The Adsorption Behaviors of Thermosensitive poly(DMAAPS) Grafted Onto EVA Porous Support

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Abstract. The adsorption ability of poly(DMAAPS) grafted onto ethylene vinyl acetate (EVA) porous support prepared using various polymerization times was investigated at a variety of temperatures and permeated sample volumes. The permeability coefficient through Poly(DMAAPS) was also investigated. The poly(DMAAPS) was successfully grafted onto a EVA porous support through graft polymerization in water containing DMAAPS monomer with polymerization time of 4, 6 days, and 7 days. The permeability coefficient of Poly(DMAAPS) onto a EVA porous support decreased with increasing the temperature. Additionally, the adsorption amount of cation increased as permeated volume increased.

1. Introduction

The biggest challenge confronting wastewater produced by industrial is about the removal of the heavy metal ions. This topic becomes the point of interest since the heavy metal ions causing water pollution is non biodegradable substance and bio-accumulate over a period of time in human tissues. When it is consumed above the bio-recommended limits, it will give biotoxin effects on the human body which induces various diseases [1]. The treatments including physical and chemical such as precipitation, neutralization, coagulation/flocculation, ion exchange, and complexation which involve the formation of a complex or chelating agent have been practiced to remove the heavy metals; each has its merits and limitations in its application [2,3]. Several innovative approaches have been considered to overcome this limitation and among these, the use of polymer grafted onto supporting substrate is promising.

The change generally happens in the environment with sensitive polymers and hydrogel ions is the changes in pH or temperature. It also includes water polymer precipitation or hydrogel collapse completed with the expulsion of water large fraction in gel pores [4–6]. Such polymer can be grafted or absorbed onto the other polymer surface presents or porous membrane pores when it is stimulated environmentally which leads to the changes of wettability or permeability [5].

A research was conducted to study the molecular imprinted thermosensitive gels grafted onto PP substrate by plasma-initiated graft polymerization [7]. The thermosensitive N-isopropylacrylamide microgel adsorbent was prepared by emulsion polymerization using anionic polymerizable surfactant and the molecular imprinting technique using Cu(II) ions as the target ion. These microgels were suspended stably even when the temperature of the suspension exceeded the transition temperature of poly(NIPAM) which is about 32 °C and the adsorption amount of Cu(II) ions on the microgel at the shrinking state of 50 °C was quite large compared to the swollen state of 10 °C. Although the adsorption of these microgels was quite rapid compared to the grinding gels, however it is difficult to handle in the industrial application due to the small size of the particle.

In this study, we intend to employ the DMAAPS polymer grafted onto EVA porous support in order to regenerate the heavy metal ions from salt solution. This method could overcome the adsorption
limitations in the use of gel adsorbent. In this research, the adsorption and desorption mechanism of DMAAPS polymer could be simply controlled by tuning the temperature of the system. By grafting DMAAPS polymer onto EVA porous support and after thin film is contacted with a salt solution containing metal ions, the ions directly approach and bind to the opposite charge of betaine polymer DMAAPS without any hindrance. In this system, the ability of ions to infiltrate into the network as occurred in gel does not need to be considered. At temperatures above its upper critical solution temperature (UCST), adsorption occurs due to the polymer swells on the surface-grafted from of EVA porous support leading to the attachment of metal ions into the betaine DMAAPS. At temperatures below its critical solution temperature (UCST), the polymer collapse, the intrachain and/or interchain interactions between the side chains of the polymer are strong and betaine is forced to release the binding with ions and desorption would take place.

Based on the previous reports, most work has been done on the swelling behavior of gels and thermosensitive microgel. This paper reports the study on the ability of DMAAPS polymer grafted onto EVA porous support in recovering and regenerating various kinds of heavy metal ions. The adsorption properties of ground DMAAPS gel are also reported as a comparison.

2. Experimental Section

2.1 Materials

The material used in this work such as N,N-dimethylaminopropylacrylamide (DMAPAA), 1,3-propanesultone (PS) was obtained from Kohjin Co. Ltd and purified through reduced distillation. Additionally, 1,3-propanesultone (PS) was used as received without further purification. Other reagents such as acetonitrile and acetone were purchased from Sigma-Aldrich Co. (USA).

