ISSN = 1980-993X – doi:10.4136/1980-993X
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RECEIVED 06 Jul 2012 16 Dec 2012 ACCEPTED

UV/H_2O_2 process performance improvement by ultrafiltration and physicochemical clarification systems for industrial effluent pretreatment

(http://dx.doi.org/10.4136/ambi-agua.926)

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ABSTRACT

The present study evaluated the removal of TOC from an effluent with high organic load resulted from the treatment of oil-water emulsion by thermal process. Hollow Fiber Ultrafiltration membrane (HF-UF) and physicochemical clarification process were used as pretreatment options to assess the influence of feed effluent quality on the UV/H_2O_2 oxidation process. Results for TOC removals showed HF-UF and physicochemical clarification processes can significantly improve the efficiency of UV/H_2O_2 oxidation process, when compared with the direct effluent oxidation. Reaction time for obtaining a TOC removal higher than 90% was reduced to approximately half of the time needed when no pretreatment was applied. Considering both pretreatment processes it was not possible to notice any significant difference on the UV/H_2O_2 oxidation process performance. However, the complexity of physicochemical process due to the use of three different chemicals and sludge production made the HF-UF process the best pretreatment alternative, without increasing the Total Dissolved Solids of the effluent, a very important issue when water reuse is considered.

Keywords: UV/H_2O_2, ultrafiltration, physicochemical process.

Melhora do desempenho do processo UV/H_2O_2 usando sistemas de ultrafiltração e de clarificação físico-química como pré-tratamento de efluente industrial

RESUMO

O presente trabalho teve por objetivo avaliar a remoção de COT de um efluente com elevada concentração de matéria orgânica proveniente do tratamento de emulsão (água/óleo) por processo térmico. Um processo de separação por membranas de fibra-oca e outro de clarificação físico-químico foram usados como opções de pré-tratamento para avaliar a influência da qualidade do efluente sobre o processo de oxidação UV/H_2O_2. Os resultados de remoção de COT demonstraram que tanto o processo de membranas quanto o físico-químico podem melhorar significativamente a eficiência do processo de oxidação UV/H_2O_2. O tempo de reação necessário para uma remoção de 90% de COT foi reduzido pela metade quando comprado com a oxidação direta do efluente. Considerando ambos os processos de pré-tratamento não foi possível observar nenhuma diferença significativa sobre o desempenho do processo de oxidação UV/H_2O_2. Entretanto, a complexidade do processo físico-químico devido ao uso de três diferentes compostos e a produção de lodo faz do sistema de membranas a melhor alternativa de pré-tratamento.

Palavras-chave: UV/H_2O_2; ultrafiltração; processo físico-químico.

1. INTRODUCTION

The industrial development is one of main causes for environmental degradation of urbanized areas in Brazil, mainly of water bodies. Over the past two decades, environmental regulatory requirements have become more stringent because of increased awareness of the human health and ecological risks associated with environmental contaminants.

Metal working fluids are used in many small companies for metal forming and machining process, like cutting, grinding, and milling, however considering the complexity of the effluents produced, most of those companies has no capacity to treat it, then they hire a specialized company to do this job. Companies that provide such kind of service collect effluents from many sources and them treat it by specific ways, charging their service according the volume processed. One of the technologies used for treating such king of effluent is the thermal separation process (Gutiérrez et al., 2011; 2010; Fakhru'l-Razi et al., 2009). The use of thermal separation processes, depending on the inflow effluent characteristics can result in a condensate with a high organic load, because of stripping of volatile and semi-volatile compounds, besides a small fraction of non-volatile substances (Mao et al., 2010), which not allows releasing it to the environment or reusing it. Therefore, a complementary treatment step is necessary in order to cost-effectively meet environmental standards.

