



## Research article

# A hybrid froth flotation–filtration system as a pretreatment for oil sands tailings pond recycle water management: Bench- and pilot-scale studies



Kavithaa Loganathan <sup>a, \*\*</sup>, David Bromley <sup>b</sup>, Pamela Chelme-Ayala <sup>c</sup>,  
Mohamed Gamal El-Din <sup>c, \*</sup>

<sup>a</sup> Canadian Natural Resources Ltd., Fort McMurray, Alberta, T9H 3H5, Canada

<sup>b</sup> David Bromley Engineering Ltd., West Vancouver, British Columbia, V7S2N6, Canada

<sup>c</sup> Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta, T6G 2W2, Canada

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## ABSTRACT

Through sustainable water management, oil sands companies are working to reduce their reliance on fresh water by minimizing the amount of water required for their operations and by recycling water from tailings ponds. This study was the first pilot-scale testing of a hybrid technology consisting of froth flotation combined with filtration through precoated submerged stainless steel membranes used to treat recycle water from an oil sands facility. The results indicated that the most important factor affecting the performance of the hybrid system was the influent water quality. Any rise in the levels of suspended solids or total organic carbon of the feed water resulted in changes of chemical consumption rates, flux rates, and operating cycle durations. The selections of chemical type and dosing rates were critical in achieving optimal performance. In particular, the froth application rate heavily affected the overall recovery of the hybrid system as well as the performance of the flotation process. Optimum surfactant usage to generate froth (per liter of treated water) was 0.25 mL/L at approximately 2000 NTU of influent turbidity and 0.015 mL/L at approximately 200 NTU of influent turbidity. At the tested conditions, the optimal coagulant dose was 80 mg/L (as Al) at approximately 2000 NTU of influent turbidity and <40 mg/L (as Al) at approximately 200 NTU of influent turbidity. Precoat loading per unit membrane surface area tested during the pilot study was approximately 30 g/m<sup>2</sup>. The results of this study indicated that this hybrid technology can potentially be considered as a pre-treatment step for reverse osmosis treatment of recycle water.

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## 1. Introduction

The Athabasca oil sands in northern Alberta, Canada, are one of the largest known crude oil reserves in the world with over 167.2 billion barrels of recoverable bitumen available, making Canada the country with the third largest oil reserves in the world

(Energy Resources Conservation Board, 2014). During oil extraction, after separation from the bitumen, the waste product, consisting of residual bitumen, clays, slit and water, is sent to a tailing area, where the water (i.e., recycle water; RCW) is separated from solids and returned back into the process.

RCW (also known as oil sands process-affected water) is a very complex mixture of suspended solids, salts, inorganic compounds, dissolved organic compounds, and trace metals (Allen, 2008; Holowenko et al., 2002). Organic compounds found in RCW include naphthenic acids (NAs), benzene, humic and fulvic acids, and polycyclic aromatic hydrocarbons (PAHs), among others (Allen, 2008; Grewer et al., 2010). RCW from tailings ponds has been reported to cause both acute and chronic toxicity to a variety of organisms, including fish, amphibians, phytoplankton, and mammals (Debenest et al., 2012; Leung et al., 2001; MacKinnon and Boerger,

\* Corresponding author. NSERC Senior Industrial Research Chair in Oil Sands Tailings Water Treatment, Helmholtz – Alberta Initiative Lead (Theme 5), Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta, T6G 2W2, Canada.

\*\* Corresponding author. Technology Development-Horizon Oil Sands, Canadian Natural Resources Ltd., Fort McMurray, Alberta, T9H 3H5, Canada.

E-mail addresses: [Kavithaa.Loganathan@cnrl.com](mailto:Kavithaa.Loganathan@cnrl.com) (K. Loganathan), [mgamaleldin@ualberta.ca](mailto:mgamaleldin@ualberta.ca) (M. Gamal El-Din).

1986; Pollet and Bendell-Young, 2000; Yamano et al., 2006).

Through progressive water management, oil sands companies are working to reduce their reliance on fresh water by minimizing the amount of water required for their operations and by recycling water from tailings ponds where possible. Various treatment processes have been tested at the bench-scale level to treat RCW, including adsorption, advanced oxidation processes (AOPs), membrane processes, and biological treatments, among others (Islam et al., 2014; Kim et al., 2013; Pourrezaei et al., 2014; Zubot et al., 2012). However, to date there has been no full-scale treatment process implemented for the remediation of RCW. Natural *in situ* microbial degradation in tailings ponds has proven to be very slow (Han et al., 2009). Ozonation and AOPs have been used, at the bench-scale level, as treatment alternatives to remediate RCW (Martin et al., 2010; Perez-Estrada et al., 2011; Scott et al., 2008). As illustration, ozonation has been found to degrade NAs and acid-extractable fraction (AEF), increase RCW biodegradability, reduce the toxicity of RCW towards *Vibrio fischeri* (Gamal El-Din et al., 2011; Wang et al., 2013) and attenuate the RCW impacts on the growth and development of *Chironomus dilutes* (Anderson et al., 2012a, 2012b).

Among physical treatments, membrane filtration has been found to be an effective method of removing impurities from RCW (Alpatova et al., 2014; Kim et al., 2011; Loganathan et al., 2015). In particular, reverse osmosis (RO) and nanofiltration (NF) membranes have showed excellent capability of rejecting ionic species from RCW (Kim et al., 2011). However, the successful application of RO and NF membranes for RCW treatment is hindered by membrane fouling caused by colloids, organic matter, and bitumen residues that adhere to the surface and pores of the membrane (Peng et al., 2004). Due to the high solid and ionic contents in RCW, feed water pretreatments able to reduce foulants such as suspended and dissolved solids are required to minimize membrane fouling (Kim et al., 2011). As illustration, coagulation, flocculation and sedimentation (CFS) process has been effectively used to reduce solids and colloidal materials from RCW (Kim et al., 2011). This process causes the destabilization of suspended solids by reducing the surface ionic charges, resulting in the formation of flocs; then these flocs are precipitated in the sedimentation process.

Froth flotation, a surfactant-based separation processes, has been effectively used to remove emulsified oil from wastewater (Bunturongpratoomrat et al., 2013; Chavadej et al., 2004b), to control acid mine drainage in the mining industry (Alam and Shang, 2012), and to deink paper pulp (Theander and Pugh, 2004), among other applications. This process relies on the difference in surface chemistry of particles and their behavior in the gas/liquid, gas/solid and liquid/solid interphases (Al-Zoubi et al., 2009). In this process, a surfactant is added to an aqueous solution and air is sparged through the solution. The presence of surfactant located at the air–water interface in the flotation operations promotes the formation of froth. Dissolved molecules or ions, solid particles, or droplets of emulsified oil can attach to the air bubbles and be carried over to the top of a flotation cell with the froth, which is continuously skimmed off.

Hybrid flotation–membrane filtration systems have been found to be more effective not only in removing contaminants but also in reducing membrane fouling when compared to the single processes (Nenov et al., 2008; Peleka et al., 2009). In the present study, a pilot-scale test was conducted to demonstrate the ability of a hybrid system consisting of froth flotation combined with filtration through precoated submerged stainless steel membranes to effectively treat RCW from an oil sands facility. In this pilot-study, the use of high intensity mixing to generate froth produced a highly ionic and turbulent environment which caused rapid particle

destabilization (Al-Zoubi et al., 2009). In the hybrid system, the membranes were precoated in an *in situ* operational environment with a highly charged precoat material to reduce the membrane fouling (Cai et al., 2013; Malczewska et al., 2015). The charged environment of the precoat caused solid destabilization in the water passing through the precoat where the colloids attached to the precoated powder or alternatively to each other, resulting in entrapment within the precoated powder. When the precoat was fouled, the precoat was removed by backwashing the membrane and was replaced with a new precoat. Instead of making the membrane surface a barrier for filtration, the precoat was a media. This media attracted the solids in the water to the media surface by dispersion interaction and polar interaction forces (Israelachvili, 2011).

This feasibility study evaluated and analyzed the potential of the hybrid system to achieve water quality requirements to feed unit effluent to a RO system. Along with the optimization of system performance, the target for treated water was to consistently maintain a silt density index (SDI) of less than 5. Another objective for the pilot-scale study was to determine the optimum ranges for operating parameters that impacted the full-scale sizing of the treatment system, including operating flux rates and maximum sustainable recovery rates. A significant amount of effort was placed on a bench-scale testing in order to identify the best chemicals and process settings to be examined in the pilot-scale experiments.

## 2. Materials and methods

### 2.1. Source water

RCW from Canadian Natural Resources Limited (CNRL) Horizon operation was used as feed water for this study. The water was drawn from a header of the main hydro-cyclones of the CNRL cooling water recycle system. The RCW in the storage tank was recirculated continuously in order to prevent the settling out of solids or separation of the hydrocarbon materials. Because significant variations in the source water quality were observed, the RCW was characterized before and after each stage of operation. Table 1 shows the main water quality parameters of the untreated RCW used in this pilot-scale study.

### 2.2. Pilot-scale tests

The pilot-scale facility was located on the CNRL Horizon site next to plant 99A, which is on the north side of the site, adjacent to a tailings pond. The pilot study was conducted in two stages. The first stage was initiated on September 16, 2012 and terminated on November 04, 2012, after major optimization activities were completed. The second phase of the pilot study required a modification to the existing system design and was started on December 18, 2012 and terminated on December 31, 2012.

