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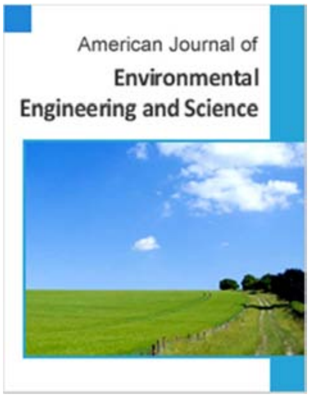

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Forward Osmosis Using Temperature-Responsive Slurries as a Draw Solution

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Abstract

Forward osmosis has emerged as a method for desalination. The development of the efficient forward osmosis process strongly depends on the development of a high performance draw solution. In this study temperature-responsive slurries, consisting of a mixture of temperature-responsive polymer and inorganic powder, were evaluated as draw solutions for the process of forward osmosis. Various copolymers were synthesized via copolymerization of N-isopropylacrylamide (NIPAM) with varying amounts of 2-acrylamido-2-methylpropanesulfonicacid (AMPS). Synthesized copolymers were mixed with alumina powder and then the osmotic pressure of the slurry mixtures was measured. The water flux of the mixed slurry in forward osmosis was also measured repeatedly. Subsequently, the water that had been sucked into the slurry was separated by gravitational settling of the alumina powder and copolymers. It was found that the osmotic pressure and water flux in forward osmosis increased with an increase in the ratio of AMPS to copolymer because the ionic concentration of the mixed slurry increased. It was also demonstrated that these temperature-responsive slurries could be used repeatedly, maintaining the water flux in forward osmosis, because the almost all temperature responsive polymers were completely separated from the diluted draw solution together with the alumina powder. In addition the water recovery ratio from the diluted draw solution became larger when using the temperature responsive slurry as draw solution compared when using the temperature responsive polymer solution as draw solution, because the alumina powder in the temperature responsive slurry enhance the polymers' settling, forming the closely packed sediment of the polymer and powder.

1. Introduction

Forward osmosis (FO) is a separation process in which water in a treated solution, called a feed solution (FS), permeates through a semi-permeable membrane to a high-osmotic pressure solution, called a draw solution (DS) due to the osmotic pressure difference between the FS and DS [1–5]. Recently, much research has been conducted relating to the FO process, especially for application in desalination [6–8] due to the growing water shortage concerns on a world-wide level. The FO process is also being investigated for application in waste-water treatment [9]. It is claimed that the FO process has several advantages compared with the conventional pressure-driven reverse osmosis (RO) process; (1) the FO process is operated at a relatively low cost because of the absence of hydraulic pressures, (2) the water recovery ratio through the FO process becomes higher, (3) the FO process can reject many contaminants, (4) the FO process exhibits low membrane fouling [10-13].

In FO, the water must in some way be recovered from the DS after osmosis is completed. As such, there are two requirements for the desirable DS: (1) highly soluble in water (generating high osmotic pressure relative to that of FS, and (2) easy recycling such that there is a simple method available for water recovery. Currently the researches about the former point, generating high osmotic pressures have been progressed. For example, Ling et al. reported that 2 M KOH solution as DS could generate an osmotic pressure of 89.3 atm and a water flux of 22.6 LMH [14]. Darwish et al. used 0.065 M PEG-$(COOH)_2$-MNPS solution as DS, generating an osmotic pressure of 73 atm and a water flux of 13 LMH [15]. In addition, in review articles about FO process [16], there were many draw solutions which can generate the higher osmotic pressure than that of seawater, almost 28 atm. However, the recovery of pure water from the diluted DS is the most important concern in successful selection of a suitable draw solute because it is still difficult to recover the water from DS by a simple method. Many different types of draw solution have been investigated in order to improve the water recovery method, including salts, fertilizers, saccharides, hydrogels, hydrophilic nano-particles, and polyelectrolytes. For example, some researchers reported that volatile draw solutes like ammonium bicarbonate (NH_4HCO_3) solution [17], carbon dioxide gases [18], and SO_2 [19], can be separated from product water by means of heating or distillation and the regeneration of draw solutions can be achieved by dissolving the volatile gases back into water. However, most early patents on volatile compounds as draw solutes had insufficient experimental data to demonstrate their superiority or advantages. However, most early reports on volatile compounds as draw solutes had insufficient experimental data to demonstrate their superiority or advantages. On the other hand, Na et al. synthesized superhydrophilic, citrate- coated magnetic nanoparticles (cit-MNPs) through a co-precipitation method, and then systemically investigated their osmotic potential as draw solutes for FO, however, the recovery of the diluted cit-MNPs via magnetic separation from the diluted DS have not been done, yet [20]. In other previous reports related to the novel DS have often proposed unique methods of water recovery from the diluted DS, however, there are still issues such as increasing cost, time and labor. In summary, although the most of tested draw solutions have high osmotic pressures, it remains difficult to recover pure water from the diluted DS following FO.

