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Preparation and characterization of polymer–carbon composite membranes for the removal of the dissolved salts from dye wastewater

Yong Hwan Lee [a,*], Jae Yun Jeong [a], Jonggeon Jegal [b], Joong Hwan Mo [c]

[a] Department of Molecular System Engineering, Hanyang University, 17 Haengdang-Dong, Seongdong-Ku, Seoul, South Korea
[b] Membrane and Separation Research Center, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusung, Daejon, South Korea
[c] School of Materials Science and Engineering, Seoul National University, Seoul 151-742, South Korea

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Abstract

Polymer–carbon composite membranes (PCC membranes here after) were prepared and used for the removal of the dissolved salts from dye wastewater. The dye wastewater used in this study was prepared by filtering with a membrane of MWCO 3500 the solution coming out of the synthetic process of Reactive Red 195. The PCC membrane system turned out to remove effectively the salts dissolved in the dye wastewater. The TDS removal efficiency increased with decreasing flow rate of the wastewater. As the flow rate was 0.5 LPM, it appeared to be about 98%. With increasing rinse time, the adsorption–desorption efficiency of the ions by the PCC membrane was improved, showing better efficiency for the TDS removal. As the TDS concentration of the wastewater decreased, its removal efficiency increased and reached about 99% at the TDS concentration of less than 2000 ppm.

Keywords: Membrane; Carbon; Salt; Dye wastewater; Removal; Electric adsorption; TDS

1. Introduction

With industrialization, water-deficient state is getting worse because of the water pollution and dry-up of the water resource. Over 40% of the people in the world have been suffering from water-shortage. According to report from the United Nations (UN), the amount of water possible to be used right now in Korea is estimated to be about 66.1 billion m^3, which can be converted into about 1472 m^3 per person [1,2]. Being compared with the water amount of 3247 m^3 per person in year 1950, Korea can be classified as a water-deficient country. With the estimated amount of water in year 2025 of 1258 m^3, it is very urgent for the Korean government to make plan to cope up with this kind of water-shortage problem.

For the Korean government, it is now needed to strengthen the guideline for the release of the effluent and to come up with an efficient wastewater treatment method. The best solution to solve this kind of water-shortage problem is to reuse wastewater after perfect treatment, then to decrease the amount of effluent released to the river again, protecting the water resource from secondary pollution. So far, many studies have been carried out for the wastewater treatment and for protecting the water resource, but the techniques that have been developed have limited capabilities of desalting sea water or treatment of wastewater with low TDS (total dissolved solid) concentration, using membranes and ion-exchange resins. The main reasons for the limited capabilities of the current techniques for the water treatment are related to the high operating cost for the treatment of the wastewater with high TDS concentrations.

With increasing interests in the wastewater reuse and in the efficient treatment of sea water, there are strong needs for the economically favorable techniques for the water treatment. On

* Corresponding author. Tel.: +82 2 3665 1102; fax: +82 2 3663 6551.
E-mail address: iyhlee@ihanyang.ac.kr (Y.H. Lee).

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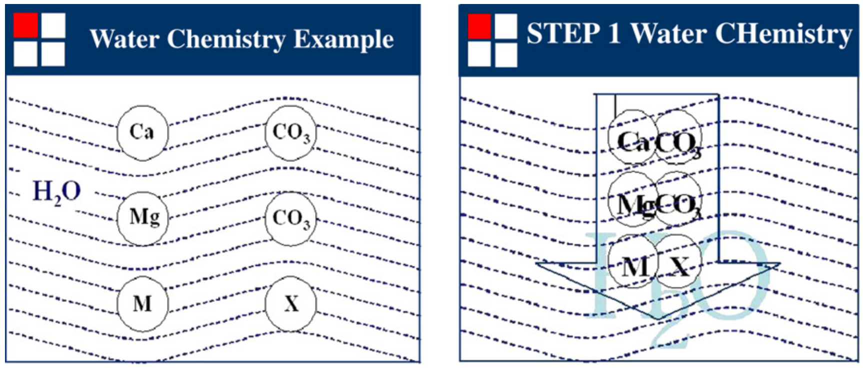

Fig. 1. Water chemistry example.

this basis, polymer–carbon composite (PCC) membranes that can remove the TDS effectively from wastewater through the electronic adsorption–desorption mechanism were prepared and used for the effective treatment of dye wastewater, in this study.

