Treatment of petroleum refinery sourwater by advanced oxidation processes

Alessandra Coelho, Antonio V. Castro, Márcia Dezotti, G.L. Sant'Anna Jr. *

Chemical Engineering Program-COPPE, Federal University of Rio de Janeiro, P.O. Box 68502, CEP 21941-972 Rio de Janeiro, Brazil

Abstract

The performance of several oxidation processes to remove organic pollutants from sourwater was investigated. Sourwater is a specific stream of petroleum refineries, which contains slowly biodegradable compounds and toxic substances that impair the industrial biological wastewater treatment system. Preliminary experiments were conducted, using the following processes: H_2O_2, H_2O_2/UV, UV, photocatalysis, ozonation, Fenton and photo-Fenton. All processes, except Fenton and photo-Fenton, did not lead to satisfactory results, reducing at most 35% of the sourwater dissolved organic carbon (DOC). Thus, further experiments were performed with these two techniques to evaluate process conditions and organic matter removal kinetics. Batch experiments revealed that the Fenton reaction is very fast and reaches, in a few minutes, an ultimate DOC removal of 13–27%, due to the formation of iron complexes. Radiation for an additional period of 60 min can increase DOC removal up to 87%. Experiments were also conducted in a continuous mode, operating one 0.4 L Fenton stirred reactor and one 1.6 L photo-Fenton reactor in series. DOC removals above 75% were reached, when the reaction system was operated with hydraulic retention times (HRT) higher than 85 min. An empirical mathematical model was proposed to represent the DOC removal kinetics, allowing predicting process performance quite satisfactorily.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Sourwater; Petroleum refinery wastewaters; Fenton process; Photo-Fenton process

1. Introduction

Large amounts of water are used in the petroleum refinery activity and, consequently, significant volumes of wastewater are generated (0.4–1.6 times the volume of processed oil) [1]. Some of the industrial wastewater streams should be segregated and submitted to specific treatments, to avoid organic overloading or toxic impacts on the downstream wastewater biological treatment process [2,3]. Sourwater is an industrial stream that should be segregated and treated by combined processes because it presents complex chemical composition, containing emulsified oil, phenols, sulfides, mercaptans, ammonia, cyanides and other micropollutants. Despite its complex composition, sourwater may be considered a candidate stream for industrial reuse if submitted to efficient treatment processes.

Sourwater is produced when steam is injected in some of the refinery processing units to reduce hydrocarbon partial vapor pressures, allowing operation under less drastic temperature conditions. After separation at the top of the refinery towers, sourwater may be fed to a rectification tower to remove ammonia and hydrogen sulfide. Besides its pollution load, sourwater is a corrosive liquid. The amount of sourwater generated in a refinery depends on several factors, including process configuration and type and characteristics of the processed oil. Typical specific sourwater production in large refineries is comprised between 0.2 and 0.5 m^3 ton^{-1} of crude oil processed.

Works on sourwater treatment are scarce in the scientific literature. However some patents were proposed, dealing with oxidation by the Fenton process [4] and membrane process (reverse osmosis) [5].

Since, sourwater has a detrimental effect on the biological treatment process implanted in the petroleum refineries; physical–chemical techniques should be investigated to treat that stream. Sourwater presents the following general characteristics: absence of suspended solids, translucent aspect and moderate levels of oxidable pollutants. Such characteristics favor the utilization of advanced oxidation techniques to treat sourwater.

The first aim of this work was to investigate the performance of several oxidation processes (UV radiation, peroxidation, UV + peroxidation, ozonation, photocatalysis, Fenton and

---

* Corresponding author. Tel.: +55 21 25628342; fax: +55 21 2562 8300.
E-mail address: lippel@peq.coppe.ufrj.br (G.L. Sant'Anna Jr.).