Temperature-responsive polymer solutions are one type of draw solution, which can be relatively easily recycled [21-30]. Temperature-responsive polymers have an additional interesting feature: the solubility of the polymer can be changed by altering the surrounding temperature. There is a report in which a typical temperature-responsive polymer solution using poly (N-isopropylacrylamide) (denoted as PNIPAM) was used as a draw solution in FO process [21]. It was seen that the PNIPAM solution could generate a relatively high osmotic pressure below its lower critical solution temperature (LCST), because PNIPAM becomes more hydrophilic and highly water soluble under this condition. Above the LCST, PNIPAM becomes more hydrophobic and can thus be separated from water due to formation of the hydrogel. However, previous papers used intensive and difficult separation techniques for removing water from the diluted DS, the diluted temperature-responsive polymer solutions, such as ultrafiltration using a 4,000 Da membrane [21] and membrane distillation [23]. Similarly to the other DS presented in the previous works, a much easier separation method is desired for the temperature responsive polymer solutions.

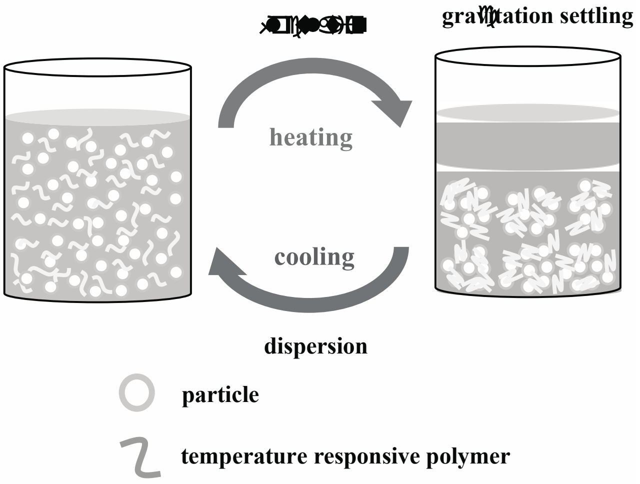


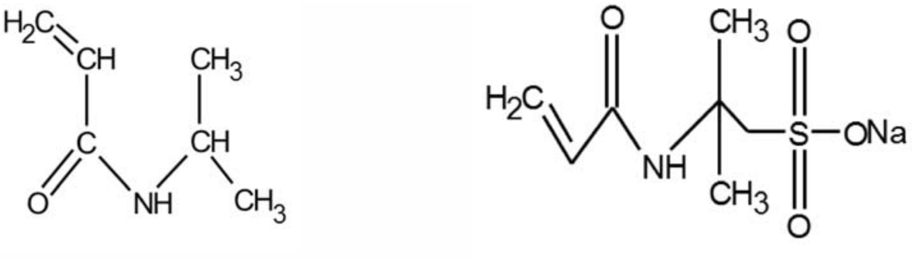
Figure 1. *Schematic of the developed draw solution.*

In our previous report, using our developed characterization method of particle dispersion state, the hydrostatic pressure measurement [31-37], it was reported that the alumina slurry containing temperature-responsive polymers exhibited reversible changes in particle dispersion and flocculation caused by changing its temperature below or above the LCST of the synthesized polymer [31]. It was also demonstrated that the reversible change in particle dispersion states was a result of the reversible adsorption and desorption of the temperature-responsive polymers to alumina particles [31]. The most remarkable result in the paper was that alumina particles with adsorbed temperature-responsive polymers formed large flocs, enabling relatively quick gravitational settling without the use of a centrifugal field as long as the slurry temperature was kept above LCST. In addition the behavior of the reversible change in particle dispersion states strongly depended on the type of the temperature-responsive polymer [31]. Based upon these results, this study investigated the feasibility of using temperature-responsive slurries containing temperature-responsive polymers and fine inorganic particles as draw solutions for FO process. This research aimed to develop the temperature-responsive slurry as a draw solution illustrated in Figure 1, which can generate a relatively high osmotic pressure below LCST (due to well dispersion of both fine particles and polymers) and easily separates pure water from the diluted draw solution after FO process above LCST (due to formation of flocs containing both fine particles and polymers).

2. Experiment

2.1. Synthesis of Temperature-Responsive Polymers

PNIPAM and copolymers of NIPAM and 2-acrylamido-2-methylpropanesulfonicacid (denoted as AMPS) were synthesized as temperature-responsive polymers. The raw materials were N-isopropylacrylamide (KJ Chemicals Corporation, Japan) and 2-acrylamido-2-methylpropanesulfonicacid (Wako Pure Chemical Industries, Japan) monomers. Ammonium peroxodisulfate (Tokyo Chemical Industry Co., Ltd., Japan) and N', N', N', N'-tetramethyl-ethylenediamine (denoted as TEMED, Tokyo Chemical Industry Co., Ltd., Japan) were used as the polymerization initiator and promoter, respectively. Figure 2 shows the chemical structure of the monomers used in this study. Four types of polymer were synthesized by changing the mixing ratio of AMPS to NIPAM. The ratios of each component are summarized in Table 1. First the monomers were dissolved in deionized water at the ratios given in Table 1, and then TEMED was added. The solution was then subjected to an hour of bubbling treatment using nitrogen gas. Finally, APS was added into the solutions, which were then left to rest for one day in sealed containers. The synthesis of the polymers was conducted at room temperature.



