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Application of flocculation–flotation followed by ozonation in vehicle wash wastewater treatment/disinfection and water reclamation

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ABSTRACT

This article provides the results of flocculation–flotation followed by sand filtration and ozonation (FFO), applied for the treatment of car wash wastewater in a water reclamation system in Brazil. The assessment of the efficiency of the process in enhancing reclaimed water quality, especially aesthetic, microbiological, and chemical issues is reported. The FFO process provided disinfected (*Escherichia coli* $< 1.8\,\mathrm{CFU}\,100\,\mathrm{mL}^{-1}$) and clarified water (10 NTU), minor foaming (residual surfactants = $1.30\,\mathrm{mg}\,\mathrm{L}^{-1}$MBAS), and no odor-related problems from reclaimed water. Comparative studies were carried out at bench scale; ozone (AOP) and chlorine were applied separately as oxidation procedures and a mass balance was assessed as a function of the number of water cycles. Results revealed that besides higher oxidation of organics and water clarification, both conductivity and dissolved solids concentrations for the ozone-treated water were lower than those obtained with the chlorinated water. A cost–benefit analysis performed for two different Brazilian scenarios showed that the payback period of the FFO equipment might be as short as one year, depending on water prices and daily wash demand. Thus, it appears that the FFO process has a great potential to be gradually introduced in sustainable vehicle wash water reclamation systems both in Brazil and worldwide.

Keywords: Water reuse; Flotation; Ozonation; Car wash; Disinfection; Oxidative process; Chlorination

1. Introduction

Some European countries began adopting policies that were aimed at restricting the consumption of drinking water (60–70 L per car) and/or imposing water recycling ratio (70–80%) in commercial vehicle washes [1]. Hence, the development and application of new vehicle wash wastewater treatment processes, which complies with the low technology/low cost/controlled risk approach [2], have become a challenge in scientific research and sanitation engineering projects. Recent findings suggest that the implementation of water reclamation systems in vehicle wash units can enhance the urban water efficiency, by reducing water demand by approximately 0.7%. More so, this fact may decrease pollution load at receiving bodies and/or municipal sewage treatment plants by reducing at least

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2.5% of the surfactant load [3]. In developing countries, where there are no specific laws imposing a rational use of water in the car wash industry, several vehicle wash units have implemented recycling systems, stimulated by a cost decrement in drinking water consumption from public supply.

A number of technologies, mostly physicochemical processes, have been employed for the treatment and reuse of water in the vehicle wash industry [3]. Zaneti et al. [4] validated a so-called Flocculation/Column Flotation (FCF) technique [5] in a car wash water recycling system at full scale, where approximately 70% of odorless and clarified water was attained in a period of 22 weeks. However, the authors reported some limiting aspects of such a system, namely: (i) Water contamination by micro-organisms (Total Coliforms and *Escherichia coli*) and microbiological risk associated to reclaimed water; (ii) Organic concentration and BOD buildup (BOD/COD ratio of about 0.4), this increasing the disinfectant demand and promoting re-growth of micro-organisms; and (iii) Foaming (surfactants) and odor generation in the washing pit.

With regard to the microbiological risk, Zaneti et al. [3] proposed a limit (determined by QMRA) of 200 CFU 100 mL^{-1} of *E. coli* in reclaimed water, and this target was obtained by a final chlorination stage (15 mg Cl_2 L^{-1}) with sodium hypochlorite. However, this dosage may significantly increase with the organic load (COD) of the reclaimed water [6], which is higher in water recycling systems of heavy vehicles [7,8]. Another disadvantage of chlorine application is the dissolved solids (salts) buildup concentration as a function of recycling ratio and the number of water cycles, which may end up with corrosive action of the reclaimed water. Surprisingly, up to date, there are no articles reporting the application of alternative disinfectants in these water reclamation systems.

Due to safety reasons and a high oxidation efficiency process with ozone [9–13], the present study investigates the application of flocculation–flotation, followed by sand filtration and the ozonation process (FFO) for water reclamation in a car wash wastewater recycling system.

2. Materials and methods

The FFO process was studied in a hand wash carwash installed in Porto Alegre-South Brazil, with 40–50 cars per day capacity (Fig. 1). Reclaimed water (~70% of total water usage) was attained in the first rinse of vehicles, and fresh water (~30% of total water usage) was used for the final rinse, before the cars were dried. In the wash procedure, neutral and alkali detergents were employed; these products contain dodecyl benzene sulfonate $–CH_3(CH_2)11C_6H_4SO_3Na–$ as the main surface active agent.