2.2 Synthesis of DMAAPS monomer

The DMAAPS monomer was synthesized through the ring-opening reaction of N,N-dimethylaminopropylacrylamide (DMAPAA) and 1,3-propanesultone (PS) [8–11]. A mixture of PS (75 g, 11.4 M) and acetonitrile (75 g) was added by a dropwise to the mixture of DMAPAA (100 g, 5.1 M) and acetonitrile (200 g) with continuous stirring at 30°C for 90 minutes. After the completion of the addition, the mixture was then stirred at 30°C for 6 h and allowed to stand for two days. The precipitated white crystal was collected by filtration and washed several times with 500 ml of acetone. Finally, the crystal obtained was dried under reduced pressure for 24 h. The structure of DMAAPS is shown in Figure 1.

\[
\text{CH}_3\text{CONH}-(\text{CH}_2-\text{N}^+-(\text{CH}_2-\text{CH}_2-))^{-}\text{SO}_3
\]

Figure 1. Chemical structure of DMAAPS.

2.3 Plasma and peroxide-initiated graft polymerization

As previously reported by Tokuyama et.al, the procedure of the graft polymerization consists of three steps. A piece of ethylene vinyl acetate (EVA) porous support with size of 20x20x0.82 mm to be grafted was treated with Ar plasma in a reactor in order to promote the graft-polymerization of the monomer. Initially, air in the reactor was displaced with Ar gas and evacuated to approximately 10 Pa, and the radio-frequency-plasma treatment was then started for the activation for 60 s (power input 40 W and 13,56 MHz). It was followed by treating the porous support with O$_2$ gas for 60 s to produce peroxide on the surface of activated EVA porous support. Activated EVA sample was then contacted with a graft monomer solution of the desired concentration, e.g., solution containing monomers of DMAAPS 1000 mol/m$^3$. The graft polymerization was carried out under nitrogen atmosphere for four days at 80°C. Finally, the grafting polymers product was washed by water and dried to calculate the amount of grafting as the mass ratio of the grafted polymer to the initial EVA. The plasma initiated graft polymerization apparatus is presented in Figure 2.
Figure 2. Apparatus of plasma-initiated graft polymerization: (A) reactor, (B) inductively-coupled coil, (C) radio-frequency power source, (D) matching unit, (E) vacuum gauge, (F) vacuum pump, (G) flowmeter and (H) gas reservoir.

Table 1. Polymerization condition of DMAAPS graft

| Monomer                          | (mol/m³) |
|----------------------------------|----------|
| N,N-dimethyl(acrylamidopropyl)ammonium propane sulfonate (DMAAPS) | 400, 1000 |
| N,N,N',N'-tetramethylethylenediamine (TEMED) | 4        |

| Measurement of permeability coefficient and concentration of permeated solution |
|--------------------------------------------------------------------------------|
| The permeability through the porous material grafted with poly(DMAAPS) was evaluated by the permeability coefficient \( \kappa \) defined by the following equation. |

\[
Q = A \kappa \frac{\Delta P}{\mu L}
\]

where, \( Q \) is the flow rate, \( \mu \): viscosity, \( L \): the thickness of the porous material, \( A \): the cross sectional area of the porous material, and \( \Delta P \): the pressure difference between the both ends of the porous material. Pressure was conducted by an aqueous solution column on the porous material, and the flow rate was measured by the change in the solution level in the column with time. First, the salt solution of 50 °C was permeated through the porous material to form the open-chain conformation of the grafted polymer. Then, the salt solution of the temperature was permeated.

2.5 Adsorption Experiment

The metal ion adsorption experiment was performed by the similar method as the permeability mentioned above of the desired. The salt solution concentration was permeated through the porous material grafted with poly(DMAAPS) and the permeated samples solution was collected at the desired volume. When the desired volume was reached, the adsorption process was stopped and washed EVA porous support by HCl 0.01 M, followed rinsed several time by water. The permeate concentration and
initial feed concentration of nitrate solution were measured by an ion chromatography. The adsorption amount was calculated from the concentration difference between the feed solution and permeated solution per gram of the grafted polymer.