Table 1
Sourwater average characteristics

Parameter	Range or average
COD ($mg\,L^{-1}$)	850–1020
DOC ($mg\,L^{-1}$)	300–440
BOD_5	570
Phenol ($mg\,L^{-1}$)	98–128
Ammonia ($mg\,L^{-1}$)	5.1–21.1
TSS ($mg\,L^{-1}$)	n.d.[a]
VSS ($mg\,L^{-1}$)	n.d.[a]
pH	8.0–8.2
Turbidity (NTU)	22–52
Sulfide ($mg\,L^{-1}$)	15–23
Toluene ($\mu g\,L^{-1}$)	1.1
Ethyl benzene ($\mu g\,L^{-1}$)	3.7
m,p-Xylene ($\mu g\,L^{-1}$)	15.4
o-Xylene ($\mu g\,L^{-1}$)	3.7
Oil and grease ($mg\,L^{-1}$)	12.7

[a] Non-detectable.

photo-Fenton) to remove dissolved organic content (DOC) of petroleum refinery sourwater. Since Fenton and photo-Fenton were the oxidation processes that led to the best results, they were further investigated in more detail in this work.

2. Materials and methods

2.1. Sourwater source and characteristics

Samples of the wastewater were collected in different days, when the petroleum refinery was operated under normal conditions, in sunny periods. Samples were transferred to the laboratory and stored under refrigeration (4 °C) until use. Sourwater samples come from a petroleum refinery, which has a nominal processing capacity of 5000 ton of oil per day. The characteristics of the sourwater used in the oxidation experiments are shown in Table 1. The wastewater presents high levels of phenols and sulfide and a moderate level of organic matter content.

2.2. Reagents and materials

Hydrogen peroxide was supplied by Merck (Rio de Janeiro, Brazil), at the concentration of 30% (v/v), and stored under refrigeration. The concentration of hydrogen peroxide was periodically determined and the results confirmed that the solution remained stable under the storage conditions. Iron sulfate (hep-
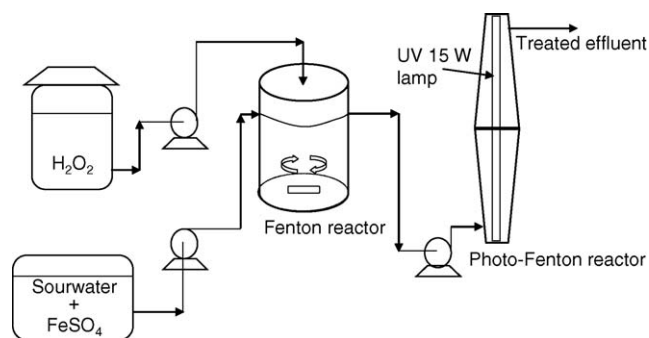

Fig. 1. Experimental set-up used in continuous oxidation experiments.

tahydrated) was supplied by Vetec (Rio de Janeiro, Brazil). In the radiated experiments two different lamps were used: 250 W UV light supplied by Phillips (batch experiments) and 15 W UV light (continuous experiments). The radiant flux in photo-Fenton experiments was measured using a calibrated radiometer (Cole Parmer, model VLX).

2.3. Experimental procedures

A first set of experiments was performed to access the potential of each oxidation technique to remove the organic matter content of sourwater. The preliminary experiments were carried out to evaluate the extent of DOC removal that could be attained, using drastic oxidation conditions (high reagents concentrations), as indicated in Table 2.

Oxidation experiments were further conducted in batch and continuous systems, using selected reagents concentrations. The experimental apparatus used in batch oxidation tests consisted of a small magnetically stirred reactor (100 mL). Under non-radiated conditions, the Fenton reaction was conducted for a given period of time (30 min). Then, the 250 W UV light (placed 12 cm above the water surface) was switched on, assuring a radiant flux of $5.5\,J\,m^{-2}\,s^{-1}$, and the photo-Fenton reaction was conducted for an additional period of 60 or 70 min. Hydrogen peroxide was employed at the concentration of $4\,g\,L^{-1}$, while different concentrations of $FeSO_4$ were tested (0.13, 0.20 and $0.40\,g\,L^{-1}$). Some batch experiments were also carried out under permanent radiation (photo-Fenton) during 90 min.

