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Reclaiming polymer-flooding produced water for beneficial use: Salt removal via electrodialysis

Guolin Jing*, Lijie Xing, Shulin Li, Chunjie Han

College of Chemistry and Chemical Engineering, Daqing Petroleum Institute, Daqing 163318, China
Tel. +86 (459) 650-3502; Fax +86 (459) 650-3502; email: jingguolin@yahoo.cn

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ABSTRACT

This paper discusses the use of electrodialysis (ED) to remove salts from polymer-flooding produced water (PFPW) in order to meet confecting polymer solution standards. Specifically, the ED treatment of PFPW with total dissolved solids (TDS) concentrations and varying cations and anions distributions was evaluated at three voltage settings. The removal rates of cations, anions, and TDS increased rapidly with time at the same voltage; their removal rates also simultaneously increased with voltage. With Neosepta® CMX-SB/AMX-SB membranes, cations and anions were generally found to be removed in the following order (from the fastest to the slowest): $Ca^{2+} > Mg^{2+} > K^+ \approx Na^+$ and $Cl^- > SO_4^{2-} > CO_3^{2-} > HCO_3^-$. The viscidity of the polymer solution confected by treated PFPW was found to be superior compared with the polymer solution confected by fresh water.

Keywords: Electrodialysis; Polymer-flooding produced water; Total dissolved solids; Water treatment; Removal rate

1. Introduction

Polymer-flooding oil production in the Daqing oilfield in China has entered the industrial stage [1]. Currently, it produces an annual amount of about 6×10^7 m^3 of polymer-flooding produced water (PFPW) with its production of oil and gas [2]. Polymer-flooding produced water is a complex multi-phase system containing solid and liquid impurities as well as dissolved gases and salts, among others. Its main characteristics include [3] (1) high polymer concentration; (2) high suspended solid concentration; (3) high oil concentration; (4) PFPW-rich HCO_3^-, Na^+ and Cl^- concentrations; (5) high PFPW pH, conductivity and salinity; and (6) serving as the breeding places of sulfate reducing bacteria and saprophytic bacteria caused by rich organic compounds and suitable water temperature. The successful treatment of PFPW generally requires a series of operations to remove different contaminants. Separation techniques tested for the removal of oil, grease, and suspended solids from PFPW include walnut shell filtration [4], fiber ball media filtration [5], gravity-type crossflow pack separation [6], ceramic crossflow microfiltration [7,8], and ultrafiltration [9]. As shown in previous studies, the removal of organic compounds from PFPW has been achieved through eletroflocculation [10], carbonaceous adsorbent [11], bioreactors [4,8,12], wetland treatment [13], ultrafiltration [14] and nanofiltration [15]. Upon the removal of oil, grease, suspended solids, and organic compounds, PFPW can then be reclaimed for beneficial use.

As a new type of industrial wastewater, PFPW has three kinds of usage approach [16]. First is direct dis-

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* Corresponding author.

charge or treated discharge which entails tremendous processing costs. Second, PFPW can be used for oil field injection water. The treatment of oil field PFPW normally uses two-stage settlement and two-stage filtration technology to meet water injection standards for high permeability layer. However, because of excessive polymers, oil and suspended solid particles, the treatment of PFPW can plug the middle or low permeability layer, decrease permeability, and produce physical harm. As such, treated PFPW cannot be used as injection water for middle or low permeability layer. Third, treated PFPW can be used for confecting polymer solution. Polymer increases the viscosity of water and residence time in a porous medium, reduces water permeability and the mobility rate of water and oil, as well as increases the spreading coefficient to improve the oil recovery ratio. By increasing PFPW polymer concentration to meet the injection standards of polymer solution viscidity, the economic benefits of polymer flooding will be far below that of water polymer flooding [17]. Given that higher polymer concentrations harm the stratum, hence, there is a demand to study new ways of treating oilfield PFPW to meet confecting polymer solution standards. Therefore from a long-term economic point of view, treated PFPW has great potential as polymer solution prepared water. It does not only eliminate major pollution sources caused by PFPW discharge, but also solves the prevailing water problem during the development of polymer production as well as achieves a favorable cycle for wastewater reclaiming.