2. Theory [3–7]

An electronic adsorption method can remove the materials such as mineral, silica and metals consisting of TDS of the organic and inorganic wastewaters through the electronic adsorption reaction with the help of the electrical current flowing through the membranes working as an electrode (Fig. 1). There are electronic adsorption reactions of oxidation, reduction, dissociation and precipitation by the movement of ions into anode and cathode, and the product of electronic adsorption reactions such as coagulation, sedimentation, adsorption and floatation above the water surface. Anions and cations in the water are in the state of being associated with water and trying to move to anions and cations each other when no electric current is applied from outside. Once the electric current is applied, anions move to cathode and cations to anode (Fig. 2).

During the water treatment, after installing the electrodes in the adsorption bath for electric adsorption, as the voltage between the electrodes is increased, electric current begins to flow, and at 2–3 V, the electric current become suddenly strong. The certain voltage inducing strong electric current is so called adsorption–dissociation voltage. In Fig. 3, it has been shown that electric current increases slowly up to 2–3 V, and then abruptly increases as the voltage increases over that point.

As explained above, there are two kinds of electric adsorption in water: one is electric adsorption under the adsorption–dissociation voltage and the other is the one above the adsorption–dissociation voltage. For the electric adsorption under the adsorption–dissociation voltage, if there is no separating membrane between the electrodes, H^+ is attracted to the anode to become H_2 by the reduction, and OH^- is to be attracted to the cathode, but there is no oxidation and no oxygen evolvement. Consequently, H^+ is being consumed, but OH^- is accumulated in the water without being dissociation, making the water automatically alkali. For the electric dissociation of the NaCl aqueous solution of 0.005–0.10 wt.%, the equations for the reaction occurring in the anode and cathode are as follows.

The oxidation reaction occurring in the cathode as the current flows through the electrode:

$$2Cl^- \rightarrow Cl_2 + 2e^- + 1.3583\ V(\varepsilon^0)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 1.229\ V(\varepsilon^0)$$

where ε^0: the standard electromotive force – when the solute concentration is 1 mol/L, and each gas pressure is 1 atm.

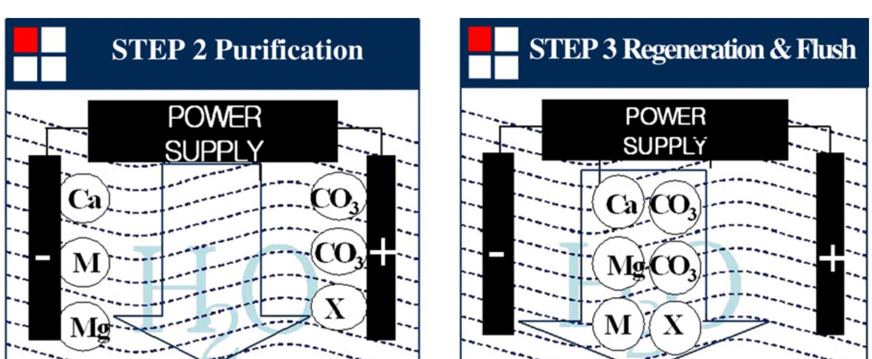

Fig. 2. Water electric purification, regeneration and flush.

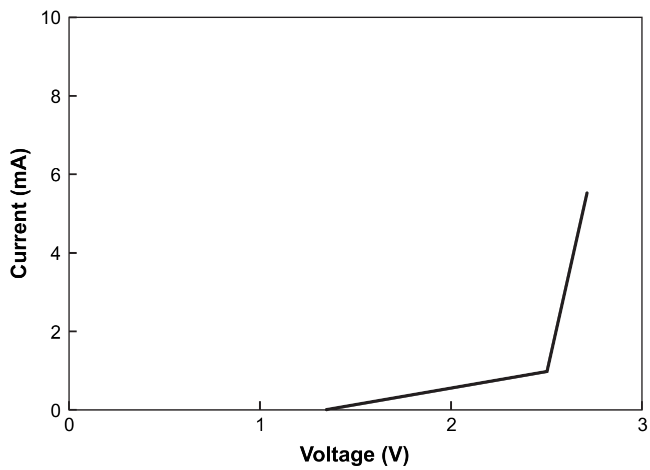

Fig. 3. Graph of the electrolysis and electrolysis voltage.

