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Article

Stripped Sour Water Treatment by Advanced Oxidation Processes

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No presente trabalho foi avaliada a aplicação dos processos de fotólise (UV), peroxidação (H_2O_2), peroxidação assistida por radiação ultravioleta (UV/H_2O_2), reagente de Fenton (H_2O_2/Fe(II)) e foto-Fenton (H_2O_2/Fe(II)/UV) no tratamento de água ácida retificada proveniente da Refinaria de Petróleo Replan da Petrobras, Paulínia-SP. Para avaliação da eficácia dos processos, a concentração de carbono orgânico dissolvido (COD) foi monitorada durante todo o período de reação. Dentre os processos avaliados, a peroxidação assistida por radiação ultravioleta apresentou o melhor potencial para sua aplicação no tratamento da água ácida retificada.

This study assessed the application of photolysis (UV), peroxidation (H_2O_2), peroxidation combined with ultraviolet light (UV/H_2O_2), Fenton's reagent (H_2O_2/Fe(II)) and photo-Fenton (H_2O_2/Fe(II)/UV) processes in the treatment of stripped sour water from the Petrobras Replan Oil Refinery in Paulínia City, São Paulo State, Brazil. To evaluate the efficiency of the process, the concentration of dissolved organic carbon (DOC) was monitored throughout the reaction period. Among the evaluated processes, peroxidation combined by ultraviolet radiation showed the best potential for its application in the stripped sour water treatment.

Keywords: Fenton, oil refinery, photo-Fenton, reuse, UV/H_2O_2

Introduction

The oil refining industry uses a large amount of water in its production process, generating a large volume of effluent. At the Replan Refinery in Paulínia City (São Paulo State, Brazil), 700 L of water are consumed *per* 1000 L of oil processed. There is a great interest in improving wastewater management in petrochemical facilities by optimizing water use and introducing technologies which enable water to be reused in production units.[1]

Sour water is one of the most significant issues in a refinery mainly due to its composition and its corrosive nature. It is produced by various different processes and thus its composition varies. In addition, the management cost of this type of water is quite high. Sour water is defined as any processed water containing hydrogen sulfide, ammonia, phenols, cyanides, dissolved oils, mercaptans, hydrocarbons, suspended solids and high levels of dissolved organic carbon (DOC) and chemical oxygen demand (COD).[2] It usually has pH values above 7, though it gets its name from its characteristic smell. Sour water may result from water vapor injected into oil processing units in order to reduce the partial pressures of hydrocarbons, which provides less extreme temperature conditions. Some is generated by injection of wash water to prevent salt deposition inside pipes or equipment such as heat exchangers. According to Coelho *et al.*,[3] typical sour water production in large refineries is between 0.2 and 0.5 m^3 ton^{-1} of crude oil processed.

Sour water is typically not treated along with the effluents from the refinery. It is separated and stripped in order to remove sulfide and ammonia, so they can be reused in the refining process. Though stripped sour water from the Petrobras Replan Refinery in Paulínia City is H_2S-free, it contains high levels of ammonia, mercaptans and hydrocarbons, in addition to oils and greases. For this reason, it is not possible to reuse all the sour water produced at Replan.

Due to the great variety of recalcitrant compounds in stripped sour water, studies are needed to look for clean and efficient treatment alternatives that compensate for the limitations of conventional methods when the effluent

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is intended to be reused. Advanced oxidation processes (AOPs) are technologies that involve the generation of hydroxyl radicals ($^{\bullet}OH$), which are highly oxidizing and non-selective. Due to their high reactivity, these radicals can react with a wide variety of complex organic compounds, oxidizing them to simple molecules, or even mineralizing them.[4,5]

Biodegradation,[6] membrane bioreactor methods,[7] electrocoagulation,[8] enhanced photo-degradation,[9] electrochemical methods,[10,11] microwave-assisted catalytic wet air oxidation[12] and photocatalytic degradation methods[1] are used for the treatment of effluents from oil refineries. However, there are still few works about sour water treatment in scientific literature.

Coelho *et al.*[3] evaluated reduction of DOC from sour water from a petroleum refinery by several oxidation processes and verified that Fenton and photo-Fenton led to the best results. Bhargava *et al.*[13] employed the catalytic wet oxidation process for treating stripped sour water from an oil shale refinery in Australia, with a 9 g L^{-1} DOC initial concentration, and they reduced DOC by 73% after a 3 h reaction at 200 °C using a copper and palladium bimetallic catalyst. Prasad *et al.*[14] adopted the wet oxidation with hydrogen peroxide technique to treat the same effluent used by Bhargava *et al.*[13] DOC removal was 80% in 1.5 h at 150 °C, using 64 g L^{-1} of H_2O_2.[14]

It is also important to emphasize that studies based on treatment of industrial effluents for the purpose of reusing them in the production process have become very important. Reusing treated water consolidates alternatives and actions that use water more rationally, minimizing waste. Among various published works, Ismail and Al-Hashimi,[15] El-Salam and El-Naggar,[16] Oliveira *et al.*[17] and de Feo *et al.*[18] reported reuse proposals in different kinds of industrial plants.

