

Promoted wet air oxidation of polynuclear aromatic hydrocarbons

F. Javier Rivas*, Ruth García, Juan F. García-Araya, Olga Gimeno

*Departamento de Ingeniería Química y Química Física, Edificio José Luis Sotelo, Facultad de Ciencias,
Universidad de Extremadura, Av. Elvas S/N, 06071 Badajoz, Spain*

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Abstract

The treatment of an aqueous solution of four polycyclic aromatic hydrocarbons, namely acenaphthene, phenanthrene, anthracene and fluoranthene, under moderate conditions of temperature and pressure has been conducted in the presence and absence of free radical promoters (hydrogen peroxide or potassium monopersulfate). With no addition of promoters, the process achieves PAH conversion values in the range 80–100% at 190 °C and 50 bars of air pressure (80 min of reaction). Similar results are obtained in the presence of hydrogen peroxide, however, in this case, the time required is just 60 min with a sharp decrease in PAH concentration in the first 10–20 min. Additionally, temperature can be lowered to values in the range 100–150 °C. If potassium monopersulfate is used instead of hydrogen peroxide, an analogous behaviour is experienced, in the latter case, temperatures above 120 °C lead to an inhibition of anthracene oxidation, likely due to ineffective decomposition of the monopersulfate molecule. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals naturally occurring in coal, crude oil and gasoline. Additionally, PAHs can appear in products derived from fossil fuels, such as coal-tar pitch, creosote and asphalt, and can also be released into the environment during the incomplete burning of fossil fuels and garbage [1]. Given the hydrophobic nature of PAHs (especially high molecular weight PAHs), these compounds tend to be adsorbed onto suspended solid particulates and sediments. PAH contaminated soil remediation technologies include two different processes: direct PAHs removal with no extraction or, alternatively, PAHs can be first extracted from soils and further treated in a fluid phase. Thus, for instance, gaseous ozone can be injected into contaminated soils with no need of extraction [2] or, contrarily, an organic or inorganic extracting agent can be used previously to remove PAHs from soils and thereafter the solvent is regenerated by oxidation of organics or adsorption onto a suitable adsorbent [3].

One of the technologies that can be used to simultaneously extract and oxidise organics from soils is the subcritical

wet air oxidation (WAO) under moderately elevated temperatures (150–300 °C) and pressures (30–200 bars). The process is normally performed in the presence of water and an oxygen containing gas as the oxidising agent, although other possibilities include the use of inorganic peroxides (promoted wet air oxidation). Several works have detailed the results of applying the WAO technology to polluted soils [4–8], however, the efficiency of WAO in the remediation of contaminated soils depends not only on the extraction capability but also on its potential to oxidise the target contaminants. In this sense, most of the literature has reported the PAHs removal level attained in the specific soils treated with none or little attention paid to the oxidation degree and kinetics occurring in the water phase. The present study is focused on the fate of four selected PAHs under WAO conditions in the presence and absence of oxygen and with the addition of free radical promoters, for instance a hydroxyl radical promoter (hydrogen peroxide) and a sulfate radical promoter (peroxymonosulfate).

2. Experimental

Wet air and promoted (either H₂O₂ or OXONE®) oxidation experiments were carried out in a PARR stainless steel autoclave of 600 mL of capacity. A titanium vessel was placed inside the reactor to avoid corrosion of the reactor walls. The rest of

* Corresponding author. Tel.: +34 924 289300x6951; fax: +34 924 289385.
E-mail address: fjriv@unex.es (F.J. Rivas).

components inside the reactor were kept in 316 SS. The experimental set-up consisted basically of the following components: sampling port equipped with a heat exchanger to cool down samples, injection port, meant to inject the promoter after reaching the working operating conditions, a magnetic system to agitate the reaction mixture and finally the corresponding pressure and temperature sensors. Reaction temperature was kept constant by a digital PI controller. The operating procedure was as follows: 325 or 350 mL of PAH saturated water were placed inside the reactor and pressurized to 5 bars with air (or nitrogen). Thereafter, the heating system was switched on to reach the desired operating temperature. Once the temperature achieved the set point, the reactor was finally air (or nitrogen)-pressurized to the working pressure and this was taken as time zero. When a promoter was added, a 25 mL solution of a predetermined concentration was injected immediately after reaching the operating temperature. Steadily and after flushing of the injection port, 2 mL of sample were withdrawn from the reactor to analyse the remaining PAH concentration. Further details of the experimental setup can be found elsewhere [9].