Fig. 1 shows the continuous reaction system, which consisted of two reactors in series. The first one was a stirred vessel (400 mL) where Fenton reaction occurred and the sec-

Table 2
Preliminary oxidation experiments conducted to evaluate the performance of several oxidation techniques: experimental conditions and corresponding DOC removals

Process	Experimental conditions	DOC removal (%)
UV	Batch reactor, volume = 100 mL, pH = 3, time of reaction 1 h, Hg vapor lamp (250 W), radiant flux = $5.5\,J\,m^{-2}\,s^{-1}$	20
H_2O_2	Batch reactor, volume = 100 mL, pH = 6.2, time of reaction 1 h, $[H_2O_2]_0 = 6\,g\,L^{-1}$	8
$UV + H_2O_2$	The same conditions as above, excluding pH value, which was fixed at 6.2	25
Ozonation	Batch reactor, volume = 1 L, pH = 8, reaction was extended until ozone consumption reached $1\,g\,L^{-1}$	35
Photocatalysis	Batch reactor, volume = 100 mL, suspended TiO_2 concentration of 0.2 g/L, time of reaction 1 h, Hg vapor lamp (250 W), radiant flux = $5.5\,J\,m^{-2}\,s^{-1}$	21
Fenton	Batch reactor, volume = 100 mL, reaction time of 1 h, $[H_2O_2]_0 = 15.4\,g\,L^{-1}$, $[FeSO_4]_0 = 1.1\,g\,L^{-1}$	55
Photo-Fenton	Batch reactor, volume = 100 mL, reaction time of 1 h, $[H_2O_2]_0 = 15.4\,g\,L^{-1}$, $[FeSO_4]_0 = 1.1\,g\,L^{-1}$, Hg vapor lamp (250 W), radiant flux = $5.5\,J\,m^{-2}\,s^{-1}$	83

Table 3
Preliminary Fenton and photo-Fenton experiments performed at different reagents concentrations—Fenton reaction lasted 30 min and UV radiation was further applied (photo-Fenton) during 60 min

$[H_2O_2]$ (g L^{-1})	$[FeSO_4]$ (g L^{-1})	DOC removal (%) Fenton	DOC removal (%) Photo-Fenton	Overall DOC removal (%)
8	0.8	34	82	88
4	0.4	26	76	82
4	0.2	24	79	84
2	0.2	21	68	75
2	0.1	17	62	69
1	0.1	10	64	68
1	0.2	14	64	69

ond one was a vertical rector (1600 mL), which contained a germicide lamp (15 W) along its axial shaft. The liquid flowed upwards, passing through the space between the lamp and the tube wall. The radiant flux was 60 J m^{-2} s^{-1}. Hydrogen peroxide was continuously added to the first reactor and iron sulfate was previously added to the stored influent. The amounts of hydrogen peroxide and iron sulfate added to the wastewater corresponded to 4 and 0.4 g L^{-1}, respectively. These values were selected based on results obtained in previous batch oxidation experiments. The overall hydraulic retention time in the reaction system varied in the range of 40–1200 min.

2.4. Analytical determinations

The organic matter content was expressed as dissolved organic carbon (DOC) and its determination was performed in a Shimadzu TOC analyzer, model 5000A. To follow organic matter removal in the oxidation experiments, DOC was used instead of COD, because the residual hydrogen peroxide interferes on COD determination. Oil and grease (O and G) was quantified, using the partitioning method with organic solvent (S-316, Horiba Instruments Industry) and the O and G analyzer (Horiba, model OCMA 350). Ammonia, phenols, sulfide, and turbidity were determined according to the standard methodology [6]. Benzene, toluene, ethyl benzene and xylene were determined by gas chromatography (Trace GC 2000, Thermo Finnigan), using OV-5 column (5% phenyl, 95% methyl, Ohio Valley Specialty Chemical), 30 m length, 0.53 mm internal diameter and 3 μm phase thickness.

3. Results and discussion

3.1. Preliminary oxidation experiments

The results obtained in preliminary tests are shown in Table 2. It may be observed that UV radiation contributed to improve the DOC removal and that Fenton and photo-Fenton processes were the most effective ones.