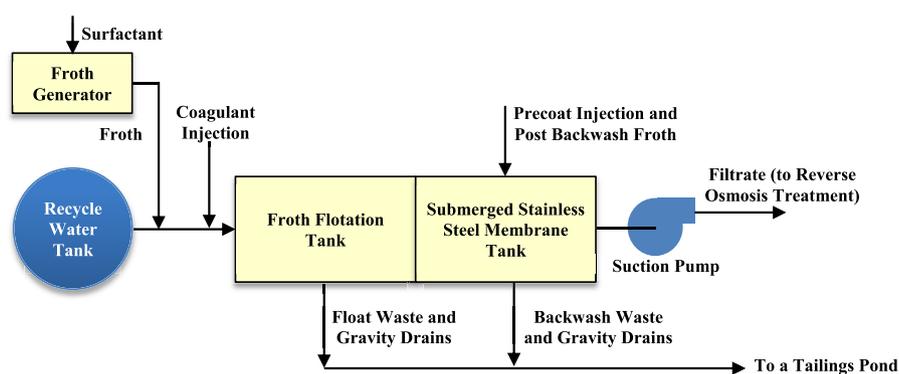
The hybrid system was a stand-alone system fed with untreated RCW. The system incorporated three major processes: (1) froth flotation; (2) filtration using a precoat material applied directly on the membrane surface; and (3) filtration through submerged stainless steel membranes (Fig. 1). All process equipment used in the pilot study was supplied by David Bromley Engineering Ltd. (Vancouver, Canada).

The froth flotation system was similar to conventional flotation based solid–liquid separation. During regular operation of the system, froth was created in a froth generator using water, air, and surfactant. The generated froth was then injected in the raw water line before the RCW was pumped into the flotation tank. For the froth generation, the air–water ratio was 50/50. The air, however,

**Table 1**  
Water quality of the untreated RCW.

Parameter	Units	Average value	Maximum value	Minimum value	Standard deviation	Number of observations
pH	–	8.29	8.39	8.16	0.08	13
Total alkalinity	mg/L as CaCO <sub>3</sub>	725	780	680	32	17
TSS	mg/L	359	880	6.7	315	17
Turbidity	NTU	489	1000	100	312	17
Conductivity	µS/cm	2988	3200	2800	122	17
TDS	mg/L	2094	2500	1700	284	17
Total sodium	mg/L	631	700	570	39	17
Chloride	mg/L	450	520	350	47	17
Bicarbonate	mg/L	876	930	830	32	17
Total hardness	mg/L as CaCO <sub>3</sub>	47	56	36	6	17
TOC	mg/L	47	69	29	14	11
Oil & grease	mg/L	25	32	14	6	17
Acid-extractable fraction	mg/L	54	68	39	11	11
COD	mg/L	425	530	310	89	17

TSS: total suspended solids; TDS: total dissolved solids; TOC: total organic carbon; COD: chemical oxygen demand.



**Fig. 1** Schematic diagram of the hybrid froth flotation–filtration system.

was not added from a compressed air system; it was sucked into the froth generator using a venture concept. Coagulant was also added to the raw RCW, upstream of the flotation tank. The addition of coagulant into the feed water allowed particle destabilization and promoted the formation and growth of flocs. The froth was intended to capture the flocs and help the captured solids to rise to the surface of the flotation tank where the float layer could be effectively removed using a skimmer system (Al-Zoubi et al., 2009). Heavier solids sank to the bottom of the membrane tank and could be drained at desired intervals. The bubble size for the hybrid system was about 20 µm. Typically, bubbles sizes <100 µm are generated in dissolved air flotation, while bubble size higher than 600 µm are generated in dispersed air flotation (Al-Zoubi et al., 2009; Mathur, 2002).

After the separation of solids in the flotation tank, the RCW was further filtered using a submerged membrane bundle. A 316 stainless steel tube membrane system with 1 µm pore size was used in this study. The membrane tube was a hollow fiber stainless steel which allows for high temperature and highly corrosive waters to be treated. The membrane tubes were the membrane substrate that would be used to place an affixed precoat skin layer. Before the hybrid system went into a production cycle, a layer of precoat material was applied to the surface of the membrane tubes. The precoat layer prevented colloidal particles and other scalants to deposit on the membrane surface during filtration and protected the membranes from rapid fouling. The precoat layer also contributed to the filtration process, as the colloidal particles attached to the surface of the precoat material.

The typical operating sequence for the hybrid system included a filtration cycle followed by a backwash, a froth injection and finally

a precoat injection cycle. During a filtration cycle, solids accumulated on the outside surface of the precoat layer as filtrate was pulled through using a suction pump. When the filtrate flow rate dropped or the required suction (vacuum) increased to a predetermined level, the membrane bundle was cleaned using a backwash cycle. After backwashing was complete, a dose of froth was injected into the membrane tank followed by the injection of the precoat material. Then, the membrane bundle was coated with the precoat material by operating the suction pump that created a pressure differential. The pressure differential drew the precoat media to a surface of the membrane screen. The post backwash froth dosing was intended to improve the ability of the precoat material to stay in suspension and form a uniform layer on the membrane tubes.

In the hybrid system design, the final barrier for solids rejection was the membrane tubes. The minimum pore size for the membrane substrate was 1 µm. A precoat material with a mean size range of 30 µm and 95% less than 46 µm was used. The resulting water quality was equivalent to a 0.01 µm ceramic membrane. The layer of precoat material formed on the surface of the membrane tubes should allow the rejection of even smaller particles via adsorption, physical attachment, and straining. During the pilot tests, the waste streams and effluent streams generated by the hybrid system were directed back to the tailings pond.

### 2.3. Bench-scale experiments

Bench-scale experiments were conducted to narrow the parameters to be tested in the pilot study and to understand the significance of certain operating parameters impacting the RCW

quality. The bench-scale experiments were also developed to evaluate the effect of different types and quantities of coagulants for destabilization, surfactant for froth flotation, and precoat material for membrane coating.

Three coagulants were tested, including aluminum sulfate (alum; from Marsulex), ferric sulfate (Kemira PIX 312 from Kemira), and polyaluminum chloride (PACl; GC Hyper Ion 1090 from General Chemical). For surfactants, an anionic (negative charge, KR-SAF900), a cationic (positive charge; KR-SAF050) and a non-ionic (neutral charge; KR-SAF330) surfactant, purchased from Kroff Chemical Company, were selected. For precoat materials, pseudoboehmite alumina (G-250) and gamma phase alumina (GA-200) from BASF Catalysts LLC, activated alumina 90  $\mu$  (ActiGuard 100) and activated alumina 10  $\mu$  (ActiGuard 101) from Axens, as well as powdered activated carbon (PAC; HydroDarko W from Norit) were tested.

Major apparatus used during the bench-scale testing included a bench top dissolved air flotation (DAF) jar tester (EC Engineering, Edmonton) and a small froth generator supplied by David Bromley Engineering Ltd. Tables S1 and S2 in the Supplementary Material (SM) provides a summary of the operating parameters and mixer settings, respectively, used in the laboratory-scale experiments. Details of the froth generation and a description of the experiments conducted to select the precoat materials are also included in the SM.

#### 2.4. Analytical methods

Onsite analytical testing conducted during the pilot study included the following parameters: pH, turbidity, temperature, total suspended solids (TSS), alkalinity, hardness, oxidation-reduction potential (ORP), UV absorbance at 254 nm, SDI, and conductivity. The onsite testing was primarily intended to provide rapid feedback on process conditions in order to guide operational settings and adjustment. These tests were conducted following the standards methods (American Public Health Association, 2005). External analytical testing was also carried out by a commercial laboratory (Maxxam Analytics, Calgary, Alberta).

### 3. Results and discussion

#### 3.1. Selection of surfactants, coagulants and froth doses in bench-scale experiments

The selection of the surfactant is a key parameter to improve the froth flotation performance. Surfactants not only increase the dispersion of air bubbles in the flotation system, but also reduce the coalescence of individual bubbles, enhancing the froth formation and stability (Buntungratoomrat et al., 2013). When a surfactant is added to water, the interfacial tension of the solution decreases as a result of preferential adsorption of surfactant molecules at the air/water interface (Chavadej et al., 2004a), resulting in high colloidal removals (Buntungratoomrat et al., 2013). To select the surfactant type, the same coagulant and coagulant dose were used. Accordingly, PACl (Hyper Ion 1090) at 85 mg/L (as Al) was used along with the three different surfactants. Before conducting the tests, the amount of surfactant required to create optimum froth was investigated and it was found to be 0.8 mL per L of clean water.

Fig. S1 shows the results of the tests conducted to select the surfactant type during the bench-scale tests. Although a higher destabilization was expected due to the reduction of the electrostatic repulsion between the negative particles in RCW by adsorbing a cationic surfactant (Jódar-Reyes et al., 2006), only marginal differences were observed among the performances of the three surfactants. Turbidity removal was greater than 95% for all of them, with the anionic surfactant producing the highest percent removal.

It has been found that independently of the charges of both the surfactant and the particle surface, the colloidal stability strongly depends on the ionic surfactant concentration (Jódar-Reyes et al., 2006). This may explain the marginal difference between surfactants observed in this study. The bulk prices for the three surfactants indicated that the anionic surfactant was the most economic selection (Fig. S1). Based on these considerations, the anionic surfactant KR-SAF 900 was selected for subsequent experiments and pilot testing.

After the selection of the surfactant type, bench-scale tests were conducted to select the best coagulant in terms of turbidity removal. The selected coagulants are all widely used in the industry for water and wastewater treatment (Verna et al., 2010). The RCW had high alkalinity and very strong buffering capacity with pH in the range of 7.5–8.5. PACl was found to be the most effective coagulant compared to alum and ferric sulfate. This result is in agreement with previous publications that have showed higher turbidity and organic matter removals using PACl compared to alum when using same aluminum doses at pH values >8 (Wu et al., 2012; Yan et al., 2008). Fig. 2 shows the results of coagulant selection tests at low froth dose set at 70 mL per L of water to be treated. The results showed that the turbidity removal using the ferric sulfate (Kemira PIX 312) was negligible at all doses (data not shown). Alum and PACl performances were close in removing turbidity, with negligible removals at doses below 20 mg/L and >95% turbidity removals at doses above 40 mg/L. Fig. 2 also shows the results of coagulant selection tests at high froth doses (140 mL per L of water to be treated). Negligible turbidity removals were observed using ferric sulfate. Doses below 20 mg/L for alum or PACl did not produce good separation of solids. Visual observation during the experiments indicated that the best floc formation and the most well-defined separation between the float layer and treated water could be obtained at higher doses (above 80 mg/L) of the PACl coagulant.