Among these technologies the Advanced Photochemical Oxidation Processes (APOP) are very promising, because it could be considered a green technology, involving the generation and use of powerful but relatively nonselective transient oxidizing species, primarily the hydroxyl radical (●OH) for contaminant destruction. The ●OH can be generated by both photochemical and non-photochemical processes to oxidize many contaminants (USEPA, 1998). Among the different available AOP, the one which uses UV light and hydrogen peroxide (UV/H_2O_2) was the first one to be used for wastewater treatment (Litter, 2005). This process proceeds in two main steps: hydroxyl radicals production by direct H_2O_2 photolysis and oxidation of organic compounds by these radicals (Braun e Oliveros, 1997). In some cases the photon energy is enough to break chemical bounds of organic molecules, resulting on its degradation. The UV/H_2O_2 process has been shown very efficient on the degradation of various organic pollutants. Many successful application of UV/H_2O_2 could be found in the literature, for instance, the works of Beltrán et al. (1997), for phenol oxidation, Cater et al. (2000), for gasoline contaminated groundwater treatment, Arslan et al. (2000), for the treatment of dyes contaminated effluents, Einschlag et al. (2002), for oxidation of nitro-aromatic compounds, and more recently the work of Gao et al. (2009), for the treatment of ametryn contaminated waters. The advantage of UV/H_2O_2 processes is that the H_2O_2 is the only chemical that needs to be added, and is easily converted to oxygen and water.

Even with the spread use of UV/H_2O_2 process, most of them are applied for degradation of specific contaminants, present in relatively clean matrices, which is not the case for industrial wastewaters. In a recent review developed by Diya'uddeen et al. (2011), it is pointed out that wastewater composition could reduce the UV activated efficiency and even make its application unfeasible. The presence of discoloring substances or suspended solids can reduce the process efficiency by adsorbing or reducing UV light transmittance, which makes necessary the use of pretreatment systems, in order to improve contaminant degradation. Many technologies could be used as a pretreatment for the application of UV/H_2O_2 oxidation process. However the best option should consider not only the improvement on the oxidation process efficiency, but the overall system performance. In some cases AOP are used as a pretreatment for improving the efficiency of biological process for treating complex wastewater focusing water reuse (Oller et al., 2011), where they concluded that is necessary to improve the knowledge about organics degradation kinetics and

reactor modeling considering the combined process. Considering the contaminants presents in condensates from thermal separation process will probably be partially emulsified, presenting high color and turbidity, the efficiency of UV/H_2O_2 oxidation process will be reduced. To overcome this problem a clarification pretreatment process will be necessary, and for this purpose, physicochemical clarification or membrane filtration processes could be efficiently applied (Yahiaoui et al., 2011; Fakhru'l-Razi et al., 2009).

Focusing the overall performance of a treatment system for industrial effluent treatment, the aim of this study was to evaluate the influence of two pretreatment technologies: (i) physicochemical clarification (ii) Hollow Fiber Ultrafiltration Membrane – on the performance of UV/H_2O_2 oxidation process for treating an industrial effluent with a high organic load. The pretreatment technologies were chosen based on the effluent characteristics.

2. MATERIAL AND METHODOLOGY

2.1. Effluent Composition

In the experiments an effluent arising from a thermal separation process (vapor compression evaporator), treating oil-water emulsions with a high TOC load was used. Because of evaporation process characteristics, a high level of organic contaminants is still present in the condensate, which not allows its releasing to the environment or even its reuse for industrial purposes. The main composition of raw effluent generated in the thermal separation process is given in Table 1.

Table 1: Mean composition of raw effluent (N=7).

Parameter	Concentration	Unit	Analytical Method or Instrument
pH	7.2±0.7	--	Electrometric – Quimis pH-meter
Turbidity	141±51	NTU	Policontrol Turbidimeter
Color	507±492	Color unit	Policontrol Colorimeter
COD	4321±1015	mg/L	Standard Methods, 5220 – D*
TOC	827±109	mg/L	TOC-V CPH Shimadzu
Oil & Grease	168±42	mg/L	Standard Methods, 5520 – B*
Total Dissolved Solids	106±19	mg/L	Standard Methods, 2540 – C*
Electrical Conductivity	1703±179	µS/cm	Standard Methods, 2510 – B*
Total Phosphorus	12±2.3	mg/L	Standard Methods, 4500 – PB*
N-Ammonia	450±89	mg/L	Standard Methods, 4500 - NH_3D*
N-Organic	64±16	mg/L	Standard Methods, 4500 - Norg B*

***** APHA (1999)

According to the data presented in Table 1, most appropriated pretreatment technologies should be able to remove effluent color and turbidity, because it could significantly affect the UV/H_2O_2 performance, justifying the use of ultrafiltration and physicochemical clarification as pretreatment processes.