NIPAM AMPS

Figure 2. *Structures of NIPAM and AMPS.*

Table 1. *Composition of synthesized polymer.*

Polymer No.	Molar ratio			
	NIPAM	AMPS	TEMED	APS
1	1000	0	20	15
2	985	15	20	15
3	970	30	20	15
4	950	50	20	15

Table 2. *LCST of synthesized polymer.*

Polymer No.	LCST [°C]
1	33
2	39
3	43
4	47

In order to eliminate any residual unreacted monomers and polymers with low molecular weight, the solutions of synthesized polymers were heated in hot water bath and the white bodies of the polymers that formed were collected and dried. This procedure was repeated at least 3 times for the following experiments. The LCST of the synthesized polymer was measured by the colour change of the solution with a certain amount of the synthesized polymer when subjected to changes in temperature by visual inspection. The measured LCST of each synthesized polymer is summarized in Table 2.

2.2. Preparation of Temperature-Responsive Slurries

Alumina particles (an abrasive powder of #6,000 with an average particle size of 2.0 µm, Fujimi Inc., Japan) and the synthesized polymers from section 2.1 were mixed in deionized water. The polymer was added as aqueous solution at a concentration of 3.0% of total mass. The zeta potential of the alumina powder was measured by electrophoresis, changing slurry pH by the addition of HCl and NaOH. Figure 3 shows the pH dependence of the measured zeta potential for the alumina particle. The isoelectric point of the alumina particle was about pH 7.0. A certain amount of the alumina particles, polymer solution and deionized water were mixed to prepare the slurry with a volumetric particle concentration of 0.16%. The prepared slurries were mixed for 4 min using a planetary centrifugal mixer (ARE-300, Thinky Inc., Japan). The revolution and rotation speeds were 2,000 and 60 rpm, respectively. The mass ratio of alumina powder to synthesized polymer was held constant at 0.2: 1.0.

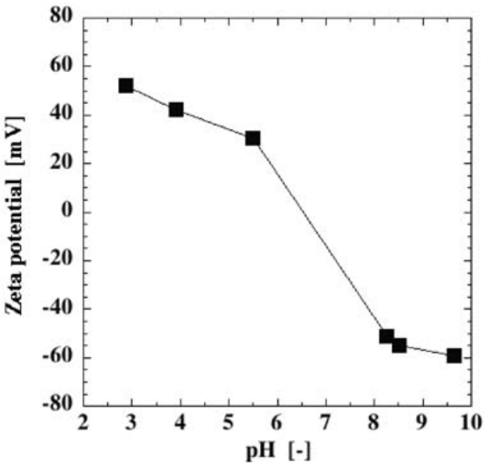


Figure 3. *Zeta potential of alumina powder.*

2.3. Osmotic Pressure Measurement of Temperature-Responsive Slurries

The osmotic pressure at room temperature (around 20°C) of the temperature-responsive slurries was measured using the apparatus illustrated in Figure 4 [38, 39]. The apparatus in Figure 4 can be measured the osmotic pressure of the sample solutions (slurries in this paper) as negative pressure in the chamber of the deionized water. The detail of the apparatus and measurement procedure is provided elsewhere [38]. The slurry was brought into contact with deionized water via semipermeable membrane (RO membrane ES20, Nitto Denko Corporation, Japan), and the pressure in the chamber of the deionized water was measured by a pressure sensor such that the osmotic pressure of the slurry was determined by subtraction the measured pressure in the chamber of the deionized water from the hydrostatic pressure of the slurry. Since this apparatus measured the hydrostatic pressure of the slurry above the pressure sensor at the same time, thus, the true osmotic pressure of the slurry was determined by subtracting the measured pressure at a given time from the hydrostatic pressure. These measurements were continued until the pressure reached an almost constant value.