The application of the coagulants was considered necessary to neutralize the surface charge of the particles in the RCW in order to achieve effective flocculation and removal of solids. It has been found that the coagulation-flocculation chemistry is a key operating parameter affecting the flotation performance (Al-Zoubi et al., 2009). Typically, organic constituents have negative surface charge compared to typical inorganic colloidal solids. It has been reported that the surface of particles present in RCW was negatively charged,

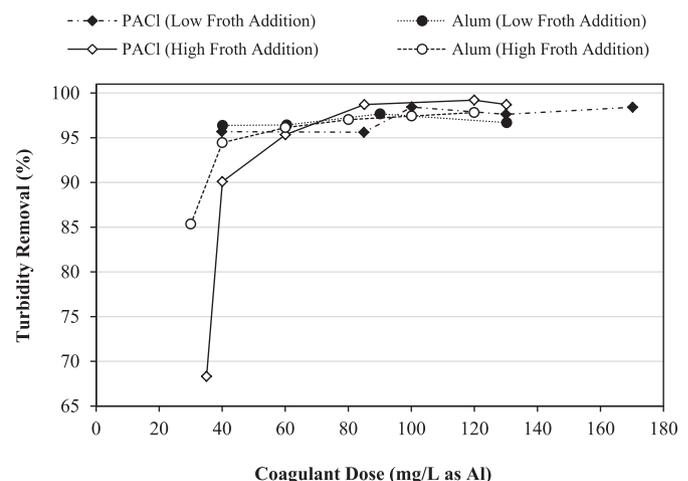


Fig. 2. Selection of coagulant doses at low and high froth doses. Untreated RCW turbidity = 930 NTU; low froth dose = 70 mL/L; high froth dose = 140 mL/L; surfactant to clean water ratio = 0.8 mL/L.

with an average zeta potential value of  $-40$  mV (Pourrezaei et al., 2011). Because the RCW contained high levels of TOC ( $>50$  mg/L), high doses of coagulants were required for effective treatment; this is in agreement with previous publication. Pourrezaei et al. (2011) reported that high doses of coagulants were needed to remove suspended solids from RCW to achieve charge neutralization.

The pH of the treated RCW was also monitored. Treatment with alum reduced the RCW pH significantly with near neutral pH obtained at doses between 20 and 40 mg/L. Alternatively, very small reduction in pH was observed with PACl even at very high ( $>100$  mg/L) doses. This result is consistent with previous publication that has showed minimum effect of PACl on the water pH (Duan and Gregory, 2003).

Pourrezaei et al. (2011) reported that aluminum salts were preferred over ferric salts because the latter added color to the treated RCW due to the formation of iron(III)-organics complexes. In addition, the toxicity of the alum-treated RCW towards *C. dilutes* increased compare to that of raw RCW (Pourrezaei et al., 2011). Based on these considerations, the PACl based Hyper Ion 1090 coagulant was selected for subsequent experimentation and pilot testing.

Fig. 3 shows the results of the tests conducted to select the optimal range of froth addition to be used during the pilot testing. PACl was used for these tests at 130 mg/L. Poor separation of solids and negligible turbidity removal was observed at or below a froth dosage of 35 mL/L. This is equivalent to 0.028 mL of surfactant usage per L of treated water. Improved performance was observed at higher volumes of froth addition, with up to 98.6% removal obtained at a froth dosage of 140 mL/L (0.112 mL of surfactant per L treated water). This is consistent with previous publications that have showed increasing froth flotation efficiency when the surfactant concentration increases (Pondstabodee et al., 1998). The results of these tests highlight the importance of froth addition and indicate that the application of coagulant alone is not sufficient in order to achieve effective solids separation.

### 3.2. Selection of precoat material

Fig. 4a shows the results of the tests conducted to evaluate the precoat materials by assessing their impact on solids and organics removal efficiency. Prior to conducting these tests, a large volume of froth flotation treated water was generated using PACl coagulant at 130 mg/L and the anionic surfactant with a froth dose of 140 mL/L. The precoat materials were applied on 47 mm diameter, 1.2  $\mu$ m

Millipore Nylon filters using a vacuum filtration apparatus. The filtrate qualities from these experiments indicated noticeable removal of turbidity and UV absorbing organics with or without the precoat layer. The PAC precoat produced filtrate with the lowest turbidity levels. The PAC had higher surface area compared to the other precoat materials, resulting in higher organics removals.

In addition to the filtrate quality, the precoat materials were also evaluated for flux rates, suspension quality, and ease of washing after filtration. Fig. 4b shows the flux rates obtained using different precoat materials. Overall flux rates are representative of the time required to filter 1 L of froth treated water. The Pseudoboehmite based precoat materials had the highest overall flux rates with values exceeding 250 l/m<sup>2</sup>/hour, while the PAC produced the lowest overall flux rates. Studies have showed that PAC combined with organic and/or inorganic material would affect the resistance to the permeate flow in PAC/UF systems (Saravia and Frimmel, 2008). It was suggested that organic matter could bind strongly with both the PAC particles and the membrane surfaces at the same time. Thus, the layer on the membrane gives a high resistance to permeate flow (Zhang et al., 2003). Zhao et al. (2005) also suggested that metal ions could neutralize the charge on PAC particles, enabling them to form a more compact structure, resulting in an increase of the PAC cake resistance. Therefore, it is possible to conclude that the precoat material had a large impact on the efficiency of the membrane portion of the system, with respect to overall water recovery, as well as on the efficacy and frequency of cleaning cycles (Thiruvengkatachari et al., 2004).

Results shown in Fig. 4 indicate comparable filtration performance even without the application of a precoat layer. It should be noted that in pilot- or full-scale operations, when the filtration cycle is longer, precoat application will be essential to maintain the system performance. RCW contained high concentration of suspended solids that could be deposited on the membrane surface, increasing its hydraulic resistance and trans-membrane pressure (Kim et al., 2011). Therefore, the precoat layer was intended to prevent colloidal particles and other scalants to deposit on the membrane surface during filtration, thereby protecting the membranes from rapid fouling (Thiruvengkatachari et al., 2004). The precoat layer also increased the available surface area for the adsorption and physical rejection of suspended solids, which permitted the implementation of longer filtration cycles.

It was observed during the experiments that the alumina-based materials from BASF chemicals had the highest suspension quality, while the other precoat materials tended to settle fairly quickly in the absence of mixing. The ability for the precoat to stay in suspension is essential to form an even and uniform layer on the stainless steel membrane surface during the piloting process. After filtration, the spent filter discs were washed with distilled water using a spray bottle. Most of the cakes formed with the precoat materials flaked off without difficulty; however, PAC left a non-washable black film on the surface of the filter. It has been found that organic matter can bridge PAC particles, resulting in the formation of irreversible fouling (Saravia and Frimmel, 2008). Based on the above considerations, the BASF G-250 and GA-200 were selected for subsequent experiments and pilot testing.

### 3.3. Optimization of operating cycles in the pilot-scale tests

After selecting the coagulant, surfactant and precoat material, pilot-scale tests were conducted. The typical operating sequence for the hybrid system included a filtration cycle followed by a backwash, a froth injection and finally a precoat injection cycle. Fig. 5 shows the changes in suction pressure and effluent flow rate over four consecutive filtration cycles. On average, the 60 min filtration cycles resulted in a 15% reduction in effluent flow rate and

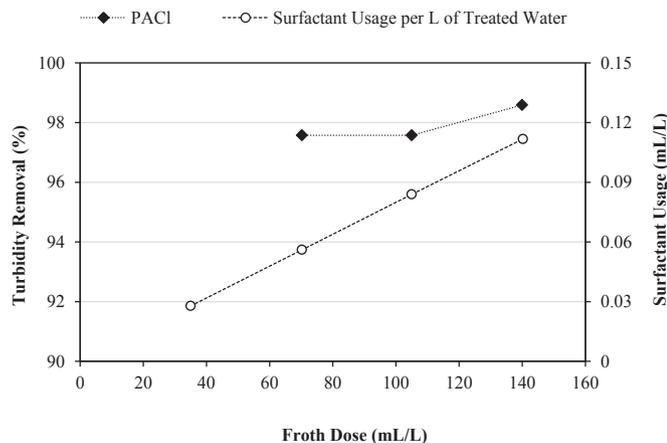


Fig. 3. Effect of froth addition on the turbidity removal. Untreated RCW turbidity = 930 NTU; PACl dose = 130 mg/L as Al; surfactant to clean water ratio = 0.8 mL/L.

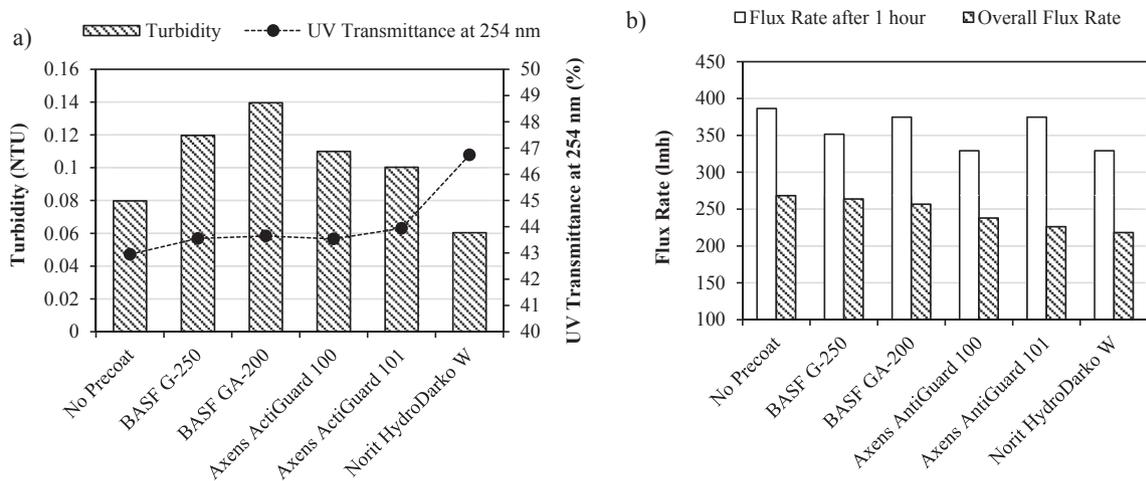


Fig. 4. Effect of different precoat materials on (a) turbidity and UV transmittance at 254 nm; (b) flux rates through 1.2  $\mu\text{m}$  membrane. Lmh = liters/m<sup>2</sup>/hour.