2.2. Membrane Separation Process – HF-UF

The membrane separation process was carried out using a laboratory scale ultrafiltration unit (Demofilter - Koch Membrane Systems). Prior to the experiment, the effluent was filtered through a 100 µm bag filter in order to remove coarse suspended solids, if present. Experiments were carried out using a hollow fiber membrane module from Koch Membrane

Systems, 1" HF 1.0-45-XM50, with a Molecular Weight Cut-off (MWCO) of 50,000 Daltons. The temperature in all experiments was 20±0.9 °C and the transmembrane pressure (TPM) was kept at 1.26 bar. Membrane system was operated in batch, with full concentrate recirculation to the feed tank. Permeate from UF system was used in the oxidation experiments.

2.3. Physicochemical Clarification Process

Effluent clarification was carried out in Jar-test equipment (Milan JT 203/6) with the addition of three different chemicals from Procytek Industria e Comercio Ltda. The chemical doses are presented in Table 2. Each chemical was added separately according to the data presented in Table 3. Thirty liters of effluent were treated using chemical clarification. The clarified effluent was used in oxidation experiments with UV/H_2O_2.

Table 2 - Chemical doses used in clarification experiment.

Chemical brand	Density (g/mL)	Dosage (ppm/L of effluent)
Procytrat 110B	1.35	200
Procytrat 100C	1.15	700
Procytrat 130C	0.85	500

Table 3 - Operation condition during clarification step.

Process	Mixing gradient (s^{-1})	Time (s)	Chemical added
Rapid mix	120	180	Procytrat 110B
	120	180	Procytrat 100C
	120	240	Procytrat 130C
Flocculation	40	240	---------
Settling time	-	30 min	-

2.4. UV/H_2O_2 Process

Effluents from the ultrafiltration and physicochemical clarification processes, besides the raw effluent were then treated using the UV/H_2O_2 oxidation process in order to obtain the TOC degradation kinetic constants. The photochemical reactor from Germetec UV/IR Technology Ltd. was equipped with a 1,600 watts medium pressure UV lamp. All tests were performed in batch with full effluent recirculation (Figure 1). Samples from the photochemical reactor effluent were taken each hour during the tests for the analysis of TOC and at the end of test for the analysis of the same parameters presented in Table 1. For the evaluation of TOC degradation kinetic constants a pseudo first order reaction was considered according equations 1 and 2, derived from a mass balance based on the diagram of Figure 1. Since H_2O_2 was added in excess a pseudo first order kinetics can be assumed (USEPA, 1998). Equation 1 refers to the TOC degradation in the UV reactor and equation 2 refers to the TOC concentration leaving the storage tank, where no TOC degradation is expected. Oxidation kinetic constant was obtained by plotting the natural logarithm of TOC concentration with time, according the linearization of Equation (2). Operational conditions for the oxidation assays are presented in Table 4.

$$C_S = C.e^{-k.\tau} \quad [1]$$

$$C = C_0.e^{\frac{\left(e^{-k.\tau}-1\right)}{\theta}.t} \quad [2]$$

where:

- C, C_S and C_0 = TOC concentration in the photochemical reactor influent and effluent and in the effluents from UF and physicochemical processes (mg/l);
- k = TOC degradation kinetic constant (h^{-1});
- τ = photochemical reactor detention time (h);
- ɵ = storage tank detention time (h);
- t = reaction time (h).