Acenaphthene (Ac), phenanthrene (Ph), anthracene (An) and fluoranthene (Fl) (Sigma–Aldrich) were used as received. Saturated solutions were obtained by vigorous stirring of an excess of PAHs in MilliQ ultrapure water in the dark. After 3 days the non-dissolved fraction of PAHs was removed from solution by consecutive filtrations on Schleicher & Schuell 589³, 2° filtration paper and 0.47 mm diameter Millipore membranes (MF Millipore 0.45 μm). Hydrogen peroxide and OXONE[®] (2KHSO₅·KHSO₄·K₂SO₄) were purchased from Aldrich and used as received. OXONE[®] is a double potassium salt being the active ingredient the peroxymonosulfate, commonly known as monopersulfate. It derives from the peroxymonosulfuric acid H₂SO₅ (also known as Caro's acid, $\text{p}K_1 = \infty$, $\text{p}K_2 = 9.4$) whose structure is a tetrahedron with a S atom in the centre surrounded by a perhydroxyl group and two oxygen atoms.

Aqueous PAHs were analysed by injecting 25 μL of a sample into a HPLC system (Rheodyne injector, 1050 Hewlett Packard pump, 1046A, Alltech Prevail C18 column (4.6 mm \times 150 mm), Hewlett Packard fluorescence detector, Chromjet Spectra Physics integrator) in isocratic mode using an acetonitrile–water mixture 70:30 (v/v) as mobile phase.

3. Results and discussion

3.1. Wet air oxidation experiments

3.1.1. Inert atmosphere

Although in most of cases the absence of oxygen in WAO processes avoids the elimination of organic contaminants, the literature reports several examples in which the hydrolysis or other non-oxidising processes (i.e. isomer transformation) might take place to a significant extent [10,11]. Consequently, due to the aforementioned non-oxidising reactions, in this work it was decided to check for the possibility of PAH removal under typical WAO conditions in the absence of oxygen. For this purpose, once the reactor was filled with the PAH solution, it was thereafter purged with nitrogen for 60 min, previous to the heating and

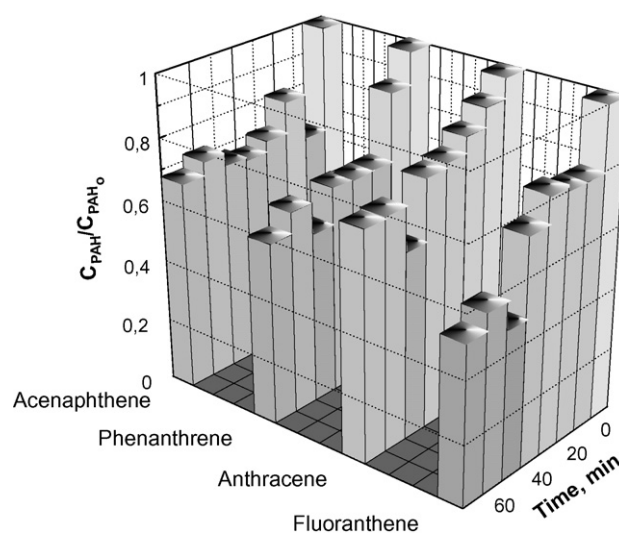


Fig. 1. Wet nitrogen treatment of PAHs. Experimental conditions: $V = 0.350 \text{ L}$, $T = 180^\circ \text{C}$, $P_T = 16 \text{ bars}$, $\text{pH} = 6.0$, $C_{\text{Ac}_0} = 1.20 \text{ ppm}$, $C_{\text{Ph}_0} = 0.26 \text{ ppm}$, $C_{\text{An}_0} = 5.77 \times 10^{-3} \text{ ppm}$, $C_{\text{Fl}_0} = 1.86 \times 10^{-2} \text{ ppm}$.

pressurising stages. Fig. 1 shows the results obtained for a run conducted at 180°C and 16 bars of total pressure. As observed, the different PAHs tested partially disappear after 70 min of reaction. Thus an average removal of approximately 30, 35, 25 and 50% for acenaphthene, phenanthrene, anthracene and fluoranthene was experienced, respectively. Since adsorption of PAHs to the reactor walls is unlikely at this temperature, it seems that the hydrocarbons have suffered some type of hydrolysis reaction. In this sense, hydrolysis of pyrene at 300°C has been reported by detecting the presence of 2-methyl-pyrene, 1,3-dimethyl-pyrene, 1-pyrene-carboxaldehyde and some phenol derivatives [12].

