# Removal of Chromium from Water Environment by Forward Osmosis System

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**Abstract** Forward osmosis (FO) technology has been applied for removal of chromium (Cr) from water environment. Comparison of the removal efficiency of Cr(VI) and Cr(III) was investigated by changing several operational conditions. The pH of feed solution plays an important role in rejection of Cr. The Cr(VI) rejection was increased with increasing pH, while Cr(III) rejection was stable. It also demonstrated that the rejection of Cr was higher when the membrane active layer faces the feed solution compared to the rejection when the membrane active layer faces the draw solution.

## 1 Introduction

Heavy metals are naturally occurring elements that have high atomic weight and a density at least 5 times greater than that of water. Their multiple industrial, domestic, agricultural, medical, and technological applications have led to their wide distribution in the environment; raising concerns over their potential effects on human health and the environment (Tchounwou *et al.*, 2012). Chromium (Cr) is a toxic industrial pollutant that is classified as human carcinogen by several regulatory and non-regulatory agencies. The health hazard associated with exposure to Cr depends on its oxidation state, ranging from the low toxicity of the metal form to the high toxicity of the hexavalent form (Velma *et al.*, 2009; Atsdr, 2012). Therefore, development of more effective treatments for mixtures of harmful compounds is required.

In previous studies, the removal of heavy metals with several traditional treatments was examined, and advanced technologies were developed (Barakat, 2011). Membrane technology has been proven as a feasible option in wastewater treatment, due to its high rejection to contaminants, such as organic compounds or dye molecules, and low fabrication cost. Nanofiltration (NF) and reverse osmosis (RO) were proved their effectiveness in removing heavy metals from polluted water. However, both processes are operated at high pressures and have relatively low water–recovery rates. Therefore, comparatively high costs are incurred, and there is a high risk of severe membrane fouling (Alzahrani *et al.*, 2013). Forward osmosis (FO) is an emerging water treatment technology, and has gained increasing interest in recent years. FO is a membrane process in which water flows across a semi-permeable membrane from a feed solution of lower osmotic pressure to a draw solution of higher osmotic pressure (Cath *et al.*, 2006). FO is highly attractive due to its lower fouling potential, simplicity, and higher recovery (Cath *et al.*, 2005), although energy consumption could be high if draw solution regeneration is required. Potential applications of FO include seawater desalination (McCutcheon *et al.*, 2006), wastewater reclamation, liquid food processing (Petrotos *et al.*, 1999), and electricity generation *via* a derivative pressure retarded osmosis process. When evaluating FO as a treatment process for water treatment, it is important to ensure that trace contaminants such as Cr are removed from the treated water. Thus, a fundamental understanding of Cr transport in FO membrane processes is critical to the effective development of FO membrane technology. Despite the importance of this aspect, very few studies on the removal of trace contaminants by FO have been reported in the literature. However, the performance of FO membranes in removing the various Cr species from aqueous solution in the presence of different environmental conditions, has not yet been reported. The various factors and related mechanisms that control the removal of Cr by FO membranes need to be elucidated for a better understanding of the separation mechanisms.

The aim of this study is to find out the effectiveness of FO to be used for the removal of Cr. In this work, the separation behavior was studied by a set of experiments at various conditions including pH, membrane orientation, feed and draw solution concentration.

## 2 Experimental

All chemical reagents were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

The FO experiments were carried out using commercial flat thin–film composite (TFC) FO membrane (Sterlitech Corporation, WA, USA). The FO membrane cell was made of natural acetal copolymer (CF042 FO, Sterlitech Corporation, WA, USA), a thin polyamide layer (around 200 nm) deposited on top of a polysulfone porous layer (about 50 μm) on top of a non-