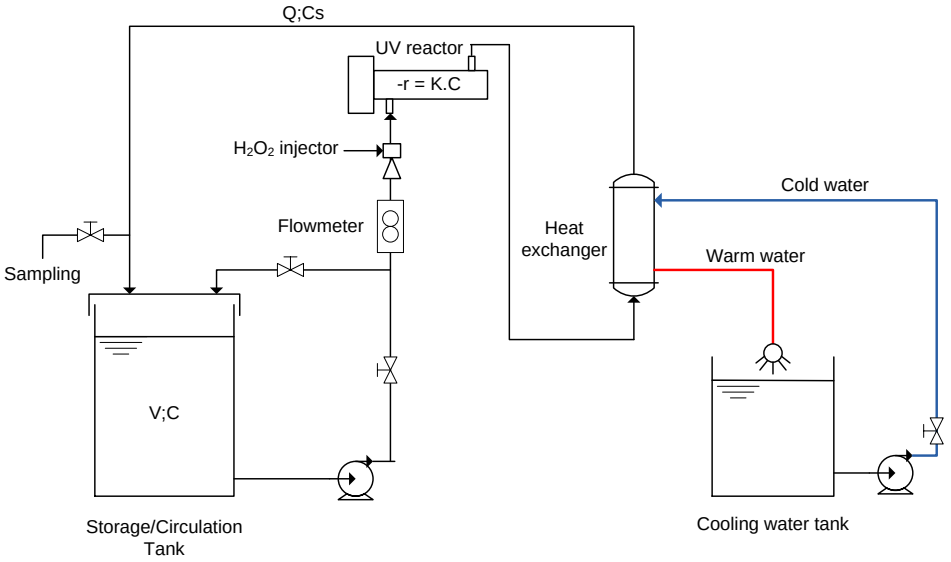

Figure 1: Advanced Oxidation Process diagram.

Table 4: - Operational parameters during UV/H_2O_2 oxidation tests.

Parameters	Value	Unit
Effluent volume per batch	25	L
Effluent circulation flow	360	L/h
Experiment length	9,3	hours
UV reactor retention time	6,7	Seconds ($1.86x10^{-3}$ h)
α (H_2O_2/TOC)	10	mg H_2O_2/mg TOC
UV dose	2,39	w.s/cm^2
Operation temperature	40 – 50	ºC

2.5. H_2O_2 dosage

Commercial hydrogen peroxide dosage was determined based on the concentration of TOC fed to the UV reactor according to alpha (α) correlation stated in Table 4, using Equation 3.

$$V_{H2O2} = \frac{0.1 \times \propto \times TOCo.\ V_{effluent}}{\rho_{H_2O_2} \cdot \%_{H_2O_2}} \quad [3]$$

where:

V_{H2O2} : hydrogen peroxide volume (mL);
$TOCo$: total organic carbon in the effluent fed to the UV reactor (mg C/L);
$V_{effluent}$: effluent volume (L);
ρ_{H2O2}: density of the hydrogen peroxide solution (g/cm^3)
$\%_{H2O2}$: mass content (m/m) of hydrogen peroxide solution (%).
0.1: correction factor.

3. RESULTS AND DISCUSSION

3.1. Pretreatment Performance

As it was mentioned, two types of pretreatment were applied prior oxidation experiments were initiated: (i) physicochemical clarification using 3 different chemicals and (ii) Hollow Fiber Ultrafiltration Membrane with MWCO of 50,000 Da. Those pretreatments were studied in order to verify the effect of feed water quality on TOC kinetics removal by UV/H_2O_2 oxidation process, mainly with respect of turbidity and color removal which may prevent the penetration of UV light through wastewater during the oxidation experiments.

Thirty eight liters of effluent were treated by ultrafiltration, with a water recovery of 84%. In this experiment, the permeate stream was collected separately for subsequent oxidation experiment. Mean permeate flow rate was 21.6 ± 9.0 L/h, which could be considered adequate for effluent treatment. The clarification process resulted in a production of 670 mL of sludge resulting in a production rate of 22 liters of sludge per cubic meter of treated effluent. Compared to the concentrate produced by the ultrafiltration system, the sludge from the physicochemical process is a drawback because it will be necessary to implement a sludge conditioning process before its final disposal, while the concentrate from UF system could be sent back to the evaporation system.