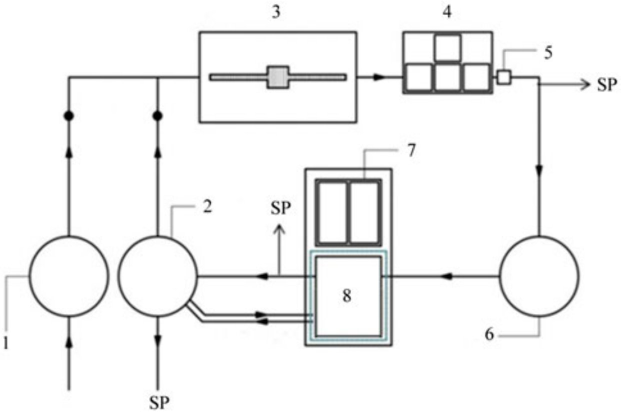

Fig. 1. Car wash wastewater reclamation system scheme: (1) Water from public supply tank; (2) Ozonation tank; (3) Washing pit; (4) Oil–water separator; (5) Pump; (6) Wastewater tank; (7) Sludge drying bed; (8) FFO unit; SP: Sampling points.

2.1. Full-scale studies: FFO process application

Main equipment design and operating data of the FFO process are summarized in Table 1. In the flocculation stage, a derivative of tannin (Tanfloc SL) was used as coagulant–flocculant (1,200 mg L^{-1}) and sodium hydroxide was dosed for pH adjustment (pH 7). This pH was chosen to perform ozonation, because both the reactions of the mechanisms were expected to occur simultaneously (molecular ozone and OH radical).

After flotation and sand filtration stages, the effluent was pumped to a sheltered ozonation tank (Fig. 2—10 m^3) and the sludge was collected in a sand drying bed. One corona effect ozone generator was utilized (4 g O_3 h^{-1}) with atmospheric dried air feed, and ozone gas was injected into the effluent through a venturi placed after the discharge extension of a recycling pump. The water was continuously ozonized and recirculated in this tank over 22 h per day during 5 weeks. Reclaimed water from this tank was employed in the car wash pit, and the water level was monitored with an electric level sensor. Therefore, the FFO treatment process was turned on automatically when the water level of the tank was lowered.

The characteristics of the wastewater and reclaimed water of the reclamation system were monitored along 5 weeks. Samples were collected once a week (total of five sampling days) at the sampling points shown in Fig. 1, and the following quality parameters were analyzed: pH, total solids (TS), total

Table 1
FFO unit employed (1 $m^3.h^{-1}$ flow rate): operating parameters and constructive characteristics

Bubbles generation unit (CMP)	
Saturation pressure, atm	2–4
Bubbles diameter range[a], μm	5–250
Bubbles Sauter diameter (D_{32})[a], μm	75
Needle valve, inch	0.5
Flocculation unit (FGR)	
Pipe diameter, m	0.0352
Total length, m	21.6
Retention time (tr), s	75.7
Head loss, atmospheres	2.6
Velocity gradient (G), s^{-1}	573
Tanfloc SL, mg L^{-1}	300–1,200
Dosing pump	Diaphragm
Aerated flocs characteristics[b]	
Average diameter, μm	860–1,600
Theoretic average strength (σ), N m^{-2}	49–82
Fractal dimension (D_2)	1.64
Rise rate, m h^{-1}	45–165
Flotation unit (column)	
Diameter, m	0.4
Height, m	1.32
Retention time (t), s	882
Hydraulic load, m h^{-1}	5,4
Ozonation unit	
Ozone generator (crown effect)/model	Aqua OZ—Brazil
Air flow rate	10 L min^{-1}
Feed air	Atmospheric dried air
Ozone gas production ratio	4 g h^{-1}

[a] Measured according to the technique reported by [14].
[b] Measured as in [5].

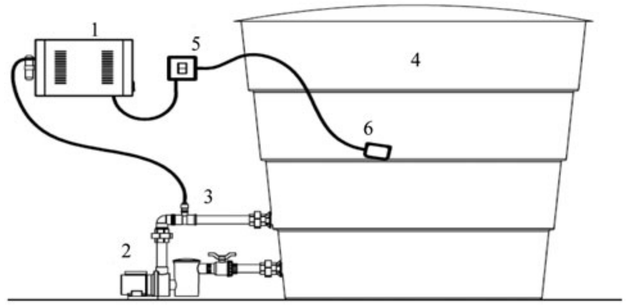

Fig. 2. Ozonation system: (1) Ozone generators; (2) Recirculating pump; (3) Venturi tube; (4) Ozonation tank; (5) Electrical controllers; (6) Level controller.