3.1.2. Oxygen containing atmosphere

The next step in this study was to assess the effect of oxygen presence at high temperature and pressures. The most important parameter in WAO processes is temperature; accordingly, the influence of this parameter was checked in the interval $170\text{--}200^\circ \text{C}$. Fig. 2 illustrates the results obtained. The presence of oxygen significantly enhances the conversion of PAHs. PAH removal even starts in the heating period, which takes approximately 40–50 min (see embedded figure for the 170°C run). Broadly speaking, it can be inferred a positive effect of temperature. After 70 min of treatment, PAH conversion values are located in the interval 45–60% at 170°C , while if temperature is raised to 180 or 190°C , the conversion range increases to values in the interval 80–100%. In terms of mol of PAH reacted per unit of time, acenaphthene seems to be the most reactive hydrocarbon. It is noticeable the considerable elimination of this PAH in the heating period when the starting temperature is 190°C . In any case, at the latter temperature the rest of PAHs also suffer a significant 40% depletion in the aforementioned heating period if compared to the 10% observed at 170°C . Reactivity order, under the operating conditions investigated, follows the order: $\text{Ac} > \text{Ph} > \text{Fl} > \text{An}$. This order coincides with the solubility sequence. Likely, a more accurate analysis

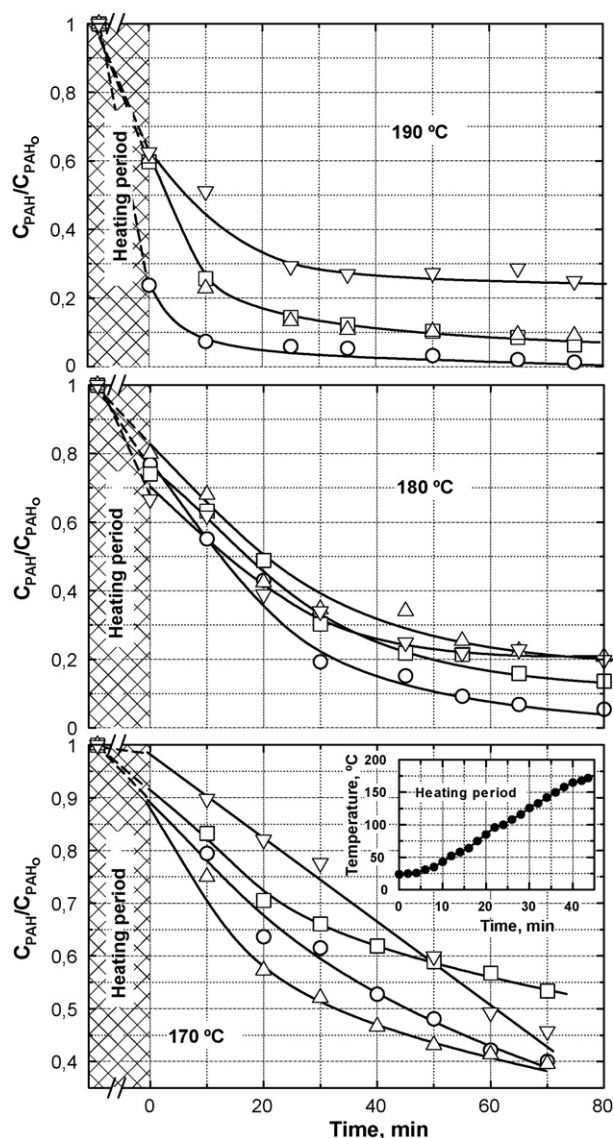
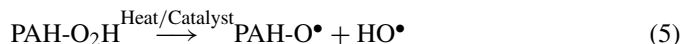
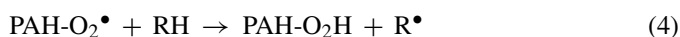
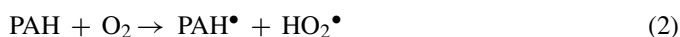
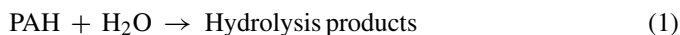