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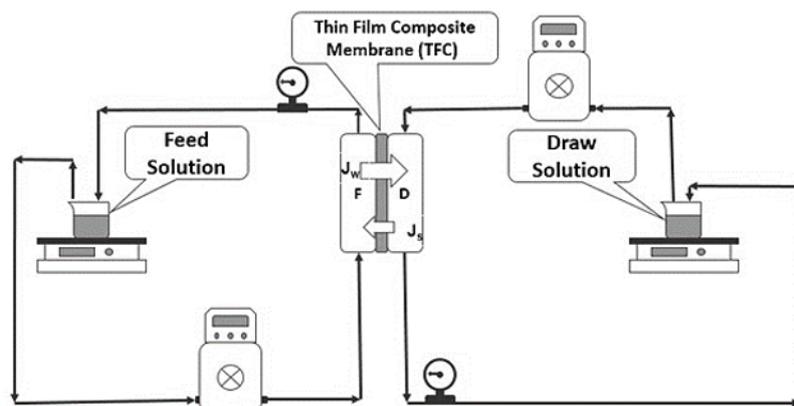
**Figure 1.** Forward osmosis experimental set-up

woven fabric support sheet. The FO membrane module comprised a cross–flow membrane cell with two channels for the feed and draw solution. The channel has dimensions of 9.2 cm length, 4.6 cm width, and 0.2 cm height, providing an effective membrane area of 42 cm². A peristaltic pump was used to recirculate the feed and draw. A constant cross–flow rate of 0.25 L/min was maintained between the two closed loops for the feed and draw solution in the system. Reservoirs were digitally weighed, and their weight changes were recorded at regular time intervals. pH and conductivity meters were used to monitor the quality variation of the solutions in 60 min intervals.

Feed solution having concentration of Cr(VI) and Cr(III) were prepared by dissolving the required amount $Na_2CrO_4 \cdot 4H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ in deionized water. Temperature of the feed and draw solutions were maintained at room temperature (25±1˚C). The experiment was conducted after stabilizing the system (~30 min), and the samples were collected from both the feed and draw solution, respectively, in 60 min time intervals to quantify the total concentration of tested metals. The solution conductivity and pH were measured in 60 minutes time interval, respectively. Due to the pure water was transported from feed to draw by the FO process, the volume of the feed reservoir decreased and the volume of draw solution increased over time were recorded continually. Solution pH was adjusted to 4 – 8 by adding 0.1 M [= mol/L] HCl or 0.1 M NaOH. The total feed solution volume was 0.5 L. Deionized water was used for preparing sodium chloride (NaCl) as draw solution with concentration of 0.5, 1, 1.5 and 2 M. The total draw solution volume was 0.5 L. This sodium chloride NaCl was selected in preparation of draw solutions because it has low molecular weight, low viscosity, high solubility, high osmotic pressure that can be given by this solution, nontoxic, easily and economically separated and recycled.

The schematic of lab-scale FO system and the module picture were shown in the Figure 1. The membrane was used in active layer facing feed solution (AL-FS) mode, with draw solution facing the membrane support layer and the feed solution facing the active layer. The performance of the FO process was investigated by varying the operating factors pH, solutes initial concentration, draw solution concentration, and membrane orientation. During the experiment, the conductivity and pH of the solutions were measured at 1 hour time intervals, and 1 ml sample was collected from draw solution in each hour for analysis. The volumes variation of 2 tanks within the experiment period were measured and the mass balance was calculated after each experiment.

The FO water flux ($J_w$) was obtained by measuring the weight change of the draw solution according to the Eq. (1):

$$J_w = \Delta V/(A_m\Delta t) = (\Delta m/\rho)/(A_m\Delta t) \qquad (1)$$

where $\Delta V$ and $\Delta m$ is the volume change and weight change of the draw solution over the operation time interval $\Delta t$, $\rho$ is the density of feed solution, and $A_m$ is the effective membrane area. The solute rejection $R$ [%] was defined as the percentage of feed solutes that were retained by the membrane. It was calculated as:

$$R = [1 - (C_dV_d/V_pC_f)] \times 100 \qquad (2)$$

where $C_d$ [mg/L] is the Cr concentration in the draw solution at the end of each FO test, $V_d$ [L] is the final volume of draw solution, $V_p$ [L] is the volume of the permeate water, and $C_f$ [mg/L] is the Cr concentration in the feed solution. $C_d$ [mg/L] was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Conductivity and pH of the solutions were also measured by using a conductivity (Horiba DS-51) and pH meter (Horiba model F-74). The average and standard deviation of Cr removal and water flux was obtained experimentally following the time from the collected data. The error bars for each experiment represent the standard deviation of 3 measurements.