suspended solids (TSS), total dissolved solids (TDS), turbidity, conductivity, surfactants, BOD, COD, sulfide, *E. coli*, and total coliforms.

pH, turbidity, and conductivity were measured by a pHmeter (EcoSense pH100, YSI), a nephelometric turbidimeter (model AP 2000, Policontrol®) and a portable conductivity meter (model C 702, Analion®), respectively. All microbiological and physicochemical parameters were measured according to APHA [15]. *E. coli* and total coliforms were determined by the methods "Escherichia coli Procedure" (9221 F) and "Enzyme Substrate Test" (9223 B), respectively. COD was measured by the "Open Reflux Method" (5220 B) and BOD by the "5-Day BOD Test" method (5210 B). For the measurement of sulfide, the "Methylene Blue Method" (4500-S2-B) was employed. Surfactants were determined as MBAS (anionic surfactants—5540 C). TS and TSS were measured according to the methods 2540 B and 2540 D, respectively. TDS were estimated by the difference between TS and TSS.

2.2. Bench-scale studies: comparison between ozonation and chlorination as polishing stages

A comparative study was conducted at bench scale, utilizing either ozone or chlorine (sodium hypochlorite) as an oxidizing agent, for samples of treated water collected after the flotation stage of the FFO process (see sampling point in Fig. 1).

Ozonation experiments were carried out in the laboratory with an ozone generator ($4\,\mathrm{g\,h^{-1}}$ capacity), with 1.5 L samples in a glass flask and an ozone injection through a porous diffuser. Aliquots (100 mL) were collected at intervals of 10, 30, 60, and 120 min for an analysis of the parameters of interest. The ozone generators were calibrated through ozone bubbling in an aqueous solution containing $20\,\mathrm{g\,L^{-1}}$of potassium iodide. The iodine formed was quantified by titration with sodium thiosulfate ($Na_2S_2O_3$), and gas ozone concentration was measured by the iodometric method [15].

The same sampling procedure was carried out on a different sampling day for chlorination studies, and all water samples and solutions were allowed to equilibrate to room temperature (20˚C) before their use in the experiments. Chlorine solutions were prepared in deionized water with sodium hypochlorite on the day of use. The first chlorination method applied was the breakpoint chlorination [6], which consists of adding sufficient chlorine to react with all of the organic compounds; thus, chlorine is added beyond this concentration to end up with some free chlorine in solution.

Then, experiments were conducted to inactivate *E. coli*, using a sodium hypochlorite solution that was prepared at different concentrations for a fixed contact time of 2 h. This solution was titrated, shortly before use, according to [15]. At the end of the contact time, a calculated amount of sodium thiosulfate solution was added to 0.025 N for complete dechlorination.

All ozonated and chlorinated samples were analyzed by the parameters described in Section 2.1. The chemical risk (corrosion and scaling) of the treated chlorinated and/or ozonated water was evaluated by employing a mass balance model (Eqs. (1)–3). The parameter utilized was TDS, as its buildup concentration, along the water cycles of a reclamation system, is a matter of concern [6]. The bench-scale results were used in the mass balance equations, and the following hypotheses were considered:

(1) The mass value added during the car wash and wastewater treatment process is constant (Eq. (2)), in each water cycle, and there is no water loss (Eq. (3));

(2) One water cycle is considered to occur when the total water volume used in the washes reaches the storage capacity of the system (10 m in the full-scale study);

(3) The recycling ratio is fixed at 0.7 [16].

$$C_{\mathrm{R+I}}\frac{\mathrm{CS}+(F\cdot V_{\mathrm{Li}}\cdot C_{\mathrm{Ri}}+(1-F)\cdot V_{\mathrm{Li}}\cdot C_{\mathrm{N}}}{V_{\mathrm{Li}}} \tag{1}$$

$$\mathrm{CS}=V_{\mathrm{Li}}\cdot(C_1-C_{\mathrm{N}}) \tag{2}$$

$$V_{\mathrm{Ei}}=V_{\mathrm{Li}}=F\cdot V_{\mathrm{Ri}}+(1-F)\cdot V_{\mathrm{Ni}} \tag{3}$$

where C_{Ri} and $C_{\mathrm{Ri+1}}$ = the TDS concentration in reclaimed water during cycle Ri and Ri + 1, $i = 1,\ldots, n$; CS = Mass of the quality parameter added during the car washing/water treatment processes; F = Recycling ratio (0.7); V_{Li} = Total volume of water used in the car wash; V_{Ei} = Wastewater volume; V_{Ni} (L) = Fresh water volume; C_{N} = TDS concentration in fresh water.

