Heavy-Metal-Anion Adsorption and Desorption Properties of \(N,N\)-Dimethylaminoethylacrylamide/Acrylamide Gels

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The authors have investigated heavy-metal-anion (hexavalent chromium, \(\text{Cr(VI)}\)) adsorption and desorption properties of \(N,N\)-dimethylaminoethylacrylamide/acrylamide (DMAEAAm/AAm) gels successively. Though the DMAEAAm/AAm gels show relatively low \(\text{Cr(VI)}\)-capturing efficiencies, the hydrogels have a possibility of actual use as a heavy-metal-anion recovering material because the DMAEAAm/AAm gels with some compositions show high desorption efficiency of the captured-\(\text{Cr(VI)}\), which is advantageous to a heavy-metal-anion recycling system with repetitive use of the hydrogel.

Key words: recyclable, heavy metal anion, recovery, environment, \(N,N\)-dimethylaminoethylacrylamide gel

1. INTRODUCTION

Triggered by the \textit{Itai-Itai} Disease in 1968, the heavy-metal pollution received a great deal of public attention \cite{1}. Therefore, the discharge of the heavy-metal wastes into the environment has been strictly regulated; and their pollution becomes much reduced in these days. However, the heavy metals themselves will not crumble to nothingness nor become harmless automatically. In fact, the polluted areas can become larger by diffusion \cite{2}. In such a situation, prompt emergency treatment to recover the heavy metals should be important in order to block their spread. Under the circumstances, the authors have considered that some hydrogels can be utilized as the quick heavy-metal recovering materials because, as mentioned in the following sections, they can capture the hazardous heavy metals with high efficiency. However, the authors have also noticed several problems for practical use on the post-processing of the hydrogels after use: the hydrogels themselves can be thorny wastes with inappropriate treatments, therefore, reusable adsorbents are desirable from the viewpoint of resource saving and less repository-site possession. It should be noticed that the hydrogel’s reusability indicates the necessity of the captured-heavy-metal desorption, preferably by simple treatments.

By attaching functional-group side chain to the backbone of network polymer, the hydrogels show interesting properties \cite{3}. Some hydrogels capture the heavy metals by introducing ionized group in the side chain. By utilizing this functionality, Jacson \textit{et al.} developed a metal-ion detecting hydrogel made of interpenetrating poly(vinyl alcohol) and NIPA/AAc \cite{4}, however, they did not mentioned the capturing efficiency in spite of its importance. In contrast, the authors have noticed the high heavy-metal capturing efficiency of the hydrogels and the great advantage as an environment purifying material. Since then they have been investigating the heavy-metal capturing efficiency of some hydrogels, as mentioned below.

Since the authors found the high heavy-metal-adsorption efficiencies of the some hydrogels (estimated \(-20wt\% of network polymer in the case of poly(acrylamide/ sodium acrylate) [PAAm/SA] gel \cite{5}) over other adsorbents, they have been studying the heavy-metal capturing property \cite{5-9}: in the early stages, mainly on the hydrogels which captures heavy-metal cations \cite{5}. However, because there are also harmful heavy-metal anions which are notorious for causing the environment pollution, such as AsO\(_4^{3-}\), Cr\(_{2}O_{7}^{2-}\) and SeO\(_2^{2-}\), they have been also developing heavy-metal-anion capturing gels and investigating their capturing efficiency \cite{6-9}.

As the first examination of the heavy-metal-anion capturing property of hydrogels, copolymer gels of dimethylaminoethylmethacrylate quaternised with methylchloride (DMAEAMA-MeCl) and acrylamide (AAm) was adopted as the adsorbent \cite{6}. In the examinations, their high heavy-metal-anion capturing efficiency and a possibility as an environment purifying material were revealed \cite{6}: the amounts of the captured heavy-metal anions by the DMAEAMA-MeCl/AAm gels \cite{6} are higher than PAAm/SA \cite{5} and CMC-Na \cite{5} gels, which capture...
heavy-metal cations, and needless to say, higher than other adsorbents such as zeolite, ion-exchange resins.

Next, in order to examine the hydrogels' structural effect on the heavy-metal-anion capturing property, the authors measured the heavy-metal-anion capturing amount of dimethylaminoethylacrylate-methylchloride (DMAEAmMeCl) / acrylamide (AAm) gels [7]. The structural difference between DMAEAmMeCl/AAm gels and DMAEA-MeCl/AAm gels are only on the side-chain group in the opposite side of the functional group across the main chain: hydrogen in the DMAE-A-MeCl/AAm gels and methyl-base in the DMAEAm-MeCl/AAm gels. In the investigations, it was observed that the Cr(VI)-capturing behaviors with changing the functional-part ratio and total network concentration are similar to those of the DMAEAm-MeCl/AAm gels: The recovered Cr(VI) amount increases with DMAEAm-MeCl molar ratio in the lower ratio range while the fashion becomes saturated in the higher DMAEAm-MeCl molar ratio region, besides the similar trends can be also confirmed in the total network concentration dependences [7]. In addition to the above-mentioned features, it is noteworthy that that the Cr(VI)-adsorbing efficiency of the DMAEAm-MeCl/AAm gels are clearly surpass those of the DMAEAm-MeCl/AAm gels [7], which may come from the difference in the network configuration.