# 3 Results and Disscussion

## 3.1 Effect of Cr initial concentration on As rejection and water flux

The effect of Cr feed solution concentration on removal efficiency and water flux in AL-FS mode membrane orientation is shown in Figure 2. Average water flux for Cr(VI) and Cr(III) were 5.3 Lm⁻²h⁻¹ and 6 Lm⁻²h⁻¹, respectively, which were constant over the entire range of feed solution concentration investigated (10

mg/L to 100 mg/L). The Cr(VI) rejection was increased with increasing feed solution concentration, while the Cr(III) rejection was stable. The Cr(VI) rejection was increased, because the ratio between the feed solution concentration and solute flux is not proportional. Increase in the Cr(VI) concentration in the feed solution simultaneously increases the Cr(VI) solute flux passing through membrane. When the inital concentration of Cr(VI) increases in tenfold from 10 mg/L to 100 mg/L, the Cr solute flux ($J_s$) however increases just 7 times. Therefore, the ratio ($J_s/J_wC_f$) (Eq (2)) was decreased while rejection was increased. The rejection of Cr(III) occurs due to larger hydrated radii (0.9 nm) (Al-Haj-Ali and Marashdeh, 2014) and larger than 2 times of membrane pore (Xie *et al.*, 2014). As a result, a significant effect of initial Cr(III) concentration on rejection was observed.
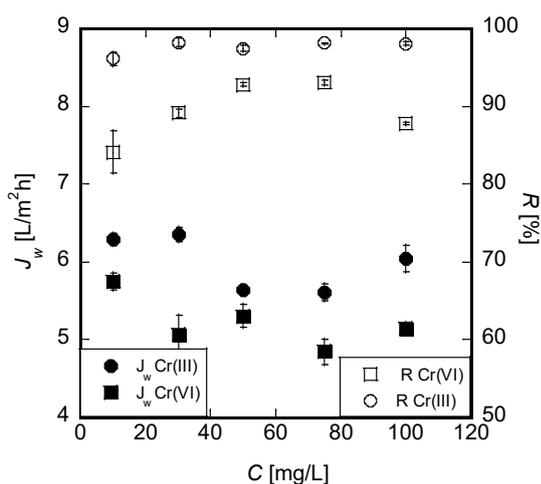


**Figure 2**. Effect of feed concentration on water flux and Cr removal

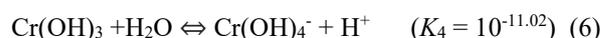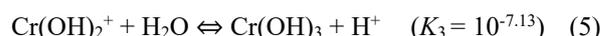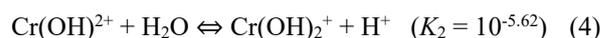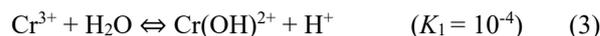### 3.2 Effect of draw solution concentration on Cr rejection and water flux

Figure 3 shows the effect of draw solution concentration on the water flux and Cr rejection in FO system. Due to the increase of the osmotic pressure for both case of Cr, the water flux increase with increase of draw solution concentration. The water flux in the case of Cr(III) was higher than that of Cr(VI). The rejection of Cr(VI) increased with increasing draw solution concentration, due to the related increase of the applied osmotic pressure, which yields a dilution effect, however, this was not as significant as the water flux. The rate of increase in water flux $J_w$ was much higher than the rate of Cr solute flux $J_s$ across the membrane, with the increase of the draw solution concentration. Therefore, the rejection increase (from 83.7% to 87.3%) as the effective concentration of solutes ($J_s/J_w$) permeated through the membrane was low due to comparatively high water flux (Eq. (2)). The rejection of solute is dependent on the characteristics and properties of the membranes used for separation, so the Cr(III) rejection was stable for the range of draw solution concentration (from 0.5 M to 2 M) because of its larger hydrated radii.
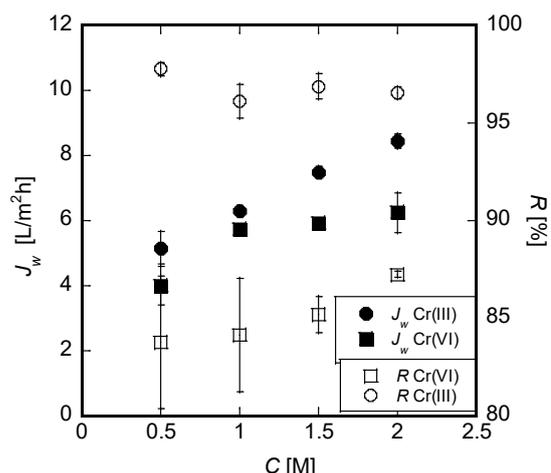