2.3. Cost–benefit analysis

The cost estimation and assessment for the present technique (FFO) and recently, flocculation–flotation–chlorination (FFC—reported by Zaneti et al. [4]) equipment needed for the present vehicle wash reclamation system are based on a market survey. The updated market value for the devices ($1{,}000\,\mathrm{L\,h^{-1}}$ capacities) in Brazil is US$ 7,929.00 (FFC) and US$ 9,470.00 (FFO).

The cost–benefit analysis of the processes presented in the present work for car wash water reclamation in Brazil was conducted based on the cost of FFO and FFC equipment plus operating and maintenance costs (here: chemicals, makeup water, energy consumption, and sludge disposal). Manpower was not considered in the calculation due to the simplicity of the operation of the both process (operated semi-automatically by the car wash team). The amortization (payback time) was calculated as the ratio of the cost of FFO and FFC equipment to the economy (monthly savings afforded by implementing the system)—Eqs. (4) and (5).

$$a=c/e \tag{4}$$

$$e=x-(y+z) \tag{5}$$

where a = amortization (months); c = equipment cost (US$); e = economy (US$ month^{-1}); x = monthly cost of water with no water recycling (US$ month^{-1}); y = monthly cost of the process with 70% reclamation rate

Table 2
Water consumption and costs in Brazil

Number of daily washes	Water consumption (m^3 $month^{-1}$)[b]	Water costs (US$ m^{-3})[a]	
		São Paulo	Porto Alegre
Cars—15	46.8	11.09	2.86
Cars—45	140.4	11.56	4.00
Cars—71	221.52	11.56	4.66

[a] Sewage collection and treatment rate are included.
[b] Considering 26 d of operation per month and 130 L per car.

Table 3
Processes of maintenance and operating costs

Item	FFO (US$ m^{-3})	FFC (US$ m^{-3})
Chemicals	0.34	0.67
Sludge disposal	0.04	0.04
Energetic consumption	0.73	0.14
Total	1.12	0.85

(US$ $month^{-1}$); z = monthly cost of makeup (fresh) water—70% reclamation rate (US$ $month^{-1}$).

Fresh water prices vary among the different cities in Brazil; therefore, the amortization was calculated for two different state capitals—São Paulo and Porto Alegre—considering 15–70 cars washed per day.

The water prices in the cities of São Paulo and Porto Alegre are shown in Table 2, and the FFO maintenance and operation costs are depicted in Table 3.

3. Results and discussion

3.1. Wastewater treatment process: full-scale studies

Table 4 shows the characteristics of the car wash wastewater, collected after the oil–water separator and compared with local standards. Main results show that total coliforms and *E. coli* counting are fairly high, and, therefore, water reclamation in this system should be preceded by a disinfection stage, in order to control and/or reduce the microbiological risk of the reclaimed water to a safe level.

The average concentration of surfactants was within the range of values already reported in the literature for these wastewaters [1,4]. The results showed an average concentration of 14.6 mg MBAS L^{-1}, above the local emission standard (2 mg MBAS L^{-1}), which indicates that the oil–water separator is not enough to reduce the load of these contaminants, overloading municipal sewage treatment plants.

The oxygen demand values of the wastewater were also above the local emission limit (COD = 683 mg L^{-1}; BOD = 397 mg L^{-1}), and these concentrations are at least thrice higher than those reported by [4,17] but lower than [8] results. It seems that detergents and wax are the most prominent factors that are responsible for oxygen consumption in this car wash wastewater, and, therefore, different product suppliers may result in different organic concentrations in those wastewaters.

Table 4
Characterization of the car wash wastewater after the oil–water separator

Parameters	Min–max	Media (± 1/2 standard deviation)	Local emission standards
Turbidity, NTU	194–254	229 (21.9)	–
pH	6–6.6	6.4 (0.2)	6–9
TSS, mg L^{-1}	85–279	182 (63)	180
TDS, mg L^{-1}	546–797	700 (88.5)	–
E. coli, CFU.100 mL^{-1}	4.5E + 01–2.4E + 03	1.2E + 03	10^5
Total coliform, CFU.100 mL^{-1}	1.6E + 06–1.3E + 07	5.3E + 06	–
BOD, mg O_2 L^{-1}	203–496	397 (108.9)	180
COD, mg O_2 L^{-1}	249–873	683 (224.2)	400
Sulfide, mg S^{2-} L^{-1}	3.9–5.1	4.8 (0.5)	0.2
Conductivity, μS cm^{-1}	730–1,530	933 (303.8)	–
Surfactants, mg MBAS L^{-1}	11.26–22.3	14.6 (3.9)	2