The reduction reaction occurring in the anode:

$$Na^+ + e^- \rightarrow Na - 2.713\ V(\varepsilon^0)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- - 0.8277\ V(\varepsilon^0)$$

For electric adsorption, direct current is used.

3. Experimental

3.1. Materials

3.1.1. Synthetic dye wastewater

The synthetic dye wastewater used in this study was prepared by filtering with a membrane with MWCO 3500 purchased from GE Co., the reaction solution of Reactive Red 195 whose chemical structure is shown in Fig. 4. Reactive Red 195 has usually been prepared by the synthetic process using cyanuric chloride, H-acid, $NaNO_2$, NADS (sulfo tobias acid), P-base, and so on. The Reactive Red 195 solution was filtered at 15 kgf/cm^2 of pressure to prepare the synthetic dye wastewater and the TDS concentration of the resulting wastewater ranged from 15,000 ppm to 17,000 ppm.

3.1.2. Polymer–carbon composite membrane

The polymer–carbon composite membrane (PCC membrane) is of utmost importance in this study. The electrical characteristics of the carbon material such as capacitance, density, pore volume, and electrical resistance affect the performance of the PCC membrane. The electrode with high specific surface area, high conductivity, high adsorption property, and high mechanical property usually has good adsorption of ions in water. The PCC membrane (CND Co., Korea, Model: CM20) was used in this study as a carbon electrode and its preparation method was as elaborated as follows: carbon powder and polyvinylidene difluoride (PVDF) (95:5 wt.% in composition) was dissolved into *N*-methylpyrrolidone, and the solution was cast on the glass plate followed by the phase inversion process using water vapor and drying at room temperature. Fig. 5 shows the FESEM photographs of the PCC membrane prepared in this study. The features of these PCC membranes were high specific surface area, high conductivity and high salts' rejection performance. This PCC membrane is possible to be used at low electrical power and no need of chemical treatment before using, and also has advantages of long time use by cleaning the salts attached to the PCC membrane continuously.

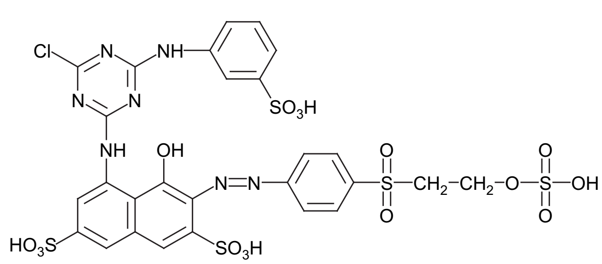

Fig. 4. Chemical structure of Reactive Red 195.

3.1.3. PCC membrane system

The structure of the PCC membrane system of this study is shown in Fig. 6. This system consists of water reservoir (PE, 100 L), micro-filter with 5 μm pores (PP, Shinyang Filter) and carbon composite membranes with a surface area of 1.0 m^2. The electrical power was applied to the system by using a power supply system (JIE Co., Korea) for the electrical adsorption of ions dissolved in the water. The voltage used in this study was controlled at 1.2 V. The treated water and concentrated water were sent to each reservoir after being checked using TDS meter of ISTeC Co. (Model: 460CP, USA) for their TDS concentrations.

3.1.4. Salts removal using PCC membrane system

Experiment for the salt removal from dye wastewater was carried out in this study using the PCC membrane system. The operation conditions employed in this experiment were as follows: the first and second stops were at 1 min and 15 s, respectively, and operation and rinse time and flow rate of the wastewater were controlled. The concentration of the dye wastewater ranged from 15,000 ppm to 17,000 ppm but in order to keep the membrane from the overloading, the dye wastewater was diluted before to the PCC membrane system. The TDS of the dye wastewater used for this experiment was 1170 ppm, 2900 ppm, and 6120 ppm.