**Figure 3**. Effect of draw solution concentration on water flux and Cr removal

### 3.3 Effect of pH on Cr rejection and water flux

The effect of the pH of the feed solution on Cr removal and water flux in AL-FS mode membrane orientation is shown in Figure 4. The experiment was carried out in pH varied from 4 to 8. The water flux for Cr(VI) was stable at 5.2 $Lm^{-2}h^{-1}$ while water flux for Cr(III) was slightly bell shape against pH. This can be explained by the range of difference in dissociated form of trivalent chromium in water environment (Girard, 2013):

$$Cr^{3+} + H_2O \Leftrightarrow Cr(OH)^{2+} + H^+ \qquad (K_1 = 10^{-4}) \qquad (3)$$

$$Cr(OH)^{2+} + H_2O \Leftrightarrow Cr(OH)_2^+ + H^+ \quad (K_2 = 10^{-5.62}) \quad (4)$$

$$Cr(OH)_2^+ + H_2O \Leftrightarrow Cr(OH)_3 + H^+ \quad (K_3 = 10^{-7.13}) \quad (5)$$

$$Cr(OH)_3 + H_2O \Leftrightarrow Cr(OH)_4^- + H^+ \quad (K_4 = 10^{-11.02}) \quad (6)$$

It can be seen that at pH 8, the dominant form of Cr(III) was $Cr(OH)_3$, precipitation form, therefore it might block membrane pore and hinder the water permeating through membrane. As the result, reducing water flux was observed. The effect of pH on the rejection of Cr(III) was insignificant, the rejection was stable around 97.5%. The Cr(VI) rejection increased with an increase in the pH. The Cr(VI) rejection increase from 60.9% to 89.9%. This can be explained by considering the following dissociation equilibrium (Kučić *et al.*, 2018):

$$H_2CrO_4 \Leftrightarrow HCrO_4^- + H^+ \qquad (K_1 = 1.21) \qquad (7)$$

$$Cr_2O_7^{2-} + H_2O \Leftrightarrow HCrO_4^- \qquad (K_2 = 35.5) \qquad (8)$$

$$HCrO_4^- \Leftrightarrow CrO_4^{2-} + H^+ \qquad (K_3 = 3.10^{-7}) \quad (9)$$

From the above equation it is clear that with an increase in pH of the solution, the dominant Cr(VI) species becomes more negatively charged. As a result, electrostatic repulsion increases between the negatively charged FO membranes (Kim *et al.*, 2012) and the negative oxy-anionic Cr species. Therefore, a higher rejection of Cr(VI) with increasing pH was achieved.
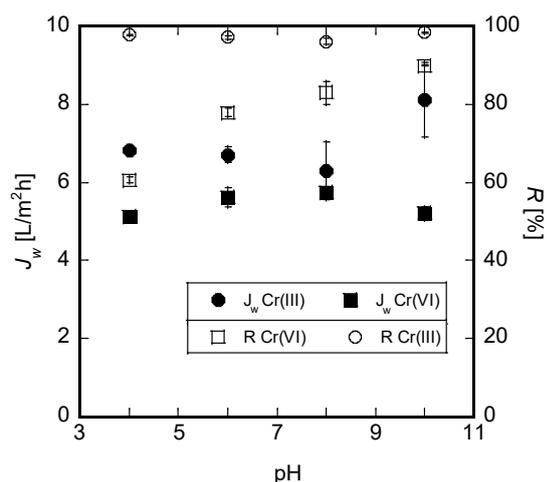
**Figure 4**. Effect of pH on water flux and Cr removal