Toward this goal, desalting PFPW TDS is the key to solving the problem of confecting polymer solution with PFPW. Separation technologies that are currently available for desalting PFPW include filtration with bentonite membrane [18], reverse osmosis [4,20], evaporation, crystallization, membrane distillation, ion exchange [21,22] and electrodialysis (ED). Reduction of TDS in PFPW with ED is the focal point of this paper. In addition to PW, ED has been successfully used to reduce TDS from surface water [23], groundwater [24,25], brackish water [26] and seawater [27].

In ED, electrolytes are transferred through a system of solutions and ion exchange membranes by an applied electric potential gradient [28]. An ED stack consists of cation-exchange membranes, which are permeable only to positively charged ions. It also consists of anion-exchange membranes, which are permeable only to negatively charged ions. In the stack, cation-exchange membranes alternate with anion-exchange membranes to form solution compartments. When an electrical potential is applied between the electrodes at the end of the stack, all cations in the solution circulating through the stack tend to move toward the cathode, while all the anions tend to migrate toward the anode. The cations that migrate through cation-exchange membranes toward the cathode are rejected by the anion-exchange membranes; simultaneously, while the anions that pass through the anion-exchange membrane toward the anode are rejected by the cation-exchange membrane. As a result, ion depletion and concentration are accomplished in alternating solution compartments. Diluted streams from alternating compartments are the combined and distributed back to the same compartments to continuously remove the ions. An analogous process occurs to continuously increase the number of ions in the concentrate.

In this experiment, the ED treatment of PFPW and the varying distributions of different cations and anions were evaluated at three voltage settings. The removed orders of cations or anions were respectively compared. In addition, the problem of membrane fouling has already been studied and described in another paper [29].

2. Experimental

2.1. Feed water

Feed water was obtained from the Daqing Oilfield in China. The anionic polymer (partly hydro-lyzed polyacrylamide, HPAM) was supplied by S.N.F. Company (France), with an average molecular weight (MW) of 2.72×10^6 and a degree of hydrolysis of about 25/30%. Usage of actual PFPW would require significant upstream treatment of the ED system to remove oil, grease, suspended solids, and organic compounds. Details of the anion and cation distributions of the PFPW are listed in Table 1.

2.2. Analytical methods

The concentration of cations was measured with an atom-absorbing spectrum (PERKIN-ELMER 703), the concentration of anions was measured with ion chromatogram (DLONEX 4500i), and the sum amount of the ionic concentration became the TDS.

2.3. Electrodialysis experiments

The electrodialysis stack was equipped with a NEO-

Table 1
Components and concentrations of feed water

K^+	3.8
Na^+	1100
Ca^{2+}	6.1
Mg^{2+}	2
Cl^-	670
SO_4^{2-}	11.1
HCO_3^-	2772
CO_3^-	3.4
TDS	4568.4

All concentrations are in mg/L

SEPTA ACS and CMX membranes manufactured by Tokuyama Co The electrodialysis apparatus was supplied by the Eurodia Co. It is a TS-2-10 pilot which is a batch type dialysis unit. It has a stack with 15 cell pairs of Neosepta CMX (strongly acidic cation exchange) membranes having an effective area of 770 cm^2 and electrical resistance of about 8 $\Omega\cdot cm^2$. The pumps have a maximum capacity of 5.0 L/min. The DC power at constant potential (max 30 V) per current (max 5 A) was provided by a rectifier. Three solution tanks (each 10 L) were used for holding dilute, concentrated, and electrode rinse solutions. The electrodes used were platinum-plated titanium (anode) and stainless steel (cathode).

The two electrode compartments were separated from the others to prevent a modification in the composition of the concentration sides, which could be caused by electrode reactions. About 10 L solution of 0.1 mg Na_2SO_4 was used as an electrode rinse. For the concentrate and diluted compartment, 10 L PFPW was used for both. The experiment was conducted under the direct current voltage, and the three applied direct current voltages were 5 V, 10 V and 15 V. Conductivity was directly measured in the diluted compartment, and all the solutions were allowed to circulate in a closed loop. The number of replicated experiments that provided the basis for the calculation of the mean and standard deviation values was five. The layout of the experimental set-up is shown in Fig. 1.

