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# Impact of polymeric membrane filtration of oil sands process water on organic compounds quantification

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## ABSTRACT

The interaction between organic fractions in oil sands process-affected water (OSPW) and three polymeric membranes with varying hydrophilicity (nylon, polyvinylidene fluoride and polytetrafluoroethylene) at different pHs was studied to evaluate the impact of filtration on the quantification of acid-extractable fraction (AEF) and naphthenic acids (NAs). Four functional groups predominated in OSPW (amine, phosphoryl, carboxyl and hydroxyl) as indicated by the linear programming method. The nylon membranes were the most hydrophilic and exhibited the lowest AEF removal at pH of 8.7. However, the adsorption of AEF on the membranes increased as the pH of OSPW decreased due to hydrophobic interactions between the membrane surfaces and the protonated molecules. The use of ultra pressure liquid chromatography-high resolution mass spectrometry (UPLC/HRMS) showed insignificant adsorption of NAs on the tested membranes at pH 8.7. However, $26 \pm 2.4\%$ adsorption of NAs was observed at pH 5.3 following the protonation of NAs species. For the nylon membrane, excessive carboxylic acids in the commercial NAs caused the formation of negatively charged assisted hydrogen bonds, resulting in increased adsorption at pH 8.2 (25%) as compared to OSPW (0%). The use of membranes for filtration of soluble compounds from complex oily wastewaters before quantification analysis of AEF and NAs should be examined prior to application.

Key words | acid-extractable fraction, filtration, naphthenic acids, oil sands process-affected water, polymeric membrane

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## INTRODUCTION

The oil sands in Canada are one of the largest unconventional oil resources in the world. A billion litres of oil sands process-affected water (OSPW) are produced yearly by the oil sands industry and are currently stored in huge tailing ponds (Del Rio *et al.* 2006). According to the US EPA's toxicity identification and evaluation protocol, organic acids are considered to be the most toxic compounds in OSPW (MacKinnon *et al.* 1993). In particular, naphthenic acids (NAs), a persistent fraction of organic acids in OSPW, have been reported as primary sources of toxicity and are considered as target pollutants (MacKinnon *et al.* 1993).

Classical NAs are a group of aliphatic and alicyclic carboxylic acids, with a general empirical formula $C_nH_{(2n-Z)}O_2$, where $n$ is the carbon number, $-Z$ is the hydrogen deficiency (Allen 2008). Oxidized NAs with the formula $C_nH_{2n+Z}O_x$ ($x > 3$), where x represents the number of oxygen atoms, have also been detected in OSPW (Grewer *et al.* 2010). Few techniques have been used to qualitatively detect NAs in OSPW. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR FT-IR) has been used to characterize different NA mixtures or single NA model compounds (Pourrezaei *et al.* 2011). The evaluation of the aromatic organic content in OSPW, including naphtheno-aromatic acidic compounds, can be done using synchronous fluorescence spectroscopy (SFS) (Kavanagh *et al.* 2009). The concentration of NAs in OSPW can also be estimated as a part of the extractable organic fraction (AEF) by FT-IR, which is based on the detection of carbonyl stretches (Syncrude Canada Ltd 1995; Frank *et al.* 2006; Grewer *et al.*

2010; Martin *et al.* 2010). On the other hand, the estimated concentration and distribution of NAs in OSPW can be obtained by ultra/or high pressure liquid chromatography-high resolution mass spectrometry (UPLC/HRMS, HPLC/HRMS) (Martin *et al.* 2008; Han *et al.* 2009; He *et al.* 2010; Anderson *et al.* 2012). However, FT-IR remains the most common technique for the estimation of the concentration of AEF compounds in OSPW due to its simplicity and low cost (Bataineh *et al.* 2006).

Raw OSPWs from different tailing ponds contain AEF at concentrations between 40 and 130 mg/L at different pH values (7 to 8.7) (Allen 2008; Han *et al.* 2009). In addition, the pH of OSPW could significantly change after treatment. Sample filtration using 0.45 μm polymeric membranes precedes the analysis of OSPW to remove suspended solids. In this study, it is hypothesized that this filtration could bias the quantification of classical NAs. The main goal of this research was to report the impact of the interactions between the organic fraction in OSPW and polymeric membranes during the filtration of OSPW on further quantifications of AEF and NAs in solution. In addition to OSPW, commercial NAs (refined Merichem NAs mixture) were used to investigate the differences in behavior between a commercial NA mixture and classical NAs in OSPW during filtration. Three commercial 0.45 μm polymeric membranes with different hydrophilicity (nylon, polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE)) were tested in this study.