4. Results and discussion

4.1. Characterization of the dye wastewater

The dye wastewater used in this study was analyzed using ICP/AES (Spectro Co., Germany, Model: Spectro CCD) and its composition was given in Table 1. Among the many different metals, Na, Mg, K, and Ca were relatively in their high concentrations.

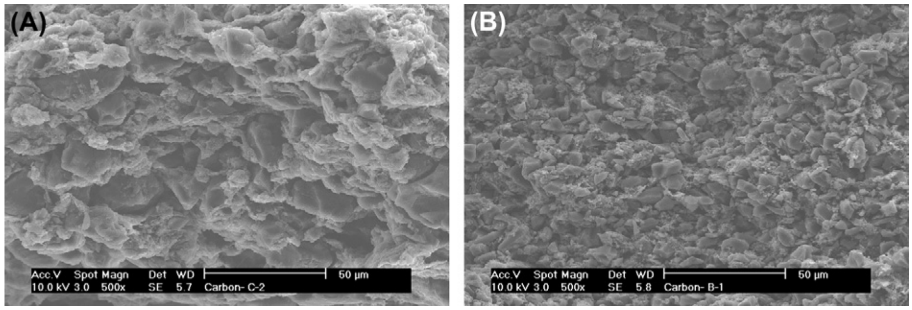

Fig. 5. The SEM images of the PCC membrane: (A) cross-section and (B) surface.

4.2. Removal of TDS from dye wastewater using a PCC membrane system

The TDS of the original dye wastewater was in the range of 15,000–17,000 ppm. Knowing from the previous study that in the TDS removal experiment with NaCl solutions using the PCC membrane system, with increasing TDS, the efficiency of the PCC membrane for the electric adsorption decreased, we diluted the TDS of the original dye wastewater to 4280 ppm. The operation conditions for the PCC membrane system were as follows: with constant running time of 4 min, the rinse time and water flow rates were varied for three cycles of operation to study the efficiency of the PCC membrane for the removal of the TDS from dye wastewater.

First of all, effect of rinse time on the removal of TDS from dye wastewater was studied under the operation condition as follows: water flow rate: 0.5 LPM, running time: 4 min, stop time: 15 s, water flow pressure: 0.5 kgf/cm^2, and Fig. 7 shows the result. It is found that as the rinse time was 3 and 4 min, the efficiency was the best. The TDS of the treated was relatively low as the rinse time was 3 or 4 min. This result indicates that for the better electric adsorption of TDS by the PCC membrane, it is needed to be cleansed for rather a longer time after one cycle of operation.

The high TDS of the treated water right after the end of each cycle of operation is because of the reverse charges applied to the PCC membrane for rinsing the membrane. In other words, because for the effective cleaning of the PCC membranes after running time, during the rinsing time, reverse charges are applied to the PCC membrane, the TDS adsorbed onto the membrane gets out of the membrane, so that for a short period of time, the TDS of the cleaning water is usually high. Therefore, when the rinse time is not long enough, the TDS of cleansing water is mixed into the treated water, increasing then the TDS of the treated water. Accordingly, as the rinse time increased from 1 to 4 min, the high TDS of the treated water right after each cycle become much lower.

4.3. Factors affecting the performances of the PCC membrane system

4.3.1. Effect of water flow rate

When the rinse time was changed from 1 to 4 min, to study the effect of the water flow rate on the performance of the PCC membrane for treating the dye wastewater, the operation condition of the PCC membrane system was given as follows: TDS of feed solution: 4280 ppm, water pressure: 0.5 kgf/cm^2, running time: 4 min, and stop time: 15 s.