Table 5 presents the results for contaminant removal obtained by each pretreatment process. Comparing these results it could be observed that HF-UF pretreatment system showed a best performance, except for oil & grease and N-organic removal. Another point that should be mentioned is the increasing of electrical conductivity (34%), and Total Dissolved Solids (191%), in the effluent from clarification process, mainly because chemicals added during treatment. With regard the TOC removals both processes were inefficient, indicating the necessity of one additional treatment step, before its final disposal or reuse. Figure 2 presents the results for turbidity, color, COD, and TOC removal efficiencies.

Table 5. Characteristics of HF-UF and Physicochemical effluent.

Parameter	Raw Effluent	Physical-Chemical	HF-UF	Unit
pH	8.5±0.7	7.9±0.5	8.4±0.3	--
Turbidity	141±51	2.7±1.0	1.9±0.7	NTU
Color	507±492	59±41	10±7.8	Color unit
COD	4321±1015	3283±786	3076±565	mg/L
TOC	827±109	763±79	748±54	mg/L
Oil & Grace	168±67	4.0±3.8	6.0±2.5	mg/L
TDS	106±19	309±28	55±9.2	mg/L
Electrical Conductivity	1703±179	2283±181	1648±141	µS/cm
P-total	12±2.3	13±2.6	7.9±1.7	mg/L
N-Ammonia	450±89	296±55	232±44	mg/L
N-Organic	64±16	18±4.3	21±4.1	mg/L

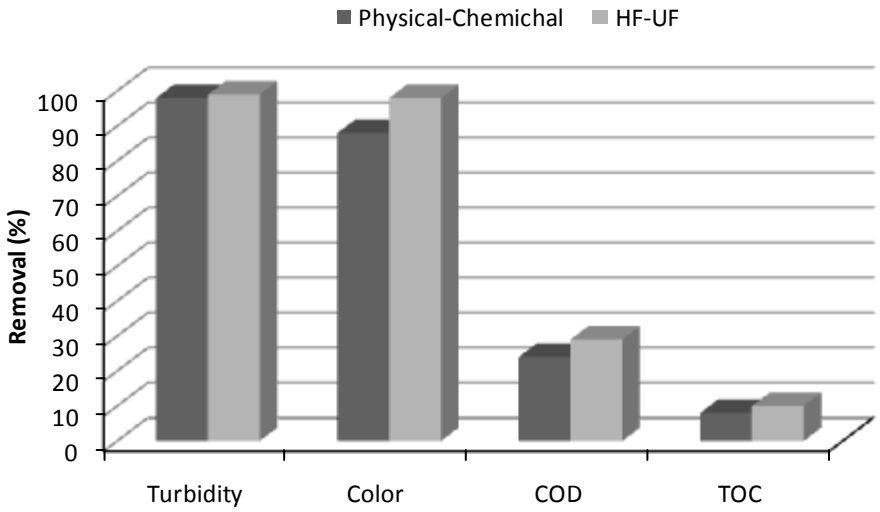

Figure 2: Efficiency of pretreatment systems for turbidity, color, COD, and TOC removal.

3.2. TOC removal using UV/H_2O_2 oxidation process, and kinetics constants

TOC removals by UV/H_2O_2 oxidation process were close to 90% in all experiments (Figure 3). However, when the pretreatment processes were applied the rate of TOC degradation increased, showing that effluent pretreatment is necessary for improving the UV/H_2O_2 oxidation performance (Figure 4 and Table 6). These results are most probably related to the effluent clarification, which resulted in a better UV light transmission in the photochemical reactor, since color and turbidity can absorb UV light. Reaction time for obtaining a TOC removal of 90% was reduced to approximately 4 hours, half of the time needed when no pretreatment was applied. It is in accordance to the work developed by Benítez et al. (2008).

The results presented in this study are not in agreement the ones obtained by Saquib, Vinckier, and Van der Bruggen (2010), where they concluded that ultrafiltration process has no influence on the performance of an oxidation process using O_3/H_2O_2 oxidation process. This could most be associated to the differences on inflow streams characteristics and experimental procedures. It should be mentioned that Saquib et al. (2010), used previously filtered natural water in the experiments, and no mention about water turbidity or color were made.