## MATERIALS AND METHODS

### Oil sands process-affected water

Three different OSPWs were obtained from two oil sand companies located in Fort McMurray, Alberta, Canada. OSPW 1 and OSPW 2 were collected from the same settling basin, but at different sampling periods (September 2010 for OSPW 1 and June 2012 for OSPW 2), while OSPW 3 was collected from a second oil sands company. The pH values of the OSPWs ranged from 7.0 to 8.7.

### Chemicals and reagents

Refined Merichem NAs were provided by Merichem Chemicals and Refinery Services LLC (Houston, TX, USA). Sodium hydroxide (NaOH) and tetradecanoic acid-1-^{13}C were purchased from Sigma Aldrich (Edmonton, AB, Canada). Sulfuric acid ($H_2SO_4$), potassium hydrogen phthalate ($C_8H_5KO_4$), dichloromethane ($CH_2Cl_2$), methanol ($CH_3OH$), sodium chloride (NaCl), and Optima-Grade water were purchased from Fisher Scientific (Edmonton, AB, Canada). Milli-Q water (Synergy® UV instrument, Millipore, Molsheim, France) was used through the entire study. Naphthenic acid (NA) standards were purchased from Sigma-Aldrich (Edmonton, AB, Canada).

### Filtration set-up and membranes

The OSPW samples were centrifuged at 16,000 rpm to remove suspended solids. A 200 mg/L stock solution of Merichem NAs was prepared in 100 mmol/L NaOH. The pH of OSPW and Merichem NA mixture was adjusted with $H_2SO_4$ or NaOH to 2.5, 5.5, 6.5, 9.2, 10 and 2.5, 5.5, 6.5, 8.2, 9.4, 10, respectively. The filtration set-up consisted of a 300 mL filtration funnel (Gelman Sciences, MI, USA) and a 500 mL receiving Büchner volumetric flask connected to a vacuum pump. Three types of 0.45 μm polymeric membranes (nylon: Cat. # HNWP04700; PVDF: Cat # HVLP04700; and PTFE: Cat # FHLC04700, Millipore, ON, Canada) were used in the tests. A 100 mL aliquot of each sample was filtered at a time; permeates were collected and used for AEF, SFS and classical NA analyses.

### Quantification of acid-extractable fraction (AEF) and classical NAs

AEF was quantified using FT-IR spectroscopy (Perkin Elmer Spectrum, 100 FT-IR Spectrometer, Waltham, MA, USA) based on a standard calibration curve ($R^2 = 0.999$ for 9 points) as described elsewhere (Gamal El-Din *et al.* 2011). Stock solution was prepared by dissolving 0.2 g of NAs in 200 g of dichloromethane ($CH_2Cl_2$, DCM). The quantification of AEF was based on the absorbance of wave numbers at 1,743 and 1,706 cm$^{-1}$ for the monomer and dimer carboxylic acids, respectively (Syncrude Canada Ltd 1995; Frank *et al.* 2006). Each analysis was performed in triplicate and the results are reported as an average ± standard deviation.

A Waters Acquity UPLC System (Milford, MA, USA) was used for the chromatographic separation of classical NAs. Two millilitres of each sample were centrifuged for 5 min at 10,000 rpm. Five-hundred microlitres of the supernatant were placed in a 2 mL glass vial with 400 μL of Optima-grade methanol and 100 μL of 400 mg/L tetradecanoic acid-1-[13]C (internal standard) to make a final 1 mL sample solution with 0.4 mg/L internal standard for the final injection. Further details can be found in the Supplementary material (SM), available online at http://www.iwaponline.com/wst/070/282.pdf.

An acid–base titration with the linear programming method (LPM) was used to identify and quantify the relative intensities of the functional groups present in AEF from OSPW and Merichem NAs as described previously (Brassard *et al.* 1990; Cox *et al.* 1999) with further details available in the SM.

## Synchronous fluorescence spectroscopy (SFS) analysis

SFS was used to evaluate the variation in aromatic residues of organic compounds in solution due to filtration. Duplicate fluorescence measurements were performed on a Cary Eclipse fluorescence spectrometer (Varian, Australia PTY LTD, Australia), and the synchronous fluorescence method was applied (Kavanagh *et al.* 2009). The $\Delta$ offset value ($\Delta = \lambda_{\text{Emission}} - \lambda_{\text{Excitation}}$) was 18 nm. The excitation wavelength ($\lambda$) ranged from 200 to 600 nm. The excitation and emission slits were set at 5 nm. The scan speed was 10 nm/s, and the photomultiplier tube voltage was set at 800 V (Peuravuori *et al.* 2002).