Fig. 2. Wet air oxidation treatment of PAHs. *Experimental conditions:* $V=0.350$ L, $P_T=50$ bars, pH 6.0. $C_{Ac_0} = 1.5$ ppm, $C_{Ph_0} = 0.27$ ppm, $C_{An_0} = 8 \times 10^{-3}$ ppm, $C_{Fl_0} = 6 \times 10^{-2}$ ppm (average values). ○, Acenaphthene; □, phenanthrene; △, anthracene; ∇, fluoranthene.

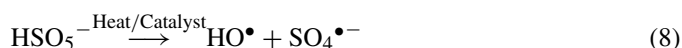
of the reactivity should have been conducted by starting the experiments with the same initial PAH concentration for each organic, however, the methodology followed to prepare the original aqueous solutions impedes the uniformity in PAHs initial concentration.

Commonly, the mechanism of organics oxidation in WAO processes is intimately related to the generation of radical species, either inorganic and/or organic radicals [13]. The following general stages can proceed:



Reactions ((1)–(6)) constitute an oversimplified scheme of the actual number of reactions occurring in the WAO process, nevertheless, since reaction (2) is normally quite slow, they highlight the importance of radicals to achieve acceptable oxidation rates in WAO systems.

As a consequence, it was decided to operate the system under less extreme conditions of temperature and pressure by adding a suitable radical promoter. Hydrogen peroxide and monopersulfate were chosen as effective generators of HO^\bullet and $\text{SO}_4^{\bullet-}$, respectively [9]:



3.2. Wet promoted oxidation

3.2.1. Hydrogen peroxide promoted wet air oxidation

3.2.1.1. Influence of temperature. As described previously in the bibliography [14], hydrogen peroxide might decompose to free active radicals provided that temperature is sufficiently high and/or a suitable catalyst is added into the reaction media. In the present study some experiments were conducted at different temperatures in the range 100–150 °C (well below the normal temperatures used in non-promoted wet air oxidation processes) after addition of a pre-determined initial amount of hydrogen peroxide. As illustrated in Fig. 3, a value of temperature of just 100 °C in the presence of 0.01 M of hydrogen peroxide is enough to efficiently oxidise the PAHs dissolved in the aqueous matrix. With the exception of the run conducted at 100 °C, the conversion of the different PAHs with time follows the order: $\text{Ac} > \text{Ph} \approx \text{An} > \text{Fl}$.

The curves represented in Fig. 3 show an initial fast period of reaction followed by a second stage in which PAHs removal rate is slowed down. Thus, a plot of the depletion rate of individual PAHs versus normalized PAHs concentration leads to straight lines of intercept different of the origin (see embedded plots in Fig. 3). The previous plot suggests that the kinetics of the process can be well described by a first order differential equation of the type:

$$\tau \frac{dC_{\text{PAH}}}{dt} + C_{\text{PAH}} = K \quad (9)$$

where τ is a parameter related to the rate of the oxidation process and K is a constant indicative of the extension of the reaction at long times, i.e. the conversion percentage at high reaction times is: $(1 - K/C_0) \times 100$ (%).

Solving (9) analytically by the integrating factor finally yields:

$$C_{\text{PAH}} = C_{\text{PAH}_0} \exp\left(-\frac{t}{\tau}\right) + K \left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \quad (10)$$

Table 1 shows the results obtained after fitting expression (10) to experimental data by the KYPLOTT v13 spreadsheet.