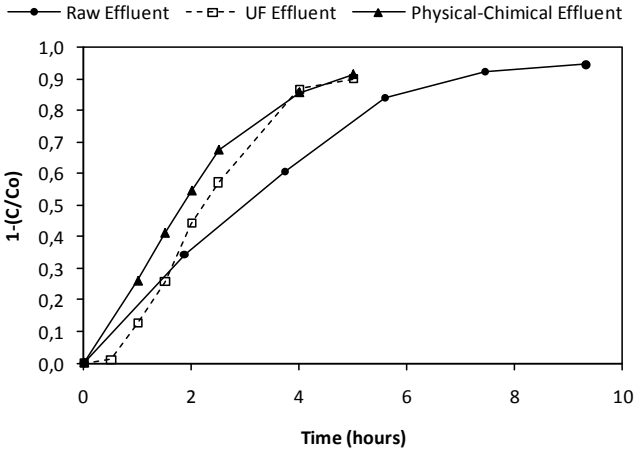

Figure 3. TOC efficiency removal with the UV/H_2O_2 process

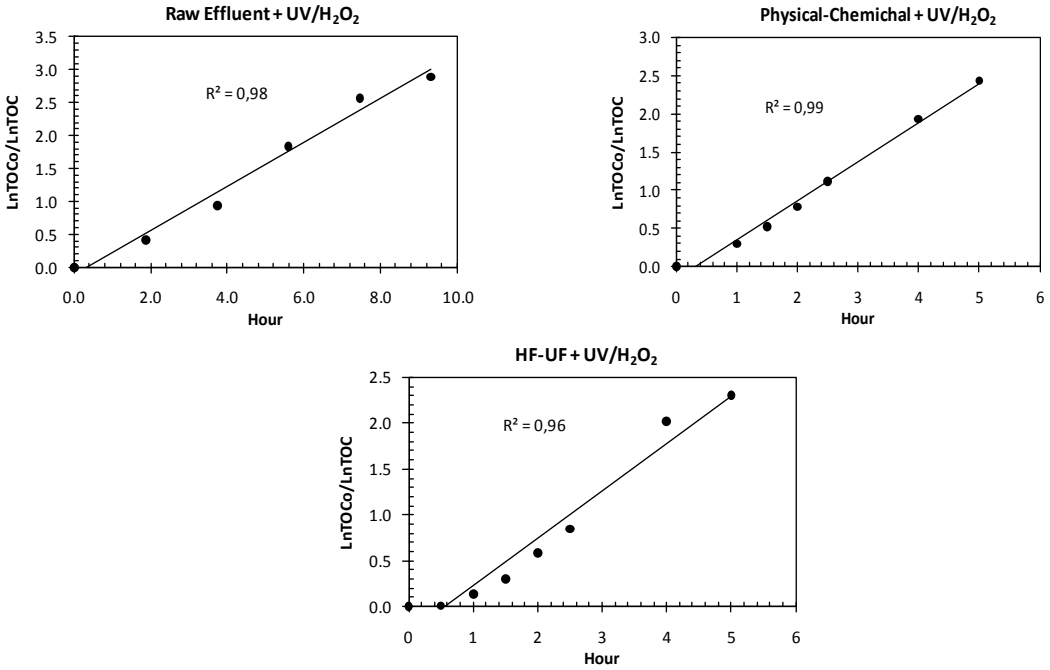

Figure 4. Data linearization for TOC removal by the UV/H_2O_2 oxidation process.

Besides the analyses of the contaminants presented in Table 5, samples of all streams were sent for a private laboratory Bioagri Ambiental, in order to analyze the concentration of volatile and semi-volatile contaminants by gas chromatography. The results of gas chromatography analyses are presented in Figure 5, where it could be seen that the physicochemical clarification process was slightly more efficient than the UF one, and that UV/H_2O_2 oxidation process was very efficient for all conditions evaluated, because the concentration of these contaminants in all samples analyzed were below the equipment detection limit.

Table 6. TOC degradation kinetics constants obtained.