## X-ray photoelectron spectroscopy (XPS)

An AXIS 165 spectrometer (Kratos Analytical, Japan) analytical chamber was maintained below $3 \times 10^{-8}$ Pa. A monochromatic Al K$\alpha$ source (h$\nu = 1{,}486.6$ eV) was used at a power of 210 W. The analyzed area had dimensions of $400 \times 700$ μm. Duplicate survey scans were collected for binding energies in a range of 1,100 to 0 ev with analyzer pass energy of 160 eV and a step of 0.4 eV and 20 eV with a step of 0.1 eV for the high-resolution spectra. No charge neutralization was required due to sample conductivity.

## Characterization of the surfaces of polymeric membranes

The contact angles of pristine membranes were estimated using a sessile drop method (FTA-200, FOLIO Instruments Inc., Kitchener, ON, Canada). Four microlitres of Milli-Q water was dropped on each membrane (five replicates) and the contact angle was determined by the FTA32 software.

The chemical functionality of the membranes' surface before and after filtration was determined in duplicate by ATR FT-IR using a multi-reflection Smart Performer® instrument (Nicolet 8700, Thermo Electron Corp., West Palm Beach, FL, USA) with a zinc selenide (ZnSe) crystal at a nominal incident angle of 45°. The spectra were collected in the range of wave numbers from 600 to 4,000 cm$^{-1}$ with 128 scans at a resolution of 4.0 cm$^{-1}$.

## RESULTS AND DISCUSSION

### Identification of functional groups in AEF by acid–base titration and LPM

Table 1 showed the pK$_a$ values and relative percentages of the detected groups in OSPW 1 and Merichem NAs, respectively. Site 1 with a pK$_a$ value of 5.8 and 5.5 ± 0.1 for OSPW 1 and Merichem NAs, respectively, was attributed to the presence of carboxylic functional groups (Fein *et al.* 1997). Site 2 had a pK$_a$ of 6.4 ± 0.1 and 6.6 ± 0.2 for OSPW 1 and Merichem NA mixtures, respectively, and was attributed to the presence of phosphoryl functional groups (Cox *et al.* 1999). The intensity of this site was lower than that of site 1 for both Merichem NA mixture and OSPW 1 by 20% and 50%, respectively. Site 3 had a pK$_a$ of 7.9 ± 0.1 and 7.8 ± 0.1 for OSPW 1 and Merichem NA mixture, respectively. It was suggested that this could be attributed to the presence of amine functional groups. Both amine and phosphoryl functional groups have been reported previously using LPM for a water matrix at similar pH values (Cox *et al.* 1999). Sites 2 and 3 had the lowest intensity among all four detected sites in both Merichem NA mixture and OSPW 1. However, further studies are required to confirm that sites 2 and 3 belong to phosphoryl and amine functional groups, respectively. Site 4 was ascribed to hydroxyl functional groups, with pK$_a$ values of 9.9 and 9.4 ± 0.1 for OSPW 1 and Merichem NA mixture, respectively. The presence of hydroxyl functional groups could be an indication of the oxidized NA (Cox *et al.* 1999; Bataineh *et al.* 2006; Grewer *et al.* 2010; Martin *et al.* 2010). This site had the highest intensity in OSPW 1, but its intensity was significantly lower in Merichem NA mixture. This alteration in site percentages could significantly affect the further quantification processes due

**Table 1** │ pK$_a$ values and percentage of functional groups in AEF from OSPW 1 and Merichem NAs as measured by LPM

| Sample | Site number | pK$_a$ | Relative response | Percentage (Average) |
|---|---|---|---|---|
| OSPW | (1) | 5.8 ± 0.0 | 3.4 ± 0.2 | 32 |
| | (2) | 6.4 ± 0.1 | 1.8 ± 0.4 | 17 |
| | (3) | 7.9 ± 0.1 | 1.0 ± 0.3 | 10 |
| | (4) | 9.9 ± 0.0 | 4.3 ± 0.3 | 41 |
| Merichem | (1) | 5.5 ± 0.1 | 6.1 ± 0.6 | 64 |
| | (2) | 6.6 ± 0.2 | 1.1 ± 0.5 | 12 |
| | (3) | 7.8 ± 0.1 | 0.6 ± 0.5 | 7 |
| | (4) | 9.4 ± 0.1 | 1.7 ± 0.6 | 17 |

to the corresponding formation of different bonds with membrane surfaces (Ni et al. 2011). More specifically, focus on the carboxyl and hydroxyl groups would be useful as they characterize classical and oxidized NAs (Bataineh et al. 2006; Grewer et al. 2010; Martin et al. 2010).

