agent. In these circumstances, the authors consider that ionized gels can be a most suitable heavy-metal recovery agent and have been investigating their properties.

Gel is a two-component system composed of three-dimensional network and solvent, of which properties are much influenced by the interaction between the components [8]. For example, with elevating temperature from room temperature, an *N*-isopropylacrylamide hydrogel exhibits a continuous reduction up to 36°C due to a change in the nature, from hydrophilic to hydrophobic, of the *N*-isopropylacrylamide group. By introducing ionic-group to the network, the reduction is considerably affected by the Donan potential [9]; an *N*-isopropylacrylamide/acrylic acid copolymer hydrogel is a typical example because the acrylic-acid-group can be easily ionized, which causes a considerable discrete volume change at a higher transition temperature than that of the *N*-isopropylacrylamide hydrogel [10, 11]. This interesting phenomenon is well known as a volume phase transition [9, 12]. It is also known that a polymer which has ionic groups in the side chains can trap ions; multivalent-ion capture with chelation mechanism is a typical case. With utilizing this feature, Jacson et al. invented an ion sensor made of an interpenetrating {poly(vinyl alcohol)} and {*N*-isopropylacrylamide/acrylic acid} hydrogel, which can distinguish several metal ions [13].

The authors estimate that the ionized gel can be also utilized as a heavy-metal recovery agent. Merits of the utilizing ionized gels are:

- i. Organic hydrogel can reduce the cost for conveyance, since the {captured heavy metal / recovery agent} weight ratio is much larger than that of inorganic substances like zeolite.
- ii. Because the network of organic chemical hydrogel is mainly formed by covalent bonds, the chemical gel is proof against to wide-range condition changes such as temperature, pressure, which is advantageous as a recovery agent usable in various conditions.

Under these circumstances, the authors adopted the poly(acrylamide/sodium acrylate) co-polymer gel (abbreviated as PAAm/SA gel) as the first specimen for examining possibility of utilization of the ionized hydrogel for the environmental purification. As described below, we have observed that the PAAm/SA gel has an enough capability of recovering heavy metal. The first half of this paper is allotted to the experimental results on the heavy-metal recovery of the PAAm/SA gel.

The authors have been also aware that a post-recovery process should be important in order to establish the new environment purification technique, for which a good choice of recovery agents seems essential. With this viewpoint, we surveyed bio-related and biodegradable polymers neither toxic nor expensive, as well as the capability of the heavy-metal recovery, and found sodium carboxymethylcellulose (abbreviated as CMC-Na) can be a candidate for that purpose. The

CMC-Na is a derivative of cellulose, which is colorless, odorless, nontoxic and water soluble. With these properties, it has been used in detergents, soaps, food products, and cosmetics, etc. It should be also noted that the authors have utilized the  $\gamma$ -ray irradiation method for preparing CMC-Na gel because gelation can be performed without toxic cross-linker and at room temperature [14-15]. The latter half of this paper is assigned for the heavy-metal recovery property of the  $\gamma$ -ray irradiated CMC-Na gel.

In order to examine the heavy-metal recovery ability of both the specimens, we adopted  $\text{Cu}^{2+}$  ion as a model cation, and amount of  $\text{Cu}^{2+}$  ion adsorption was estimated by the atomic absorption spectrometry method.

## 2. EXPERIMENTALS AND DISCUSSIONS

### PAAm/SA Gel

Several 700 mM PAAm/SA pregel solutions were prepared, of which the molar ratios of [AAm]:[SA]'s are 6:1, 5:2 and 4:3, respectively. Then, gelation was conducted at room temperature for 24 hrs after adding 0.133 wt% of *N,N'*-methylenebisacrylamide (crosslinking agent), 0.04 wt% of ammonium persulfate (polymerization initiator) and 0.24 wt% of *N,N,N',N'*-tetramethylethylenediamine (reaction accelerator) to the pregel solutions. After the gelation, 10 g cubic portions were cut out and immersed in pure water for 24 hrs in order to wash out unreacted ingredients.

The purified cubic gel blocks were immersed in aqueous  $\text{CuCl}_2$  solutions with concentrations in a range from 1 to 15 mM for 24 hrs in order to measure the concentration dependence of the cupric ion adsorption. After removing the cupric-ion adsorbed gels from the cells, concentrations (by atomic absorption spectrometry) and volumes of the remaining solutions were measured. The amounts of the adsorbed cupric ion were estimated by subtracting the concentrations multiplied by the volumes from the initial amounts of cupric ion before the immersion of the cubic gel blocks.