From Fig. 8, it was found that the water flow rate is very important factor to be considered for the effective removal of TDS using this PCC membrane system. As one can see, when the water flow rate was over 1.0 LPM, the TDS removal

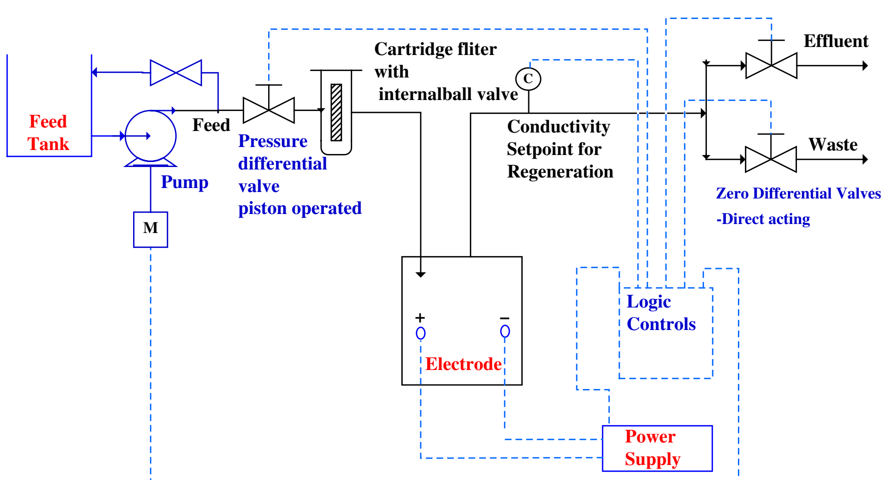

Fig. 6. Schematic diagram of the continuous reactor combined by electrolysis apparatus containing the PCC membranes.

Table 1
Analysis of dye wastewater elements

Concentrations of the metals contained in the dye wastewater					
Al	0.1 ppm	Ni	0.2 ppm	Na	3914 ppm
Cr	<0.1 ppm	Cu	0.1 ppm	Mg	4.4 ppm
Mn	0.1 ppm	Zn	<0.1 ppm	K	396.1 ppm
Fe	0.9 ppm	Cd	<0.1 ppm	Ca	131.6 ppm

efficiency was very low (about 30% for 1 LPM, and about 20% for 2 LPM), but at 0.5 LPM, the TDS removal efficiency was over 98%. This result means that when water flow rate was high, the TDS in the water is moving too fast to be captured by the PCC membrane, but as the water flow rate is slow enough for the TDS to get contact with the PCC membrane, the performance of the PCC membrane system is good for the removal of TDS from dye wastewater.

From this result, it can be concluded that for the effective removal of the TDS from dye wastewater, using the PCC membrane system, the water flow rate better be as slow as possible and the rinse time be long enough for the membranes to be cleansed completely.

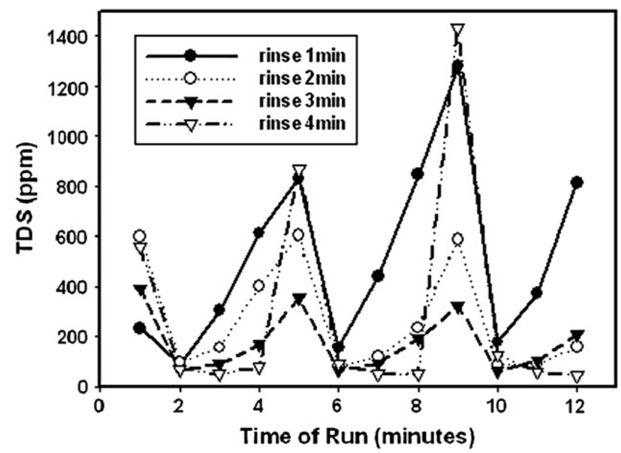

Fig. 7. The effect of rinse time on the TDS of the treated water along the running time when the operation condition of the PCC membrane system is as follows: water flow rate: 0.5 LPM, running time: 4 min, stop time: 15 s, and water flow pressure: 0.5 kgf/cm^2.