Table 5
FFO process: characterization of FF- and FFO-treated water at full scale (five samplings)

	FF-treated water[a]		FFO-treated (reclaimed) water		
Parameters	Min–max	Mean values (±1/2 standard deviation)	Min–max	Mean values (±1/2 standard deviation)	Local emission standards
Turbidity, NTU	13–28	21 (5.7)	4–18	10 (5.6)	–
pH	6.7–7	6.7 (0.2)	6.9–8.2	7.3 (0.5)	6–9
TSS, mg L^{-1}	2–50	27 (17)	0–49	22 (19)	180
TDS, mg L^{-1}	667–937	828 (91)	653–848	686 (92.5)	–
E.coli CFU.100 mL^{-1}	1.8E + 00–4.5E + 01	1.7E + 01	1.8E + 00–1.8E + 00	1.8E + 00	10^5
Total coliform, CFU.100 L^{-1}	2.4E + 04–2.4E + 06	6.3E + 05	1.3E + 04–8.4E + 04	3.6E + 04	–
BOD, mg O_2 L^{-1}	106.3–415.5	290 (120)	2.0–122.2	60.5 (43.2)	180
COD, mg O_2 L^{-1}	129–536	415 (155)	12–167	96 (50.2)	400
Sulfide, mg/L S^{2-}	1.0–2.2	1.5 (0.4)	0.1–1.0	0.6 (0.3)	0.2
Conductivity, μS cm^{-1}	879–1,332	1,149 (153)	1,045–1,125	1,068 (29.6)	–
Surfactants, mg MBAS L^{-1}	2.46–4.93	4.1 (0.9)	0.03–4.3	1.3 (1.6)	2

[a] Samples collected after flotation stage.

The characteristics of wastewater treated by the FFO process are shown in Table 5. Most of the total suspended solids were removed at the flocculation–flotation stage, as the turbidity dropped from 229 NTU in the wastewater to 21 NTU in the FF-treated water. This corresponds to the expectations, as it is the main role of this solid–liquid separation step. Moreover, an enhanced water clarification was observed in the FFO-treated water (10 NTU). In the present system, many colloidal nanocomposites and macromolecular compounds should be present as a result of residual flocculant-based tannin (polyphenol chemicals) and surfactants. Gottschalk et al. [10] reported that a kind of microflocculation caused by particle-induced destabilization of the ozone may occur as a part of the disintegration of biosolids. However, these mechanisms are specific to the system and appear to be not fully understood, and then, more basic research is needed.

With regard to microbiological quality, *E. coli* counting in the FFO-treated water always remained under the detection limit (1.8 CFU.100 mL^{-1}), and, therefore, this concentration complies with the microbiological risk of 200 CFU.100 mL^{-1}, proposed by Zaneti et al. [3] for safe water reclamation in car washes. Since the efficacy of ozone disinfection is closely linked to the presence of suspended particles, the flotation–flocculation stage of the FFO process appears to match well with the ozonation stage, as it removes particles efficiently and prevents them by shielding microorganisms from inactivation [18]. Furthermore, the average concentration of sulfides in the reclaimed water was 0.6 mg L^{-1} S^{2-}. Then, odor generation, which is related, among other factors, to the microbial process and the release of hydrogen sulfide to the atmosphere [19], was not observed in the car wash pit.

Regarding organics, it was observed that the average concentrations of COD and BOD decreased after FF, reaching values in the order of 290 mg O_2 L^{-1} (BOD) and 415 mg O_2 L^{-1} (COD). The ozonation stage (FFO-treated water) also decreases the concentrations of COD and BOD to 96 and 60 mg L^{-1} O_2, respectively. According to Gottschalk et al. [10], the oxidation of organic compounds by ozonation can occur by molecular ozone (direct reaction) or hydroxyl radical (indirect reaction), although a combination of mechanisms may occur. In acidic or neutral pH, ozone reacts with the dissolved organic matter. Under alkaline pH, ozone decomposes, releasing hydroxyl radicals (OH·), which react rapidly with most organic compounds. The hydroxyl radicals are known to be more reactive and less selective in their reactions when compared with molecular ozone. The oxidation of the residual dissolved organic matter occurs by the combination of the two mechanisms, whereas medium pH ranges between pH 7 and 8.

The surfactants that were not satisfactorily reduced by the FF stage (residual 4.1 mg MBAS L^{-1}) were drastically decreased by the ozone oxidation to about 1.3 mg MBAS L^{-1}. Accordingly, no foaming was visually observed when the reclaimed water was utilized in the car wash pit.