The objective of this study was to evaluate reduction of dissolved organic carbon present in stripped sour water flow by five processes: photolysis (UV), peroxidation (H_2O_2), peroxidation with ultraviolet radiation (UV/H_2O_2), Fenton's reagent (H_2O_2/Fe(II)) and photo-Fenton (H_2O_2/Fe(II)/UV). The effects of initial concentrations of hydrogen peroxide and ferrous ions (Fe(II)) on the treatment of this effluent were also investigated.

Experimental

Reagents and effluent

Ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), concentrated sulfuric acid and hydrogen peroxide (30% v/v) were supplied by Synth (Diadema, Brazil).

Stripped sour water samples from the Replan Refinery in Paulínia City were collected and transferred to the Laboratory of Oxidation Processes (LABPOX) of the Department of Sanitation and Environment (DSA) (School of Civil Engineering, Architecture and Urbanism, at University of Campinas (Unicamp)). The sample was characterized (Table 1) and stored in a refrigerator (ca. 10 °C).

Table 1. Characterization of stripped sour water sample

Parameters	Values	Units
COD	553	mg O_2 L^{-1}
BOD	147	mg O_2 L^{-1}
DOC	160.5	mg L^{-1}
EC	396	µS cm^{-1}
pH	9.5	
Turbidity	30	UT
Apparent color	624	PtCo

Notable levels of COD, BOD (biochemical oxygen demand) and DOC were found, suggesting the presence of dissolved oil, phenols and hydrocarbons. The low BOD/COD ratio (0.27) indicates the low biodegradability of this effluent. The pH value is high because caustic soda is added to remove ammonia gas in the stripping tower. The electrical conductivity (EC) value might indicate the presence of salts dissolved in the sample. The effluent had pink-orange coloring.

Experimental system

The batch system used in this study is presented in Figure 1. The batch was made using a photochemical reactor, a magnetic stirrer, a 600 mL vessel and a peristaltic

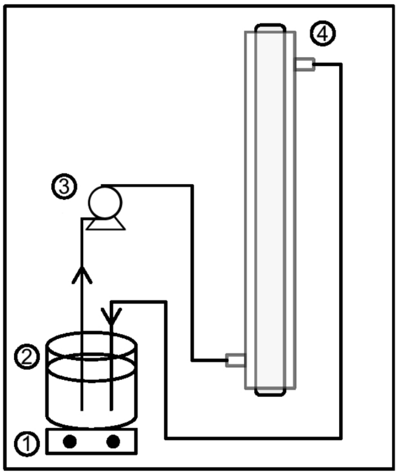

Figure 1. Experiment setup: (1) magnetic stirrer, (2) vessel, (3) peristaltic pump and (4) photochemical reactor.

pump to recirculate the solution at a flow of approximately 207 mL min^{-1}. This system was based on works by da Silva *et al.*[19] and Guimarães *et al.*[20]

The bench photochemical reactor consisted of a 42.5 cm long and 4 cm internal diameter borosilicate glass cylinder with a low pressure mercury vapor lamp inserted in the center (15 W, λ_{max} of 254 nm, 2.5 cm internal diameter, brand Ecolume). The lamp was in direct contact with the circulating solution. The internal volume of the reactor was approximately 270 mL. The radiation intensity (I) of the UV lamp was 8.3 mW cm^{-2}. It was obtained by a VLX 3Wr model Cole Parmer radiometer calibrated to 254 nm.

In this experimental system, the effluent was continuously stirred inside the vessel, pumped into the reactor with an upward flow and returned to the vessel, forming a closed-circuit. In tests using UV radiation, the UV light exposure time of the effluent was different from the total trial time, and was calculated according to equation 1.

$$t_{irrad} = t_{tot} (V_{react} / V_{sol}) \quad (1)$$

in which t_{irrad} is exposure time to UV radiation (min), t_{tot} is total trial time (min), V_{react} is useful volume of the photolytic reactor (mL) and V_{sol} is total volume of the solution (mL).

A volume of 500 mL of the sample was used in all tests. In peroxidation and UV/H_2O_2 trials, H_2O_2 was added once at different DOC:H_2O_2 mass ratios between 1:2 and 1:7, giving 360 to 1260 mg L^{-1} H_2O_2 concentrations. For Fenton and photo-Fenton processes, 1:5 and 1:7 DOC:H_2O_2 (900 and 1260 mg L^{-1} H_2O_2) mass rations were evaluated, and ferrous ion concentration varied from 31 to 500 mg L^{-1}. Photolysis, peroxidation and UV/H_2O_2 trials were performed at the original pH of the sample, while the value was adjusted to pH 3.0 in Fenton and photo-Fenton processes using diluted sulfuric acid.