## Surface characterization of pristine polymeric membranes

The nylon membrane was composed of 77% carbon, 10% oxygen and 13% nitrogen atoms (Figure S1, available online at http://www.iwaponline.com/wst/070/282.pdf). The curve fitting of C1s peak resulted in binding energies ($E_B$) of 284.9, 285.6 and 287.8 eV, attributed to C–C, C–N and O = C–N species, respectively (Xie et al. 2007). PVDF membrane consisted of 56% carbon, 10% oxygen and 34% fluoride atoms. The deconvolution of C1 s peak resulted in four $E_B$ values at 284.8, 286.2, 288.7 and 290.7 eV, assigned to C–H, H–C–H, C = O and F–C–F groups, respectively (Xie et al. 2007). The PTFE membrane consisted of 56% carbon, 20% oxygen and 24% fluorine atoms. The deconvolution of C1 s peak resulted in peaks with $E_B$ values of 284.8, 286.1, 288.7, and 291.9 eV. These binding energies were assigned to C–C, C–O, O–C = O and F–C–F groups, respectively (Chebbi et al. 2009; Chandler-Temple et al. 2010). Contact angles measurements indicated that nylon membrane was the most hydrophilic, having a contact angle of $34.5 \pm 3.1$. The PTFE membrane was the less hydrophilic with contact angle of $82.0 \pm 5.5$ and the PVDF membrane slightly higher at $69.8 \pm 1.5$. The XPS and contact angle results indicate that nylon membranes should be the best for filtration due

to their relatively high hydrophilicity as indicated by previous work (Wang et al. 2011; Yang et al. 2011).

## Effects of centrifugation and solution pH on the adsorption of AEF on membrane during filtration

It was found that centrifugation did not affect the quantification of AEF, with the AEF concentrations being $80.1 \pm 0.5$ mg/L and $79.9 \pm 0.5$ mg/L for as-received and centrifuged OSPW 1, respectively. This may be attributed to the very low insoluble matter concentration in the water matrix received as compared to OSPW matrices used in previous work (Pourrezaei et al. 2011). The centrifuged OSPW 1 was further subjected to membrane filtration to evaluate the effect of pH on the adsorption of AEF (Figure 1). The highest reduction in AEF concentration after filtration of OSPW 1 was observed at pH 2.5, with $33.0 \pm 0.5$, $26.0 \pm 0.8$ and $24.0 \pm 0.5\%$ adsorption on nylon, PVDF and PTFE membranes, respectively. Because the sizes of AEF molecules are significantly smaller than the pore sizes of polymeric microfiltration membranes used in this study, the size exclusion mechanism is not expected to play a significant role in the adsorption of AEF at any tested pH.

As shown by the LPM results (Table 1), at pH 2.5 the functional groups in AEF molecules were mostly protonated. Hence, the hydrophobic interactions between the non-charged AEF molecules and membrane surface could result in the adsorption of AEF molecules on the membrane surface, decreasing the concentration of AEF in permeate. The adsorption of AEF decreased when the pH increased from 2.5 to 5.5. This is consistent with the LPM results,
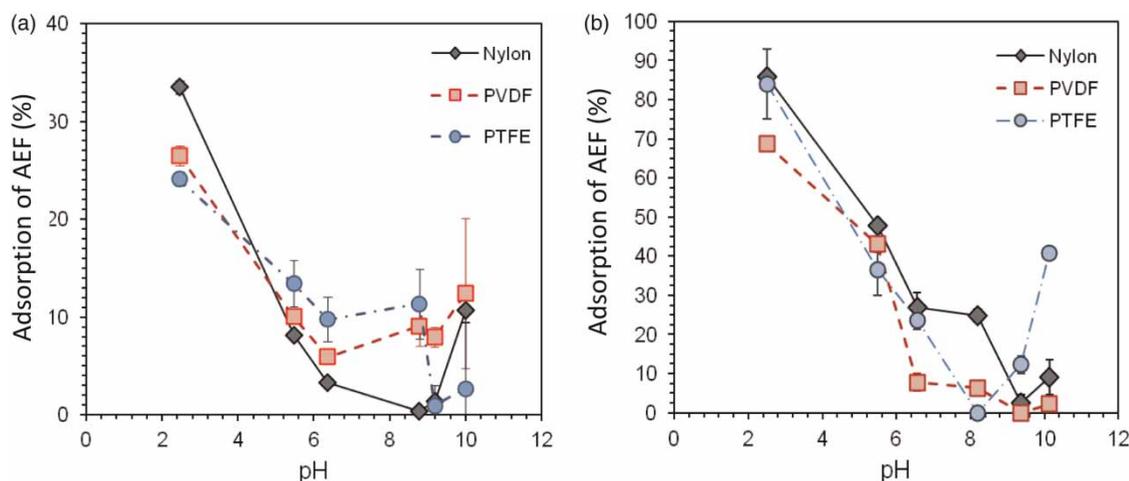