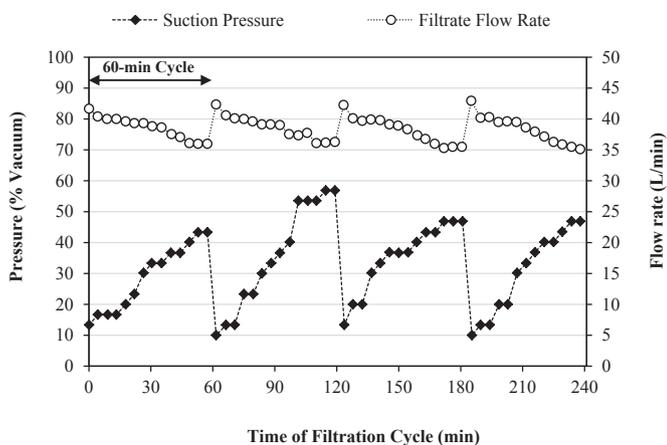


Fig. 5. Change in pressure and flow rate during a typical flotation–filtration cycle.

a 327% increase in applied vacuum. At the end of each filtration cycle, the backwash was fully effective in returning the flow rate and pressure to baseline conditions of approximately 42 L/min and 12% vacuum, respectively. The optimal operating conditions were highly dependent on the quality of the influent water. Although the influent water quality was stable and consistent during the second phase of the pilot study, some significant variations were observed during the early stages of the study. Table S3 lists the range of operating cycle durations tested during the pilot study and the optimum durations selected based on performance. The selection of optimum duration was made based on the rise in suction pressure and the reduction in effluent flow rate. The achievable length of filtration cycle was dependent on several factors, including the suspended solids content of the influent water and the separation of solids in the flotation stage. It has also been reported that to achieve stable membrane performance with higher fluxes, backwashing has proved to be necessary (Blöcher et al., 2003).

#### 3.4. Optimization of chemical dosing rates

Based on the bench-scale tests, PACI, an anionic surfactant, and Pseudoboehmite (G-250) and Gamma Phase Alumina (GA-200), were used as coagulant, surfactant, precoat material, respectively, for the pilot-scale tests. Fig. S2 shows the range of coagulant doses used during the first and second phase of the pilot study. The

coagulant dose was initially adjusted based on variations in influent water turbidity. During the first phase of the study, high raw water turbidity was experienced with a maximum of approximately 2300 NTU. The high solids content and relatively unstable raw water quality made it difficult to achieve steady operating conditions. However, by the end of October 2012, the hybrid system was operated with steady 60 min filtration cycles using coagulant dosage in the 80–90 mg/L (as Al) range. During the second phase of the study, the turbidity of the influent water was significantly lower with a maximum of approximately 115 NTU over the test duration. Consequently, the coagulant dose was lowered to a minimum of 44 mg/L (as Al). The lowest coagulant dose achievable was limited by the metering pump used for dosing this chemical.

Fig. S3 shows the surfactant and precoat dosing rates applied during the entire pilot study. The froth application rate refers to the amount of froth injected per liter of influent water into the raw water supply line during a filtration cycle. The froth was injected directly from the pilot froth generator unit and the amount of froth injected was highly dependent on the pressure differential between the froth dosing line and the raw water line. The surfactant usage rate refers to the amount of surfactant added to the froth generator to produce 1 L of treated water from the hybrid system. The volume of surfactant added to the system was manually changed and different levels were tested over the duration of the study. It was observed that when the influent water contained higher levels of suspended solids, a higher volume of surfactant would allow better solids separation in the flotation tank (Pondstabodee et al., 1998). Alternatively, a very low amount of surfactant was sufficient for treatment during the second phase of the study, when influent turbidity was lower. For the precoat material, different loading rates were tested by varying the concentration of the slurry that was injected into the submerged membrane tank. Each of the two selected precoat materials was tested individually. However, no noticeable difference was observed in hybrid system performance by changing only the precoat material.

Table S4 lists the range of chemical doses tested during the pilot study and the optimum rates selected based on performance. The performance target was to achieve maximum possible length of filtration cycle, thereby maximizing the recovery, under the existing raw water conditions. Reasonable agreement was found among results from the bench and pilot-scale experiments. The coagulant and surfactant doses at comparable treatment conditions appeared to be scalable from the bench to the pilot-scale tests.

Further optimization of the froth injection rate and precoat loading rate was possible but it would require modifications to the existing design of the system. The required precoat loading rate could potentially be reduced if the size of the submerged membrane tank is reduced to minimize the unused volume of the tank (volume not occupied by the membrane tubes). The froth injection rate could potentially be reduced by allowing a flow rate-based control for the froth dosing in addition to minimizing the backpressure at the injection point.

3.5. Flux and recovery

Figs. 6 and S4 show the recovery and flux rates, respectively, obtained during the first and second phases of the pilot study. As mentioned, throughout the first phase of the study, clean water was used to generate and dose froth into the system. The introduction of water from outside of the treatment loop resulted in significant dilution of the feed water. Furthermore, the very high raw water turbidity (>600 NTU) encountered during this period, in conjunction with different optimization efforts, resulted in high volumes of backwash water usage. Without considering cleaning water usage, the maximum recovery achieved from the system during the first phase was approximately 83%, and 64% allowing for the regular cleanings. It should be noted that the pilot system was designed to produce effluent at the same flow rate as the incoming raw water supply. The additional water injected into the system, mainly with the froth, limited the maximum possible recovery. In order to increase the system recovery, the froth application rate will have to be reduced or the effluent draw will have to be increased, thereby reducing the volume of the waste stream.

The average flux rates encountered during the study were quite consistent under stable conditions (330–390 l/mh). Lower flux rates were observed with poor raw water quality in the early stages of operation. Flux rates were normalized to 20 °C in order to permit comparison of membrane performance as the water temperature varied (USEPA, 2005). The normalized flux rates were as high as 550 l/mh during this period. Fig. 6 shows the recovery obtained

during the second phase of the pilot study. After the design modifications were completed, all regular cleaning of the system, along with generation and dosing of froth, was done with treated water. This eliminated the dilution effect of the feed water and allowed the optimization of system recovery. During this phase of the study, cleaning frequencies and durations were optimized but the maximum achievable recovery was still approx. 85%, limited by the froth application rate. The recovery levels obtained in the present work agreed with previous studies on hybrid flotation-UF systems (Laplante et al., 1983; Lazaridis et al., 2004). Based on observations made during this pilot, the hybrid system design can potentially be improved to reduce the water usage for froth application and backwash cleaning, thereby increasing the overall recovery of the system (Al-Zoubi et al., 2009).

Fig. S4 shows the flux rates obtained during the second phase of the pilot study. The system was operated under stable conditions and the average flux rates were consistent during this phase (approximately 350 l/mh). The average normalized flux rates were also consistent at approximately 500 l/mh, as the average raw water temperature was stable during this period. It should be noted that the achievable flux rates using the hybrid system were much higher than conventional ultrafiltration treatment. This result agreed with previous work by Choo et al. (2007) that showed an increase of the flux rate in a flotation-UF system compared to the conventional coagulation-UF system.

3.6. Quality of the influent and treated RCW

Water from the tailings pond is typified by above neutral pH, high alkalinity, low to moderate TSS and turbidity, and high total dissolved solids (TDS) (Table 1). TDS is primarily composed of sodium chloride, bicarbonate and hardness-causing compounds. Fig. S5 shows the variations in influent water quality over the entire duration of the pilot-scale study. During the first phase of the study, the influent water had very high turbidity with maximum values reaching up to approximately 2300 NTU. Occasional spikes in UV absorbance were also encountered during this phase. Other water

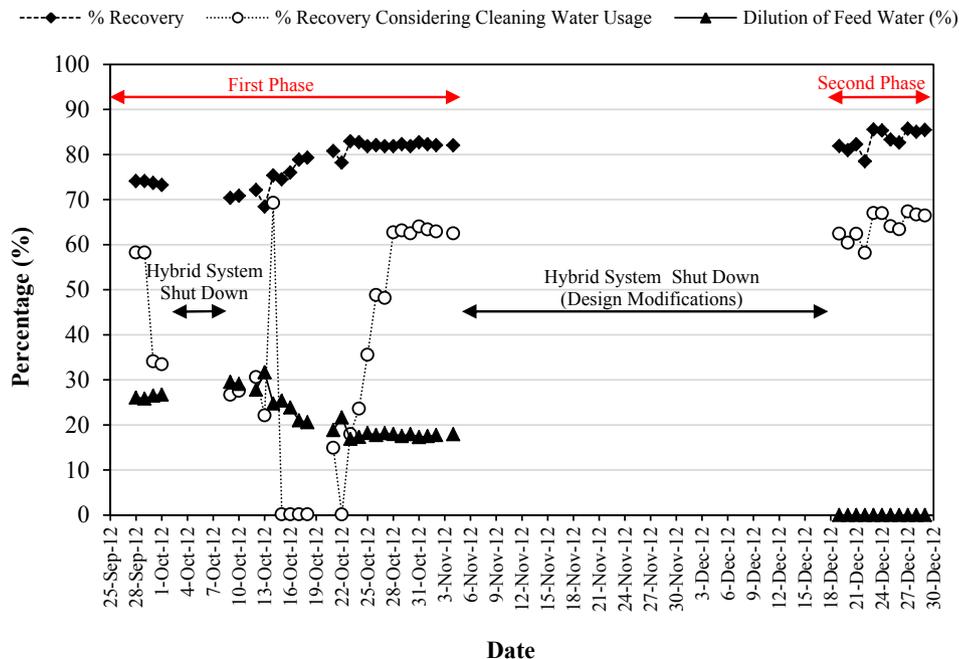


Fig. 6. Recovery during the first and second phases of the pilot-scale study.

quality parameters, such as pH, alkalinity and conductivity were more or less stable and similar to values experienced during the second phase of the study.

