Membrane processes for the reuse of car washing wastewater
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ABSTRACT
This study investigates alternative treatments of car wash effluents. The car wash wastewater was treated by settling, filtration, and membrane filtration processes. During settling, total solid concentration decreased rapidly within the first 2 hours and then remained constant. Chemical oxygen demand (COD) and conductivity were decreased by 10% and 4%, respectively. After settling, wastewater was filtered throughout a 100 μm filter. It was found that filtration had a negligible effect on COD removal. Finally, wastewater was filtered by four ultrafiltration membranes of varying molecular weight cutoff (MWCO) (1, 5, 10 and 50 kDa) and one nanofiltration membrane (NF270, MWCO = 200–400 Da). The permeate COD concentrations varied between 64.5 ± 3.2 and 85.5 ± 4.3 mg L⁻¹ depending on UF pore size. When the NF270 nanofiltration membrane was used, the permeate COD concentration was 8.1 ± 0.4 mg L⁻¹ corresponding to 97% removal. FeCl₃ precipitation and activated carbon adsorption techniques were also applied to the retentate and 60–76% COD removals were obtained for activated carbon adsorption and FeCl₃ precipitation, respectively.

Key words | car wash wastewater, nanofiltration, ultrafiltration, wastewater, water reuse

INTRODUCTION
The car wash industry is one of the leading consumers of large volumes of clean water. Water used per car varies between 150 and 600 L depending on the size of the car and equipment used (Panizza & Cerisola 2003a). Therefore, there is a growing interest in wastewater treatment and reuse in this sector, in addition to the recognition of the environmental impacts (Zaneti et al. 2011). In Queensland, Australia, water is limited to 70 L per car. Similarly, some European countries restrict water consumption to 60–70 L per car and/or impose reclamation percentages (70–80%) (Boussu et al. 2007; Zaneti et al. 2011).

Often, characteristics of the wastewater depend on the socioeconomic structure of the country. In a study conducted in Malaysia, chemical oxygen demand (COD) ranged from 75 to 758 mg L⁻¹; conductivity 150.7–260.7 μS cm⁻¹ and turbidity 34.7–86 NTU were reported (Lau et al. 2013). Another study in Brazil reported COD at 259 ± 40 mg L⁻¹; conductivity at 446 ± 55 μS cm⁻¹, and turbidity at 139 ± 45 NTU (Rubio & Zaneti 2009).

Although there is a growing interest in recycling car wash effluents and implementing different technologies, there is no comprehensive standard for recycled water conditions. Metcalf & Eddy (2005) describe reclaimed water as water that has been brought to specific criteria and suitable for its intended use. According to Brown (2000), no dust, oil, or grease should be present in the water that is to be recycled in car wash units. Any additional process for the treatment of dust, oil, and grease increases the quality of recycled water and allows the water to be used in different washing stages (pre-soak, wash, rocker panel/undercarriage, first rinse, and final rinse) (Zaneti et al. 2011).
There are many treatment alternatives, including reverse osmosis-nanofiltration ultrafiltration (Jönsson & Jönsson 1995), ultrafiltration-activated carbon adsorption (Hamada & Miyazaki 2004), electrochemical oxidation (Panizza & Cerisola 2010b), biological treatment, and flocculation (Rubio et al. 2007). In one study, high turbidity and color removal (higher than 90% and 75%, respectively) were obtained by flocculation and the column floating method (Rubio & Zaneti 2009).

In another study, Rodriguez Boluarte et al. (2016) compared the membrane bioreactor process (MBR) with chemical coagulation and ozonation in the treatment of wastewater from the car wash station and reported that the MBR provided much better effluent than coagulation. In this study, 100% of suspended solids, 99.2% of COD, 97.3% of total organic carbon (TOC) and 41% of ammonia were removed with MBR. Ferric sulphate, ferrous sulphate, ferric chloride and ferric chloride sulphate are generally used in the chemical coagulation process. However, there are alternative coagulants in the literature and significant results are reported. In the study by Rodriguez Boluarte et al. (2016), molinga oleifera was used as a natural coagulant and effluent met EQA 1974 A standards for pH and dissolved oxygen (DO), and B standards for turbidity and COD.

Electrocoagulation is another widely used method. Mohammadi et al. (2017) used electrocoagulation to remove COD and biochemical oxygen demand (BOD) with iron and aluminum electrodes. On the other hand, electrocoagulation can be combined with ultrasound to give better results. Chu et al. (2012) found that the efficiency of COD and turbidity removal were 68.77% and 96.27%, respectively (I = 1.2 A, pH = 6.0, d = 1.5 cm, and t = 20 min). Compared to traditional approaches, membrane technology is convenient to remove all contaminants in wastewater. Membrane reactors can achieve a high permeate quality with a small area.