3. Results and discussion

It has been found that PFPW contains K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-}, CO_3^{2-}, and so on, in which Na^+, Cl^-, and HCO_3^- are the main ions comprising TDS. The content of Ca^{2+} and Mg^{2+} comprise the most important factors influencing solution viscidity.

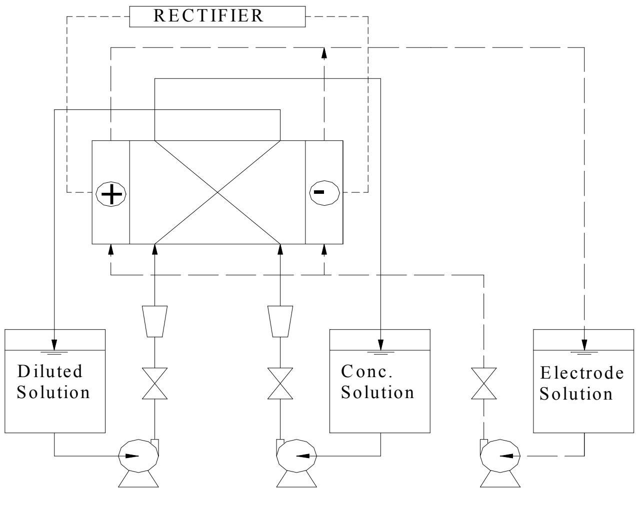

Fig. 1. Batch mode operation of the electrodialysis system.

Fig. 2 shows the variation with time of the removal rate of K^+, Na^+, Ca^{2+} and Mg^{2+} in PFPW at three applied voltages: 5 V, 10 V, and 15 V (flow rate is 150 L/h). The removal rates of K^+, Na^+, Ca^{2+} and Mg^{2+} increase rapidly with time at the same voltage for PFPW. Simultaneously, the removal rates of K^+, Na^+, Ca^{2+} and Mg^{2+} increase rapidly with increased voltage for simulated PFPW. As shown in Fig. 2, the removal rates of K^+ and Na^+ are very similar for three applied voltages: 5 V, 10 V, and 15 V. On the other hand, the removal rate of Mg^{2+} increases with time, and then stops increasing with time to a certain value at 15 V. However, the removal rate of Mg^{2+} increases rapidly with time at 5 V or 10 V, while the removal rate of Ca^{2+} also increases rapidly with time for three applied voltages: 5 V, 10 V, 15 V.

Fig. 3 shows the variations with time of the removal rates of Cl^-, HCO_3^-, SO_4^{2-} and CO_3^{2-} in PFPW at the three applied voltages: 5 V, 10 V and 15 V with a flow rate of 150 L/h. The removal rates of Cl^-, HCO_3^-, SO_4^{2-} and CO_3^{2-} increase rapidly with time at the same voltage for PFPW. From Fig. 3 we can see that the removal rates of Cl^-, HCO_3^-, SO_4^{2-} and CO_3^{2-} increase more rapidly with time at 15 V than at 10 V or 5 V.

Fig. 4 shows the variations with time of the removal rate of TDS in PFPW at the three applied voltage with a flow rate of 150 L/h). The removal rate of TDS increases rapidly with time at the same voltage for PFPW. In addition, in the same time the TDS removal rate increases rapidly with voltage increase in PFPW. The removal rate of TDS increases more rapidly with time at 15 V than at 10 V or 5 V. As seen from Figs. 3, 4 and 5, 10 V is identified as the optimal voltage. Therefore, the selected voltage for comparing the removal order of cations and anions is 10 V.