The effect of UV radiation was very significant when utilized together with Fenton reagents. This effect was somewhat expected because UV causes the photolysis of iron-organic complexes produced by the Fenton reactions [7,8].

Since the reagents concentrations used in the preliminary batch experiments were significantly high, further experiments were performed with Fenton and photo-Fenton processes in order to select more appropriated reaction conditions. The results obtained are shown in Table 3. Overall DOC removals higher than 80% could be achieved using H_2O_2 and $FeSO_4$ concentrations above 2 and 0.2 g L^{-1}, respectively. The effect of iron sulfate concentration showed to be significant and was further investigated (results shown in Section 3.4). It was observed that the oxidation could be conducted even at the original sample pH 8.0. The addition of hydrogen peroxide, even at small amounts, was enough to drop the pH value to 4.0, which is very adequate for Fenton and photo-Fenton processes.

3.2. Batch oxidation experiments

Similar experiments conducted in two steps (non-radiated plus radiated periods) or one step (permanent radiation) led to different DOC removals, 82% and 70%, respectively. Thus, permanent radiation did not contribute to improve process performance. In addition, permanent radiation for a 100 min period leads to higher energy consumption. Hence, the sequential oxidation procedure (Fenton plus photo-Fenton) was adopted and further investigated.

Fig. 2 shows a typical result of a batch oxidation experiment conducted with the reagents concentrations of 4 and 0.4 g L^{-1} (H_2O_2 and $FeSO_4$, respectively). The non-radiated (Fenton) and radiated periods lasted 30 and 70 min, respectively. It may be observed that the Fenton reaction reached very fast a plateau of
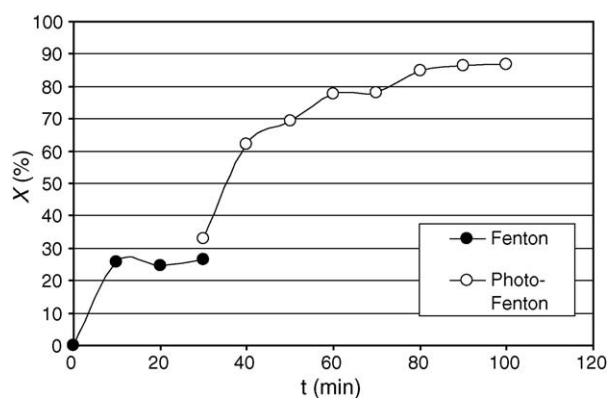

Fig. 2. Typical DOC removal (*X*) obtained during batch oxidation (Fenton and photo-Fenton processes). Experimental conditions: $[H_2O_2]_0 = 4$ g L^{-1}, $[FeSO_4]_0 = 0.4$ g L^{-1}.

Table 4
Summary of conditions and results obtained in continuous experiments

Influent DOC (mg L^{-1})—C_0	Fenton reactor influent DOC (mg L^{-1})—C_i	Photo-Fenton reactor effluent DOC (mg L^{-1})—C_e	HRT$_{FF}$ (min)	HRT (min)	Overall DOC removal (%)—X
300	225	157	35	45	0.48
345	260	79	48	60	0.77
352	265	77	72	90	0.78
345	260	52	96	120	0.85
440	330	70	240	300	0.84
309	230	19	960	1,200	0.94

DOC removal ($X = 0.27$), as a consequence of iron-complexes formation [9,10]. The utilization of UV radiation assured the reaction progress until an ultimate plateau was attained (87%). During the reaction, low molecular mass compounds, resistant to the oxidation, could be formed, like acetic and formic acid [11]. Thus, a residual amount of organic matter would be present in the medium even after 100 min of reaction. A mathematical model was proposed to represent the variation of DOC removal with reaction time and it will be further commented in this text, when the effect of iron sulfate concentration will be also discussed.