**Figure 1** | FT-IR results for the adsorption of AEF from (a) OSPW 1 by different membranes (the original concentration of AEF in OSPW 1 was $80.00 \pm 0.48$ mg/L), (b) FT-IR results for the adsorption of AEF from Merichem NAs solution by different membranes (the original concentration of AEF was $50.10 \pm 0.63$ mg/L).

which indicated that carboxylic functional groups became totally or partially ionized at pH 5.8 (Table 1). The ionization reduced the hydrophobic interactions between the AEF molecules and the membrane surface, which resulted in more soluble AEF molecules passing through the membrane pores. Further deprotonation of functional groups in AEF at pHs 6.4 and 7.9 rendered higher net negative charge on AEF molecules. The development of a negatively charged assisted hydrogen bond (NAHB) between the ionized acids and carbonyl groups on the membrane surface depends on the pKa of organic acids (Ni *et al.* 2011); however, nylon filters showed no removal at pH 8.7. For the Merichem NAs, the carboxylic acid functional group concentration was about two times higher than the OSPW that caused the development of NAHB and subsequent adsorption to the nylon membrane at pH 8.7 (Figure 1). On the other hand, the tested PVDF and PTFE membranes are expected to be negatively charged at the circumneutral and basic pHs due to the presence of the fluoride groups on the surface (Han *et al.* 2011; Lin *et al.* 2011). As such, the electrostatic repulsion between the negatively charged AEF molecules and the membrane surface would be a primary adsorption mechanism in this pH range.

According to the contact angle measurements, the adsorption of AEF molecules by the nylon membrane was the lowest, with no rejection observed at pH 8.7 (natural pH of OSPW 1) due to its higher hydrophilicity. Taking into account that PTFE and PVDF membranes are more hydrophobic than the nylon one, the hydrophobic interactions between the surfaces of PTFE and PVDF membranes and AEF molecules would be higher, resulting in an increase in AEF rejection on these membranes at pH 8.7. When pH was further increased to 10.0, the adsorption of AEF molecules increased for all membrane types. This can be explained by the LPM results, which indicated that hydroxyl (OH) functional groups in AEF are deprotonated at pH 9.9. Given the prevalence of OH groups in AEF (41%, Table 1), the complete ionization of AEF molecules increased its net negative charge. Therefore, the repulsive forces between the membrane surface and the AEF molecules will repel AEF molecules from the membrane surface during filtration, increasing their rejection by all tested membranes.

The PTFE membrane, which had the lowest hydrophilicity, had 100% recovery of AEF from the Merichem NA mixture ($50.4 \pm 1.2$ mg/L) at pH 8.2. This is due to the higher content of carboxylic groups in the Merichem mixture which may not be able to form NAHB with the low concentration of carbonyl groups on the PTFE membrane.

## Identification of adsorbed aromatic compounds from OSPW and Merichem NA solutions

The FT-IR analysis, which was used for the quantification of AEF, is based on the detection and quantification of carbonyl stretches. However, these stretches could represent NAs and other organics in AEF, including aromatic compounds (Kavanagh *et al.* 2009; Grewer *et al.* 2010). To investigate the impact of the aromatic fraction in AEF on FT-IR measurements, the SFS analyses of OSPW 1 and Merichem NAs were performed at pH 8.7 and 8.2, respectively (Figure S2, available online at http://www.iwaponline.com/wst/070/282.pdf).

The characteristic peaks of aromatic compounds were obtained in OSPW 1 at the emission wavelengths of 273, 310 and 325 cm$^{-1}$, indicating the presence of one and two aromatic rings (Figure S2) (Kavanagh *et al.* 2009). The observed wavelengths slightly deviated from the reported values (282.5, 320 and 340 cm$^{-1}$), likely due to the pH effect on the peak shape (Cabaniss & Shuman 1987; Pullin & Cabaniss 1997). The intensity of the peaks for non-filtered and PVDF- and PTFE-filtered OSPW 1 was similar, indicating that there was no adsorption of aromatic compounds by these membranes. However, the intensity of the peaks corresponding to the compounds with two rings was lower for the nylon-filtered OSPW 1, indicating that some of the two-ring compounds were removed during filtration. Comparing this finding with the results of FT-IR analysis, it can be concluded that the compounds in the removed fraction did not contain carboxyl groups in their structure which is corroborated in the NA quantification section below.