During the second phase, turbidity and UV absorbance values were more stable with approximately 100 NTU for average raw water turbidity and 0.7 to 0.9 for UV absorbance. The dilution of feed water caused by froth dosing rendered the treated water quality data, from the first phase of the study, unrepresentative in terms of dissolved constituents. For this reason, no other quality parameters except for turbidity and SDI of the treated water, were considered for analysis from the first phase of the study.

Fig. 7 shows the turbidity and SDI of the hybrid system effluent related to feed water turbidity conditions during the first and second phases of the pilot-scale study. During both phases, the hybrid system was able to consistently produce effluent water with turbidity of less than 1.5 NTU and SDI less than 3. This confirms that the treated water from the hybrid system can be considered for RO treatment. Although the feed water underwent 20–30% dilution during initial operation, the residual suspended solids concentration going to the system was still much higher than the suspended solids levels encountered in the raw water during the second phase of the study. Based on the overall piloting experience, it is expected that the hybrid system will be able to produce adequate effluent quality even during challenging raw water quality conditions. However, such challenging conditions will most likely trigger increased consumption of chemicals, increased frequency of regular backwash, and ultimately a reduced system recovery.

Fig. S6 shows the pH of the treated water as compared to the influent pH. The minor reduction in pH was caused by the application of coagulant and the amount of reduction depended on the doses (Duan and Gregory, 2003). The range of pH reduction encountered during the pilot varied from about 1% at approximately 45 mg/L (as Al) coagulant dosage to almost 7% at approximately 190 mg/L (as Al) coagulant doses. Fig. S7 shows the alkalinity and conductivity of RCW and treated water during the second phase of the study. No noticeable reduction in conductivity was observed across the hybrid system, indicating that the system was not capable of rejecting dissolved metal-based constituents from the untreated RCW. Minor reductions in total alkalinity were

also observed.

Fig. S8 shows the UV absorbance values of RCW and treated water during the second phase of the study. Significant reductions in UV absorbance were observed ranging from 15 to 40%, indicating possible rejection of organic constituents. Measurements done on corresponding pre-filtration samples, taken from the membrane tank, indicated that the majority of the removal took place in the froth flotation stage. The organics removal may be caused by the adsorption of organic constituents on the surface of the flocs formed by the surfactant-enhanced coagulation (Tansel et al., 1995). Another likely contributing factor could be the pH reduction, which could potentially result in the precipitation of the acid extractable fraction (AEF) from solution (Masliyeh et al., 2004).

Table 2 shows the average water quality data from the hybrid system during the second phase of the study. The froth flotation step of the hybrid system was able to remove the majority of the suspended solids from the RCW along with some silica (approximately 13% reduction), TOC (approximately 14% reduction), oil & grease (approximately 20% reduction), and AEF (approximately 13% reduction). Moderate reductions in the levels of sulphides, barium, iron, manganese and silicon were also observed. In general, metals with low pKa values (e.g.,  $Al^{3+}$ ) showed higher removal compared to metals with high pKa values. Metals with low pKa values were readily hydrolyzed, and were more likely to complex with the functional groups (e.g. carboxylic and hydroxyl groups) on the flocs surfaces, resulting their high removal (Schindler and Stumm, 1987) during the flotation step. The subsequent membrane filtration step was successful in further reducing the levels of suspended solids, dissolved mercury, and dissolved aluminum in the treated effluent. Minor additional reductions in TOC and DOC levels were observed across the membranes. However, the filtration step did not seem to have an effect on the concentration of oil & grease and AEF.

### 3.7. Deficiencies in the pilot-scale design

At the conditions tested, the hybrid system was able to effectively remove suspended solids and turbidity from the raw RCW. It has been found that using flotation combined with ultrafiltration has reduced membrane fouling and extended their useful working

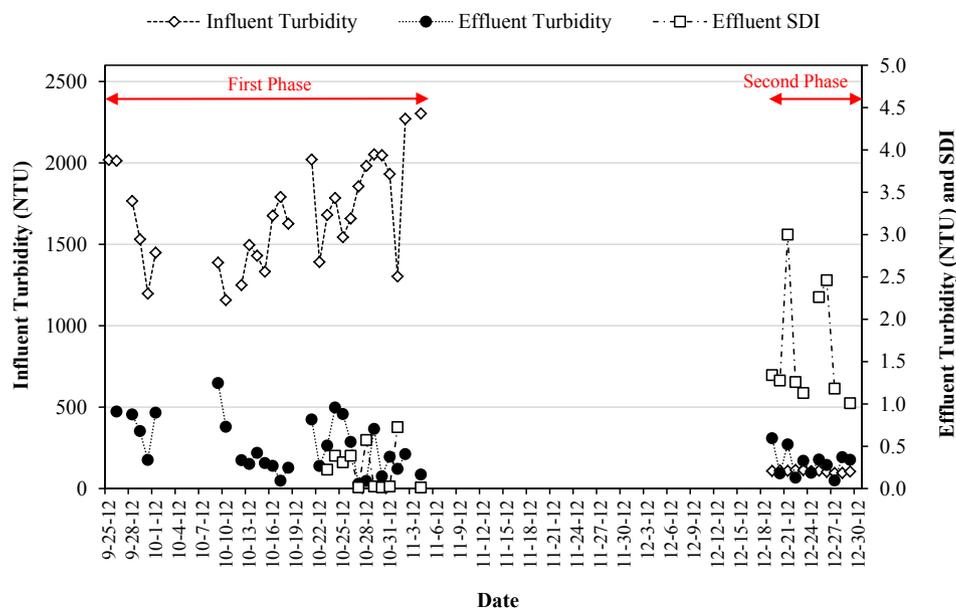


Fig. 7. Influent and effluent turbidity as well as silt density index (SDI) during the first and second phases of the pilot-scale study.

**Table 2**  
Average water quality of untreated and treated RCW.

Parameter	Units	Average RCW	Average membrane tank	Reduction by flotation (%)	Average hybrid system effluent <sup>a</sup>	Reduction by filtration (%)	Overall reduction (%)
pH	–	8.27	8.08	2.4%	8.07	0.1%	2.5%
Turbidity	NTU	115	12	89.2%	5	58.0%	95.5%
Electrical conductivity	μS/cm	2983	2817	5.6%	2850	NA	4.5%
Total dissolved solids	mg/L	1750	1600	8.6%	1650	NA	5.7%
Hardness (as CaCO <sub>3</sub> )	mg/L	48	52	NA	53	NA	NA
Bicarbonate	mg/L	853	780	8.6%	790	NA	7.4%
Total alkalinity (as CaCO <sub>3</sub> )	mg/L	700	638	8.8%	647	NA	7.6%
Silica	mg/L	4.94	4.32	12.6%	4.58	NA	7.3%
Ammonia	mg/L	1.38	1.33	3.6%	1.37	NA	1.2%
Chloride	mg/L	473	443	6.3%	452	NA	4.6%
Sulfide	mg/L	0.0057	0.0022	62.2%	0.0026	NA	55.2%
Total organic carbon (C)	mg/L	36	31	13.8%	30	5.9%	18.8%
Dissolved organic carbon (C)	mg/L	34	30	11.8%	28	6.7%	17.6%
Oil & grease	mg/L	30	24	19.8%	24	NA	17.5%
Acid-extractable fraction	mg/L	63	55	12.7%	56	NA	11.1%
F1 hydrocarbons (C6–C10)	μg/L	50	50	NA	50	NA	NA
Dissolved aluminum	mg/L	0.37	0.43	NA	0.12	71.4%	66.8%
Dissolved barium	mg/L	0.26	0.18	33.5%	0.17	1.9%	34.8%
Dissolved Boron	mg/L	2.30	2.10	8.7%	2.22	NA	3.6%
Dissolved calcium	mg/L	10.3	11.8	NA	11.8	NA	NA
Dissolved iron	mg/L	0.30	0.26	15.0%	0.26	NA	15.0%
Dissolved Magnesium	mg/L	5.30	5.33	NA	5.67	NA	NA
Dissolved manganese	mg/L	0.032	0.021	35.1%	0.020	4.0%	37.7%
Dissolved mercury	μg/L	0.001	0.001	8.0%	0.001	25.0%	31.0%
Dissolved phosphorus	mg/L	0.50	0.45	9.7%	0.43	5.9%	15.0%
Dissolved potassium	mg/L	10.2	9.2	9.3%	9.9	NA	2.5%
Dissolved silicon	mg/L	3.00	1.93	35.6%	2.07	NA	31.1%
Dissolved sodium	mg/L	640	593	7.3%	637	NA	0.5%
Dissolved strontium	mg/L	0.30	0.28	7.8%	0.29	NA	3.3%
Dissolved sulfur	mg/L	30.5	28.8	5.5%	30.2	NA	1.1%

<sup>a</sup> Hybrid system effluent refers to the effluent after flotation and filtration treatments.

time (Al-Zoubi et al., 2009). Although the hybrid system shows several advantages, several design limitations were identified during the course of this study. A major limitation of the system, discovered during the first stage of the study, was that the initial design required a constant supply of potable water for batching chemicals and implementing regular cleaning steps. The substantial volume of water required to generate and inject froth into the raw water line resulted in up to a 30% dilution of the feed water entering the system. As a result, the actual performance of the system, in rejecting dissolved constituents of the source water, was very difficult to assess. During the second stage of the study, all chemical batching and regular membrane cleaning steps were conducted using treated water, thus allowing the proper assessment of effluent water quality and actual system recovery.