Then, the authors investigated Cr(VI)-capturing property of the copolymer gels of N,N-dimethylaminoethylacrylamide (DMAEAm) and AAm in order to make clear the role of the terminal group [8]: the structure of DMAEAm is almost identical with DMAEAm-MeCl except for polarizing terminal group in the side chain. In the investigations, it was found that the DMAEAm/AAm gels capture ~1/2 the amount of Cr(VI) that the DMAEAm-MeCl/AAm gels adsorb, which indicates an important role of the terminal group. Though the Cr(VI)-capturing efficiencies of the DMAEAm/AAm gels are low compared with those of the DMAEAm-MeCl/AAm gels, they are still larger than those of other adsorbents such as zeolites or ion-exchange resins.

Then, the author explored another aspect of the side-chain substitution effect terminal-group by examining the heavy-metal-anion capturing features of the copolymer gels of AAm and N,N-dimethylamino-propylacrylamide (DMAPAA) [9]. The structure of DMAPAA is almost identical with DMAEAm except for the number of alkylene groups (2 in DMAEAm and 3 in DMAPAA) from the main chain to the terminal group. In the investigation, the largest Cr(VI) capturing amount was found in the DMAPAA/AAm gels among the heavy-metal capturing gels which the authors investigated [5-9]. Because the polarization intensity of the side-chain terminal group of the DMAPAA/AAm gel (tertiary amine group) is not higher than that of the DMAEAm-MeCl gel (quaternary ammonium group), the number of alkylene groups are also thought to play an important role in the ion-capturing mechanism.

Because the total recovering performance cannot be determined only by the capturing functionality but also by the desorption one, the authors have considered that the low Cr(VI)-capturing functionality of the DMAEAm/AAm gels should not be an inconclusive factor for the actual use. Under these circumstances, aiming at actual use, the author investigated the DMAEAm/AAm gels more comprehensively in the present study by examining Cr(VI)-adsorption and adsorbed-Cr(VI)-desorption successively.

2. EXPERIMENTALS

In the same way as the previous studies [6-9], an aqueous solution of chromium trioxide is adopted as a model fluid which contains heavy-metal anion because the hexavalent chromium oxoanions CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ occur without any treatment. In order to examine the heavy-metal-anion capturing functionality of the DMAEAm/AAm gels, prepared were the pre-gel solutions of which the molar ratios in a range from [DMAEAm]:[AAm]=1:6 to 6:1, and the total polymer concentrations, from 0.7M to 2.1M. Also, as a cross-linker, 0.133 wt% of N,N-methylenediacrylamide (BIS) was added to each the pre-gel solution. In order to initiate the gelation, 0.04wt% of ammonium persulfate was put into each the pre-gel solution with BIS, which was left intact for 24 hrs at room temperature. After the solution solidified, cubic portions of 1g (~1x1x1cm$^3$) were cut out and immersed in pure water for 24 hrs in order to wash out unreacted ingredients.

- Adsorption experiments

In the experiments of examining the DMAEAm/AAm gel’s hexavalent-chromium oxoanion capturing functionality, each the purified gel cube was immersed in a cell filled with 40 mL of aqueous 16.8 mM CrO$_3$ solution 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 (Hitachi High-Technologies, Z-2000). The amount of captured-Cr(VI) by each the gel was derived by subtracting the measured (concentration x volume) from the ingredient weight in the pre-gel solution.

- Desorption experiments

For examining the DMAEAm/AAm gel’s Cr(VI)-desorption property, each the Cr(VI)-adsorbed gel cube was put in a cell filled with 40 mL of aqueous 3 M NaOH solution for 24 hrs. During this period, the captured-Cr(VI) desorbed from the gel cubes. After the period, the Cr(VI)-desorbed gels were carefully taken out from the cells; then the Cr(VI)-concentration and volume of each the remaining solution in each the cell was measured by the atomic absorption spectrometer (Hitachi High-Technologies, Z-2000).

Similar to the procedure of the Cr(VI)-adsorption amount measurements, the amount of the desorbed-Cr(VI) was derived by the concentration multiplied by volume; and then the adsorption ratio was calculated by dividing the desorbed Cr(VI) weight by the adsorbed one obtained in the adsorption experiments.

3. RESULTS

- Adsorption of Cr(VI)

Figures 1 and 2 show DMAEAm-fraction and...
total-polymer-concentration dependences of recovered Cr(VI) weight at 1 g of the pre-gel solutions, respectively. In the similar manner to the previous studies [6-9], the authors adopted this description to express definitely the amount of the DMAEAAm and AAm in the respective gels because the DMAEAAm/AAm gels expands in a different degree with the DMAEAAm composition ratio to AAm in the rinsing procedure in pure water.