As shown in Fig. 5, the curves representing the removal rates of K^+ and Na^+ are nearly coincident, so the removal rates of $K^+ \approx Na^+$. The removal rate of Ca^{2+} is the largest, that of Mg^{2+} is the second largest, and those of K^+ and Na^+ are the least. In comparing the time required to achieve the same removal rate, Ca^{2+} is the least, followed by Mg^{2+} and K^+ and Na^+. The cations were generally removed in the following order (from the fastest to the slowest): $Ca^{2+} > Mg^{2+} > K^+ \approx Na^+$. Divalent ions are prioritized as they pass through ion-exchange membranes is a phenomenon in electrodialysis, electrodialysis dynamics can explain this phenomenon. In the case of other conditions remain unchanged, the higher ionic valence is, the current is greater caused by the ionic migration, the ionic transterence velocity is faster in channel, and ionic transporting quantity is bigger in unit time. The results show that the quantity of multicharged ions passing through the ion-exchange membranes during separation performance in unit time is larger than the low charged ions' quantity, namely the multicharged ions are prioritized as they pass through ion-exchange membranes.

As shown in Fig. 6, the removal rate of Cl^- is the largest, followed by those of SO_4^{2-} and CO_3^{2-}, with that of

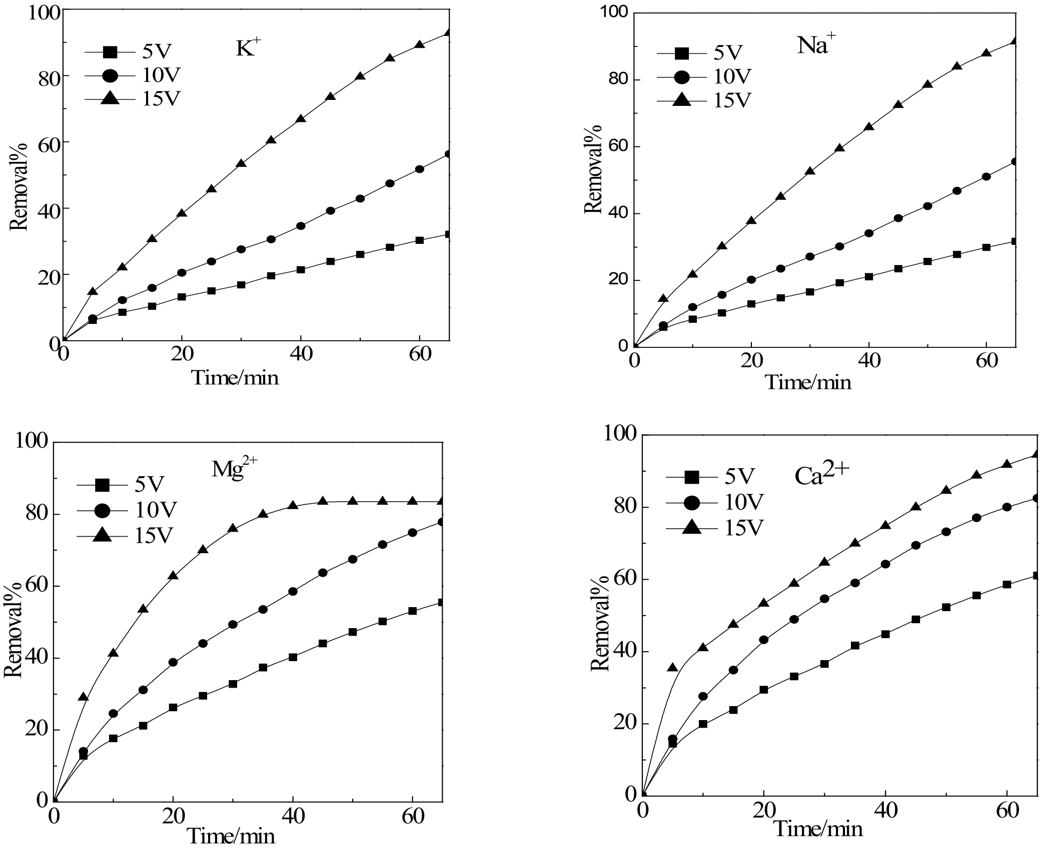

Fig. 2. Variation with time of the removal rate of cations at different voltages.