Over the past few decades, membrane separation has drawn a great deal of interest as a treatment for various types of industrial wastewater (Yurtsever et al. 2015; Sahinkaya et al. 2016). However, less attention has been given to the membrane separation treatment for car wash wastewater. According to Daneshyar & Ghaedi (2015), ignorance regarding the negative impact of polluted water may be the reason that implementing car wash best management practices remains limited. Compared with other industry wastewaters, car wash effluents are usually considered less severe. However, environmental contamination caused by various chemical agents necessitates its proper treatment.

Treatment of car wash effluents by membranes has been reported in several studies (Lau et al. 2013; Rodriguez Boluarte et al. 2016). Lau et al. (2013), investigated the treatment of car wash effluents by ultra- and nanofiltration membranes by means of flux, conductivity, total solids, COD, and turbidity. According to their results, over 92% turbidity removal was observed independently from the membrane, but COD removal depended on the membrane properties. The best COD removal was obtained with the NF270 membrane (91.5%, influent was 738 mg L$^{-1}$). For higher performance and flux, single membrane separation is insufficient and requires a pre-treatment. Surfactants and oil grease are especially difficult to remove with membranes. Therefore, many researchers emphasize the importance of pre-treatment (Hamada & Miyazaki 2004).

In the treatment of car wash effluents, membrane technologies generally focus on ultrafiltration (Istrokhatun et al. 2015; Pinto et al. 2017). However, a comprehensive study comparing UF membranes in a number of different molecular weight cutoffs (MWCOs) is still needed. Therefore, this study aims to investigate the membrane filtration alternatives for car wash effluents together with pre-treatment options. The efficiency of the treatment techniques was investigated using different UF membranes at 5–50 kDa MWCO and the data obtained with the UF membranes are also compared with the NF270, a common NF membrane.

For that purpose, car wash effluents were precipitated and filtered. Finally, four various sized ultrafiltration and one nanofiltration membrane were used to treat the wastewater. The results were evaluated with respect to COD, conductivity, and total solid rejections.

**EXPERIMENTAL**

**Car wash effluent**

Wastewater was collected from a car wash station in Atasehir/Istanbul, Turkey; its characteristics can be seen in
Table 1. Wastewater was collected during three washing periods – rinsing, foaming, and final rinsing – and subsequently mixed. Wastewater was collected in proportion to water used in each period. In order to also focus on detergent removal, detergent was also taken from the station.

Treatment process

The treatment process included three steps: settling, filtration, and membrane filtration. In the settling tests, 1 L of wastewater was taken into a 1,000 ml graduated cylinder and sampled for every 30 minutes from the 300 ml level of the cylinder. After 11 h settling, the test wastewater was siphoned up to the 300 ml level. The siphoned wastewater then passed through a ~10 μm filter (coarse filtration – Chmlab). The newly filtered water was then used in several membrane filtration tests in which four ultrafiltration membrane (1, 5, 10 and 50 kDa) and one nanofiltration membrane (NF270, 200–400 Da) were used. The properties of membranes are presented in Table 2. Membranes used were left in pure water for 1 day prior to the dead-end analysis. At the end of each process, wastewater was sampled for color, COD, total solid, pH, conductivity, and PO4 analysis.

In order to investigate high concentrations of detergent removal from the retentate, detergent from the car wash station was added to the water. This water was then treated by adsorption and chemical precipitation. Granular activated carbon and FeCl3 were used for the adsorption and chemical precipitation tests, respectively. The results were evaluated based on the COD and conductivity analysis.

Analytical methods

Total solids were measured according to the evaporation methods as reported by another study (Bhattarai et al. 2008). COD was measured according to APHA (American Public Health Association) and WEF (Water Environment Federation) by micro-digestion and then titration (Rice et al. 2005). Conductivity and pH were measured with a Hach multimeter (Hack – HQ 40 d multimeter). Total phosphate was measured with the Hach phosphate test kit (Model PO-24). PO4 was measured with the orthophosphate measurement kit (Chemetrics, 0.1–10 ppm, Stannous Chloride method with maximum detection limit of 0.05 ppm). Color was measured using the Pt-Co method by a spectrophotometer (HACH, DR/5000). The dead-end filtration unit was used for both coarse and membrane filtrations (Figure 1). In the dead-end unit, wastewater was forced by nitrogen gas pressure to pass throughout a membrane lying in the bottom of the unit. Wastewater mixing (230 rpm) was provided by the magnetic stirrer within the dead-end mechanism (Figure 1). The weight of the filtrate was measured on a scale and the data was processed by a computer connected to the scale. The volume of the filtrate was calculated based on the assumption that filtrate density is 1 g cm⁻³. These dead-end filtration tests were performed
for 1 hour under 5 bar pressure. At the end of the tests, the filtrates were subjected to chemical analysis.