Effluent	K_1 (h^{-1})	R^2 --
Raw	12,42	0.98
UF	19,03	0.96
Physicochemical	18,52	0.99

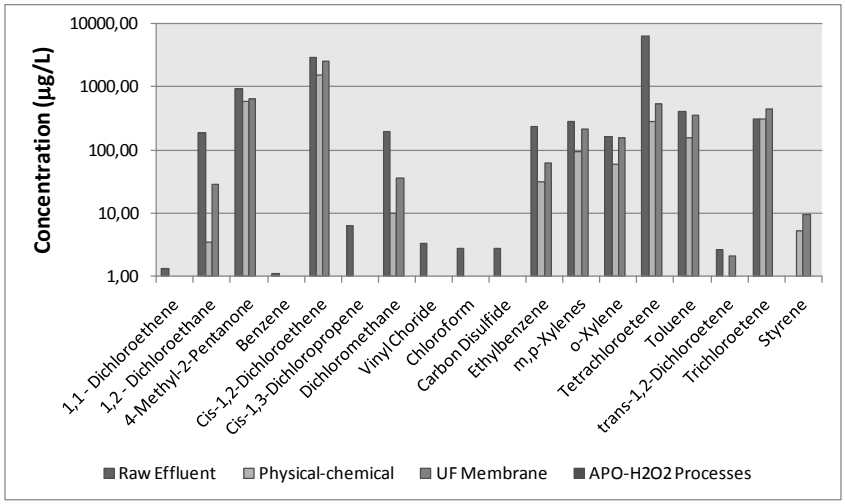

Figure 5. Gas chromatography analyses results for volatile and semi-volatile chemicals

4. CONCLUSIONS

In this work a physicochemical clarification process and an ultrafiltration separation system were evaluated as a pretreatment option for industrial wastewater treatment by UV/H_2O_2 oxidation process, in comparison to its direct treatment. The following conclusions can be drawn:

- Results obtained from the treatment of an effluent arising from an evaporation process of oil and water emulsion showed that ultrafiltration and physicochemical process, present no significant differences on contaminants removal, but that ultrafiltration system presents a better performance because there is no need for chemicals use.
- A considerable improvement on the efficiency of TOC removal from the effluents of UF and physicochemical clarification process, compared with the raw effluent, was obtained;
- Considering both pretreatment processes it was not possible to notice any significant difference on the performance of UV/H_2O_2 oxidation process. However, the complexity of physicochemical process, because of the use of three different chemicals, and because of the sludge produced, makes the UF process the best pretreatment option.

5. REFERENCES

AMERICA PUBLIC HEALTH ASSOCIATION - APHA. **Standard methods for examination of water and wastewater**. 20. ed. Washington, DC, 1999.

ARSLAN, I.; BALCIOGLU, I. A.; TUHKANEN, T.; BAHNEMANN, D. H_2O_2/UV and Fe^{2+}/ H_2O_2/UV-c versus TiO_2/UV-A treatment for reactive dye wastewater. **Journal of Environmental Engineering,** v. 126, n. 10, p. 903-911, 2000. http://dx.doi.org/10.1061/(ASCE)0733-9372(2000)126:10(903)

BENÍTEZ, F. J.; ACERO, J. L.; LEAL, A. I.; REAL, F. J. Ozone and membrane filtration based strategies for the treatment of cork processing wastewaters. **Journal of Hazardous Material**, v. 152, n. 1, p. 373-380, 2008. http://dx.doi.org/10.1016/ j.jhazmat.2007.07.007

BRAUN, A. M.; OLIVEROS, E. How to evaluate photochemical methods for water treatment. **Water Science and Technology.** v. 35, n. 4, p. 17–23, 1997. http://dx.doi.org/10.1016/S0273-1223(97)00004-8

BELTRÁN, F. J.; GONZÁLEZ, M.; GONZÁLEZ, J. F. Industrial wastewater advanced oxidation. Part 1. UV radiation in the presence and absence of hydrogen peroxide. **Water Research**, v. 31, n. 10, p. 2405-2414, 1997. http://dx.doi.org/10.1016/S0043-1354(97)00077-8

CATER, S. R.; STEFAN, M. I.; BOLTON, J. R.; SAFARZADEH-AMIRI, A. UV/H_2O_2 Treatment of methyl tert-butyl ether in contaminated water. **Environmental Science & Technology,** v. 34, n. 4, p. 659-662, 2000. http://dx.doi.org/10.1021/es9905750