HCO_3^- as the least. The time required for removing Cl^- is the least, followed by SO_4^{2-} and CO_3^{2-}, with HCO_3^- as the longest. Therefore, the anions were generally removed in the following order (from the fastest to the slowest): $Cl^- > SO_4^{2-} > CO_3^{2-} > HCO_3^-$. Normally, the ion mobility rate is related to hydrated ion radius in ED stack; the larger hydrated ion radius is, the slower the ion removal rate would be. the hydrated ion radii of Cl^- and HCO_3^- are different, the hydrated ion radius of bicarbonate ion is larger than chloride-ion hydrated ion radius, so the removal rate of Cl^- is higher than HCO_3^-.

Energy consumption (EC) was calculated using Eq. (1) during ED treatment of PFPW:

$$EC = \frac{E\int_0^t Idt}{V_D} \tag{1}$$

where E is operating voltage, I is operating electric current, t is the time of desalinating and V_D is volume of diluted solution.

Fixed flow rate at 150 L/h, changing operation voltage respectively 5 V, 10 V, 15 V, under each constant voltage, concentrate and dilute water circulated independently, and the current value were recorded at different desalinating until the conductivity reached 500 μS/cm stopped experiment. Energy consumption (EC) was calculated using Eq. (1). In order to investigate the potential gradient on the impact of energy consumption and desalination time, with voltage as abscissa and energy consumption and desalination time as vertical plotted Fig. 7. As can be seen in Fig. 7, the conductivity in the dilute compartment down to the same level required for the time was significantly decreased when the voltage increased from 5 V to 10 V, while the voltage continuously increased to 15 V, this trend became less obvious, the time required for was basically the same. The energy consumption increased linearly with voltage increased, This is because the voltage increased from 5 V to 15 V, an electrical potential difference used as the main driving force in electrodialysis (ED), its increasing would accelerate ion diffusion from dilute to concentrate compartment. While if the voltage continues increased, current density would increase to limiting current density, it will lead to concentration polarization and water dissociation, which reduces the current efficiency, increases energy consumption.

The major ion contents and properties in the treated PFPW, fresh water, and untreated PFPW are compared in Table 2. The TDS of the diluent is 826.34 mg/L and