3. Result and Discussion

3.1 Effect of polymerization time on the permeability of water

Figure 3. Permeability coefficient through poly(DMAAPS) grafted onto a EVA porous support in water containing DMAAPS monomer of 1000 mol/m^3 with polymerization time of (a) 4 days, (b) 6 days, (c) 7 days at various temperatures. As shown in Fig. 3 (a), it can be seen that in 4 days polymerization, permeability coefficient increased first and the value reached maximum and further increasing the temperature, permeability coefficient then decreased. However, in 6 days, the polymerization permeability coefficient decreased along with the increasing the temperature. This phenomenon was considered to be due to the factor affecting the permeability.
coefficient in polymerization time of 4 days which is only the viscosity of water. However, in polymerization time of 6 days, the viscosity of water and polymer characteristic at various temperatures strongly affect the permeability coefficient. As shown in Fig 3 (c), it can be seen that in 7 days of polymerization, permeability coefficient decreased along with the increasing temperature. This phenomenon was considered to be due to the factor affecting the permeability coefficient in i.e., the viscosity of water and polymer characteristic at various temperatures strongly affect the permeability coefficient.

3.2 Effect of polymerization time on the adsorption amount

Figure 4. Adsorption amount of nitrate solution by poly(DMAAPS) grafted onto EVA porous support in water containing DMAAPS monomer 1000 mol/m$^3$ at 50 $^\circ$C with polymerization time of (a). 4 days (b). 6 days. The porosity and pore size of EVA is 80 % and 20µm.

In this work, the effect of polymerization time in graft polymer solution on adsorption amount was studied. The adsorption amount of nitrate solution by poly(DMAAPS) grafted onto the EVA porous support in water containing DMAAPS monomer 1000 mol/m$^3$ at 50 $^\circ$C with polymerization time of (a). 4 days (b) 6 days are shown in Figure 4. From both figures, we can conclude that the poly(DMAAPS) was successfully grafted onto the EVA porous support by graft polymerization in water solution. It was also found that in polymerization time of 4 days and 6 days adsorption amount shows the same tendency. Adsorption amount increased as permeated volume increased, however adsorption amount in 6 days is higher than 4 days of polymerization. This can be considered due to the graft ratio in 6 days polymerization which is higher than the 4 days of polymerization. The grafting ratio in 4 days was found to be 0.043 g-polymer/g-support, however for 6 days was 0.0833 g-polymer/g-support.
3.3 Effect of permeated sample volume on adsorption amount

Figure 5 shows the adsorption amount of DMAAPS polymer grafted onto a EVA porous support by graft polymerization in water containing DMAAPS monomer of 1000 mol/m$^3$ as shown in Fig. 5 (a), it can be seen that in 11 ml of permeated solution, the adsorption amount increased drastically in the first sample obtained and the value remained constant with further increasing the permeated solution. However, when the permeated volume reached 100 ml, the adsorption amount gradually decreased. This phenomenon was also observed when changing the permeated solution volume up to 3 ml. On the contrary, the adsorption amount increased significantly when the permeated solution volume was 1 ml.
4. Conclusions

The poly(DMAAPS) was successfully grafted onto a EVA porous support through graft polymerization in water containing DMAAPS monomer of 1000 mol/m³ at 50 °C with polymerization time of 4, 6 days, and at 70 °C with polymerization time of 7 days. However, the amount of polymer grafted on the porous support was too small. The permeability of poly(DMAAPS) onto a EVA porous support with polymerization time of 4 days depends only on the viscosity of water and of polymerization time of 6 and 7 days strongly depends on the thermosensitive characteristic of DMAAPS. The adsorption amount of poly(DMAAPS) was successfully grafted onto the EVA porous support by graft polymerization in water containing DMAAPS monomer of 1000 mol/m³ in sample volume of 3 ml and 1 ml.

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