RESULTS AND DISCUSSION

Pre-treatment of wastewater

The pre-treatment stage consisted of settling and coarse filtration. In settling tests, wastewater was sampled every 30 minutes during the first 150 min of the experiment. Then two more samples were taken after 210 minutes and again after 630 minutes. Results showed that most of the settleable solids were precipitated in 1 hour and then the concentration of total solids remained the same (see supplementary material, Figure S1, available with the online version of this paper). Initial total solid concentration was 1,054 ± 21 mg L⁻¹ and decreased to 609 ± 14.2 mg L⁻¹ at the end of 1 hour corresponding to 42% solid removal. At the end of 10.5 hours, removal efficiency was 47% (Figure 2).

Wastewater was then filtered throughout a coarse filter (∼10 μm). Filtration efficiency was not affected by the total solid or COD concentrations, indicating that the remaining solid particles were less than 10 μm in size. Influent and effluent COD concentrations were 287 ± 8 and 282 ± 7.4 mg L⁻¹, respectively. The concentration of phosphate in the wastewater was 9.05 ± 0.4 mg PO₄³⁻ L⁻¹ and decreased to 5.9 ± 0.3 and 5.8 ± 0.2 mg PO₄³⁻ L⁻¹ by the end of the settling and filtration process, respectively. As a result, pre-treatment (1 hour settling and filtration) removed 44% of total solids, 36% of phosphate, 11% of COD, and 4% of conductivity.

The COD concentration can indicate pollutants outside of the car such as bird excreta, fruit falls or dust in various composites. Detergents also cause higher amounts of COD in the effluent and were measured directly as COD in several studies (Pak & Chang 2000; Chu et al. 2012; Lau et al. 2013). To specify that the detergent used in this study can be measured as COD, 2 ml and 4 ml of detergent were added to 1 L of distilled water and the COD was analyzed. The COD concentrations were 228.3 ± 3.5 and 427.6 ± 10.6 mg L⁻¹ for 2 and 4 ml L⁻¹ detergents, respectively (COD ml⁻¹ detergent ratio was calculated as 110 ± 4 mg COD ml⁻¹ detergent).

Membrane filtration – flux

In the membrane filtration tests, four 1,000–50,000 Da UF membranes and one NF (NF270) membrane were used. The flux variations were investigated for a single 1 hour period and decreases were monitored. The highest flux decrease was observed for the 50,000 Da UF membrane. While the initial flux was 177.9 L m⁻² h⁻¹, it rapidly decreased to 68.9 ± 1.9 L m⁻² h⁻¹ in 10 min. After the 1 hour filtration, the final flux was 35.2 ± 2.1 L m⁻² h⁻¹. As MWCOs decreased from 50,000 to 1,000 Da, the flux...
decline also decreased. For the 10,000 Da UF membrane, the initial flux of 156.5 ± 2.05 L m⁻² h⁻¹ decreased to 24.8 ± 5 L m⁻² h⁻¹ corresponding to 82% flux loss. The 1,000 Da UF membrane showed the lowest flux with an average of 13.97 L m⁻² h⁻¹ (Figure 3). The flux decrease for NF270 membrane was 35% at the end of the experiment.

Pore size is one of the most important parameters affecting the flux in membrane filtrations. Flux is also affected by the membrane structure, constituents in the water, and wastewater pH. In some studies, it has been reported that NF membranes (especially NF270) can provide a higher flux than UF membranes (Lau et al. 2013). This is primarily due to electrostatic interactions between the membrane surface and wastewater constituents as reported (Chidambaram et al. 2015).