4.3.2. Effect of the concentration of feed water

For this experiment, three different concentrations of dye wastewater were prepared by diluting the original wastewater with distilled water. Fig. 9 shows the effect of the concentration of the feed water on the performance of the PCC membrane system. The operation condition employed for this study was as follows: water pressure: 0.5 kgf/cm^2, water flow rate: 0.5 LPM, running time: 4 min, stop time: 15 s, and rinse time: 4 min.

As one can see from Fig. 9, the TDS removal efficiency was increased with decreasing concentration of the feed water. For the wastewater with 1170 ppm of TDS, the removal efficiency was over 99%, for the wastewater with 2900 ppm of TDS, over 98%, and for wastewater with 6120 ppm of TDS, about 20–30%.

From this result, it is found that when the TDS concentration of the feed solution is too high, the capability of the PCC

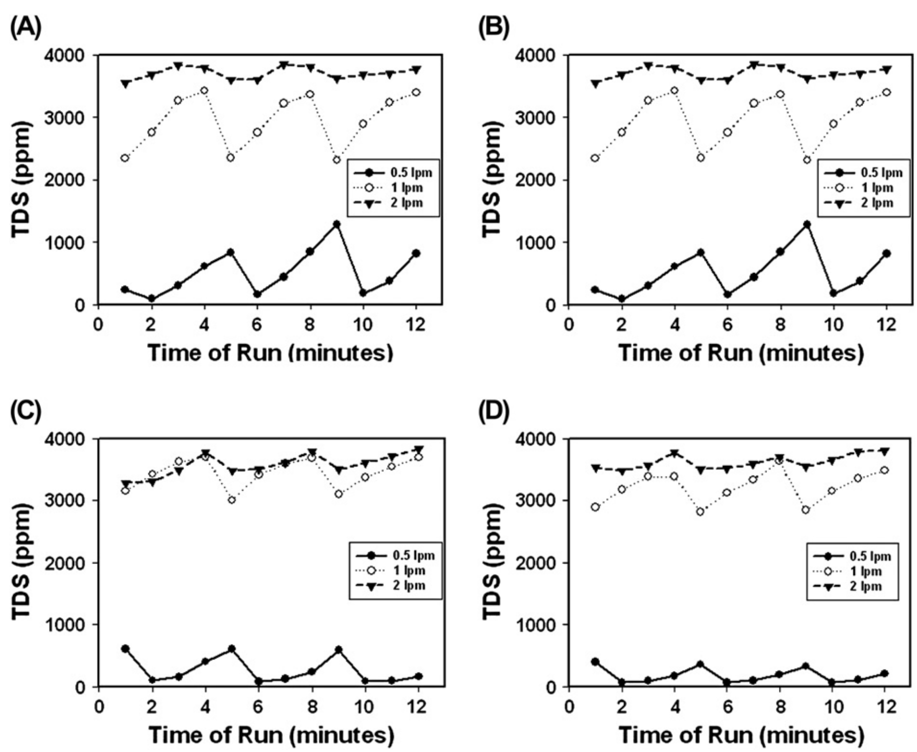

Fig. 8. The effect of the flow rate on the performance of the PCC membrane system as the rinse time was changed from: (A) 1 min, (B) 2 min, (C) 3 min, and (D) 4 min.

