pH-Effect on Heavy-Metal Adsorption and Desorption of Sodium acrylate/Acrylamide and \(p\)-Styrenesulfonicacidsodiumsalt/Acrylamide Gels

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pH-dependences of Ni(II)-adsorbing and -desorbing properties of \(p\)-styrenesulfonicacidsodiumsalt/acrylamide (\(p\)-SSAS/AAm) and sodium acrylate/acrylamide (SA/AAm) gels have been investigated. Though the \(p\)-SSAS/AAm gel can capture more amount of Ni(II) even at a low pH region, its desorption ratio is below \(
\sim 92\) wt% even in \(3\) M of HCl concentration. On the other hand, though Ni(II)-capturing efficiencies of the SA/AAm gel is lower; its Ni(II)-desorption ratio is \(
\sim 100\) wt% in all the measured HCl concentrations.

Key words: gel, heavy metal cation adsorption, pH dependence, Sodium acrylate, \(p\)-Styrenesulfonic acid sodium salt

1. INTRODUCTION

As well as heavy metals are famous as indispensable materials for industry, they are notorious for their toxicity by which once many environment pollution issues occurred in Japan [1]. With much of the efforts by all parties concerned, the environment pollution by the hazardous heavy metals is improved to a great extent in these days. However, it should be remembered that the heavy metal cannot be nontoxic by itself nor perish spontaneously. In a sense, it can be said that the heavy metals can spread by diffusion [2]. Owing to this circumstance, an easy and effective recovery method has been desired; therefore, the authors have measured some hydrogels’ heavy-metal-capturing functionalities useful for the environment purification as described below. The hydrogels show valuable properties by introducing functional groups [3], some of them can capture the heavy metals. By utilizing this property, Jacson et al. developed a metal-iodetecting hydrogel [4]. However, they did not notice its capturing efficiency. The authors recognized its importance and have been investigating the heavy-metal capturing efficiency of the hydrogels [5-9].

The captured-Cu(II) efficiency of sodium acrylate/ acrylamide (SA/AAm) gel is \(\sim 20\) wt% of the network polymer [5] and that of sodium carboxymethylcellulose (CMC Na) gel is comparable to the SA/AAm gel [5]. The heavy-metal anion capturing gels have been also investigated [6-9] by authors and it was observed that their heavy-metal capturing efficiencies are larger than those of SA/AAm and CMC-\(\text{Na}\) gels. Though some hydrogels can effectively capture hazardous heavy metals compared with other adsorbents such as zeolites as mentioned above, there are some problems for practical applications. Among them, that on the hydrogel’s post-processing after the adsorption is thought to be serious because the hydrogel itself will be a waste by unsuitable treatments. In order to solve this problem, the authors thought of the repetitive reuse of the hydrogels, which can be serviceable for both the resource saving and less repository-site possession. Along this line, the authors have been investigating the heavy-metal adsorption and desorption properties of the hydrogels.

In the present study, pH-dependence of Ni(II)-adsorption and -desorption properties of \(p\)-styrenesulfonicacidsodiumsalt/acrylamide (\(p\)-SSAS/AAm) and sodium acrylate/acrylamide (SA/AAm) gels have been investigated in order to examine the conditions in practical uses as environment purifying materials as well as the terminal group effect.

2. EXPERIMENTALS AND RESULTS

\* Adsorption experiments at a fixed pH

The pre-gel solutions of which the molar ratios in a range from [\(p\)-SSAS or SA] : [AAm] = 1 : 6 to 6 : 1; and the total polymer concentrations, from 0.7 M to 2.1 M were prepared to begin with. Next, as a cross-linker, 0.133 wt% of \(N,N'\)-methylenebisacrylamide (BIS) was added to each the pre-gel solution. Then, in order to initiate the gelation, 0.04 wt% of ammonium persulfate was put into each the pre-gel solution after adding BIS. After then, the pre-gel solutions were left intact for 24 hrs at room temperature. After the period, cubic portions of \(\sim 1 \times 1 \times 1\) cm\(^3\) (\(\sim 1\) g) were cut out and im-
The authors immersed a gel cube in an experimental cell filled with a 40 ml aqueous NiCl₂ solution of 9.09 mM (pH~4.6) for 24 hrs in order to wash out unreacted ingredients. The Ni(II)-concentration of the remainder solution was measured by an atomic absorption spectrometer. Finally, the amount of captured Ni(II) was derived by subtracting the measured (concentration × volume) from the ingredient weight in the pre-gel solution.