Aliquots were collected after 15 min and every 30 min thereafter to monitor the concentration of DOC in order to evaluate the effectiveness of procedures. After total reaction time, COD, color, turbidity and electrical conductivity analyses were also performed.

Analytical methods

A Shimadzu model 5000A total organic carbon analyzer was used for DOC analysis. COD and BOD analyses were performed according to APHA/AWWA/WEF standard methods.[21]

Measurements of hydrogen ionic potential (pH) were performed using the electrometric method, using the ASTM D1293 methodology with a Thermo Orion 410A pH meter.[22]

Turbidity analyses were based on section 2130 B of the APHA/AWWA/WEF methodology,[21] using a HACH model 2100N turbidimeter. Electrical conductivity measurements were performed according to APHA/AWWA/WEF section 2510 B[21] on a Micronal B330 conductivity meter.

Color analyses were performed as defined in section 2120 C of the APHA/AWWA/WEF methodology[21] using a HACH model DR4000 spectrophotometer.

A colorimetric analytical method was adopted for the determination of hydrogen peroxide. It was based on redox reactions between the solution, which contained H_2O_2, and a yellow-colored acidic metavanadate ion solution. Due to the formation of red-orange-colored peroxovanadium cations with maximum absorbance at 450 nm, hydrogen peroxide concentration could be obtained by UV-Vis spectrophotometry.[23]

Results and Discussion

Photolysis (UV)

DOC reduced by 17% after 210 min of photolysis. This may be because of the degradation of compounds present in the sample and/or decreased solubility of certain volatile and semi-volatile organic compounds due to the approximately 8 °C temperature increase during the trial.

COD (16.4%) was reduced by a similar amount to DOC. Color was reduced by 58% and turbidity by 29%. The decreased values for these parameters may be due to the effect of temperature on solubility and to UV radiation modifying the structure or destroying the chromophore groups of a set of molecules present in the effluent that absorb electromagnetic radiation at a wavelength close to 254 nm.

Photolysis was found to reduce DOC by a similar amount by Coelho *et al.*,[3] who verified reduction of 20% in treatment of sour water from an oil refinery with initial DOC concentration around 1000 mg L^{-1}.

Peroxidation (H_2O_2)

There was no reduction in DOC concentration in the peroxidation process, showing that the compounds present in stripped sour water cannot be mineralized when only the oxidant hydrogen peroxide is applied.

Both turbidity reduction (0 to 5%) and COD (0 to 3.3%) values were very low. However, this process was able to remarkably reduce the color of the effluent (15 to 21%). This means that the structure of a set of component molecules of the effluent was modified and their chromophore groups may have been destroyed.

Coelho *et al.*[3] verified that peroxidation reduced DOC of sour water from an oil refinery by only 8%, confirming the results obtained in this work.

Peroxidation combined with ultraviolet light (UV/H_2O_2)

According to Figure 2, when DOC:H_2O_2 mass ratio was 1:2, DOC reduction was 47.5%. At a ratio of 1:3, DOC reduction was 60.6%. Both were slower and smaller than the higher ratios in 210 min of reaction. When the DOC:H_2O_2 mass ratio was 1:4, degradation was 82% for the same reaction time. This showed that a higher H_2O_2 concentration had a more pronounced DOC concentration decay curve, i.e., a higher degradation rate of organic compounds. However, this behavior was verified only up to 1:4 DOC:H_2O_2 mass ratio.

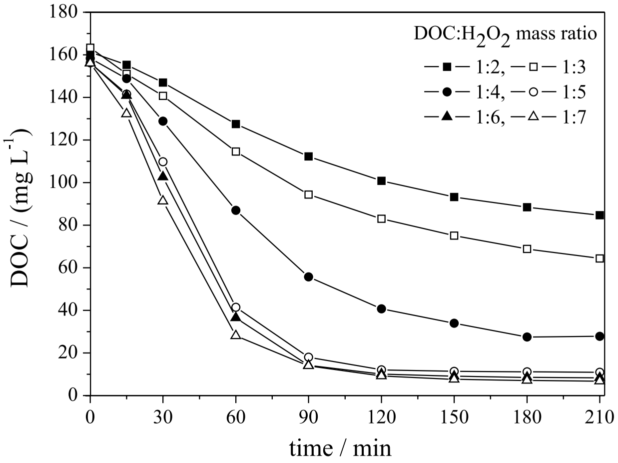

Figure 2. DOC concentration variation over time for degradation by UV/H_2O_2 at different DOC:H_2O_2 mass ratios.

No significant differences were noted in DOC reduction among DOC:H_2O_2 mass ratios of 1:5, 1:6 and 1:7: maximum organic carbon reduction values were between 93 and 95% in 150 min of reaction.