3.3. Continuous oxidation experiments

The increase of DOC removal along the time of operation of the two reactors in series (Fenton and photo-Fenton reactors), for a typical experiment, is shown in Fig. 3. In this case, the transient operation lasted 130 min, approximately. For all the experiments performed the transient period lasted for a period of time lower than twofold the overall hydraulic retention time (HRT). After that period of time the steady-state condition was reached (plateau), allowing the determination of the DOC removal (X) attained in the continuous experiment. The overall results obtained for different HRT values are shown in Table 4. As expected, the increase on hydraulic retention time (HRT) led to a higher DOC removal. DOC removals higher than 80% were attained (steady-state values) when HRT was higher than 120 min.
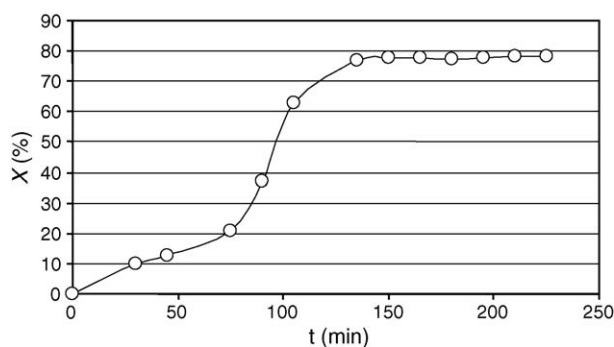

Fig. 3. Increase of DOC removal (X) vs. time of operation:–transient and steady-state periods in a typical continuous experiment (Fenton and photo-Fenton processes). Experimental conditions: $[H_2O_2]_0 = 4$ g L^{-1}, $[FeSO_4]_0 = 0.4$ g L^{-1}, pH 8 (original sourwater pH), HRT = 90 min^{-1}.

It is difficult to compare results obtained in batch and continuous tests, even when the same concentrations of reagents were employed, because the two reaction systems were significantly different (flow or mixing conditions and level of radiation).

Removal of oil and grease varied in the range of 52–73%, as shown in Table 5. Low levels of oil and grease remained in the treated effluent (<5 mg L^{-1}) when HRT was higher than 60 min. The pollutants classified as BTEX (benzene, toluene, ethyl benzene and xylene) were removed to non-detectable levels in all the experiments performed with different HRT values. The original contents of these pollutants in the sourwater were already shown in Table 2. Benzene was not detected in the sourwater neither in the wastewater from the oxidation process.

Despite the promising results obtained, combining Fenton and photo-Fenton processes, the amount of reagents used was high. This could render uneconomical the application of such process. The analysis of published papers on this field shows a large variation on reagents consumption [3,10,12]. The amount of oxidable substances present in the wastewater is a fundamental factor, which determines the necessary supply of reagents. However, an appropriate design of the photo-Fenton reactor and the utilization of a more efficient radiation system would contribute to improve process performance and, consequently, reduce reagents consumption.

3.4. Mathematical modelling—batch experiments

The development of a rigorous mathematical model should take into account the large number of chemical reactions involved on Fenton and photo-Fenton processes. Certainly such development would be a challenge task and probably will lead to a very complex model containing a large number of parameters. An empirical approach may be also considered since it can lead to simple equations which are useful to estimate process performance. First order or pseudo-first order models have

Table 5
Oil and grease removal attained in the continuous oxidation experiments

HRT (min)	O and G (mg L^{-1}) treated effluent	O and G removal (%)
300	3.8	70
120	4.3	66
90	3.4	73
60	6.0	52
45	5.7	55

Table 6
Kinetic model parameters determined in batch experiments carried out with different ferrous sulfate concentrations and $4\,g\,L^{-1}$ of hydrogen peroxide

FeSO$_4$ (g L^{-1})	X_F	X_{FF}	k_F (min^{-1})	k_{FF} (min^{-1})
0.13	0.13	0.60	0.08	0.045
0.20	0.20	0.62	0.17	0.059
0.40	0.27	0.60	0.17	0.057

Fig. 4. Predicted (X_{pred}) and experimental (X_{exp}) DOC removal attained in batch experiments conducted with, $[H_2O_2]_0 = 4\,g\,L^{-1}$ and FeSO$_4$ concentrations of $0.13\,g\,L^{-1}$ ($\triangle$), $0.20\,g\,L^{-1}$ ($\diamond$), $0.40\,g\,L^{-1}$ ($\bigcirc$).

been proposed to describe the oxidation of 2,4 dinitro-toluene by photo-Fenton process [13] and nitrobenzene and nitrophenols by the Fenton-like process [14].