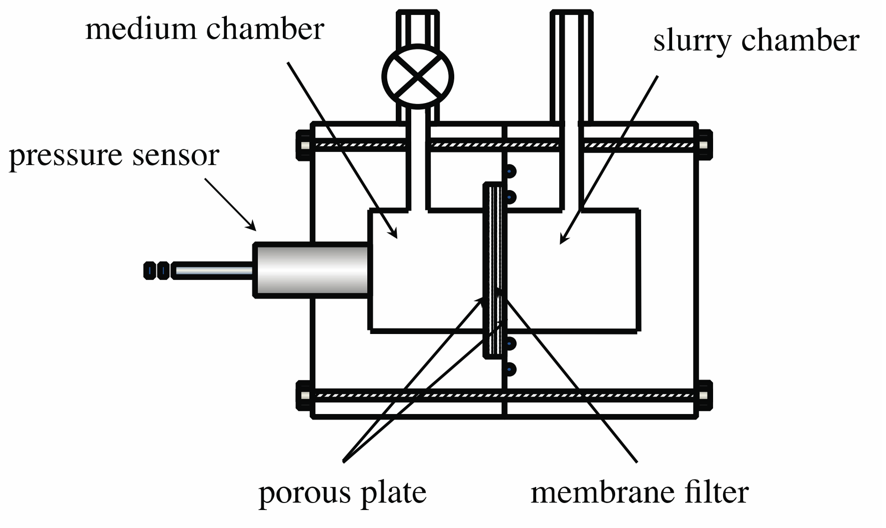


Figure 4. *Schematic of osmotic pressure measurement device.*

2.4. Forward Osmosis and Water Recovery from DS

The forward osmosis experiment shown in Figure 5 was conducted, and the permeating flux of deionized water was measured. First, the temperature-responsive slurries prepared in section 2.2 were brought into contact with deionized water via a semipermeable membrane (RO membrane ES20, Nitto Denko Corporation, Japan). The decreases in the mass of deionized water in the reservoir tank were measured by an electronic balance. As the evaporation of water from the reservoir tank could not be perfectly prevented, the rate of evaporation from this setup was determined in advance using a blank test. The true decrease in water mass resulting from FO was calculated by subtracting evaporation from the measured reduction. The permeation flux was determined by dividing the permeating rate (the true decrease in water mass of the reservoir tank) by the membrane area. The permeating amount of water was continuously measured over 48 h.

Following this stage, the temperature-responsive slurry and absorbed deionized water was kept at approximately 50°C for 3 h by circulating a hot water in the jacket of the container, after closing the valve at the bottom of the apparatus, ensuring that no more forward osmosis occurred. The supernatant created by particle and polymer settling was sampled as much as possible from the top of the apparatus and its weight was measured. Then the remaining body (alumina particles and polymers) was cooled at room temperature, and an amount of fresh deionized water equal to the removed supernatant was added during stirring for regenerating the DS. The regenerated slurry was used as draw solution for the second FO test. Figure 6 shows the schematic of the water recovery procedure. The FO and water recovery tests were repeated three times, and the change of water flux was observed.

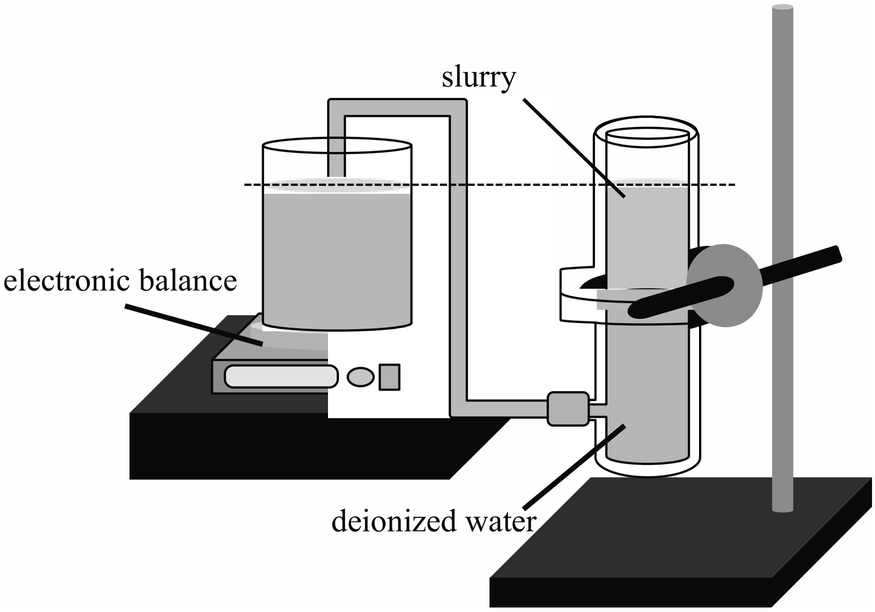


Figure 5. Schematic of forward osmosis test device.