Figures 1 and 2 show p-SSAS- and SA-fraction dependences of captured Ni(II) weight at 1 g of the pre-gel solutions of the p-SSAS/AAm and SA/AAm gels with different total network concentrations, respectively. In the similar manner to the previous studies [6-9], the authors adopted this description to express definitely the amount of the p-SSAS, SA and AAm in the respective gels because the p-SSAS/AAm and SA/AAm gels expand in different degrees with the p-SSAS- or SA-fraction ratios to AAm in the rinsing procedure in pure water. As can be seen from the figures, these experimental results demonstrate that the p-SSAS and SA work sufficiently as a heavy-metal cation capturer in the polymer network of both the copolymer gels: as a whole, the captured-Ni(II) amounts increase with p-SSAS- and SA-fractions, while the capturing amount shows a hill-shaped dependence on the total concentration with a maximum around 1.4 M.

Adsorption experiments with changing pH

In the Ni(II)-capturing experiment at pH~4.6 described above, the captured-Ni(II) amounts are found to be maximized at 85.7 mol% in p-SSAS- and SA-fractions, and 1.4 M in total network concentration in the measured ranges. Though this information can be helpful, for the practical use of the hydrogels as an environment purifying material, it should be additionally necessary to examine more of environmental condition effects on the capturing property. Among them, the effect of pH can be most important because of the direct relation to the Ni(II)-capturing mechanism. Therefore, the authors further measured the pH dependence of the Ni(II)-capturing amount of the p-SSAS/AAm and SA/AAm copolymer gels with compositions of 85.7 mol% in p-SSAS- and SA-fractions, and 1.4 M in total network concentration, at which the hydrogels show maximum Ni(II)-adsorptions in the previous experiments.

For examining the pH dependence of the Ni(II)-adsorption property of the prepared p-SSAS/AAm and SA/AAm copolymer gels, each the purified gel cube was immersed in a cell filled with a 40 ml aqueous NiCl₂ solution (~9.09 mM) of which the pH was adjusted from 1 to 8 by adding appropriate amounts of HCl and NaOH. Then the specimens were left at rest for 24 hrs at room temperature. After the period, the hydrogel cubes were carefully taken out from the cells; and then, the Ni(II) concentration and volume of each the remainder solution was measured: the Ni(II) concentration of the remainder solution was measured by the above-mentioned atomic absorption spectrometer. Finally, the amount of captured Ni(II) was derived by subtracting the measured-concentration multiplied by the measured-volume from the ingredient weight in the pre-gel solution.

Figure 3 shows pH dependences of the Ni(II) amount adsorbed by p-SSAS/AAm and SA/AAm copolymer gels of 85.7 mol%’s in p-SSAS- and SA-fractions and 1.4 M’s in total network concentrations, respectively. As can be seen from Fig. 3, the adsorbed-Ni(II) amounts show drastic decreases below certain pH’s: 2 in the p-SSAS/AAm gel and 3 in the SA/AAm gel, respectively. The feature indicates that the p-SSAS/AAm gel can capture Ni(II) in more acidic condition than the
SA/AAm gel reflecting the acidity of the functional groups of the hydrogels.

- Desorption experiments with changing pH

By taking into consideration the abovementioned resource saving and less repository-site possession, the pH effect on the Ni(II) desorption is still important because the hydrogels should be used repeatedly with a series of the adsorption and desorption processes in order to accomplish the purposes. Therefore, the authors also investigated the pH dependences of the desorption ratios of the p-SSAS/AAm and SA/AAm gels after the Ni(II)-capturing treatments.