DIYA'UDDEEN, B. H.; DAUD, W. M. A. W.; ABDUL AZIZ, A. R. Treatment technologies for petroleum refinery effluents: a review. **Process Safety and Environmental Protection**, v. 89, n. 2, p. 95-105, 2011. http://dx.doi.org/10.1016/j.psep.2010.11.003

EINSCHLAG, F. S. G.; LOPEZ, J.; CARLOS, L.; CAPPARELLI, A.L.; BRAUN, A. M.; OLIVEROS, E. Evaluation of the efficiency of photodegradation on Nitroaromatics applying the UV/H_2O_2 technique. **Environmental Science & Technology**, v. 36, n. 18, p. 3936-3944, 2002. http://dx.doi.org/10.1021/es0103039

FAKHRU'L-RAZI, A.; PENDASHTEH, A.; ABDULLAH, L. C.; BIAK, D. R. A.; MADAENI, S. S.; ABIDIN, Z. Z. Review of technologies for oil and gas produced wastewater treatment. **Journal of Hazardous Materials,** v. 170, n. 2/3, p. 530-551, 2009. http://dx.doi.org/10.1016/j.jhazmat.2009.05.044

GAO, N.; DENG, Y.; ZHAO, D. Ametryn degradation in the ultraviolet (UV) irradiation/hydrogen peroxide (H_2O_2) treatment. **Journal of Hazardous Materials**, v. 164, n. 2/3, p. 640-645, 2009. http://dx.doi.org/10.1016/j.jhazmat.2008.08.038

GUTIÉRREZ, G.; BENITO, J. M.; COCA, J.; PAZOS, CJ. Vacuum evaporation of surfactant solutions and oil-in-water emulsions. **Chemical Engineering Journal**, v. 162, n. 1, p. 201-207, 2010. http://dx.doi.org/10.1016/j.cej.2010.05.029

GUTIÉRREZ, G.; LOBO, A.; BENITO, J. M.; COCA, J.; PAZOS, C. Treatment of a waste oil-in-water emulsion from a copper-rolling process by ultrafiltration and vacuum evaporation. **Journal of Hazardous Materials**, v. 185, n. 2/3, p. 1569-1574, 2011. http://dx.doi.org/10.1016/j.jhazmat.2010.10.088

LITTER, M. I. Introduction to photochemical advanced oxidation processes for water treatment. **The Handbook of Environmental Chemistry**. v. 2, p. 325–366, 2005. http://dx.doi.org/10.1007/b138188

MAO, W.; MA, H.; WANG, B. Performance of batch vacuum distillation process with promoters on coke-plant wastewater treatment. **Chemical Engineering Journal**, v. 160, n. 1, p. 232-238, 2010. http://dx.doi.org/10.1016/j.cej.2010.03.053

OLLER, I.; MALATO, S.; SÁNCHES-PÉREZ, J. A. Combination of advanced oxidation processes and biological treatments for wastewater decontamination – a review. **Science of the Total Environment**, v. 409, n. 10, p. 4141-4166, 2011. http://dx.doi.org/10.1016/j.scitotenv.2010.08.061

SAQUIB, M.; VINCKIER, C.; VAN DER BRUGGEN, B. The effect of UF on the efficiency of O_3/H_2O_2 for the removal of organics from surface water. **Desalination**, v. 260, n. 1/3, p. 39-42, 2010. http://dx.doi.org/10.1016/j.desal.2010.05.003

UNITED STATES. Environmental Protection Agency – USEPA. **Handbook of advanced photochemical oxidation processes**. Washington, DC, 1998. Report EPA/625/R-98/004.

YAHIAOUI, O.; LOUNICI, H.; ABDI, N.; DROUICHE, N.; GHAFFOUR, N.; PAUSS, A.; MAMERI, N. Treatment of olive mill wastewater by the combination of ultrafiltration and bipolar electrochemical reactor processes. **Chemical Engineering and Processing: Process Intensification**, v. 50, n. 1, p. 37-41, 2011. http://dx.doi.org/ 10.1016/j.cep.2010.11.003