Abramovic *et al.*[24] observed the same behavior in the degradation of the insecticide thiacloprid: a rapid increase in the reaction rate occurred at H_2O_2 concentrations from 0 to 45 mmol L^{-1} (0 to 1530 mg L^{-1}), while for the range of 45-162 mmol L^{-1} (1530 to 5508 mg L^{-1}) only a slight increase was observed. It remained practically constant afterwards. Ghodbane and Hamdaoui[25] verified that up to the limit of 1543 mg L^{-1}, more color was removed as initial H_2O_2 concentration increased, supporting the results obtained here.

According to Silva *et al.*[26] and Daneshvar *et al.*,[27] when there is excess H_2O_2, there may be reactions that compete for hydroxyl radicals (equations 2 to 4). As a result, increasing hydrogen peroxide concentration does not increase DOC degradation because of competition between the oxidant and the organic compounds by $^{\bullet}OH$. Therefore, there is an optimal concentration of this oxidant at which the photo-oxidation rate is at its maximum.

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (2)$$
$$2\,^{\bullet}OH \rightarrow H_2O_2 \quad (3)$$
$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow O_2 + H_2O \quad (4)$$

Fenton's reagent (H_2O_2/Fe(II))

The 1:5, 1:6 and 1:7 DOC:H_2O_2 mass ratios were able to reduce more than 90% of DOC in the UV/H_2O_2 tests, so the 1:5 and 1:7 mass ratios were used in the Fenton tests in order to make a comparison between the processes. Iron concentrations from 31 to 500 mg L^{-1} were used, thus the oxidant/ferrous ion mass ratios varied from 1.8:1 to 40:1. Optimum H_2O_2:Fe(II) molar ratios from 1:1 to 400:1 (0.6:1 to 242.8:1 mass ratios) have been proposed to degrade different compounds in aqueous solution.[28]

The reaction rate in the first 60 min for Fenton's reagent was directly proportional to Fe(II) concentration for both 1:5 and 1:7 DOC:H_2O_2 ratios, as shown in Figure 3. This process proved to be very inefficient when low concentrations of ferrous ion (31 mg L^{-1}) were applied, reaching a maximum DOC reduction of only 8%. For initial Fe(II) contents of 125, 250 and 500 mg L^{-1}, DOC reduction was very similar in 120 min of reaction, ranging from 38 to 45%. These values stabilized after this reaction period.

Other works have also reported DOC removal of around 40% employing Fenton's reagent for the treatment of effluents.[29] This may occur due to the formation of carboxylic acids. These treatment-resistant intermediate compounds react very slowly with $^{\bullet}OH$, making the reaction unproductive.[30] Another possibility is the reaction of Fe(III) ions with these intermediate products, forming stable organic compounds that are difficult to degrade, decreasing the efficiency of the reaction, as shown in equation 5.[3,29,31]

$$Fe(III) + RCO_2^{-} \rightarrow [Fe(III)(RCO_2^{-})]^{2+} \quad (5)$$

For both concentrations of hydrogen peroxide evaluated, DOC reduction was almost the same. Increasing H_2O_2 concentration from 900 mg L^{-1} (1:5 DOC:H_2O_2) to 1260 mg L^{-1} (1:7 DOC:H_2O_2) while maintaining the same Fe(II) content did not significantly improve DOC and COD reduction within the time of the experiment. The highest efficiencies obtained were 49% for DOC and 81.7% for COD.

Varying Fe(II) and H_2O_2 concentrations, it was found the same effect by Padoley *et al.*[32] assessing Fenton's