In the same manner as the previous sections, after the preparation of the p-SSAS/AAm and SA/AAm gel cubic portions (~1×1×1 cm³, ~1 g), 85.7 mol% of p-SSAS- or SA molar ratio, 1.4 M of total polymer concentration; the hydrogel cubes were rinsed in pure water for 24 hrs. Then, each of them was immersed in an experimental cell filled with a 40 ml aqueous NiCl₂ solution of 9.09 mM (pH~4.6) for 24 hrs. After the period, the hydrogel cubes were carefully taken out from the cells. After these procedure, Ni(II)-concentration and volume of each the remainder solution was measured.

For examining the pH dependence of p-SSAS/AAm and SA/AAm gel’s Ni(II)-desorbing property, each the Ni(II)-adsorbed gel cube was put in an experimental cell filled with a 40 ml aqueous HCl solution with concentration from 0.5 to 3 M for 24 hrs. During this period, the captured-Ni(II) desorbed from the gel cubes. After then, the Ni(II)-desorbed gels were carefully taken out from the cells. Then, Ni(II)-concentration and volume of each the solution in the cell was measured by the same atomic absorption spectrometer mentioned above. The desorbed Ni(II)-amount was derived by (concentration × volume), similar to the previous experiments. Finally, the adsorption ratio was derived by dividing the desorbed-Ni(II) amount by the Ni(II)-adsorbed one measured in the previous experiments.

Figure 4 shows the HCl-concentration dependences of the Ni(II) desorption ratios of the Ni(II)-adsorbed p-SSAS/AAm and SA/AAm gels. As can be easily seen from Fig. 4, the Ni(II)-desorption ratio of the p-SSAS/AAm gel is always less than that of the SA/AAm gel. The desorption ratio of the p-SSAS/AAm gel is below ~92 wt% even at 3 M in HCl concentration. By contrast, the Ni(II)-desorption ratio of the SA/AAm gel is ~100 wt% in all the measured HCl-concentration range.

3. DISCUSSIONS

As can be seen from Figs. 1 and 2, the p-SSAS/AAm and SA/AAm gels can effectively capture Ni(II), which indicates that these hydrogels can be utilized as heavy-metal-cation capturing materials for the environment purification. The Ni(II)-capturing behaviors both of the hydrogels are similar: the captured amount increases with the functional-monomer-fraction, on the other hand, its the total concentration dependence shows a mound-like dependence on with a maximum around 1.4 M in both the hydrogels. Examining more in detail, the Ni(II)-capturing amounts of the p-SSAS/AAm gels are slightly larger than those of the corresponding SA/AAm gels, which may result from the higher dissociation degree of the p-SSAS group. The origin of the mound-like dependence of the capturing amount is not clear now, which may be related to the structure of the polymer network in the hydrogels. As for the SA/AAm gels, it may be interesting to compare their capturing behaviors of Cu(II) and Ni(II). First of all, it can be noticed that the SA/AAm gels capture more amounts of Cu(II) than Ni(II) by comparing the captured Cu(II) amounts by the SA/AAm gels reported in the previous study [5] and those measured in the present study, which may mainly result from the difference in the adsorptivity between the functional side chain group and the respective heavy metals. In addition to this quantitative adsorption difference, there is another noteworthy
difference: the SA-fraction dependence of the captured Cu(II) amounts shows a saturation phenomenon while those of Ni(II) increase monotonously, which can be related to the network structure as well as the difference in the adsorptivity between Cu(II) and Ni(II).

As for the pH dependences of the Ni(II) amounts captured by the p-SSAS/AAm and SA/AAm copolymer gels (Fig. 3), the common feature of both the hydrogels, a drastic decrease in the captured Ni(II) amount below certain pH, can be also interesting from the viewpoint of pursuing the capturing mechanism as well as that of the actual use for the environment purification. Because the amount of the captured Ni(II) of each the hydrogel is related to the number of effectively active functional side-chain groups, the pH dependence of the captured Ni(II) amount can be interpreted as the pH dependence of the number of the effectively active functional groups in each the hydrogel. Therefore, Fig. 3 indicates that the numbers of the effectively active functional groups in the p-SSAS/AAm and SA/AAm copolymer gels decrease drastically below certain pH’s: 2 in the p-SSAS/AAm gel and 3 in the SA/AAm gel, respectively; while the number is almost constant above the pH.