Another deficiency in the pilot system design was the connection between the flotation tank and the membrane tank. In the pilot design, the two tanks were separated at the bottom, but had a continuous section at the top. The float or scum layer, created by the separation of solids, extended into both tanks. The skimmer would operate along the top portion of both tanks to collect the scum for discharge. The presence of the float layer in the membrane tank and the operation of the skimmer resulted in occasional separation of solids from the float, thereby increasing the solids loading on the membranes. Based on operating experience, it is recommended that future designs include appropriate separation between the two tanks to inhibit any undesired introduction of solids into the membrane tank during filtration.

The required precoat loading rate used during the pilot could potentially be reduced if the size of the submerged membrane tank is reduced to minimize the unused volume of the tank (volume not

occupied by the membrane tubes). Reduction in the submerged membrane tank volume will also greatly enhance the effectiveness of the backwash cycle. A smaller membrane tank will allow for much less water usage during a backwash cycle thereby increasing the overall system recovery.

In the present pilot-scale study, the effects of chemical consumption rates, flux rates, and operating cycle durations on the hybrid system performance were investigated. To improve the system performance, the key parameters affecting the froth flotation performance, including the residence time in the froth flotation tank and the salinity levels in the influent water (Bunturongpratoomrat et al., 2013) should also be investigated.

#### 4. Conclusions

This study was the first pilot-scale testing of a hybrid froth flotation–filtration system to treat recycle water. At the conditions tested, the hybrid system was able to effectively remove suspended solids and turbidity (to < 1.5 NTU) from the raw RCW. The treated water can be considered for RO treatment based on SDI numbers consistently ≤3 in the hybrid system effluent. Notable removal of organics across the hybrid system was observed as represented by the UV absorbance and TOC measurements. Under stable operating conditions, approximately 19% reduction in the incoming TOC levels was achieved by the overall treatment. The majority of the reduction took place in the froth flotation stage. Removal of organics in the froth flotation stage was potentially caused by the adsorption of organic constituents on the surface of the flocs, formed by surfactant-enhanced coagulation. Another likely cause could be the reduction in pH, triggered by the coagulant

application, which could potentially result in the reduced solubility of the AEF. On average, a 60 min filtration cycle resulted in a 15% reduction in effluent flow rate and a 327% increase in required suction (applied vacuum). At the end of each filtration cycle, the backwash was fully effective in returning the flow rate and pressure to baseline conditions. Chemical dosing rates were also optimized by identifying lowest required consumption rates in order to maintain reasonable filtration cycle duration under specific raw water conditions. Lowest froth injection rate per liter of influent water, achieved during the pilot, was approximately 145 mL/L. Optimum surfactant usage to generate froth (per liter of treated water) was 0.25 mL/L at approximately 2000 NTU of influent turbidity and 0.015 mL/L at approximately 200 NTU of influent turbidity. At the conditions tested, optimal coagulant dosage was about 80 mg/L (as Al) at approximately 2000 NTU influent turbidity and <40 mg/L (as Al) at approximately 200 NTU. Precoat loading per unit membrane surface area tested during the pilot was approximately 30 g/m<sup>2</sup>. The results of this pilot-scale study indicate that the froth flotation system can be used to remove large portion of suspended solids while the membrane system can reject small particles.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2015.06.031>.

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## **SUPPLEMENTARY MATERIAL**

# **A Hybrid Froth Flotation-Filtration System as a Pretreatment for Oil Sands Tailings Pond Recycle Water Management: Bench- and Pilot-Scale Studies**

*Kavithaa Loganathan<sup>1\*</sup>, David Bromley<sup>2</sup>, Pamela Chelme-Ayala<sup>3</sup>, Mohamed Gamal El-Din<sup>3\*</sup>*

<sup>1</sup> Canadian Natural Resources Ltd., Fort McMurray, Alberta, Canada, T9H 3H5

<sup>2</sup> David Bromley Engineering Ltd., West Vancouver, British Columbia, Canada, V7S2N6

<sup>3</sup> Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta, Canada, T6G 2W2

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\* Corresponding Authors' Emails: [Kavithaa.Loganathan@cnrl.com](mailto:Kavithaa.Loganathan@cnrl.com); [mgamalel-din@ualberta.ca](mailto:mgamalel-din@ualberta.ca)

### ***Froth Generation in the Bench-Scale tests***

To produce froth using a froth generator, 0.4 mL of neat surfactant was added into 500 mL of fresh water. The surfactant solution was then placed in the vent opening of the froth generator. The pump was turned on and run for approximately 30 seconds until there was consistent froth in the line. A sample from the froth generator was collected and allowed to sit for 5 minutes to assess the approximate volumetric ratio of froth to water. If there was more froth than water, the initial surfactant amount was reduced and vice versa (the goal was to achieve equal parts froth to water). At the optimum surfactant addition, froth was created as per above and collected in a beaker. A syringe was used to take at least 35 mL of froth and inject into 1 L of recycle water (RCW) in the dissolved air flotation (DAF) jar tester. The amount of froth addition was varied from 35 to 140 mL/L to test its effect on the treated RCW quality.

A DAF jar tester typically allows the addition of a coagulant to represent the flocculation step followed by the addition of compressed air to represent the flotation aspect of the DAF unit. Under this scenario, instead of adding compressed air, froth was added from the froth generator. During the experiments, large samples of RCW were collected and analyzed for initial turbidity and pH. The sample volume was large enough so that a single batch of tests could be conducted with the same source water. Each sample was completely mixed before filling the jars. At the end of the experiment, treated RCW samples were collected and analyzed for turbidity. The tests were conducted as per the mixer settings shown in Table S2.

### ***Selection of Precoat Material at the Bench-Scale Level***

To conduct the precoat experiments, a vacuum filtration apparatus was used with 47 mm, 1.2  $\mu\text{m}$  Millipore Nylon filters. A 4,000 mg/L stock solution of the desired precoat material was

prepared by adding 2 grams of powder mixed into 500 mL distilled water. A filter disc was placed in the vacuum filter funnel and 50 mL of distilled water was poured into the funnel. 2 mL of the precoat slurry was added into the funnel representing a loading rate of approximately 5 g/m<sup>2</sup>. Vacuum was applied and all remaining water in the funnel was filtered, creating an even coat on the surface of the membrane. As the slurry in the funnel came to an end, 1 L of froth flotation treated RCW was added (the precoat layer was not allowed to dry). The volume filtered after one hour of filtration and the time required to filter the entire volume were measured. Each used filter disc was then washed off with distilled water and observations were made on how quickly and easily the cake was removed from the membrane surface. The filtrate from each experiment was collected and analyzed for turbidity, pH, and UV transmittance.

**Table S1.** Summary of the tests conducted during the laboratory-scale experiments.

Objective	Coagulant Type	Coagulant Dose (mg/L)	Surfactant Type	Surfactant to Fresh Water (mL/L)	Froth to Untreated Water (mL/L)	Precoat Type	Precoat Loading (g/m <sup>2</sup> )
<b>Surfactant Selection</b>	GC Hyper Ion 1090	85	KR-SAF 330 Nonionic	0.8	70	--	--
	GC Hyper Ion 1090	85	KR-SAF 050 Cationic	0.8	70	--	--
	GC Hyper Ion 1090	85	KR-SAF 900 Anionic	0.8	70	--	--
<b>Coagulant Selection</b>	Alum	20-170	Best of 3	0.8	70	--	--
	Kemira PIX 312	20-170	Best of 3	0.8	70	--	--
	GC Hyper Ion 1090	20-170	Best of 3	0.8	70	--	--
	Alum	20-170	Best of 3	0.8	140	--	--
	Kemira PIX 312	20-170	Best of 3	0.8	140	--	--
	GC Hyper Ion 1090	20-170	Best of 3	0.8	140	--	--
<b>Optimization of Froth Dose</b>	Best of 3	Best	Best of 3	0.8	35-140	--	--
<b>Precoat Selection</b>	Best of 3	Best	Best of 3	0.8	Best	BASF G-250	5
	Best of 3	Best	Best of 3	0.8	Best	BASF GA-200	5
	Best of 3	Best	Best of 3	0.8	Best	Axens ActiGuard 100	5
	Best of 3	Best	Best of 3	0.8	Best	Axens ActiGuard 101	5
	Best of 3	Best	Best of 3	0.8	Best	Norit HydroDarko W	5

**Table S2.** Jar test mixer setting and timing of chemical additions.

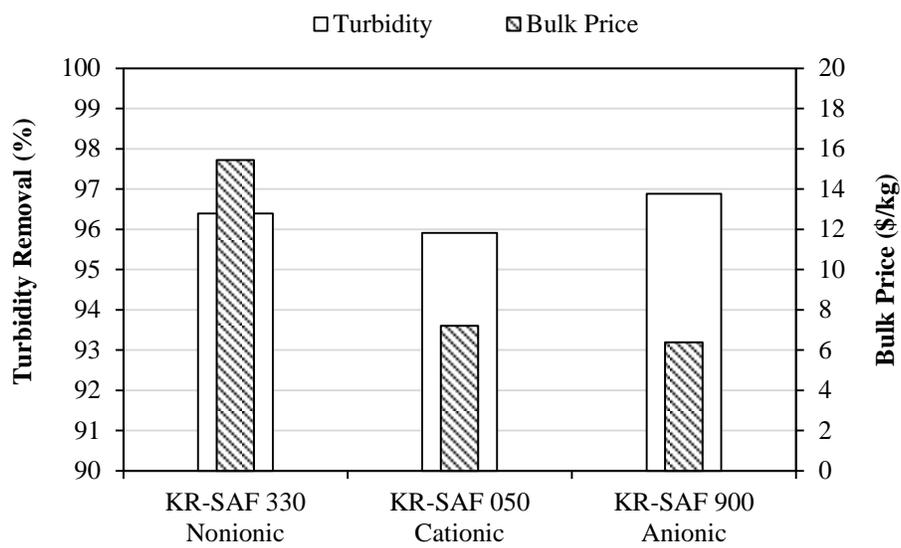
<b>Time (min)</b>	<b>Dissolved Air Flotation (DAF) Jar Test Setting</b>
0	Set stirrers to 300 rpm
1	Add coagulant, as specified
2	Reduce mixing speed to 50 rpm
12	Inject froth
13	Turn off stirrer and let stand for 5 minutes
18	Obtain clarified subnatant samples from each jar using the taps