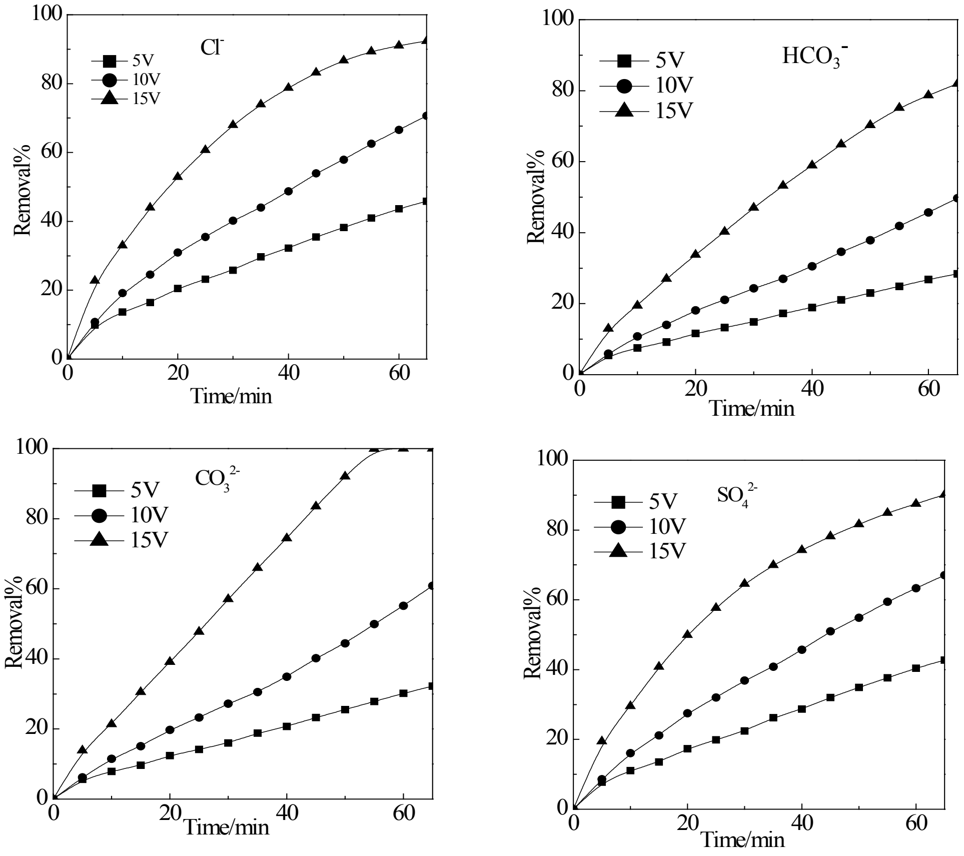

Fig. 3. Variations with time of the removal rates of anions at different voltages.

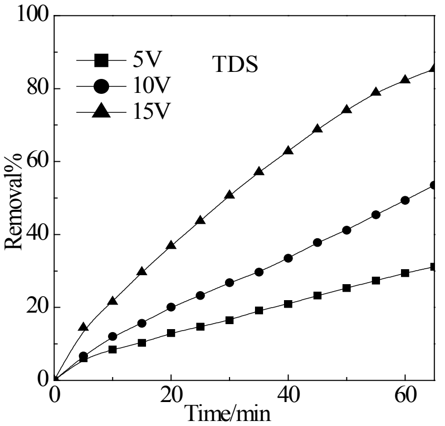

Fig. 4. Variation with time of the removal rates of TDS at different voltages.

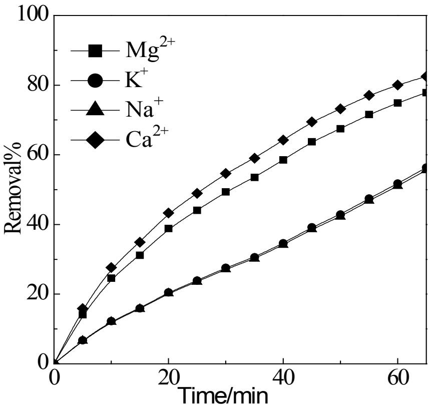

Fig. 5. The removed order of cations.

the contents of Ca^{2+}, Cl^-, Na^+, and HCO_3^- are respectively 0.8 mg/L, 38.66 mg/L, 167.47 mg/L and 613.88 mg/L. The TDS of treated PFPW is higher than that of fresh water, but the viscosity of treated PFPW is higher than that of fresh water. This is caused by the exiting of Ca^{2+}. The effect of calcium ions on the viscidity of the polymer solution is much greater than that of the sodium ions. The capability of calcium ions to neutralize negative electricity in the polymer group is higher than that of the sodium ions. These results show that the curl flexibility of the poly-

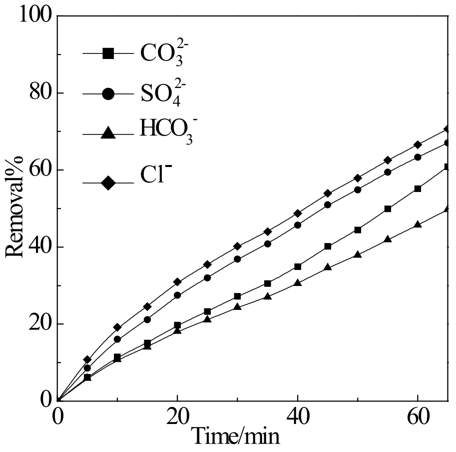

Fig. 6. The removed order of anions.