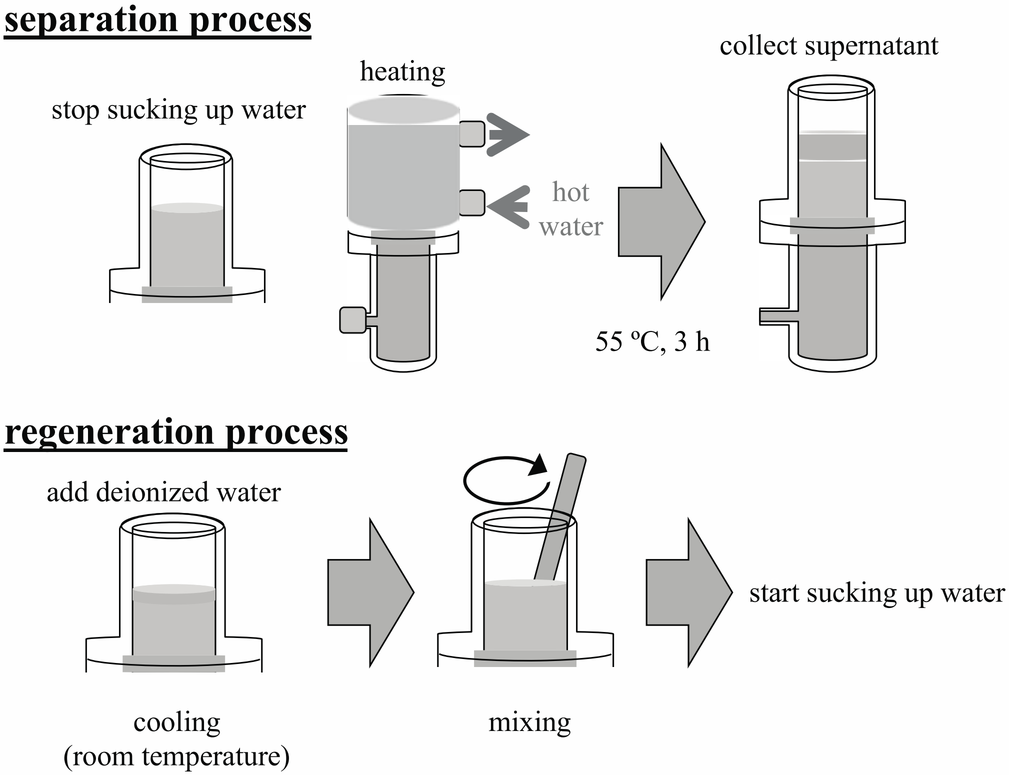


Figure 6. Schematic of separation and regeneration process for draw solution.

2.5. Comparison Between Temperature-Responsive Polymer Solution and Slurry

The efficiency of the water separation process from the draw solutions was compared between a temperature-responsive polymer solution and temperature-responsive slurry. The temperature-responsive slurry whose prepared was described in section 2.2, and its solution (temperature-responsive polymer solution) without the alumina particles, were left at rest at 50°C and their appearance was observed. The supernatant which formed was sampled and weighed after an equilibrium state was reached for both the slurry and the solution. The sampled supernatant was additionally analyzed using a thermo-gravimetric analyzer (TGA-50, Shimadzu Corporation) to determine the amount of residual polymer.

3. Results and Discussion

3.1. Osmotic Pressure of Temperature-Responsive Slurries

Figure 7 shows the time change of osmotic pressure for the temperature-responsive slurries prepared in section 2.2. The time needed to reach an equilibrium state increased as the ratio of AMPS in the synthesized polymer increased. The reason of this trend has not been clear yet, however, it may be caused by the diffusion of ions through the semipermeable membrane. Figure 8 shows the effect of the AMPS ratio on the equilibrium value of osmotic pressure for the temperature-responsive slurry. The equilibrium osmotic pressure increased linearly with the polymer AMPS ratio. This is because the amount of the counter ion in the solution increased with the AMPS ratio, leading to an associated increase in osmotic pressure. Given the ion concentration resulting from all of AMPS counterions added in polymer synthesis, the osmotic pressures could be estimated using the van 't Hoff equation [40]. The resulting values were 18.3, 36.6, and 61.0 kPa respectively for slurries 2, 3, and 4. The measured osmotic pressures for all slurries were smaller than these estimated values even though the measured values for the slurries included the osmotic pressure generated not only by counterions but also by polymers and alumina particles. This indicates that the considerable added amount of AMPS was not included in the synthesized polymer. In actuality, the recovery ratio of solid matter in the synthesized polymer purification process decreased with increases in the AMPS ratio. This fact corresponds reasonably well with the above experimental results, that is, the difference between measured and estimated osmotic pressure increased with the ratio of AMPS in the synthesized polymer. It is therefore expected that the osmotic pressure of this temperature-responsive slurry can be raised measurably by improving the polymer synthesis process – an issue which needs to be addressed in the future work.