**Table S3.** Test range and optimum cycle durations.

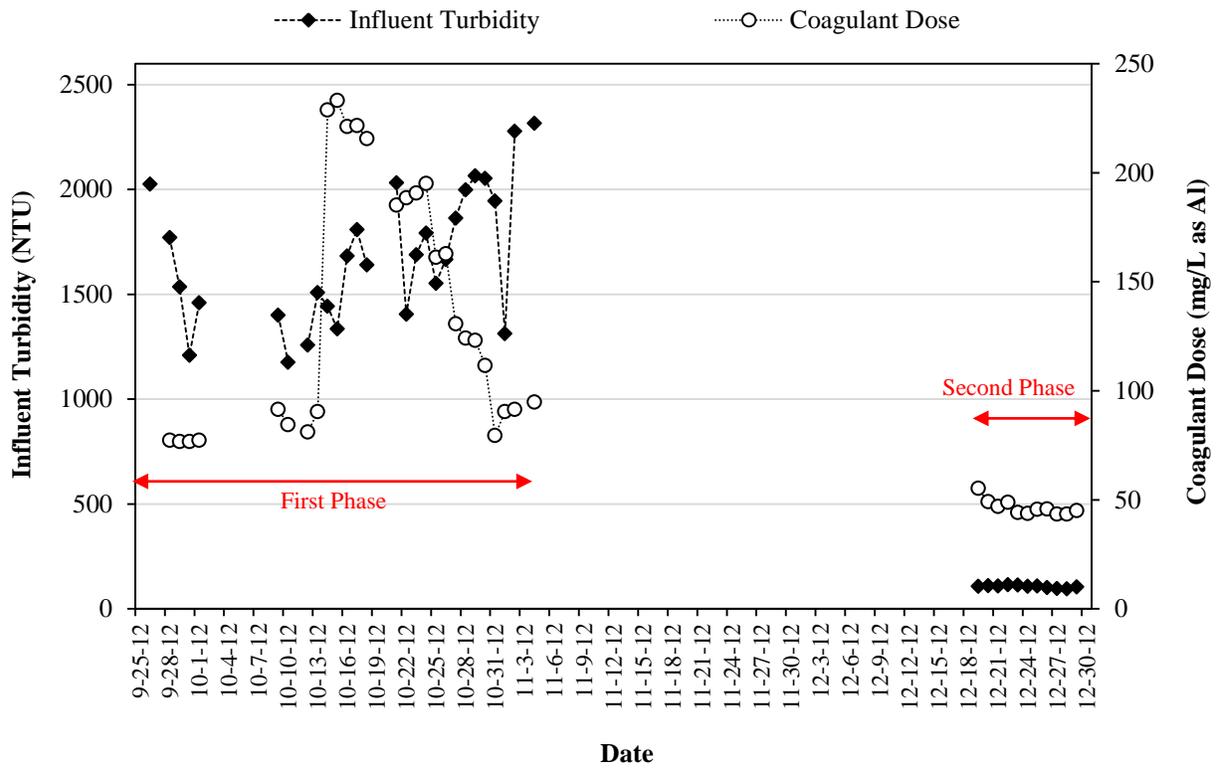
<b>Operating Cycle</b>	<b>Test Range</b>	<b>Optimum</b>	<b>Details</b>
Filtration Cycle Duration	3 to 60 minutes	60 minutes	
Backwash Cycle Duration	15 to 420 seconds	180 seconds	3 × 25 second backwashes per cycle at 35 seconds interval
Post Backwash Froth Cycle Duration	15 to 640 seconds	55 seconds	5 seconds of froth injection in membrane tank followed by 50 seconds of wait time before precoat cycle
Precoat Cycle Duration	5 to 19 seconds	19 seconds	

**Table S4.** Test range and optimum chemical doses for the pilot-scale study.

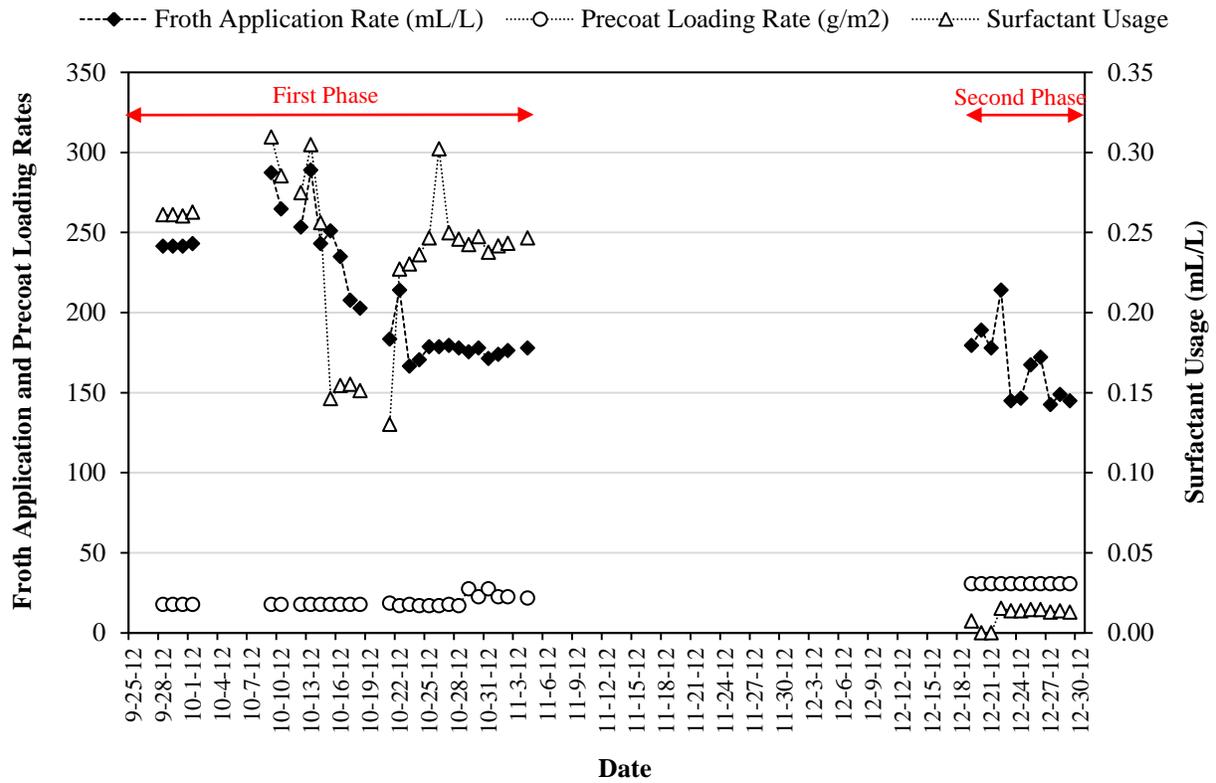
<b>Chemical Type</b>	<b>Unit of Measurement</b>	<b>Test Range</b>	<b>Optimum Values (Approx.)</b>
Surfactant	Froth Injection per L of Influent Water	143 to 290 mL/L	145 mL/L
	Surfactant Usage per L of Treated Water	0.0004 to 0.31 mL/L	0.25 mL/L at $\leq 2500$ NTU influent turbidity 0.015 mL/L at $\leq 200$ NTU
Coagulant	Dose as Al	44 to 234 mg/L	80 mg/L at $\leq 2500$ NTU influent turbidity < 40 mg/L at $\leq 200$ NTU
Precoat (G-250 or GA-200)	Loading per Unit Membrane Surface Area	18.5 to 32.5 g/m <sup>2</sup>	30 g/m <sup>2</sup>



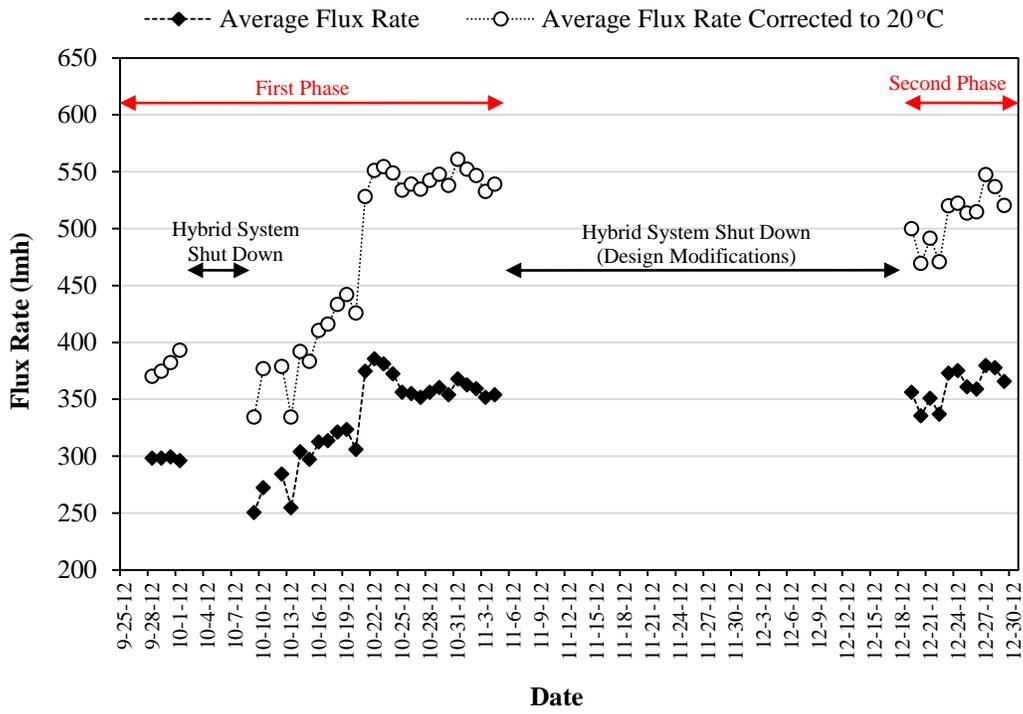
**Fig. S1.** Selection of surfactants in bench-scale experiments.