Table 6
Bench-scale studies of ozonation of car wash effluent after FF + sand filter. Effect of ozonation time on treated water quality

Parameter	Blank	10 min	30 min	60 min	120 min
pH	6.9	6.3	6.1	6.2	6.1
Turbidity, NTU	18	3	2	1	1
E. coli, CFU 100 mL^{-1}	4.7E + 02	1.8E + 00	1.8E + 00	1.8E + 00	1.8E + 00
BOD_5, mg O_2 L^{-1}	130	99	69	59	69
COD, mg O_2 L^{-1}	292	184	139	144	129
Conductivity, μs cm^{-1}	1,024	853	821	859	1,015
Sulfides, mg L^{-1} S^{2-}	1	0.6	0.7	0.7	0.6
Surfactants, mg MBAS L^{-1}	4.4	1.6	0.5	0.2	0.2

3.2. Bench-scale studies: comparison between ozonation and chlorination

3.2.1. Ozonation studies

The results of ozonation at bench scale are shown in Table 6. Total *E. coli* destruction was achieved with 10 min of ozonation, and the organic matter was also oxidized (BOD = 47%; COD = 52%), decelerating the re-growth of micro-organisms. Ozone acts as a disinfectant, mainly on the cell membrane, reacting with glycoproteins or glycolipids. More importantly, ozone degrades the substances present in the cytoplasm and nucleus, namely purines and pyrimidines of DNA, causing their cell death. Thus, first, ozone diffuses through the surface of micro-organisms and then penetrates through the membrane and into the cytoplasm [20,21]. In addition, hydrogen sulfide concentration decreased by 40% (0.62 mg L^{-1} S^{2-}). Other sulfur-bearing substances such as mercaptans (methyl, diethyl) may also be oxidized with ozone. Thus, by removing these compounds plus the coliforms, ozonation is able to control these main sources for malodor generation in the wastewater [19].

Moreover, an aesthetic gain was observed with a longer ozonation time (60 min), when the treated water attained the highest level of clarification, with a 1.0 NTU low turbidity without increasing the conductivity of the water. In the present system, many colloidal nanocomposites and macromolecular compounds should be present as a result of residual flocculant-based tannin (polyphenol chemicals) and surfactants. Gottschalk et al. [10] reported that a kind of microflocculation caused by particle-induced destabilization of ozone might take place as a part of disintegration of the biosolids. However, these mechanisms are system specific and appear to be not fully understood, and more basic research appears to be required.

Finally, the surfactant concentrations were drastically reduced from 4.4 to 0.2 mg L^{-1} MBAS at a

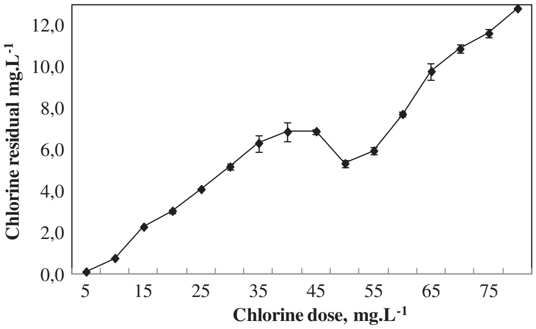

Fig. 3. Curve of breakpoint chlorination of the effluent post FF.

Table 7
Chlorination of treated water after FCF bench scale. Effect of dose of chlorine

	Blank		10 mg L^{-1} Cl_2		30 mg L^{-1} Cl_2		60 mg L^{-1} Cl_2	
Parameters	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
E. coli, CFU.100 mL^{-1}	2.2 × 10	3 × 10	1.1 × 10	1.5 × 10	<1.8	<1.8	<1.8	<1.8
Total coliforms, CFU.100 mL^{-1}	5.4×10^6	3.5×10^6	2.4×10^6	2.4×10^6	<1.8	<1.8	<1.8	<1.8
COD, mg L^{-1} O_2	319	299	329	311	321	307	309	329
Surfactants, mg L^{-1} MBAS	9.0	11.1	8.9	9.1	3.6	3.2	2.9	3.0
Turbidity, NTU	5.4	5.4	5.5	5.5	5.4	5.3	5.4	5.4
Conductivity, μS cm^{-1}	978	1,002	1,108	1,116	1,261	1,287	1,390	1,422

ozonation time of 60 in. Zaneti et al. [4] reported that the surfactants are not efficiently removed in oil–water separators, and this does not meet local emission standards (2 mg L^{-1} MBAS). Therefore, ozonation can play an important role here.

3.2.2. Chlorination studies

The curve of breakpoint chlorination (Fig. 3) shows that the concentration required for effective disinfection was higher than 50 mg $L^{-1}Cl_2$ (breakpoint). Dosages below this value may result in an oxidation of the organic matter, with the formation of chloramines, among other reactions [6].