In this study, the initial flux of the NF membrane was 57 L m⁻² h⁻¹ and decreased to 37 L m⁻² h⁻¹ (35% decrease). The NF270 membrane has a hydrophilic nature and is composed of a piperazine and benzene dicarbonyl trichloride-based polyamide layer on top of a polysulphone microporous support reinforced with a polyester non-woven backing layer (Gryta et al. 2012). With this structure, the NF270 membrane can provide good rejections at high flux values. In addition to the hydrophilic layer, the highly negatively charged surface of NF270 reduces the clogging effects and prevents flux drops in wastewater treatment (Ong et al. 2012). The reason for the low flux in the ultrafiltration membranes may be due to oil, grease, and other petroleum derivatives resulting from the engine washing process. Often the composition of oil and grease originating from the engine is quite complex and treating these materials during the process of membrane filtration can be difficult. Generally, benzene, lead, zinc, chromium, arsenic, pesticides, nitrates, and different concentrations of heavy metals are found in oil and grease (Lau et al. 2013).

Rejection

Visual improvement of wastewater was accomplished by membrane filtration. While initial conductivity was 701 ± 20 μS cm⁻¹, it decreased to 523 ± 15.7, 555 ± 16.7, 592 ± 17.8 and 629 ± 19 μS cm⁻¹ at the end of filtration with 1,000, 5,000, 10,000 and 50,000 Da UF membranes, respectively. Filtrate COD concentrations varied between 64.5 ± 3.2 and 85.5 ± 4.3 mg L⁻¹ depending on the UF membrane. For all UF membranes tested, effluent PO₄³⁻ removal efficiencies were less than 1 mg L⁻¹. Variations in water characteristics during the settling, coarse filtration, and membrane filtration are presented in Table 3.

As expected, better results were obtained with the NF270 membrane. With the NF membrane, COD, conductivity, and PO₄³⁻ removal efficiencies were 98%, 47%, and 100%, respectively (Table 3). Images showing the changes in wastewater appearance are presented in the supplementary material (Figure S2, available with the online version of this paper).

Fate of concentrate

Although high effluent quality can be obtained by membrane filtration, membrane fouling and retentate disposal are major constraints in the process. Most solid agents in the wastewater can be removed during the settling process, but dissolved matter (mainly detergent) can only be removed during nanofiltration and accumulates in the retentate. In order to remove these detergents from the retentate, chemical precipitation or adsorption can be applied. Because detergents are surfactant, adsorption of detergents is a reported approach (Narkis & Ben-David 1985; Leyval Ramos 1989). Adsorption of detergent on activated carbon was studied by preparing 2 ml L⁻¹ detergent solution. Then 2 g of activated
Carbon were added and mixed for 30 minutes. Influent 452 ± 24 mg L\(^{-1}\) COD decreased to 184 ± 4.04 mg L\(^{-1}\) corresponding to 60% detergent removal.

Chemical precipitation may be another approach for detergent removal (Aboulhassan et al. 2006; Aygun & Yilmaz 2010). 100 mg FeCl\(_3\) were added to the detergent solution (2 ml L\(^{-1}\); pH 7). Once the FeCl\(_3\) were mixed homogeneously, the solution was mixed slowly (50 rpm) for 30 seconds. Effluent COD decreased to 112 ± 8.06 mg L\(^{-1}\), showing 76% detergent removal (precipitates are presented in supplementary material, Figure S3, available with the online version of this paper).

Membrane filtration removes colloids and detergents that cannot be retained in the precipitation and filtration process, and these substances are concentrated in the brine. Some small stations may discharge the concentrate directly to the sewer depending on the sewage discharge standards. In this case, while the water recovery rate is reduced, the chemical costs used for concentrate treatment can be saved. According to Istanbul sewage discharge standards, 1,000 mg L\(^{-1}\) COD, 500 mg L\(^{-1}\) SS and 150 mg L\(^{-1}\) oil and grease are allowed (Iski 2013).

### CONCLUSIONS

Car wash effluents were treated by settling, filtration, and membrane filtration processes. Total solids decreased from 1,054 ± 21 to 609 ± 14 mg L\(^{-1}\) at the end of 1 hour of settling. Although the settling process provided 6% COD removal, further removal of COD was accomplished by membrane filtration. Removal rates of COD were between 73% and 80%, depending on UF membrane. Conductivity varied between 14% and 28% with the UF membranes. With the NF membrane, COD and conductivity removals were 98% and 47%, respectively. Results show that car wash effluents can be treated with settling, coarse filtration, and finally UF (1,000 Da) or NF (300 Da) membranes. Retentate can be treated with FeCl\(_3\) and/or activated carbon filtration.

### REFERENCES


First received 23 July 2017; accepted in revised form 9 September 2017. Available online 26 October 2017