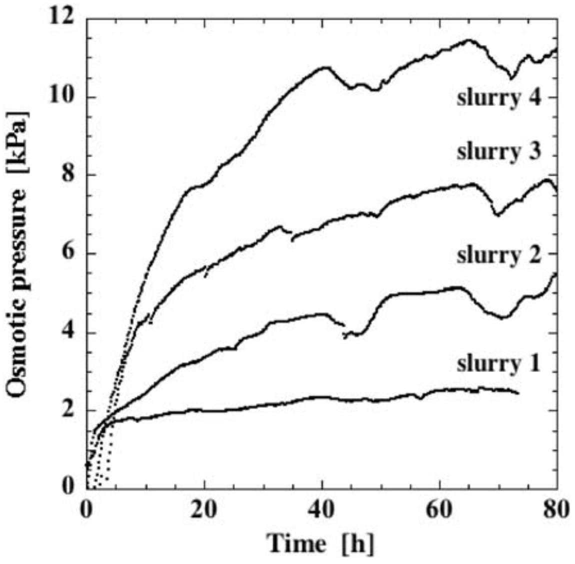


Figure 7. *Time change of osmotic pressure of all prepared slurries.*

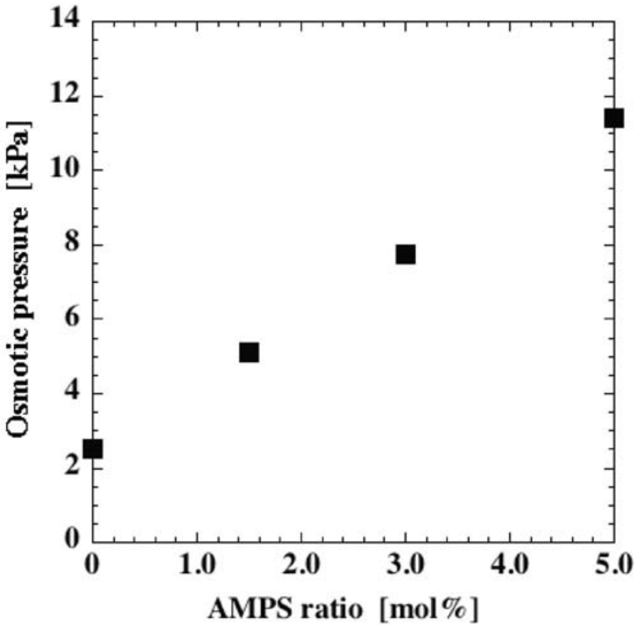


Figure 8. *Effect of AMPS ratio on the magnitude of osmotic pressure of the prepared slurry.*

3.2. FO and the Water Recovery Test for Temperature-Responsive Slurries

Figure 9 shows the water flux during FO tests of temperature-responsive slurries. These figures show the water flux resulting from each FO and water-recovery test (performed three times). It can be seen in Figure 10 corresponded to slurry 3 that there was clear supernatant while for slurry 4, which had the highest AMPS ratio in this study, there was no clear supernatant. This implies no pure water was separated by gravitational sedimentation following the temperature change for slurry 4. This result indicates that flocculation of particles and polymers, which can enhance settling and separation, did not occur for slurry 4. This is probably because the hydrophilicity and LCST of the polymer were raised due to the high ratio of AMPS. Highly hydrophilic polymer with a relatively high LCST can be adsorbed particles in the slurry at room temperature, thus, the additional adsorption of polymer which could enhance the formation of flocs did not occur for slurry 4.

Conversely, the water flux of each FO test had almost the same value for slurries 1, 2, and 3. This indicates that the almost all the added polymer was included in the particle bed formed by settling after the temperature change, rather than being included in the supernatant. To state this idea in another way, the concentration of the polymer in DS, the temperature-responsive slurry did not change for each subsequent FO test even though the temperature-responsive polymer was repeatedly used.