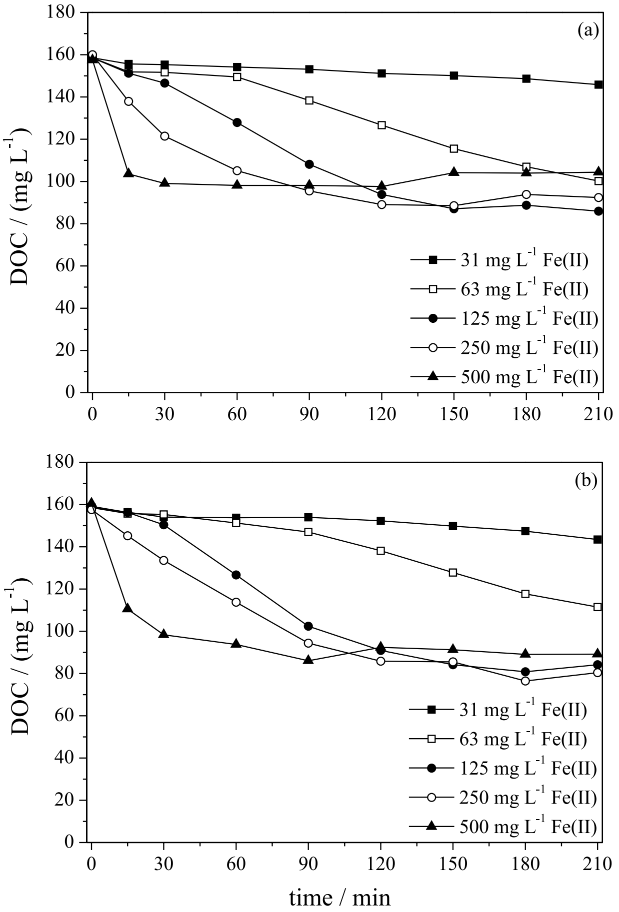

Figure 3. DOC values at different Fe(II) concentrations over time for (a) 1:5 and (b) 1:7 DOC:H_2O_2 mass ratios, for the Fenton process.

reagent as a pretreatment option for 3-cyanopyridine wastewater (which had high ammonia content, alkaline pH and extremely high COD values). Padoley *et al.*[32] verified that more COD was removed when ferrous sulfate concentration was increased up to a ferrous concentration of 2.4 g L^{-1} and increasing hydrogen peroxide concentration over 750 mg L^{-1} did not result in increasing COD reduction.

Photo-Fenton process (H_2O_2/Fe(II)/UV)

After the first 60 min of reaction in the photo-Fenton process, DOC removal was inversely proportional to Fe(II) concentration for both DOC:H_2O_2 mass ratios assessed (1:5 and 1:7), as shown in Figure 4. This is different from what happened with Fenton's reagent. It was found that the optimum Fe(II) concentration was the lowest assessed (31 mg L^{-1}). The lower concentrations of ferrous ion used resulted in more efficient DOC removal efficiencies since Fe(II) ions are regenerated by $[Fe(OH)]^{2+}$ and $[Fe(RCO_2)]^{2+}$ photolysis in the Fenton/photo-Fenton system, among other mechanisms, according to equations 6 and 7.[30,33]

$$[Fe(OH)]^{2+} + h\nu \rightarrow Fe(II) + {}^{\bullet}OH \quad (6)$$

$$[Fe(RCO_2)]^{2+} + h\nu \rightarrow Fe(II) + CO_2 + {}^{\bullet}R \quad (7)$$

It is possible that so many hydroxyl radicals are formed by the decomposition of H_2O_2 in the photo-Fenton process at high Fe(II) concentrations. Competitive reactions take place consuming a large amount of those hydroxyl radicals (equations 2 to 4) before they are effectively used in the degradation of organic compounds.[33] High Fe(II) concentration can result in increased turbidity of the solution, preventing the absorption of the UV radiation necessary for photolysis. In addition, excess Fe(II) ions can scavenge hydroxyl radicals.[31,33-36]

The test lasted 150 min. At this point, there was no notable difference between DOC reduction values at the two hydrogen peroxide concentrations assessed: 900 mg L^{-1} (1:5 DOC:H_2O_2) and 1260 mg L^{-1} (1:7 DOC:H_2O_2). The best result was around 95% DOC reduction at the 1:5 DOC:H_2O_2 mass ratio with the Fe(II) concentration of 31 mg L^{-1}. A similar result (94%) was obtained using the highest H_2O_2 concentration and the same Fe(II) concentration (31 mg L^{-1}). The highest efficiency for the COD parameter

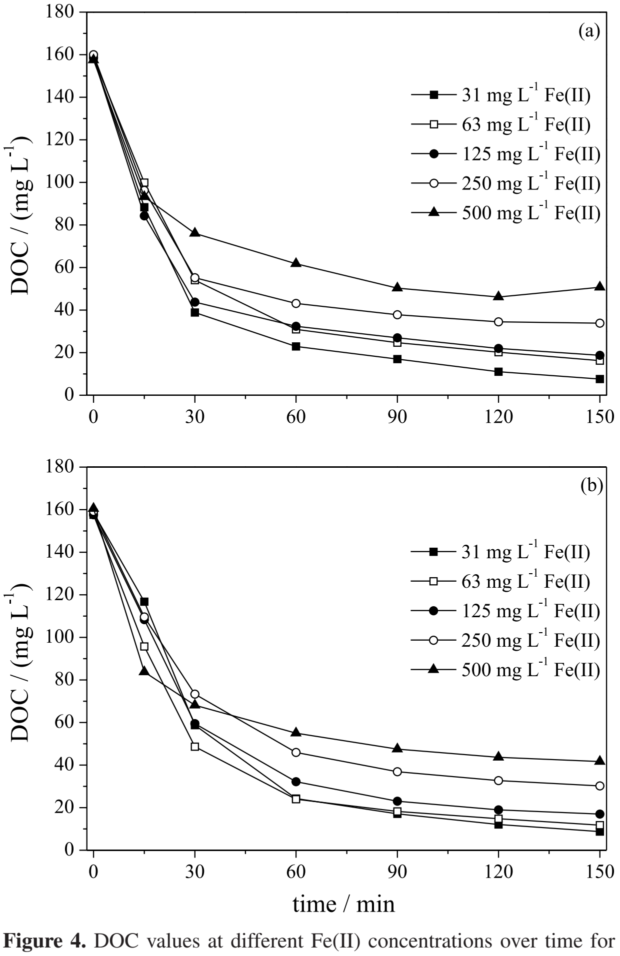

Figure 4. DOC values at different Fe(II) concentrations over time for (a) 1:5 and (b) 1:7 DOC:H_2O_2 mass ratios for the photo-Fenton process.