Table 7 shows the results of coliform inactivation at different dosages of chlorine, including a point just above the breakpoint (10, 30, and 60 mg L^{-1} Cl_2). The results showed that a concentration of 30 mg L^{-1} Cl_2 in this case was sufficient for the complete destruction of total coliforms and *E. coli*. The specific mechanism of inactivation of micro-organisms by chlorination has not yet been fully elucidated in the literature, but studies have shown that the permeability of cell membranes of bacteria is fairly changed in the presence of chlorine, causing the release of cytoplasmic material [12,18,22,23].

The results show that despite the great potential of chlorine as a disinfectant and the oxidation of surfactants, reducing the latter by 73% (3 mg L^{-1} MBAS) with a chlorine concentration of 60 mg L^{-1} Cl_2, this treatment was not effective in clarifying the water. Besides, an increase in water conductivity was observed depending on the concentration of chlorine reaching 1,422 μS cm^{-1} at a concentration slightly above the breakpoint (60 mg L^{-1}).

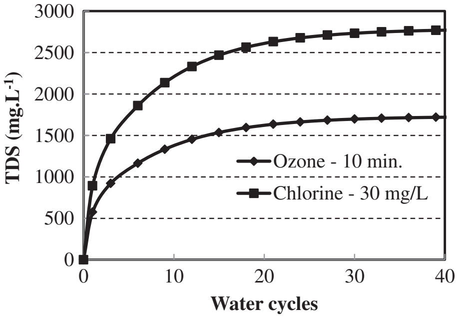

Fig. 4. TDS estimated by the mass balance for ozone and chlorine application (chemical risk studies). Conditions: TDS concentration obtained at bench scale for ozone-treated water and chlorinated water, respectively: 575 and 892 mg $L^{-1.}$

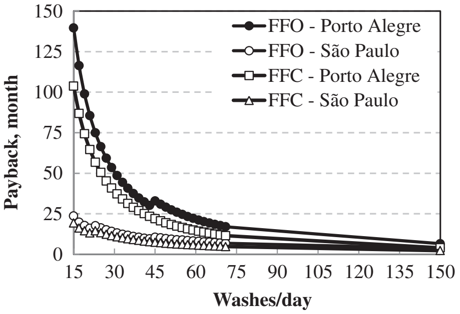

Fig. 5. Amortization of FFC and FFO equipment as a function of the oxidizing agent and daily washes.

3.2.3. Mass balance: TDS

Insofar as the chemical risks, Fig. 4 presents the concentration of TDS as a function of the oxidizing agent and the number of water cycles. When ozone was utilized, the maximum TDS concentration observed was approximately 1,700 mg L^{-1}, which was lower than the stabilized concentration of TDS when chlorine was employed (about 2,800 mg L^{-1}). Thus, ozone-treated water appears to deliver a lower potential to accelerate the corrosive process in vehicles when compared with chlorine.

3.3. Economic evaluation (approximate values)

Fig. 5 shows that the payback of the FFC and FFO equipment in Brazil is strongly dependent on the price of drinking water and water demand (number of washes per day). Thus, the amortization period decreases with an increase in the price of water and demand. As the water prices reach high values in Brazil (approximately 11.56 U$S per m in Sao Paulo), the implementation of car wash wastewater reclamation seems promising.

Regarding the two different processes assessed, results in Fig. 5 show that the payback of FFO is longer than the payback of FFC. This higher cost is due to the higher energy consumption of the ozonation process (recycling pump and ozone generator). On the other hand, when considering a car wash reclamation system in São Paulo, due to higher water prices, in all evaluated scenarios, the equipment amortization is achieved in a shorter period. Thus, water prices seem to play a more important role for equipment amortization in the assessed systems.

4. Conclusions

The results obtained suggest that the FFO process has a great potential for car wash wastewater reclamation, namely aesthetic, microbiological, and chemical-related problems. Main findings showed that the reclaimed water provided by the FFO process was fairly clarified (10 NTU), odorless, disinfected (*E. coli* < 1.8 CFU 100 mL^{-1}), and without foaming (1.3 mg L^{-1} MBAS). Bench-scale comparative studies between ozone and chlorine as oxidizing/disinfectant agents, along the process, revealed that ozone provided a higher level of clarification and organic oxidation without increasing water conductivity and salt concentration. Calculations through a mass balance estimation suggested that stabilized conductivity and dissolved solid concentrations of ozone-treated water are lower than with chlorinated water. The payback period of FFO equipment is mainly dependent on water prices and wash demand and may be shorter than one year. The high process efficiency and approximate operating costs appear to conclude that car wash wastewater could be treated and safely reclaimed at a sustainable cost using this novel process.