Along the same lines, the HCl-concentration dependences of the Ni(II)-desorption ratios of the p-SSAS/AAm and SA/AAm copolymer gels shown in Fig. 4 are also interesting. In the present study, the Ni(II) desorption process is opposite to the adsorption process because both the processes were conducted by changing \([\text{H}^+]\). In such a situation, the hydrogel capturing Ni(II) tightly cannot easily release Ni(II); in other words, the Ni(II) desorption ratio of the hydrogel which captures more amount of Ni(II) will be low as far as both the adsorption and desorption processes are executed by \([\text{H}^+]\) change. Therefore, the lower Ni(II)-desorption ratios of the p-SSAS/AAm gel than those of the SA/AAm gel (Fig. 4) are consistent with the larger Ni(II)-adsorption amounts of the p-SSAS/AAm gel than those of the SA/AAm gel in the low pH region (Fig. 3).

As reported in the present and previous studies [5-9], the authors have been examining the hydrogels’ heavy-metal adsorption and desorption properties for demonstrating their environment purifying functionality by which the current problems on both the landfillsite-depletion and the heavy-metal-resource drain can be solved. The proposed heavy-metal recycling process will be made up of the heavy-metal adsorption from waste fluid, which is followed by desorption of the adsorbed heavy metal. After then, the heavy metal released from the hydrogel will be reused as a heavy-metal resource; and the heavy-metal desorbed hydrogel, reactivated and used again in the heavy-metal adsorption process.

In order to make the abovementioned heavy-metal recycling system work efficiently, it is necessary to improve its overall functionality of the hydrogel. For achieving the purpose, there is a significant point to consider: the degree of the heavy-metal desorption functionality can be more important than the adsorption capability in the heavy-metal recycling system to which authors design. The hydrogel with a low desorption ratio cannot be adopted in the authors’ system because the heavy metal will be deposited in the hydrogel in the repeated use and will be easy to fill up the hydrogel. This situation can be worse when the hydrogel’s adsorption efficiency is higher because the hydrogel will overcrowd sooner. On the other hand, the repetitive use of the hydrogel can redeem somewhat low heavy-metal adsorption functionality.

Let us discuss on the pH dependence of the adsorption and desorption properties from this point of view. As shown in Fig. 3, the p-SSAS/AAm gel’s Ni(II)-capturing capability is higher, and is kept up even at lower pH’s than that of the SA/AAm gel. At first glance, one may think that the p-SSAS/AAm gel is suitable for the heavy-metal capturing material. In a sense, the remark will be true as far as the hydrogel is used only once as a Ni(II) adsorbent. However, the situation will be changed when the hydrogel is used repetitively together with the desorption treatment. As can be easily seen from Fig. 4, the Ni(II)-desorption ratio of the p-SSAS/AAm gel is lower than that of the SA/AAm gel in all the observed HCl concentration. Besides, the Ni(II) desorption ratio of the p-SSAS/AAm gel becomes below 70 wt% at 0.5 M which is still severe acidic condition for the practical use. Therefore, contrary to the expectation mentioned above, the SA/AAm gel can be more usable than the p-SSAS/AAm gel when the hydrogels are used repetitively together with the desorption treatment in a range above pH~3. However, the p-SSAS/AAm gel should be used if the Ni(II)-capturing treatment is carried out in a very acidic condition (below pH~1) where the Ni(II) capturing amount of the SA/AAm gel becomes very small.

Though the experimental results in the present study reveal interesting features, the investigations in more practical conditions are desired because the experimental condition and the adsorption and desorption treatment processes in the present study are very simple, and the authors are preparing some of them now.

REFERENCES


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