was also achieved using a concentration of 31 mg L^{-1} Fe(II) for both DOC:H_2O_2 mass ratios.

Comparison between the processes

Figure 5 shows the results of DOC reduction of stripped sour water subjected to photolysis, peroxidation, peroxidation assisted by ultraviolet light, Fenton and photo-Fenton processes for 210 min of testing.

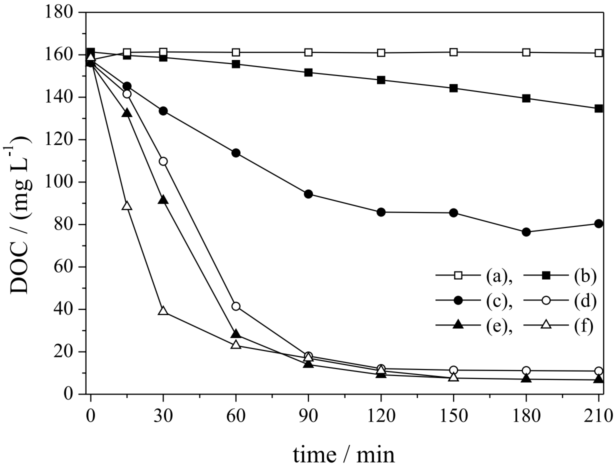

Figure 5. DOC value variation over time during treatment by (a) H_2O_2 (DOC:H_2O_2 1:7 mass ratio), (b) UV, (c) Fenton's reagent (250 mg L^{-1} Fe(II) and DOC:H_2O_2 1:7 mass ratio), (d) UV/H_2O_2 (DOC:H_2O_2 1:5 mass ratio), (e) UV/H_2O_2 (DOC:H_2O_2 1:7 mass ratio) and (f) photo-Fenton (31 mg L^{-1} Fe(II) and DOC:H_2O_2 1:5 mass ratio).

The maximum DOC reduction by photolysis after 210 min was 17%, while peroxidation was not able to reduce DOC concentration, independent of the concentration of peroxide used (360 to 1260 mg L^{-1}).

For the UV/H_2O_2 process, in 210 min of reaction, DOC reduction efficiency at 1:5 DOC:H_2O_2 was 93%, while it was 98% at a 1:7 mass ratio, and COD removal efficiencies were 95% for 1:5 DOC:H_2O_2 and 99% for a 1:7 mass ratio. Maximum color reduction was 42.3%. However, this process was not effective at reducing turbidity (maximum 4.0%). The reactions were definitely more significant for dissolved compounds.

By using 1:7 DOC:H_2O_2 mass ratio and 250 mg L^{-1} of Fe(II), DOC was reduced 45% in 120 min for Fenton's reagent. After that time, reduction efficiency stabilized. DOC removal was 95% for the photo-Fenton process using 31 mg L^{-1} ferrous ion and a 1:5 DOC:H_2O_2 mass ratio in 150 min of reaction.

It can be concluded that, considering the total testing time of 210 min, peroxidation, photolysis and Fenton's reagent processes were not very efficient at degrading the organic compounds found in stripped sour water. Photo-mediated processes using UV radiation (UV/H_2O_2 and photo-Fenton) offered the most efficient DOC reduction.

Potential reuse of the effluent treated by AOP

Among the studied processes, peroxidation combined with ultraviolet radiation (UV/H_2O_2) presented as a promising process to treat stripped sour water for the purpose of reusing. The photo-Fenton process also resulted in the reduction of most of DOC from stripped sour water (as shown in Figure 5). However, here are some disadvantages in the use of the photo-Fenton process. The pH value must be adjusted at the beginning and at the end of the reaction and precipitated iron hydroxide has to be removed as well, generating additional costs. Another restriction may relate to high electrical conductivity values of the effluent treated by photo-Fenton, around 1200 µS cm^{-1}, which could significantly reduce the possibilities of reusing of this effluent.

By comparing the two DOC:H_2O_2 mass ratios in peroxidation assisted by ultraviolet radiation (Figure 5), it can be concluded that the best treatment option is using the DOC:H_2O_2 1:5 ratio. This conclusion took the economy of hydrogen peroxide into account since the efficiency of both treatments was very similar.