In the present work, an empirical model was proposed to describe the progress of the oxidation process, taking into account the following assumptions: the oxidation of the dissolved organic matter (DOC) follows a first order kinetics; the wastewater presents a residual (non-oxidable) content of DOC. Thus, Eq. (1) represents the rate of organic matter oxidation:

$$\frac{dC}{dt} = -k(C - C_r) \tag{1}$$

where C is the DOC content of the wastewater at any time; k is the reaction constant, which corresponds to k_F and k_{FF} for Fenton and photo-Fenton processes, respectively. C_r is a limit or residual concentration, which corresponds to C_{rf} and C_{rff} for Fenton and photo-Fenton processes, respectively. The parameter C_{rf} may be understood as a limit concentration, because after a given period of time the Fenton reaction progress is stopped despite the presence of oxidable substances in the medium. The parameter C_{rff} corresponds to the organic matter which is not anymore oxidable by Fenton and photo-Fenton processes.

Taking into account the definition of conversion or organic matter removal (X) (Eq. (2)) and the residual DOC contents C_{rf} and C_{rff}, after some algebric manipulations, the final model Eq. (3) can be obtained:

$$X = \frac{C_0 - C}{C_0} \tag{2}$$

$$X = X_F(1 - e^{-k_F t}) + X_{FF}(1 - e^{-k_{FF}(t - t_c)}) \tag{3}$$

where X_F is the ultimate DOC removal attained in the Fenton process, X_{FF} the maximum increment on DOC removal attained in the photo-Fenton process; t_c is the time when the radiation period starts.

Values of X_F and X_{FF} were obtained by visual inspection of the experimental reaction progress curves, like that shown in Fig. 2. The determination of the parameters k_F and k_{FF} was made, using the mathematical software Mathcad, and further the software Statistica 6.0. The values of these parameters are shown in Table 6 for the experiments carried out with three different ferrous sulfate concentrations.

Iron sulfate concentration affected the maximum removal attained in the Fenton process (X_F) as shown in Table 6. X_F values dropped when iron sulfate concentration decreased from 0.4 to $0.13\,g\,L^{-1}$. The operation of the Fenton process using this lowest concentration did not allow extending DOC removal beyond 13% because the reaction progress was hindered by the low availability of iron ions. The kinetic parameters k_F and k_{FF}
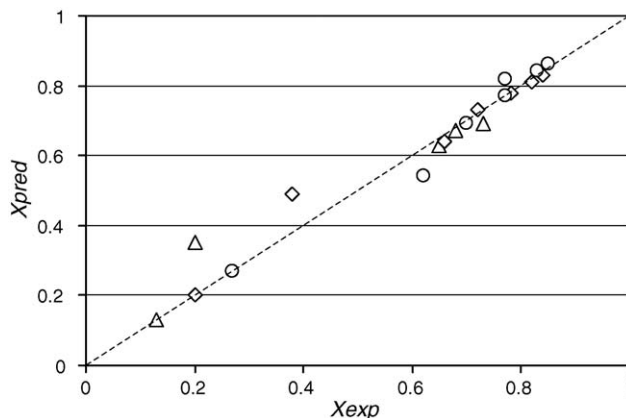
were low (0.080 and $0.045\,min^{-1}$, respectively) for this particular assay. The results obtained with iron sulfate concentrations of 0.2 and $0.4\,g\,L^{-1}$ were very similar and the model parameter values were very close (Table 6).

Fig. 4 shows that the model (Eq. (3) with the parameters shown in Table 6) was able to predict the experimental conversion attained in batch experiments conducted with different iron sulfate concentrations, since predicted and experimental values of X were very close (angular and regression coefficients of 0.999 and 0.9501, respectively).