To evaluate the impact of low pH on the adsorption of aromatic compounds from OSPW 1 during filtration, filtration on the nylon membrane was performed at pH 5.3. At this pH, the carboxyl functional groups are expected to be partially protonated (pKa 5.8) (Table 1). As shown in Figure S2, the intensity of the peaks detected in OSPW 1 after filtration on the nylon membrane was lower at pH 5.3 as compared to pH 8.7 for both one- and two-ring compounds. This implies that the aromatic compounds were removed from OSPW 1 during filtration on the nylon membrane as the pH decreased. The SFS of Merichem NA mixtures revealed three peaks at 287, 329 and 410 cm$^{-1}$, corresponding to the compounds with one, two and four or more rings, respectively (Figure S2) (Kavanagh *et al.* 2009). The intensity of the first peak did not change in the PTFE- and PVDF-filtered solutions at both studied pHs (5.5 and 8.2); however, it decreased after filtration using the nylon membrane. The intensity of the peaks corresponding to the compounds with two rings decreased after

filtration on all membranes. Consistently with the SFS of OSPW 1, it can be concluded that the removed aromatic compounds at the studied pHs (8.7 for OSPW 1 and 8.2 for Merichem NAs) did not contain carboxyl groups in their structure. No peaks corresponding to the compounds with four or more rings were detected after filtration on all membranes, suggesting that this type of organics was fully removed during the filtration. These results indicate the insignificant impact of adsorption to membranes for the OSPW aromatic compounds in addition to a minimal impact on the Merichem NA mixture.

## ATR FT-IR analysis of membrane surfaces

The decrease in AEF concentration was observed after filtration of OSPW 1 and Merichem NA solutions using different membranes (Figure 1). The nylon and PTFE membranes did not show adsorption of AEF at pHs 8.7 and 8.2 in OSPW 1 and Merichem NA mixture, respectively. The ATR FT-IR spectra of nylon, PVDF and PTFE membranes before and after filtration of OSPW 1 and Merichem NAs are shown in Figures 2 and S3, respectively (Figure S3 is available online at http://www.iwaponline.com/wst/070/282.pdf).

Two adsorption bands (C = O and OH) can indicate the presence of carboxyl functional groups on a surface, with the adsorption band near $1{,}670 \ cm^{-1}$ characterizing C = O stretching vibration, and adsorption band between 3,300 and $2{,}500 \ cm^{-1}$ characterizing OH stretching vibration (Stuart 2004; Pourrezaei *et al.* 2011). As shown in Figure S3 two adsorption peaks at 1,670 and $3{,}300–2{,}500 \ cm^{-1}$ were detected in all membranes. The wide peak that appeared in 3,300–$2{,}500 \ cm^{-1}$ region could be ascribed either to hydroxyl groups in carboxyl group or to any possible residual moisture remaining in the membranes after air-drying (Pourrezaei *et al.* 2011). The intensity of the adsorption band at $1{,}670 \ cm^{-1}$ increased two to five times after filtration on all membranes (Figure 2), with the adsorption bands for OSPW 1 and Merichem NAs mixture having similar intensities. The FT-IR analysis showed no losses of AEF in permeate from the nylon-filtered OSPW 1 at natural pH 8.7. The ATR FT-IR results confirmed the adsorption of AEF compounds on the membrane surface at natural pH 8.7. It should be noted that $CH_2Cl_2$ solvent is used for AEF extraction while ATR FT-IR allows for the direct analysis of AEF compounds retained on the membrane surface. As such, the difference between ATR FT-IR and FT-IR results might imply that FT-IR did not account
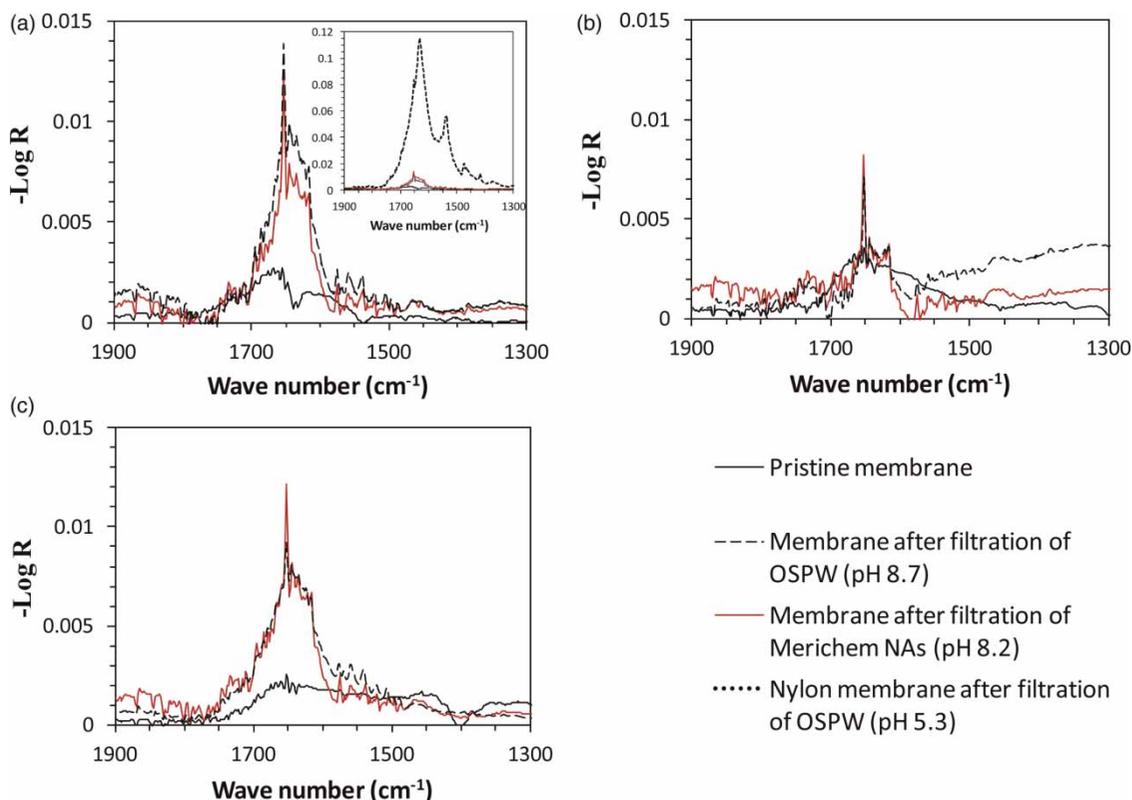