One possibility for reusing the stripped sour water treated by peroxidation assisted by ultraviolet radiation (1:5 DOC:H_2O_2 mass ratio) would be as replacement water in the cooling towers since they are responsible for consuming 49% of the water collected from the Jaguari River by Replan Refinery in Paulínia City. Table 2 shows the parameters analyzed for raw effluent and that treated by the UV/H_2O_2 process compared with values recommended by US EPA (United State Environmental Protection Agency) for cooling tower feedwater.[37] It is worth mentioning that there is no legislation governing water reuse in Brazil.

Table 2. Characterization of stripped sour water before and after treatment by UV/H_2O_2 process (DOC:H_2O_2 1:5 mass ratio; 210 min of reaction) and recommended values for replacement water in cooling towers (adapted from Oenning Jr. and Pawlowsky)[38]

Parameters	Units	Results		Recommended limits for cooling water
		Raw	Treated	
COD	mg O_2 L^{-1}	553	15	≤ 75[a]
BOD	mg O_2 L^{-1}	147	n.p.	≤ 30[b]
DOC	mg L^{-1}	160.5	10.9	n.f.
EC	µS cm^{-1}	396	520	800-1200[c]
pH		9.5	8.2	6-9[b]
Turbidity	UT	30	29.8	≤ 3.0[d]
Apparent color	PtCo	624	428	n.f.

[a]Tchobanoglous *et al.*;[39] [b]US EPA;[37] [c]US EPA San Francisco City;[37] [d]US EPA Texas State;[37] n.p.: analysis not performed; n.f.: specification not found.

By comparing the values of the parameters analyzed with the recommended limits for replacement water in cooling towers, it can be seen that the only parameter that does not fit is the turbidity value, which is much higher than the recommended one. The other values are within the range recommended in literature.[37,39] It is important to emphasize that no information was found on the recommended values for DOC and color parameters.

Therefore, in order to make the reuse of stripped sour water treated by UV/H_2O_2 process feasible as replacement water in the cooling towers, it would be necessary to pre-treat the water to reduce turbidity. The pre-treatment could be performed by means of a physical process. Furthermore, studies involving scale-up are of fundamental importance. However, a more detailed and thorough study would be indispensable in order to select the most appropriate technique, in addition to careful economic evaluation and monitoring to avoid damaging the cooling system.

Conclusions

The photo-irradiated advanced oxidation processes (photo-Fenton and peroxidation assisted by ultraviolet radiation) were highly effective at reducing DOC in stripped sour water. The photo-Fenton process (H_2O_2/Fe(II)/UV) was able to reduce 95% of DOC when 31 mg L^{-1} of Fe(II) were used at a 1:5 DOC:H_2O_2 mass ratio. DOC reduction efficiency by UV/H_2O_2 was nearly 95% when 1:5, 1:6 and 1:7 DOC:H_2O_2 mass ratios were employed.

Finally, the peroxidation assisted by ultraviolet radiation (1:5 DOC:H_2O_2 mass ratio) presented high potential for the treatment of stripped sour water for the purpose of its reuse as replacement water in cooling towers after being treated to reduce turbidity. However, scale-up studies are necessary for proper management of the treated effluent.

