Novel Treatment Process of Harmful Organic Materials in Waste Water Using Temperature-Sensitive Gel Synthesized from PVA

Hideki Yamamoto1,2*, Akihiro Kushida1, Noriyuki Heyamoto1, Yuko Takami1, Norihiro Murayama1 and Junji Shibata1,2

1Department of Chemical Engineering, Faculty of Engineering, Kansai University, Suita 564-8680 Japan
2High Technology Research Center (HRC), Kansai University, Suita 564-8680, Japan

The adsorption removal of harmful organic materials in waste water has been carried out using the adsorption and desorption characteristics of a temperature-sensitive polymer gel which is synthesized from polyvinylalcohol (PVA). A new adsorption removal process using an air lifting type vessel has been designed and examined for practical use. Three types of polymerization degrees (1000, 1700 and 2500) of PVA were used in this experiment. The gel volume in water was induced the volume contraction at around 305 K for 1000, 310 K for 1700 and 320 K for 2500, respectively. At higher temperatures, the temperature-sensitive polymer gel shrinks because of discharging water, whereas, at lower temperatures, the gel swells as a result of absorbing water. The reversibility of the volume change of the synthesized polymer gel is confirmed by changing temperature. The adsorption behavior of organic materials onto PVA polymer gels in water was investigated at various temperatures. The amount of adsorption of organic materials increases remarkably at temperatures higher than about 305 K for 1000, 310 K for 1700 and 320 K for 2500. The saturated amounts of adsorption are about 0.05 mmol/g-gel for 1000, 0.26 mmol/g-gel for 1700 and 0.20 mmol/g-gel for 2500, respectively. The organic material in waste water could be adsorbed and desorbed reversibly onto PVA polymer gel by the temperature swing. The mechanism of adsorption and desorption of organic materials onto the gel can be explained by the hydration and dehydration of the polymer gel. The driving force of the adsorption is considered to be the hydrophobic interaction between PVA polymer gel and organic compounds. The novel continuous removal process for organic materials in waste water was designed and discussed for practical use.

**Keywords:** temperature-sensitive gel, Polyvinylalcohol, volume change, adsorption, removal process, 1,2-Dichloroethane, temperature swing

1. Introduction

The adsorption removal of harmful organic materials such as dioxin, chloroform and 1,2-dichloroethane in ground water and drinking water are indispensable for the protection of the environment. In particular, the development of a new removal or disposal treatment for harmful organic materials in water is very important from a practical point of view.

Under the appropriate control of chemical and cross-link structures, certain polymer gels exhibit property or molecular shape changes in response to slight changes in the external environment such as temperature, solvent composition, magnetic field, pH and light.1–3) These gels are called environment-sensitive polymer gels, or intelligent materials, and their application in artificial muscles and drug delivery systems has been investigated. The environment-sensitive polymer gels reported to date are poly-N-isopropylacrilamide (NIPA) and poly-vinylmethylether (PVME).4–6)

The present research group identified a polymer gel that was composed of polyvinylalcohol (PVA). The gel is partially cross-linked and acts as a temperature-sensitive polymer gel that expands or contracts according to changes in temperature.7) The reversible phenomenon of volumetric contraction up to 30–40% in response to a temperature rise from 280 to 310 K was confirmed in previous work.8) The expansion and contraction behaviors of this polymer gel have been explained in terms of the hydration and dehydration of the gel. The PVA polymer gel presented in this study is found to be temperature-sensitive gel. The polymer gel is a high-functional material that has a potential application as a carrier for organic substance removal and chemical substance transportation systems.

In this work, removal experiments of harmful organic materials in water were carried out using adsorption and desorption characteristics with temperature changes applied to the temperature-sensitive PVA polymer gel.

2. Materials

The polyvinylalcohol (PVA) was supplied by KURARAY Co. Ltd. The degree of saponification was 99.8 mol%, and three types of polymerization degrees, 1000, 1700 and 2500, were used in this study.

1,2-Dechloroethane was chosen as the harmful organic compound for the adsorption removal experiments. The reagent grade 1,2-dichloroethane was supplied from Wako Pure Chemicals Co. The purity was 99.5%, and it was used without further purification.