In accordance in the previous study [8], the recovered-Cr(VI) amounts are smallest among the hydrogels which the authors investigated, however the amounts are still larger than other adsorbents. As can be seen from Figs. 1 and 2, the recovered-Cr(VI) weight increases with total network concentration, irrespective of the DMAEAAm-fraction.

As for the DMAEAAm-fraction dependence of the recovered-Cr(VI) amounts, a saturation feature was observed; the capturing amounts are almost independent of DMAEAAm-fraction in the DMAEAAm/AAm gels of which the total network concentration is 2.1 M, while those of the 0.7 and 1.4 M hydrogels increase with the DMAEAAm-fraction towards the capturing amounts of the 2.1 M hydrogels. The capturing amounts of the 1.4 M hydrogels reach the saturated amounts with the smaller DMAEAAm-fraction than those of the 0.7 M hydrogels; and around 72–86 mol% DMAEAAm-fraction range, the capturing amounts of the 1.4 M hydrogels become almost the same with those of the 2.1 M hydrogels.

- **Desorption of Cr(VI)**

Figures 3 and 4 show DMAEAAm-fraction and total-polymer-concentration dependences of the desorbed-Cr(VI) weight ratios, respectively. As can be seen from Figs. 3 and 4, irrespective of the DMAEAAm-fraction, the Cr(VI)-desorption ratio decreases with total network concentration.

As for the DMAEA-fraction dependence of the Cr(VI)-desorption ratios, the desorption ratios show a very weak DMAEA-Am-fraction dependence in all the 2.1M hydrogels and also in the 0.7 M hydrogels with the DMAEAAm-fraction smaller than ~70 mol%, while those of all the 1.4 M hydrogels and the 0.7 M hydrogels with the DMAEAAm-fraction larger than ~70 mol% decrease with the DMAEAAm-fraction towards the desorption ratios of the 2.1 M hydrogels. The desorption ratios of the 0.7 M hydrogels show very large change with the DMAEAAm-fraction and the ratios become almost the same values with those of the 1.4 M hydrogels around ~86 mol% in the DMAEAAm-fraction.

4. DISCUSSIONS

The final target of the authors’ study on the hydrogels’ adsorption and desorption of heavy metals is to develop a new environment-friendly heavy-metal-recovery process which resolves the current social problems on the landfill-site-depletion and the heavy-metal-resource drain. In order to build up such a new process, it may be necessary to weave a recycle system of the adsorbent as well as the target material, namely heavy metals; otherwise a mass of used adsorbent will turn into enormous amount of wastes, which will bring on another social problem being contrary to the initial thrust. In the heavy-metal recycling system which the authors are planning, the heavy metals in the waste fluid are captured by a hydrogel as the first step. Then, the heavy-metal-adsorbed hydrogel is treated in the heavy-metal-desorption process, in which the captured heavy metal and the adsorbent hydrogel are separated. The released heavy metals are used again as a feedstock while the heavy-metal-desorbed hydrogel is revitalized and reused to capture again the heavy metals in waste fluid. In this way, the recycle of both the waste...
heavy-metals and the hydrogel adsorbent can be realized at the same time.

The fundamental functionalities of the above-mentioned heavy-metal recovery system are the heavy-metal adsorption and desorption. Therefore, in order to examine heavy-metal-anion recovering functionality of the DMAEAAm/AAm gels, the authors carried out the Cr(VI)-adsorption and successive adsorbed-Cr(VI)desorption investigations of the DMAEAAm/AAm gels in the present study.

Because the recovery functionality is determined by the overall performance in a series of adsorption and desorption processes, it is necessary to estimate both of these processes comprehensively. If the desorption ratio of some hydrogel is high enough for practical use, it can be utilized as heavy-metal recovery materials even though its Cr(VI)-adsorption efficiency is relatively low because the hydrogel can recover enough amount of heavy metals by the repetition of the adsorption and desorption processes. On the other hand, if the desorption ratio is low, the hydrogel cannot be available as a heavy-metal recovery material because the hydrogel may stock up heavy metals inside; the situation may become even worse if its Cr(VI)-adsorption efficiency is high.

In the present investigations, as a whole, the DMAEAAm/AAm gels with high Cr(VI)-capturing efficiencies show low desorption ratios. From the point of view on the Cr(VI)-desorption, the DMAEAAm/ AAm gels of which the DMAEAAm-ratio is in a range 14~60 mol% and total polymer concentration below 0.7 M are suitable for the present purpose as shown in Figs. 3 and 4. Therefore, by taking additional consideration of the adsorption efficiency (Figs. 1 and 2), the DMAEAAm/AAm gels with ~60 mol% in DMAEAAm-ratio and ~0.7 M in total polymer concentration are most suitable for the recyclable Cr(VI)-recovery purpose.

In the present study, the authors have acquired a guideline for getting the recyclable heavy-metal-anion recovery materials. However, the examinations in the present study has been carried out in somewhat simple conditions, therefore, those in more realistic conditions are desired for the practical environment-purification use, some of which are in progress by the authors.

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