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References

1. Saien, J.; Nejati, H.; *J. Hazard. Mater.* **2007**, *148*, 491.
2. United States Environmental Protection Agency (US EPA); *Profile of the Petroleum Refining Industry*; Office of Compliance Sector Notebook Project: Washington D.C, September, 1995, http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/petrefsn.pdf accessed in August 2012.
3. Coelho, A.; Castro, A. V.; Dezotti, M.; Sant'Anna Jr., G. L.; *J. Hazard. Mater*. **2006**, *B137*, 178.
4. Malato, S.; Blanco, J.; Vidal, A.; Alarcón, D.; Maldonado, M. I.; Cáceres, J.; Gernjak, W.; *Sol. Energy* **2003**, *75*, 329.
5. Maniero, M. G.; Bila, D. M.; Dezotti, M.; *Sci. Total Environ*. **2008**, *407*, 105.
6. Wang, L.; Barrington, S.; Kim, J.-W.; *J. Environ. Manage*. **2007**, *83*, 191.
7. Rahman, M. M.; Al-Malack, M. H.; *Desalination* **2006**, *191*, 16.
8. El-Naas, M. H.; Al-Zuhair, S.; Al-Lobaney, A.; Makhlouf, S.; *J. Environ. Manage.* **2009**, *91*, 180.
9. Stepnowski, P.; Siedlecka, E. M.; Behrend, P.; Jastorff, B.; *Water Res.* **2002**, *36*, 2167.
10. Santos, M. R. G.; Goulart, M. O. F.; Tonholo, J.; Zanta, C. L. P. S.; *Chemosphere* **2006**, *64*, 393.
11. Yavuz, Y.; Koparal, A. S.; Öğütveren, Ü. B.; *Desalination* **2010**, *258*, 201.
12. Sun, Y.; Zhang, Y.; Quan, X.; *Sep. Purif. Technol*. **2008**, *62*, 565.
13. Bhargava, S. K.; Tardio, J.; Jani, H.; Akolekar, D. B.; Föger, K.; Hoang, M.; *Catal. Surv. Asia* **2007**, *11*, 70.
14. Prasad, J.; Tardio, J.; Jani, H.; Bhargava, S. K.; Akolekar, D. B.; Grocott, S. C.; *J. Hazard. Mater.* **2007**, *146*, 589.
15. Ismail, Z. Z.; Al-Hashimi, E. A.; *J. Clean. Prod.* **2011**, *19*, 197.
16. El-Salam, M. M.; El-Naggar, H. M.; *J. Clean. Prod.* **2010**, *18*, 1403.
17. Oliveira, K. D.; Cardoso, M.; Nicolato, R.; *Lat. Am. Appl. Res.* **2010**, *40*, 81.
18. De Feo, G.; Rizzo, L.; Belgiorno, V.; Meric, S.; *Int. J. Environ. Pol.* **2006**, *28*, 100.
19. Da Silva, C. R.; Maniero, M. G.; Rath, S.; Guimarães, J. R.; *J. Adv. Oxid. Technol.* 2**011**, *14*, 106.
20. Guimarães, J. R.; Santos, L. U.; Assalin, M.; Figueiredo, R. F.; *Rev. DAE* **2010**, *184*, 35.
21. American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF); *Standard Methods for Examination of Water and Wastewater*, 21th ed.; American Public Health Association: Washington D.C., 1998.
22. ASTM D1293: *Standard Test Methods for pH of Water*, American Society for Testing and Materials, Philadelphia, 1999.
23. Nogueira, R. F. P.; Oliveira, M. C.; Paterlini, W. C.; *Talanta* **2005**, *66*, 86.
24. Abramovic, B. F.; Banic, N. D.; Šojic, D. V.; *Chemosphere* **2010**, *81*, 114.
25. Ghodbane, H.; Hamdaoui, O.; *Chem. Eng. J.* **2010**, *160*, 226.
26. Silva, T. C. F.; Silva, C. M.; Reis, C.; Bellato, C. R.; Lucia, L. A.; *Ind. Eng. Chem. Res*. **2010**, *49*, 11214.
27. Daneshvar, N.; Rabbani, M.; Modirshahla, N.; Behnajady, M. A.; *Chemosphere* **2004**, *56*, 895.

28. De Souza, D. R. D.; Duarte, E. T. F. M.; Girardi, G. D. S.; Velani, V.; Machado, A. E. D. H.; Sattler, C.; Oliveira, L. D.; Miranda, J. A. D.; *J. Photochem. Photobiol., A* **2006**, *179*, 269.
29. Maciel, R.; Sant'Anna Jr., G. L.; Dezotti, M.; *Chemosphere* **2004**, *57*, 711.
30. Domènech, X.; Jardim, W. F.; Litter, M. I. *In Eliminación de Contaminantes por Fotocatálisis Heterogênea*; Blesa, M. A., ed.; Red CYTED VIII-G: Buenos Aires, Argentina, 2001.
31. Mota, A. L. N.; Albuquerque, L. F.; Beltrame, L. T. C.; Chiavone-Filho, O.; Machulek Jr., A.; Nascimento, C. A. O.; *Braz. J. Pet. Gas* **2008**, *2*, 122.
32. Padoley, K. V.; Mudliar, S. N.; Banerjee, S. K.; Deshmukh, S. C.; Pandey, R. A.; *Chem. Eng. J*. **2011**, *166*, 1.
33. Yang, M.; Hu, J.; Ito, K.; *Environ. Technol*. **1998**, *19*, 183.
34. Zang, Y.; Pagilla, K.; *Desalination* **2010**, *263*, 36.
35. Saritha, P.; Aparna, C.; Himabindu, V.; Anjaneyulu, Y.; *J. Hazard. Mater*. **2007**, *149*, 609.
36. Ghaly, M. Y.; Härtel, G.; Mayer, R.; Haseneder, R.; *Waste Manage*. **2001**, *21*, 41.
37. United States Environmental Protection Agency (US EPA); *Guidelines for Water Reuse*; US Agency for International Development: Washington D.C., September, 2004, http://www.ehproject.org/PDF/ehkm/water-reuse2004.pdf accessed in August 2012.
38. Oenning Jr., A.; Pawlowsky, U.; *Eng. Sanit. Ambient.* **2007**, *12*, 305.
39. Tchobanoglous, G.; Burton, F. L.; Stensel, H. D.; *Wastewater Engineering: Treatment and Reuse*, 4th ed.; Metcalf & Eddy: New York, 2003.

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