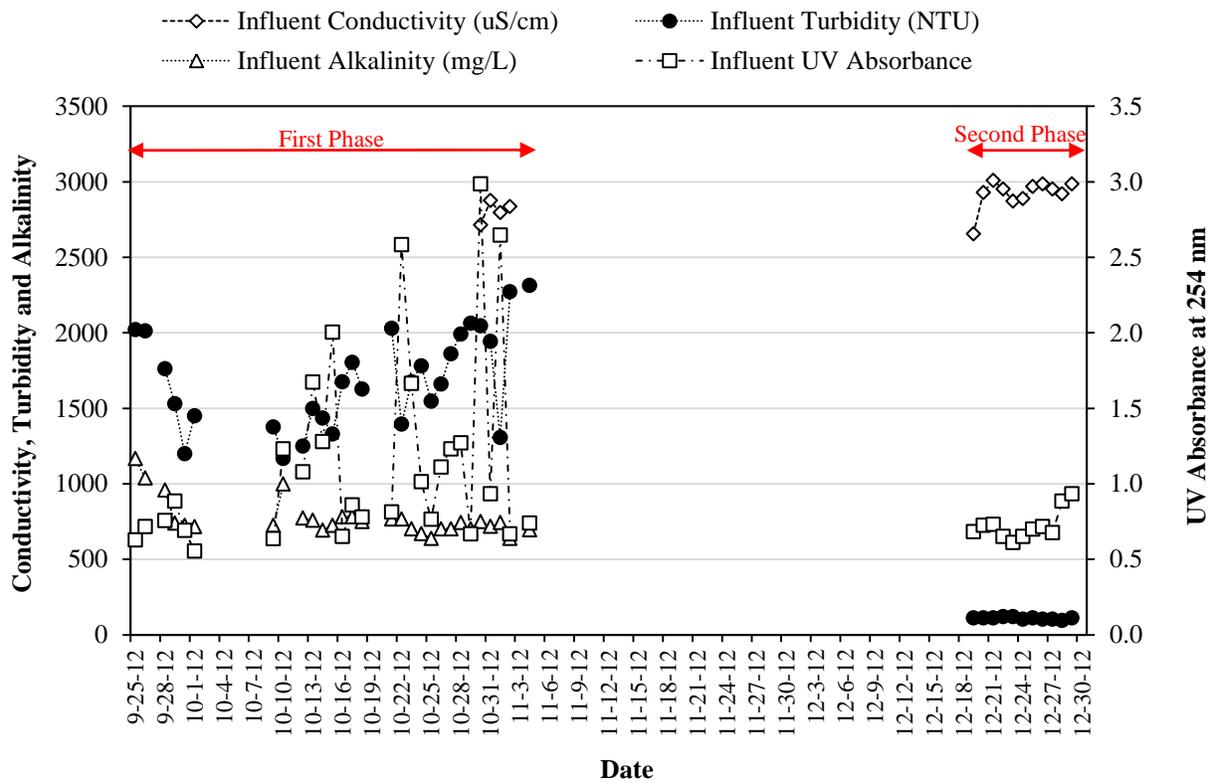
**Fig. S2.** Coagulant doses during the first and second phase of the pilot-scale tests.



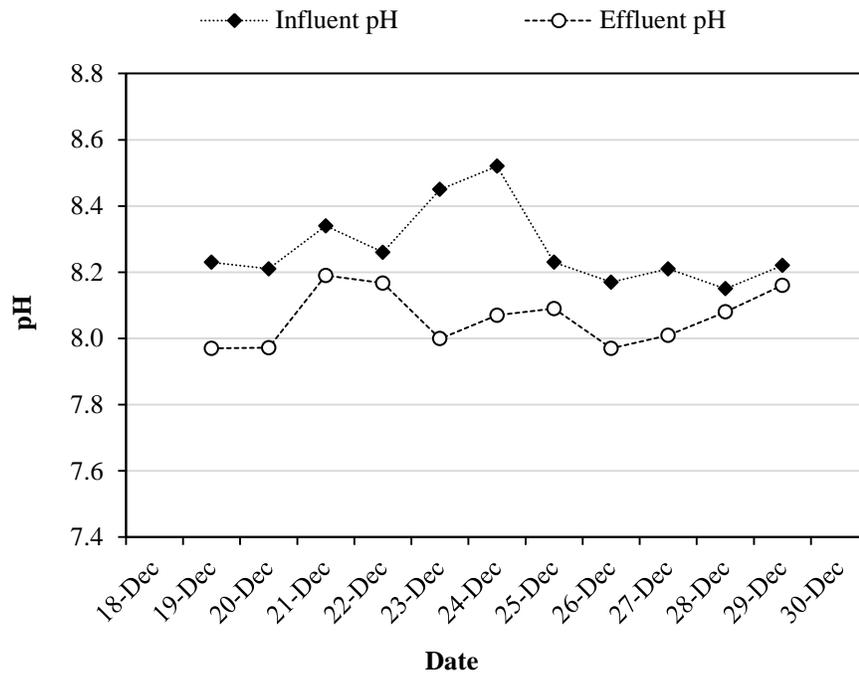
**Fig. S3.** Froth application and precoat loading rates during the pilot-scale study.



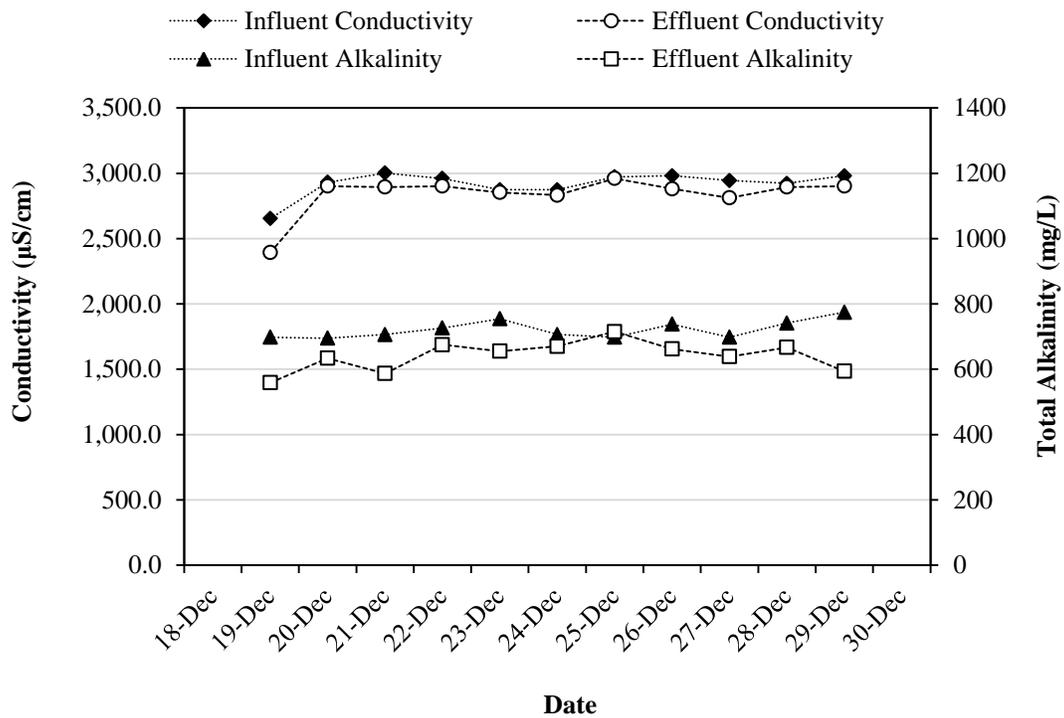
**Fig. S4.** Flux rates during the first and second phases of the pilot-scale study (lmh = liters/m<sup>2</sup>/hour).



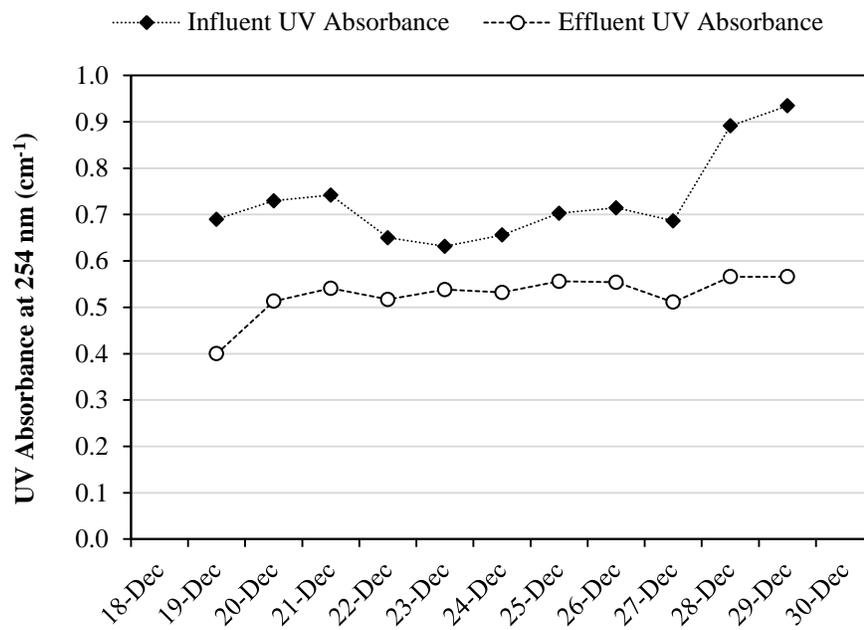
**Fig. S5.** Variations in influent water quality during the pilot-scale study.



**Fig. S6.** pH of RCW and treated water measured during the second phase of the pilot-scale study.



**Fig. S7.** Conductivity and alkalinity of RCW and treated water measured during the second phase of the pilot-scale study.



**Fig. S8.** UV Absorbance of RCW and treated water measured during the second phase of the pilot-scale study.