Figure 1 shows  $[\text{CuCl}_2]$  dependence of the recovered  $\text{Cu}^{2+}$  weight to 10 g of each the pregel solution. The authors adopted this expression to express definitely amount of the AAm and SA in the recovery experiments because the PAAm/SA gel expands in a different degree with the composition ratio of AAm to SA in the washing in pure water. As can be seen from Fig.1, the  $\text{Cu}^{2+}$  adsorption increases with  $[\text{CuCl}_2]$  and reaches saturation point, of which the amount differs with AAm/SA ratio. Figure 2 depicted SA mole fraction dependence of the average amount of the saturated  $\text{Cu}^{2+}$  adsorption, of which the dependence can be explained by a chemical equilibrium composed of carboxyl group and  $\text{Cu}^{2+}$ .

From these experimental results, it should be noted that the amount of adsorbed  $\text{Cu}^{2+}$  per adsorbent weight is much larger than that by other method, for example, which utilizes zeolite or ion-exchange resins. In the case of the present 700mM PAAm/SA gel with AAm:SA=4:3, the amount of (AAm+SA) is ~0.58 g while adsorbed  $\text{Cu}^{2+}$  amount is ~0.12 g, namely ~20wt% of (AAm+SA) of  $\text{Cu}^{2+}$  can be captured, which is extremely large value as an adsorbent.

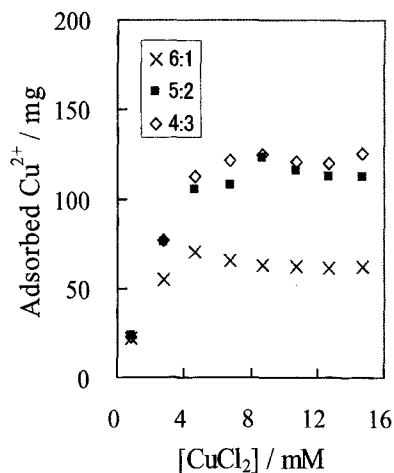


Fig. 1  
CuCl<sub>2</sub> concentration dependence of the recovered Cu<sup>2+</sup> weight to 10 g of the PAAm/SA (700 mM) pregel solution.  
The symbols, ×, ■ and ◇ denote the data of the PAAm/SA gels with molar ratios AAm:SA=6:1, 5:2, 4:3, respectively.

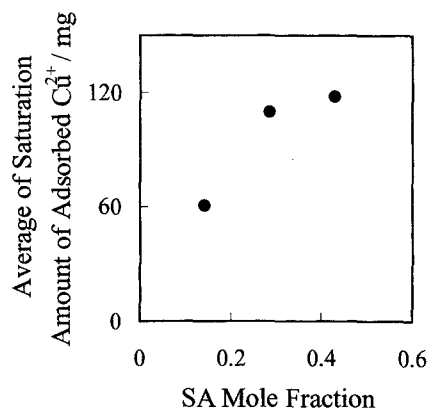


Fig. 2  
SA mole fraction dependence of the average amount of the saturated Cu<sup>2+</sup> adsorption of the 700mM PAAm/SA gel.

CMC-Na Gel

Aqueous solutions of 40 g with different concentrations (1~20 wt%) were prepared by dissolving CMC-Na (Wako Pure Chemical Industries, D=0.7~0.8, n=460~500). Then γ-ray irradiation (~20 kGy) from <sup>60</sup>Co was conducted at Koka Research Institute of the Japan Radioisotope Association.

In a CMC-Na concentration range from 1 to 6 wt%, almost no change happened by irradiating γ-ray, and from 7 to 8 wt%, several fleecy deposits were observed after the γ-ray irradiation, however, almost of all parts of the specimen were in a liquid state. There occurred drastic change in a [CMC-Na] range from 10 to 20 wt%: most of the specimen became solidified by γ-ray irradiation. Therefore, we adopted specimens of CMC-Na concentrations from 10 to 20 wt% for the heavy-metal recovery examination. The feature that the

gel can be formed in the [CMC-Na] range higher than 10 wt% by γ-ray irradiation indicates that the rate of γ-ray induced polymerization is superior to that of the decomposition above 10wt% by dense configuration of CMC-Na polymer chains [14].

The CMC-Na gels for the heavy-metal recovery experiments were also prepared by the <sup>60</sup>Co γ-ray irradiation at Koka Research Institute of the Japan Radioisotope Association. Forty grams of aqueous CMC-Na solutions with the concentrations from 10 to 20 wt% were γ-ray irradiated with doses from 20 to 50 kGy. After the irradiation, portions from each the solidified specimens were took out and immersed in pure water for ~10 hrs to wash out un-gelled ingredients. Then, in order to measure the gelled ingredient ratio, weights of the specimens were measured before and after drying at 100 °C. By these measurements, it is observed that the solidified portion fraction shows almost no change with the γ-ray dose, while that it increases and reaches saturation with [CMC-Na].