3.5. Mathematical modelling—continuous experiments

The Fenton reaction is fast, as shown in Fig. 2, and the ultimate DOC removal is attained in a few minutes. This behavior was also observed in the continuous oxidation experiments, since an average DOC removal of 25% ($X_F = 0.25$) was attained in all the experiments, even those conducted with low HRT values (10–18 min). Thus, a mass balance applied to the photo-Fenton reactor, supposing completely mixed behavior, leads to the following equation:

$$C_i - C_e = HRT_{FF} k_{FF}(C_e - C_{rff}) \tag{4}$$

where C_i is the DOC concentration in the influent of the photo-Fenton reactor; C_e the DOC concentration at the exit of photo-Fenton reactor; HRT_{FF} is the hydraulic retention time in the photo-Fenton reactor.

For the system shown in Fig. 2, DOC removal (X) is defined by Eq. (5).

$$X = \frac{(C_0 - C_e)}{C_0} \tag{5}$$

where C_0 is the DOC content of the process influent; C_e is the DOC content of the exit stream, as previously defined.

Since the removal attained in the Fenton reactor was 0.25, for all the experiments $C_i = 0.75 C_0$.

The maximum removal attainable in the process is represented by X_M, where:

$$X_M = \frac{C_0 - C_{rff}}{C_0} \qquad (6)$$

Thus, taking into account the definitions given in Eqs. (5) and (6), Eq. (4) may be re-arranged, leading to:

$$X - 0.25 = HRT_{FF} k_{FF}(X_M - X) \qquad (7)$$

The value of X_M can be obtained from the experimental data shown in Table 4, by plotting $(1 - X)$ versus the reciprocal of HRT. Thus, the value $X_M = 0.956$ can be obtained. Substituting this value in Eq. (7) results:

$$X - 0.25 = HRT_{FF} k_{FF}(0.956 - X) \qquad (8)$$

By plotting the terms of Eq. (8) containing X versus HRT_{FF}, the constant k_{FF} can be obtained, being equal to $0.044\,min^{-1}$ (correlation coefficient $R^2 = 0.974$). The value of this rate constant is lower than that obtained in the corresponding batch experiment ($0.057\,min^{-1}$). However, it should be remarked that the conditions of the continuous photo-Fenton reaction system were different from those employed in the batch experiment (radiation intensity, reactor shape, mixing characteristics).

The experimental and the predicted (Eq. (8), $k_{FF} = 0.044\,min^{-1}$) DOC removal values are shown in Fig. 5. It can be observed that the model was able to predict the process performance when moderate or high removal percentages were achieved ($X_{exp} > 0.7$), but failed to predict the lower experimental DOC removal ($X_{exp} = 0.48$).

If the flow in the photo-Fenton reactor would be represented by the plug flow model (PFR), Eq. (9) would be obtained from the mass balance, the kinetic model and Eqs. (5) and (6).

Thus, the assumption that the PFR model may be applied to the photo-Fenton reactor leads to:

$$\ln\left[\frac{X_M - X}{X_M - 0.25}\right] = (-k_{FF} HRT_{FF}) \qquad (9)$$

An adequate plotting of this equation would lead to the value of k_{FF}. However, the resulting linear relationship presents a low
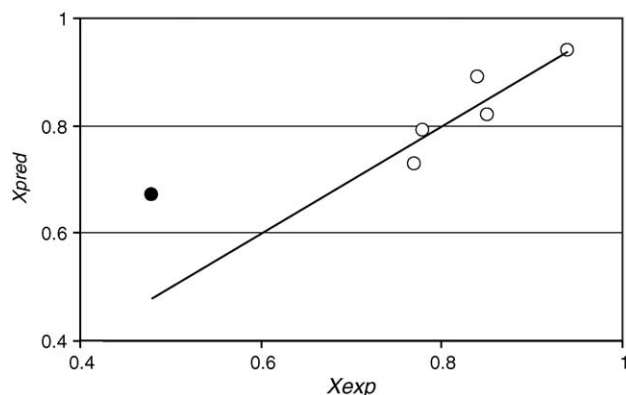
correlation coefficient ($R^2 = 0.64$). The utilization of the k_{FF} value, thus obtained, lead to a non-satisfactory estimation of the overall conversion X (results not shown), in contrast with the results obtained when the flow in the photo-Fenton reactor was assumed to be completely mixed.