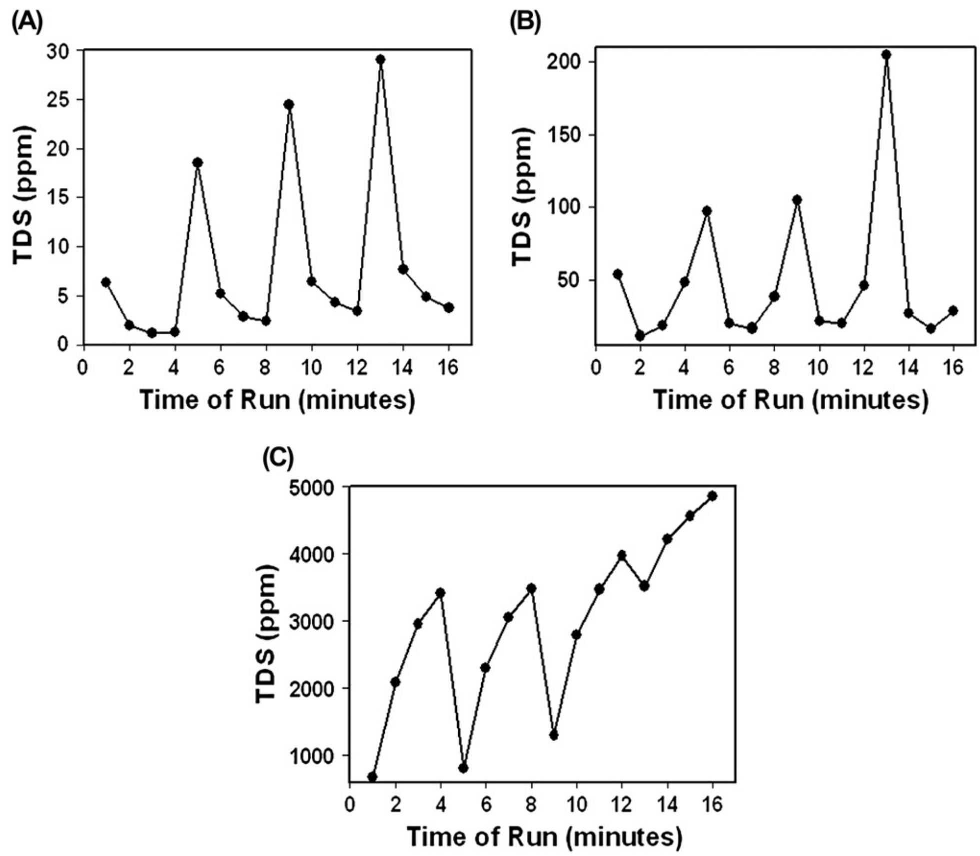

Fig. 9. The effect of the feed concentrations ((A) 1170 ppm, (B) 2900 ppm, and (C) 6120 ppm) on the performance of the PCC membrane system for the treatment of dye wastewater.

membranes to adsorb ions is saturated at the so early stage of the operation that the PCC membrane cannot adsorb the ions effectively, resulting in the high TDS concentration of the treated water. Therefore, the concentration of the feed solution should be seriously considered for the effective operation of the PCC membrane system. It can be concluded from this result that the PCC membrane system used in this study can be used effectively for the TDS removal of dye wastewater with up to 3000 ppm of TDS.

4.4. Analysis of the treated water

To see the purity of the treated water, the water treated by the PCC membrane system under the operation condition (0.5 kgf/cm^2, water flow rate: 0.5 LPM, running time: 4 min, stop time: 15 s, and rinse time: 4 min) was analyzed using ICP/AES, as shown in Table 2. It is found from Table 2 that the metals in relatively large concentration were removed mainly by the PCC membrane system. Especially, the concentration of Na^+ ion was decreased substantially, decreasing the TDS of the wastewater.

5. Conclusions

The PCC membrane system is turned out to be effective for the removal of TDS from dye wastewater. The performance of the membrane system appeared to be good when the water flow rate was low (0.5 LPM), and when the rinse time was long (4 min).

The TDS removal efficiency from the dye wastewater with 4280 ppm of TDS under the optimum operation condition was over 98%, and over 99% for lower concentration of dye wastewater.

Table 2
Analysis of the treated water by the PCC membrane system

Elements	Feed water	Treated water	Elements	Feed water	Treated water	Elements	Feed water	Treated water
Concentrations of the metals contained in the wastewater and treated water								
Al	0.1 ppm	0.1 ppm	Ni	0.2 ppm	0.1 ppm	Na	3914 ppm	85 ppm
Cr	<0.1 ppm	<0.1 ppm	Cu	0.1 ppm	<0.1 ppm	Mg	4.4 ppm	<0.1 ppm
Mn	0.1 ppm	0.1 ppm	Zn	<0.1 ppm	<0.1 ppm	K	396 ppm	10 ppm
Fe	0.9 ppm	0.3 ppm	Cd	<0.1 ppm	<0.1 ppm	Ca	131 ppm	5 ppm

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