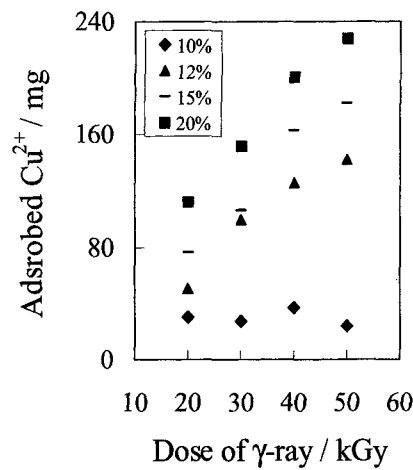


Fig. 3  
Cu<sup>2+</sup> recovery of CMC-Na gel made by γ-ray irradiation. In the figure, γ-ray dose dependence of adsorbed Cu<sup>2+</sup> amount to 10 g of CMC-Na gels is depicted at several CMC-Na concentrations. (see also text)  
The symbols, ◇, ▲, - and ■ denote the data of [CMC-Na]'s at 10, 12, 15, and 20 wt%, respectively, in the pregel aqueous solutions.

In the Cu<sup>2+</sup> recovery examination, each the CMC-Na gel was immerse in an experimental cell which contains 100 ml of 10 mM aqueous CuCl<sub>2</sub> solution for 120 hrs, then, as in the case of the PAAm/SA gel, Cu<sup>2+</sup> concentration of the residue solution in the cell was measured by the atomic absorption spectrometry after removing the Cu<sup>2+</sup>-adsorbed gel. Cu<sup>2+</sup> mounts in the residual solution were estimated by calculating product of the measured concentration and the residual solution volume. Finally, by subtracting this quantity from that before the gel immersion, the adsorbed amounts to the gel were estimated. The γ-ray dose dependences of the

estimated adsorbed amount of  $\text{Cu}^{2+}$  to 10 g of the CMC-Na gel at several concentrations are shown in Fig.3. As can be seen from the figure, it has been observed that the adsorbed  $\text{Cu}^{2+}$  amount increases with the concentration of CMC-Na. It should be also noted that the adsorbed  $\text{Cu}^{2+}$  amount also increases with dose of  $\gamma$ -rays except for the case of the 10w% gel.

As mentioned above, the adsorbed  $\text{Cu}^{2+}$  amount becomes large with [CMC-Na] and dose of  $\gamma$ -ray, which can reflect the  $\text{Cu}^{2+}$  adsorption mechanism of the CMC-Na gel. Let us discuss on the  $\text{Cu}^{2+}$  adsorbing mechanism. As is described above, the interaction fashion between carboxyl groups and  $\text{Cu}^{2+}$  can be most important in the recovery process with gels, however, there is almost no information on that point. In our estimation, two mechanisms can be possible. One possible recovery mechanism is the case where one  $\text{Cu}^{2+}$  is adsorbed by one carboxyl group; the adsorbed  $\text{Cu}^{2+}$  amount will increase with number of carboxyl group while the adsorption amount can be independent of CMC-Na polymer crosslinking degree. Another possible recovery mechanism is the case where two or more carboxyl groups take part in the  $\text{Cu}^{2+}$  recovery such as chelation; the amount of adsorbed  $\text{Cu}^{2+}$  will also increase with the number of carboxyl group. However, a different feature can occur in crosslinking degree dependence of the  $\text{Cu}^{2+}$  absorption amount. In this case, because more than one carboxyl groups participate in capturing one  $\text{Cu}^{2+}$ , spatial arrangement of the carboxyl groups should exert great influence on the  $\text{Cu}^{2+}$  recovery amount. The present experimental results support the latter mechanism as shown in Fig.3. Because [CMC-Na] of the CMC-Na gel is larger than 10wt% where the  $\gamma$ -ray polymerization rate is superior to that of decomposition as mentioned above, more dose of  $\gamma$ -ray should cause higher crosslinking degree which induces more rigid and close configurations between the CMC-Na network polymers and, as a result, more effective  $\text{Cu}^{2+}$  recovery.

The CMC-Na gel formed by the  $\gamma$ -ray irradiation has been revealed to exhibit  $\text{Cu}^{2+}$  recovering ability to almost the same extent as PAAm/SA gel (Fig.1). It should be recalled that  $\gamma$ -ray irradiated CMC-Na gel contains no toxic ingredients, such as AAm and *N,N'*-methylenebisacrylamide. Besides, because the CMC-Na is also biodegradable, the CMC-Na gel will give a new disposal method other than incineration. Taking this feature into consideration, recovery agents of this type should be very valuable.

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