Table 3. *pH of temperature-responsive slurry.*

slurry No.	slurry pH [-]
1	5.5
2	3.9
3	3.0
4	2.9

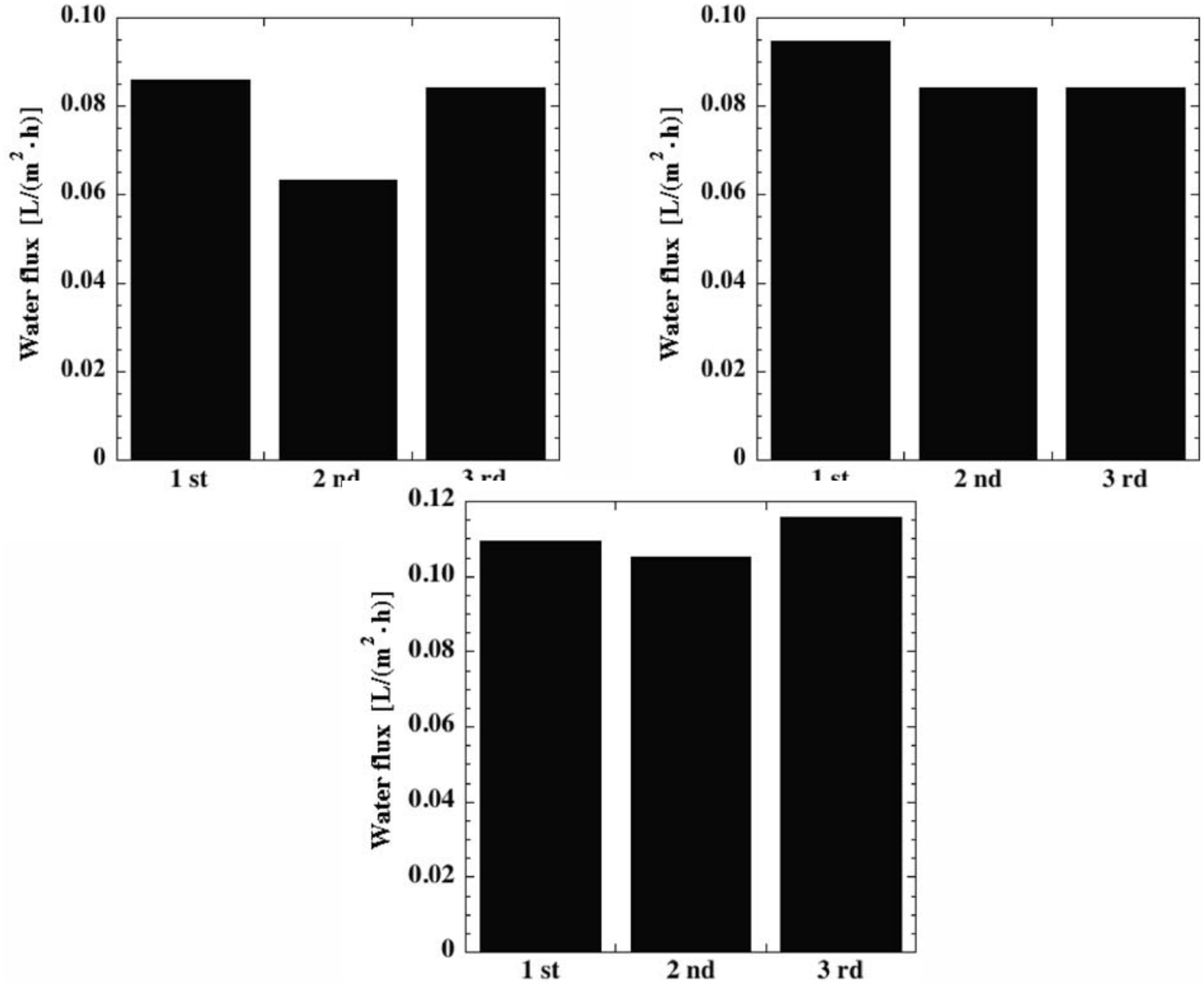


__Figure 9.__ Water flux of each slurry, (a) slurry 1, (b) slurry 2, and (c) slurry 3.

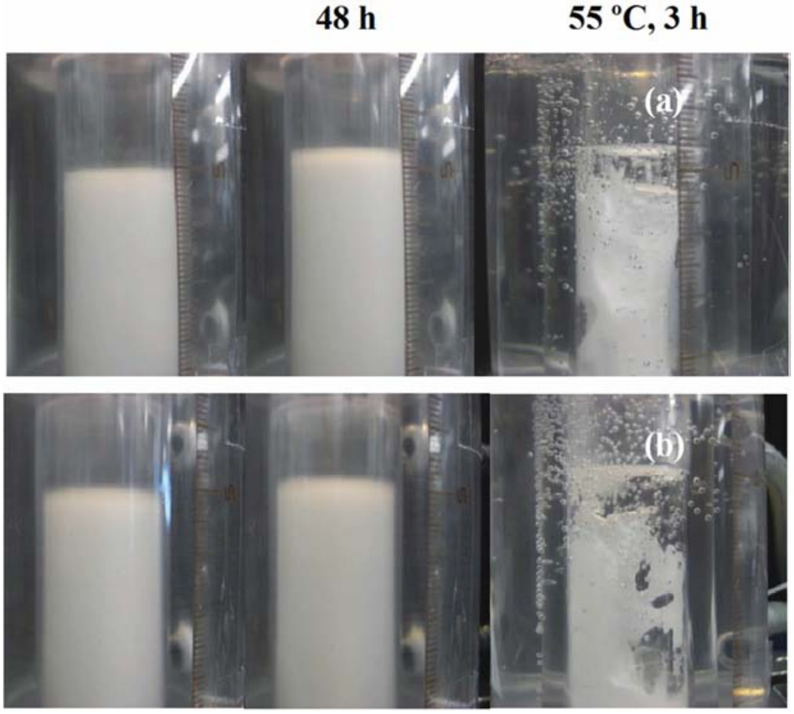


__Figure 10.__ Appearance of the draw solution (slurry 3), (a) after 48 h absorption of water and (b) after heating at 55°C for 3 h.

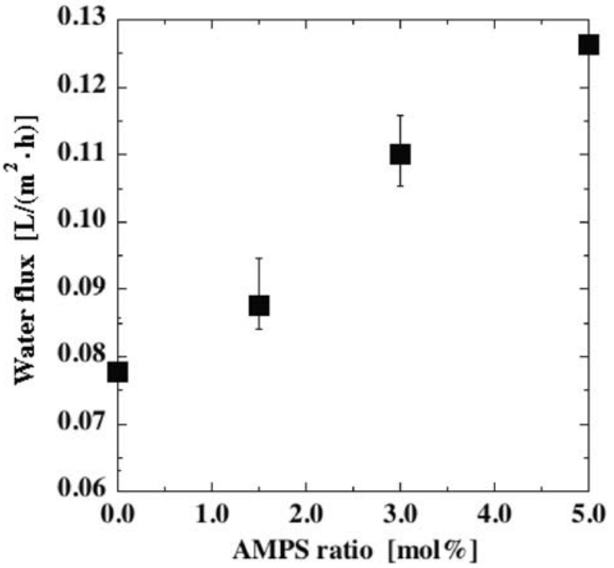


Figure 11. *Effect of AMPS ratio on the water flux.*

The pH value of each temperature-responsive slurry is listed in Table 3. From this result and Figure 3, it is shown that the synthesized copolymers which had negative charge can adsorb onto the positively-charged alumina surface in slurries 2, 3, and 4 even at room temperature. This is a result of the electrostatic interaction between the two. When the temperature was changed and became greater than the LCST, the polymer became more hydrophobic and could more easily adsorb to alumina particles. Thus, almost all the polymer adsorbed to alumina at higher temperatures, forming the large flocs with higher settling velocity except for slurry 4.