**Figure 2** │ The ATR FT-IR spectra of (a) nylon, (b) PVDF, and (c) PTFE membranes before and after filtration of OSPW 1 and Merichem NAs. An inset shows ATR FT-IR spectra of nylon membrane after filtration of OSPW 1 at pH 5.3.

for a certain fraction of carboxylic acids due to the extraction step. The $CH_2Cl_2$ might not fully extract carboxylic acids from a solution and the organic fraction of OSPW 1 reported as AEF may not account for all NAs present in OSPW 1.

To investigate the effect of low pH on the surface composition of the studied membranes due to filtration, the surface of a nylon membrane was analyzed by ATR FT-IR after filtration of OSPW 1 at a pH of 5.3. Consistent with the FT-IR analysis of membranes' permeates, which showed higher adsorption of AEF in the acidic pH range, the intensity of carbonyl peak on the membrane surface was almost eight times higher as compared to the peak detected after filtration of OSPW 1 at pH 8.7. This is caused by the higher hydrophobicity of the protonated organic fraction in OSPW 1 at the acidic conditions (pH 5.3) (Table 1) (Syncrude Canada Ltd 1995; Kannel & Gan 2012). It is noted that FT-IR results for the same sample (pH 5.3) showed $8.0 \pm 0.3\%$ adsorption of AEF, while no adsorption was observed for filtered OSPW 1 at pH 8.7.

Comparing these observations with the ATR results, it might be concluded that the detected $C = O$ groups on the filter surface could be a leftover or any possible residual moisture remaining in the membranes. An additional technique is required in order to quantify the percentage of AEF removed by the membranes.