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References

[1] K. Boussu, C. Kindts, C. Vandecasteele, B. Van der Bruggen, Applicability of nanofiltration in the carwash industry, Sep. Purif. Technol. 54 (2007) 139–146.
[2] J. Anderson, A. Adin, J. Crook, C. Davis, R. Hultquist, C. Jimenez, Climbing the ladder: A step by step approach to international guidelines for water recycling, Water Sci. Technol. 43 (2001) 1–8.
[3] R. Zaneti, R. Etchepare, J. Rubio, More environmentally friendly vehicle washes: water reclamation, J. Clean. Prod. 37 (2012) 115–124.
[4] R. Zaneti, R. Etchepare, J. Rubio, Car wash wastewater reclamation: Full-scale application and upcoming features, Resour. Conserv. Recy. 55 (2011) 953–959.
[5] J. Rubio, R.N. Zaneti, Treatment of washrack wastewater with water recycling by advanced flocculation–column flotation, Desal. Water Treat. 8 (2009) 146–153.
[6] T. Asano, F.L. Burton, H.L. Leverenz, R. Tsuchihashi, G. Tchobanoglous, Water Reuse: Issues Technologies, and Applications, McGraw-Hill, New York, NY, 2006.
[7] R. Etchepare, R.N. Zaneti, J. Rubio, Reciclagem de água em lavagem de carros (Water recycling in car washes), Saneamento Ambiental 154 (2011) 24–30 (in portuguese).
[8] N. Páxeus, Vehicle washing as a source of organic pollutants in municipal wastewater, Water Sci. Technol. 33 (1996) 1–8.
[9] N. Facile, B. Barbeau, M. Prevost, B. Koudjonou, Evaluating bacterial aerobic spores as a surrogate for Giardia and Cryptosporidium inactivation by ozone, Water Res. 34 (2000) 3238–3246.
[10] C. Gottschalk, J.A. Libra, A. Saupe, Ozonation of Water and Waste Water—A Practical Guide to Understanding Ozone and Its Applications, Wiley VCH, Weinheim, 2010.
[11] B. Langlais, D.A. Reckhow, D.R. Brink, Ozone in Water Treatment: Application and Engineering, CRC Press, Chelsea, 1991.
[12] G.C. White, White's Handbook of Chlorination and Alternative Disinfectants, John Wiley, Hoboken, NJ, 1999.
[13] P. Xu, M.L. Janex, P. Savoye, A. Cockx, V. Lazarova, Wastewater disinfection by ozone: Main parameters for process design, Water Res. 36 (2002) 1043–1055.
[14] R.T. Rodrigues, J. Rubio, New basis for measuring the size distribution of bubbles, Miner. Eng. 16 (2003) 757–765.
[15] APHA—American Public and Health Association, Standard Methods for the Examination of Water and Wastewater, American Public Health Association/ American Water Works Association/Water Environment Federation, Washington, DC, 2005.
[16] R. Zaneti, R. Etchepare, J. Rubio, Car wash wastewater treatment and water reuse—A case study, Water Sci. Technol. 67 (2013) 82–88.
[17] T. Hamada, Y. Miyazaki, Reuse of carwash water with a cellulose acetate ultrafiltration membrane aided by flocculation and activated carbon treatments, Desalination 169 (2004) 257–267.
[18] G.P. Winward, L.M. Avery, T. Stephenson, B. Jefferson, Chlorine disinfection of grey water for reuse: Effect of organics and particles, Water Res. 42 (2008) 483–491.
[19] T. Hvitved-Jacobsen, J. Vollertsen, N. Tanaka, An integrated aerobic/anaerobic approach for prediction of sulfide formation in sewers, Water Sci. Technol. 41 (2000) 107–115.
[20] V. Camel, A. Bermond, The use of ozone and associated oxidation processes in drinking water treatment, Water Res. 32 (1998) 3208–3222.
[21] B. Mariñas, N. Hunt, Inactivation of Escherichia coli with ozone: Chemical and inactivation kinetics, Water Res. 33 (1999) 2633–2641.
[22] C. Shang, E.R. Blatchley, Chlorination of pure bacterial cultures in aqueous solution, Water Res. 35 (2001) 244–254.
[23] R. Virto, P. Manas, I. Alvarez, S. Condon, J. Raso, Membrane damage and microbial inactivation by chlorine in the absence and presence of a chlorine demanding substrate, Appl. Environ. Microb. 71 (2005) 5022–5028.