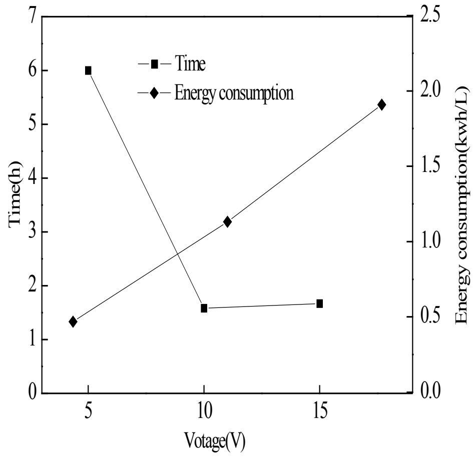

Fig. 7. The affect of voltage vs. energy consumption and desalination time.

Table 2
Water quality comparisons among untreated PFPW, treated PFPW and fresh water

State	Ca^{2+}	Cl^-	K^+, Na^+	HCO_3^-	TDS	Viscidity
Untreated PFPW	6.1	670.00	1103.80	2772.00	4567.6	18.7
Treated PFPW	0.8	38.66	167.47	613.88	826.34	66.2
Fresh water	24.05	53.19	85.8	122.04	388.47	40.5

mer molecules are larger and the equivalent volume of hydrodynamics smaller. At the same time, the viscidity of the polymer solution became decreased.

Polymer solutions were confected by PFPW, fresh water, and treated PFPW. The viscidities of the polymer solutions were determined with a DV-II type rotary viscometer at 45°C and at the speed of 6 rpm. The results in Fig. 8 show that the treated PFPW was treatable in confecting polymer solution standards after 1 h at 10 V. The viscidity of the polymer solution by the treated PFPW confecting is excelled to viscidity of the polymer solution by confecting fresh water. It may be entirely used for driving oil instead of fresh water. In this experiment, based on comprehensive consideration of energy consumption and desalination time, selecting 10 V operating voltage was more appropriate, because under this condition, required less energy consumption and the time required for desalinating was shorter.

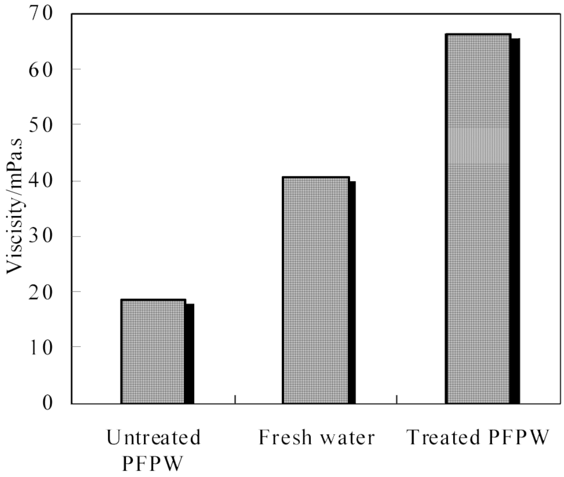

Fig. 8. Comparison of viscosities for the polymer solutions.

4. Conclusions

The ED treatment of PFPW with TDS and varying cations and anions distributions was evaluated at three voltage settings (5 V, 10 V, and 15 V). Variations with time of the removal rate of cations, anions, and TDS were studied in PFPW for the same applied voltages with a flow rate of 150 L/h. The removed orders of cations or anions were respectively compared at 10 V; from these, the conclusions were deduced. The removal rates of cations, anions, and TDS increased rapidly with time at the same voltage for PFPW. Simultaneously, the removal rates of cations, anions, and TDS increased rapidly with voltage increase in the PFPW. In addition, 10 V was confirmed as the best of the three applied voltages through variations with time of the removal rates of cations, anions, and TDS. The cations and anions were generally found to be removed in the following order (from the fastest to the slowest): $Ca^{2+} > Mg^{2+} > K^+ \approx Na^+$ and $Cl^- > SO_4^{2-} > CO_3^{2-} > HCO_3^-$. Finally, treated PFPW showed a capacity to confect polymer solution standards after 1 h at 10 V, and the viscidity of the polymer solution by the treated PFPW confecting process was improved by fresh water confecting. It may be entirely used for driving oil instead of fresh water.

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