4. Conclusions

The radiated processes showed to be more effective to remove the organic matter found in the sourwater. Among the tested processes, Fenton and photo-Fenton led to the best results.

In batch experiments, the maximum DOC removal attained was 87%, using 4 and $0.4\,g\,L^{-1}$ of hydrogen peroxide and iron sulfate, respectively. The Fenton reaction was very fast, but low levels of DOC removal were reached (13–27%), depending on the iron sulfate concentration used. The photo-Fenton process, however, was able to improve the DOC removal in a short period of time (50 min), leading to high overall process performances.

A high DOC removal (94%) was attained in the continuous operation of the combined processes (Fenton and photo-Fenton), when the system was operated with HRT of 1200 min. However, appreciable DOC removals (higher than 75%) were also attained with HRT values in the range of 60–120 min.

The kinetic model adopted was able to predict the conversion attained in batch and continuous experiments, in the latter case, especially for DOC removals higher than 70%.

Finally, it can be concluded that the combination of Fenton and photo-Fenton processes was effective for DOC and specific pollutants removal from sourwater. These promising results, however, should be further optimized to reduce reagents concentrations, keeping process effectiveness.

Fig. 5. Experimental and predicted values of DOC removal obtained in the continuous oxidation experiments: $X_{exp} > 0.7$ (○); $X_{exp} < 0.5$ (●). For values of X_{exp} higher than 0.7 the angular coefficient of the solid straight line is 0.998, the correlation coefficient is $R^2 = 0.814$.

References

[1] Fica-Piras, P., Refinery Effluent Nitrification Studies in Triphasic Bioreactors, DSc Thesis (in Portuguese), Federal University of Rio de Janeiro, 2000.
[2] EPA. Sector Notebook Project, Petroleum Refinery, September 1995.
[3] N.S.S. Martínez, J.F. Fernández, X.F. Segura, A.F. Sánchez, Pre-oxidation of an extremely polluted industrial wastewater by the Fenton's reagent, J. Hazard. Mater. B101 (2003) 315–322.
[4] Solvay Interox Inc., Hydrogen Peroxide. Controlling Reduced Sulfur Compounds, US Patent 5,621,097, 2001.
[5] Hydrometrics, Treatment of Sour Water at a Petroleum Refinery, US Patent 5,925,255, 2002.
[6] APHA, AWWA, WEF Standard Methods for Examination of Water and Wastewater, 20th ed., WPCF, New York, 1998.
[7] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today 53 (1999) 51–59.
[8] İ. Arslan, A. Balcioğlu, Oxidative treatment of simulated dye house effluent by UV and near-UV light, Chemosphere 39 (15) (1999) 2767–2783.
[9] M. Kitis, C.D. Adams, G.T. Daigger, The effects of Fenton's reagent pretreatment on the biodegradability of nonionic surfactants, Water Res. 33 (1999) 2561–2568.
[10] S. Esplugas, J. Gimenez, S. Contreras, E. Pascual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.

[11] E. Chamarro, A. Marco, S. Esplugas, Use of Fenton reagent to improve organic chemical biodegradability, Water Res. 35 (4) (2001) 1047–1051.

[12] C. Philippopoulos, S. Poulopoulos, Photo-assisted oxidation of an oily wastewater using hydrogen peroxide, J. Hazard. Mater. B98 (2003) 201–210.

[13] M.S. Celin, M. Pandit, J. Kapoor, R. Sharma, Studies on photo-degradation of 2,4-dinitro-toluene in aqueous phase, Chemosphere 53 (2003) 63–69.

[14] M.L. Rodriguez, V. Timokhin, S. Contreras, E. Chamarro, S. Esplugas, Rate equation for the degradation of nitrobenzene by Fenton-like reagent, Adv. Environ. Res. 7 (2003) 583–595.