Figure 11 shows the effect of the AMPS ratio on the water flux of FO test. For slurry 4, the plot shows only the value of the first FO test because the slurry could not be used repeatedly, as mentioned before. For all other slurries the plot shows the average value of all three FO tests, and the bar shows the minimum and maximum value of the water flux. The expected linear increase in water flux associated with the increases in polymer AMPS ration is shown in Figure 7. This result is quite natural since the driving force of FO is the osmotic pressure of the draw solution (the temperature-responsive slurry).

3.3. Comparison Between Temperature-Responsive Polymer Solution and Slurry

Figure 12 shows the appearances of slurry 1 and its solution without alumina particles after heating at 55°C for 3 h in a hot water bath. This figure clearly shows that a large volume of supernatant formed for slurry 1 relative to the total solution volume. Due to the alumina particles, the solid matter that formed at the bottom of the container for slurry 1 had a smaller volume than its associated solution without alumina. This result suggests that the added alumina particles to the temperature-responsive polymer solution made the formed flocs denser, resulting in the closely packed structure of the whole sediment. The water recovery ratio and the polymer residue ratio are summarized in Table 4. Here, the water recovery ratio and the polymer residue ratio were calculated using the following equations:

$$\left(\text{Water recovery ratio}\right)=\frac{\left(\text{Mass of collected supernatant}\right)}{\left(\text{Mass of slurry or solution}\right)}\times 100\quad\left[\%\right] \tag{1}$$

$$\left(\text{Polymer residue ratio}\right)=\frac{\left(\text{Mass of polymer in supernatant}\right)}{\left(\text{Mass of polymer in slurry or solution}\right)}\times 100\quad\left[\%\right] \tag{2}$$

Table 4. *Water-recovery ratio and polymer-residue ratio.*

sample	water recovery ratio [%]	polymer residue conc [mass%]	polymer residue ratio [%]
polymer solution	22.3	0.82	0.55
slurry	32.3	0.28	0.19

The water recovery ratio of slurry 1 was larger than that of the solution of slurry 1 without particles due to added alumina particles, also shown in Figure 11. Additionally, the polymer amount which remained in solution following separation of slurry 1 was smaller than that of the alumina-lacking solution. From these results, it can be stated that the presence of alumina particles in the solution of temperature-responsive polymers enhances the co-flocculation of particles and polymers while still allowing the hydrophobic polymer to precipitate by itself at temperatures above LCST. This results in efficient separation of water and reduced amount of residual polymer in the supernatant.

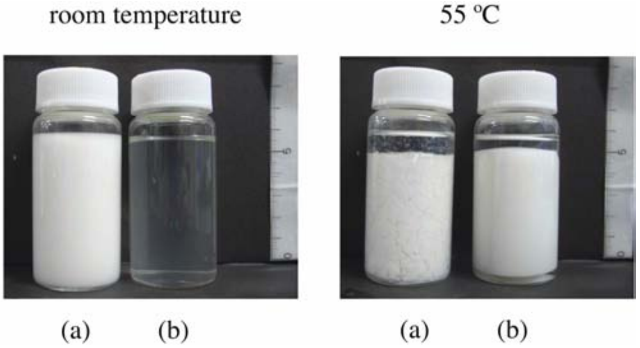


Figure 12. *Appearance change of (a) slurry, (b) polymer solutions by temperature.*

4. Conclusions

The potential of the temperature-responsive slurry as a draw solution for forward osmosis was investigated. The slurries containing the dispersed alumina particles and temperature-responsive polymers synthesized from varying ratios of AMPS and NIPAM were successfully prepared. The osmotic pressure measurement and the forward osmosis test of the prepared slurries were conducted. The following conclusions were obtained.

(1) The temperature-responsive slurries used in this study, with the exception of slurry 4, could be used repeatedly as draw solution for FO test and the water flux of each FO test did not changed. Slurry 4 could not be used in this application due to difficulty of the separation of pure water from the diluted DS, caused by the high polymer AMPS ratio.

(2) When comparing the results between a temperature-responsive polymer solution and temperature-responsive slurry, an improvement possibility was discovered. The water recovery ratio following FO was improved due to the presence of alumina particles. It was also suggested that the added alumina particles diminished the residual polymer remaining in the solution.

With these results, the temperature-responsive slurry is expected to be a promising draw solution which can be used easily and repeatedly. Increasing the generating the osmotic pressure of the temperature-responsive slurry by improving the polymer synthesis process is an issue which needs to be addressed in the future work.

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