## Measurement of classical NAs using UPLC/HRMS

The effect of membrane filtration on the adsorption of classical NAs was evaluated by quantifying classical NAs in OSPW 1 before and after filtration. The results were reported in terms of the carbon number ($n$) and hydrogen deficiency/number of rings ($-Z$) (Figures 3 and S4; Figure S4 is available online at http://www.iwaponline.com/wst/070/282.pdf). The observed $-Z$ numbers for OSPW 1 were even, ranging from 2 to 12 rings, and $n$ ranging from 9 to 20 carbons. These findings agreed with the results reported in previous studies where nylon membrane filters were
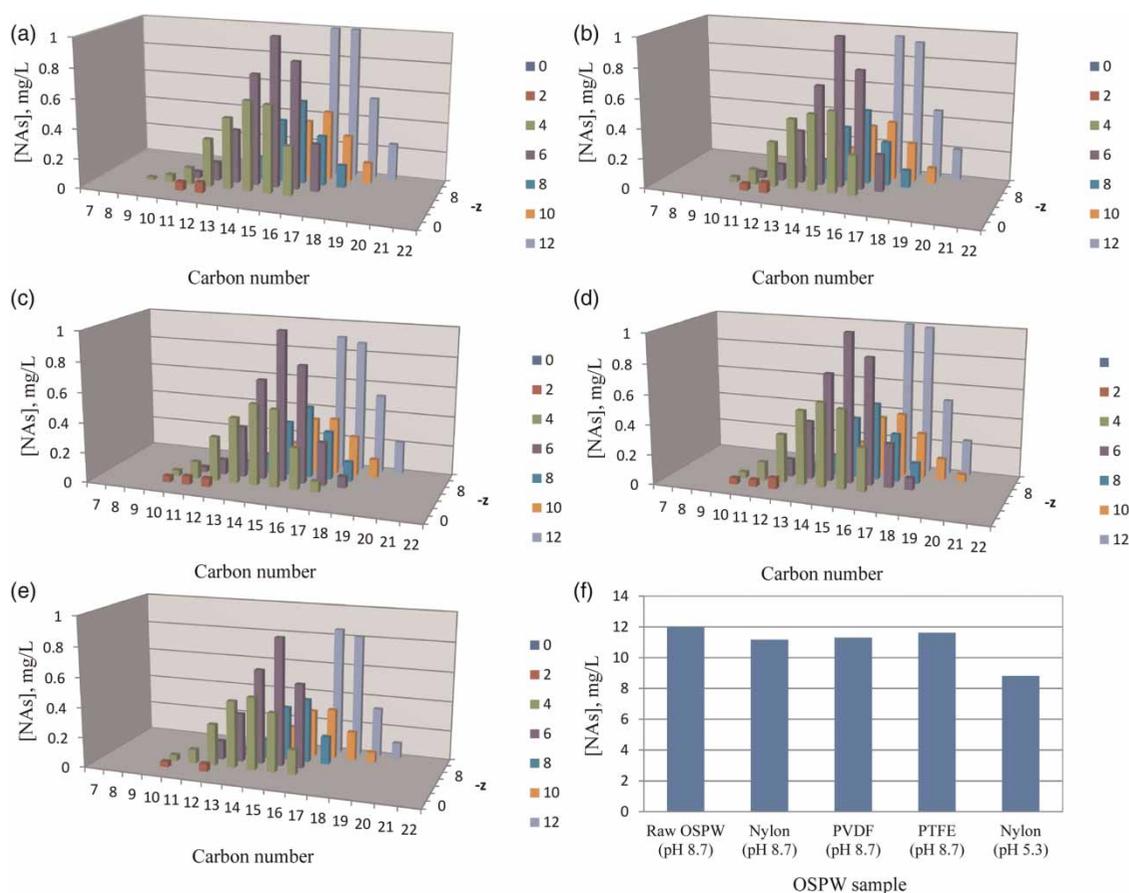


Figure 3 | Distribution and estimated concentration of classical NAs (Trial #1) in (a) OSPW 1 at pH 8.7 (11.9 mg/L), and permeates after filtration through (b) nylon membrane at pH 8.7 (11.4 mg/L), (c) PVDF membrane at pH 8.7 (11.6 mg/L), (d) PTFE membrane at pH 8.7 (11.8 mg/L), (e) nylon membrane at pH 5.3 (8.8 mg/L) and (f) summary of the estimated concentrations of NAs. The concentration of classical NAs was measured by UPLC/HRMS.

used for filtration of various water matrices (Cabaniss & Shuman 1987; Pourrezaei *et al.* 2011). The total relative responses of classical NAs did not significantly change after filtration at the natural pH of OSPW 1 (Figure 3(b) and S4(b)). A maximum of 10% adsorption of NAs was detected for nylon and PVDF membranes and less than 2% for PTFE membrane (Figures 3(c), 3(d), S4(c) and S4(d)). Consistently with the FT-IR analysis, the adsorption of classical NAs increased with the decrease in the OSPW pH. The filtration experiment conducted on nylon membrane at pH 5.3 resulted in $26\% \pm 2.4$ adsorptions of classical NAs from OSPW 1, as shown in Figures 3(e) and S4(e). To confirm these findings, classical NAs adsorption by different membranes was also estimated for OSPW 2 and 3, and the adsorption of classical NAs were also statistically insignificant (data not shown).

## CONCLUSIONS

The treatment techniques of OSPW such as adsorption and advanced oxidation are assessed based on the reduction in the concentration of NA species and their associated toxicity. Therefore, the concentration of these compounds should not be underestimated. This study showed that the use of membranes for filtration of insoluble compounds before AEF extraction can bias the quantification results, especially when OSPW pH is reduced to less than 6.2. In addition, it is interesting to note that the higher concentration of carboxylic acids in commercial NAs significantly increases the adsorption to the nylon membrane versus the OSPW due to the formation of NAHB. Therefore, the use of membranes for filtration of OSPW, commercial NAs mixtures or other oily wastewaters before the quantification analysis should be thoroughly investigated before their application. This finding should be applicable to any water matrix containing a mixture of soluble carboxylic hydrocarbons, such as the tailings water for the conventional oil and gas industries and contaminated groundwater impacted by leaking underground and aboveground storage tanks.

## ACKNOWLEDGEMENTS

## SUPPLEMENTARY MATERIAL

Supplementary material (available online at http://www.iwaponline.com/wst/070/282.pdf) includes detailed experimental methods as well as tables and figures.

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