3. Experimental

3.1 Synthesis of PVA polymer gel

The degree of saponification of polyvinylalcohol (PVA) was 99.8 mol%, and the polymerization degree was 1000, 1700 or 2500. Sodium alginate (1 mass%) and sodium hydrogen carbonate (0.3 mass%) solutions were added to the PVA (8 mass%) for the preparation of a mixed solution. Using a roller pump with silicone tube of 4 mm internal diameter and a nozzle with an internal diameter of 3 mm, the mixed solution was added to a stirred calcium chloride solution (0.1 kg/m³) at 5 cm³/min. Sodium alginate was solidified on the surface of each drop from the nozzle to make...
calcium alginate in the calcium chloride solution. The solids obtained were spherical. These spherical solids were soaked in an aqueous solution containing formaldehyde (0.02 kg/m³), sulfuric acid (0.2 kg/m³) and sodium sulfate (0.1 kg/m³) for 60 min at 313 K. Then, the solidified gel was fixed with acetal bonding and the degree of cross-linking was about 50%. The chemical structure of the PVA polymer gel is listed in Table 1.

3.2 Measurement of volumetric change with temperature swing

The spherical gels of about 5 mm diameter in water were used in the experiments in the temperature range from 275 to 353 K. The average diameter of the spherical gel was calculated from a digital image on a computer screen, and the volume was calculated assuming the PVA polymer gel to be perfectly spherical. The reversibility of the volumetric change of the gel for temperature changes in water was investigated. The accuracy of volumetric measurement and reversibility of volumetric change with temperature swing were estimated to be ±2%.

3.3 Measurement of adsorption of organic materials

Adsorption experiments of a small amount of organic materials onto PVA polymer gel in water was carried out for temperatures ranging from 293 to 333 K. The initial concentration of the organic compound in water was 200 kg/m³. An aqueous solution of 100 cm³ containing organic compound and 50 gels of 5 mm diameter were introduced into a 300 cm³ flask at room temperature. The flask was shaken using a shaker for 60 min in a constant temperature water bath. The adsorption experiments were carried out for temperatures ranging from 293 to 333 K. The amount of adsorption onto the PVA polymer gel was determined from the difference between the initial and the final concentrations of the organic compound. The concentration of organic compound in the water was measured using gas chromatography with a capillary column. The effect of the vapor-liquid equilibrium of the organic compound at the temperature swing was corrected by a blank test at each temperature.

4. Results and Discussion

4.1 Volumetric change of PVA polymer gel with temperature swing

Figure 1 shows the volumetric change of the PVA polymer gel with temperature. The volumetric changes of the PVA polymer gel of the three polymerization degrees (1000, 1700 and 2500) are shown in the figure. The spherical gel with 5 mm diameter in water at temperatures ranging from 275 to 340 K contracts with increasing temperature to about 4 mm diameter at 310 K or higher for PVA polymer gel(1700). In the case of polymer gel(1000 or 2500), the contraction takes place at 320 K or higher. It is found that the transition temperatures of the shape are different for the polymerization degree of PVA. The average diameter was obtained from a digital image on a computer screen, and the volume was calculated assuming the PVA polymer gel to be perfectly spherical.

Figure 2 shows the change in gel volume of the different polymerization degrees (1000, 1700 and 2500) in water as a function of temperature. The gel volume becomes smaller with increasing temperature. At temperatures of 310 K or higher, volumetric contraction can not be confirmed. In the case of the polymerization degree (1000 or 2500), similar results are obtained at temperatures higher than 320 K, as shown in Fig. 2.

The above results demonstrate that three types of PVA polymer gel are temperature sensitive and contract by about 30 to 40 volume% of the volume at 275 K in water, depending on temperature. The reversibility of the volumetric change of the gel in water is confirmed by five experimental trials with an accuracy of about ±3%.8) The reversibility of the volumetric expansion and contraction of the PVA polymer gel with the change in temperature was investigated by observing these behaviors.
4.2 Adsorption behavior of organic compound onto PVA gel in water