### 3.4 Effect of membrane orientation on Cr removal and water flux

The effect of membrane orientation, either AL-FS (active layer facing feed solution) of AL-DS (active layer facing draw solution) on Cr removal and water flux is shown in Figure 5. The rejection of Cr in AL-FS mode was higher than in AL-DS mode while water flux in AL-DS mode was higher than in AL-FS mode. Internal concentration polarization and external concentration polarization play an important role in the Cr separation as well as in water flux with respect to the membrane orientation.

In AL-FS mode, to obtain a considerable amount of water flux, osmotic pressure of draw solution at the draw solution side needs to be higher than osmotic pressure at the membrane surface. However, the solute concentration at the feed solution side and active layer-support layer interface is insignificant in AL-FS mode, therefore, dilutive internal concentration polarization become predominant (as water passes across the membrane from feed solution to draw solution side) resulting in decrease of water flux due to lowering of the net osmotic pressure across the active layer by diluting the draw solution (McCutcheon and Elimelech, 2006).

The higher rejection of Cr in AL-FS mode compared to AL-DS mode was attributed due to low external concentration polarization of Cr at membrane active layer. In AL-FS mode, after diffusion of Cr through active layer is immediately carried away by the water flux, leaving no chance of accumulation on active layer-support layer interface. Thus, the Cr concentration at the active layer-support layer interface was nearly the same and Cr experienced less internal concentration polarization, resulting in a high rejection. However, in AL-DS mode, the feed Cr can easily permeate through the porous support layer by diffusion and accumulate at the support-active layer interface due to the retention of Cr by the active layer. Consequently, there is a simultaneous increase in the Cr concentration gradient across the membrane active layer (concentrative internal

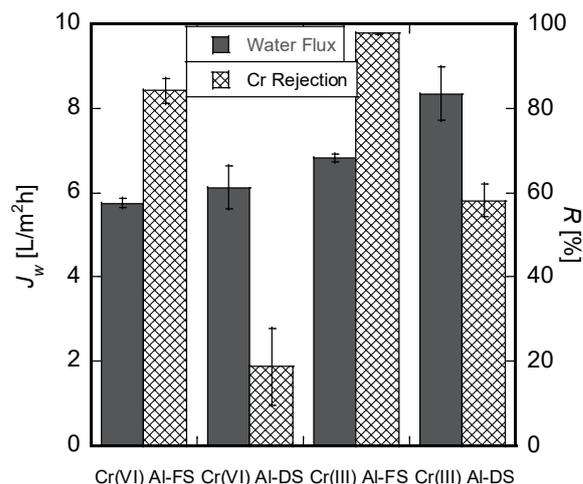concentration polarization of Cr), resulting in more permeation of Cr.



**Figure 5**. Effect of membrane orientation on water flux and Cr removal

## 4 Conclusion

A forward osmosis (FO) process for the removal of chromium from water environment was demonstrated in order to establish a more effective water treatment process. The Cr removal from water environment by FO membrane was investigated by using NaCl as the draw solution. The effect of pH of the feed solution, the draw solution concentration and the membrane orientation were examined to evaluate the efficiency of FO as a barrier for removal of heavy metal from aqueous solution. The water flux dramatically increase with the increase of draw solution concentration. It was also indicated that the rejection of Cr was higher when the membrane active layer faces the feed solution compared to the rejection when the membrane active layer faces draw solution. However, for Cr(III), it was observed that the rejection was stable at all range of pH, while it can be seen that the Cr(VI) rejection was increased with increasing in the pH. Because the electrostatic repulsion increases between the negatively charged FO membranes. In the case of Cr(III), much higher rejection was obtained, because its hydrated radii is larger than that of Cr(VI).

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