In order to examine the change in the surface property of the polymer gel with change in temperature, adsorption experiments of an organic material in water were carried out at temperatures of 298 and 323 K. As the organic material for the adsorption removal experiments, 1,2-dichloroethane was chosen. Figure 3 shows the amount of adsorption of 1,2-dichloroethane onto the PVA polymer gels at different temperatures. The PVA polymer gel adsorbs 1,2-dichloroethane in a contracted state which corresponds to temperatures of 310 K or higher, compared with that in an expanded state which corresponds to a temperature of 298 K or lower. The adsorption amount of 1,2-dichloroethane in aqueous solution at 323 K or higher is 0.25 mmol/g-drygel for 1700, which is a higher value than that at 298 K (0.01 mmol/g-drygel). This indicates that a contracted state eliminates water easily from the surface of the gel to make the surface hydrophobic. The relationship between the adsorption amount of 1,2-dichloroethane onto PVA polymer gel and temperature is shown in Fig. 3. The adsorption amount of 1,2-dichloroethane in aqueous solution at 323 K is 0.20 mmol/g-drygel, which is a much higher value than that at 298 K (0.02 mmol/g-drygel). The adsorption amount of organic material onto PVA polymer gel(1000) at 305 K or higher shows the lower value (0.05 mmol/g-gel) than that of 1700 and 2500. Figure 3 shows that the adsorption amount of organic material in water is rapidly increased at different temperatures for each polymerization degree. These temperatures show nearly similar with the terminally temperature of volume contraction given in Fig. 2.

The difference in the adsorption amount between the two temperatures can be applied to the new removal system of harmful organic materials in water using temperature change or swing. Figure 4 shows the adsorption isotherm of 1,2-dichloroethane in water onto three types of PVA polymer gels at 323 K. The saturated value of the adsorption equilibrium for 1,2-dichloroethane onto the PVA polymer gel (1700) at 323 K is the highest value of three different polymerization degrees.

4.3 Adsorption mechanism of organic compounds onto PVA polymer gel

In order to discuss the surface condition of PVA polymer gels in organic solvents, the thickness of the water film at the gel surface in toluene was examined using a digital camera. The PVA polymer gel containing water was immersed in...
4.4 Removal experiment of 1,2-dichloroethane in water

Figure 7 shows the adsorption removal experiment of 1,2-dichloroethane in water using an air lifting type reactor in a small scale. The volume of the air lifting type reactor was about $2 \times 10^{-3}$ m$^3$. Three thousands pieces of spherical polymer gels of about 5 mm in diameter were introduced into this reactor. Air is supplied by an air bomb into the reactor from the nozzle fixed at the bottom of the vessel in order to mix the polymer gels and aqueous solution uniformly. The flow rate and initial concentration of 1,2-dichloroethane were $0.5 \times 10^{-3}$ m$^3$/min and 8.0 mg/dm$^3$, respectively. The reactor was covered with insulating materials and panel heater in order to keep temperature constant. The temperature of the aqueous solution was controlled at about 315 K($\pm$2 K) by a panel heater. The outlet concentration of 1,2-dichloroethane was measured by gas chromatography with a capillary column. Figure 8 shows an example of the relationship between adsorption time and the outlet concentration of 1,2-dichloroethane in aqueous solution. The theoretical breakthrough time of 1,2-dichloroethane can be calculated from the experimental conditions of flow rate and concentration of organic material, and the saturated value of the adsorption (0.26 mmol/g-drygel) obtained in Fig. 3. In the case of this experimental condition, the theoretical breakthrough time was calculated to be about 90 min. It is confirmed that the breakthrough time for the adsorption experiments is about 60 min, which is shorter than is calculated time. This result demonstrates that the PVA polymer gel can be used in a removal system for harmful organic materials in water such as ground water or drinking water.

5. Conclusions

It is found that the polymer gel synthesized from PVA is a temperature-sensitive polymer gel. The volume of the gel in water changes at around 305 K for the polymerization degree of 1000, 310 K for 1700 and at 320 K for 2500. At higher temperatures, the PVA polymer gel shrinks because of the discharge of water, whereas at lower temperatures the gel swells because of the absorption of water due to hydrogen bonding. The adsorption amount of organic compounds onto the PVA gel increases remarkably at temperatures higher than these. The PVA polymer gel could be effective for the adsorption removal of an extremely small amount of harmful organic compounds in waste water, and they are repeatedly usable as an adsorbent. The mechanism of adsorption of
organic compounds onto the PVA polymer gel can be explained by the hydration and dehydration of the gel. The polymer gel is a high-functional material that has potential applications as a carrier for the adsorption system of organic substances and the transportation system of chemical substances. From the results obtained in this work, the PVA polymer gel is expected to have applications for a drug delivery system and a removal system of toxic organic compounds in waste water.

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