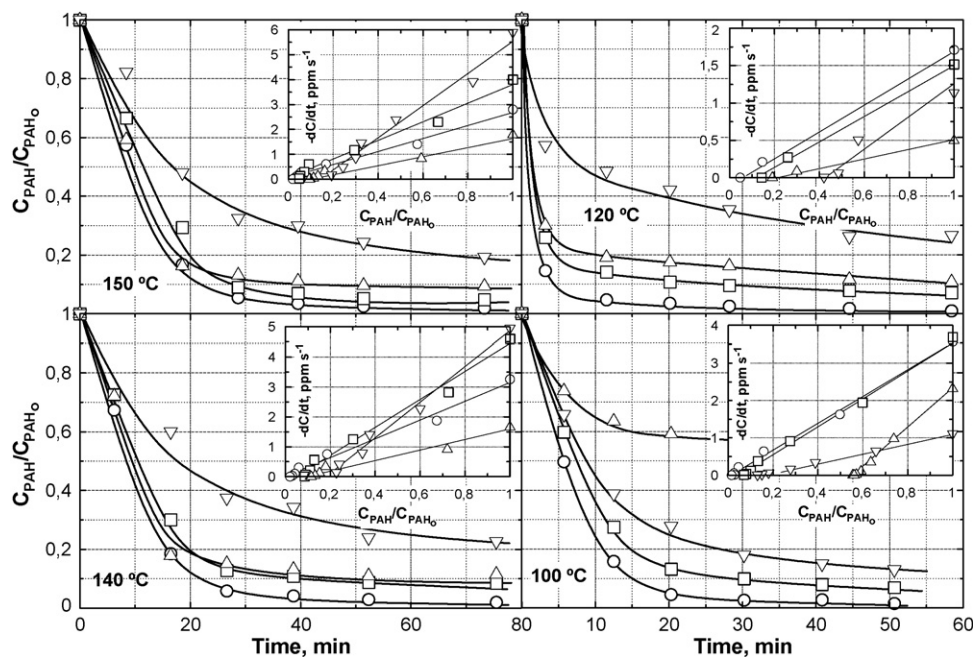


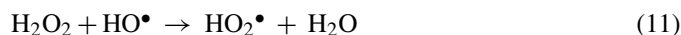
Fig. 3. Wet peroxide oxidation treatment of PAHs. *Experimental conditions:* $V=0.350$ L, $P_T=50$ bars, pH 6.0, $C_{H_2O_2}=0.01$ M, $C_{Ac_0}=1.86 \pm 0.3$ ppm, $C_{Ph_0}=0.29 \pm 0.09$ ppm, $C_{An_0}=8.2 \pm 4.7 \times 10^{-3}$ ppm, $C_{Fl_0}=7.2 \pm 2.0 \times 10^{-2}$ ppm (average values). Initial concentration of PAHs are detailed in Table 1. \circ , Acenaphthene; \square , phenanthrene; \triangle , anthracene; ∇ , fluoranthene.

When deviation variables are used, τ represents the time taken by the process to reach the 63% of the final response (conversion). Similarly in this case, the lower the τ value the faster the oxidation process. As observed from Table 1, it seems that 120 °C is, under the operating conditions investigated, the optimum working temperature. Values below 120 °C involve a slower hydrogen peroxide decomposition, while higher temperatures implicate a higher fraction of inefficient H_2O_2 decomposition to oxygen and water [15]. The ratio K/C_0 does not offer a clear trend. However, if initial PAHs concentration and temperature effects are simultaneously analysed, a simplistic linear equation relating the three parameters suggests a positive effect of temperature on K/C_0 and negative influence of the initial organic concentration.

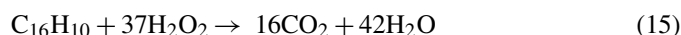
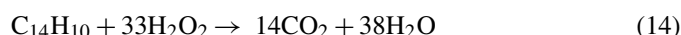
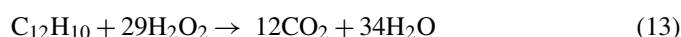
3.2.1.2. Influence of hydrogen peroxide initial concentration.

Hydrogen peroxide concentration exerts two opposite effects in the global PAHs conversion. On one hand, an increase of H_2O_2

logically should lead to a higher HO^\bullet production and hence, to a faster PAH removal. However, on another hand, an excess of hydrogen peroxide may act as a free radical scavenger according to:



In the previous experimental series, hydrogen peroxide has been used in relatively high excess according to:



For instance, the experiment carried out at 150 °C was conducted with a roughly 20-fold excess of the stoichiometric hydrogen peroxide amount needed. Similar figures can be

Table 1
Wet peroxide oxidation treatment of PAHs

T (°C)	Acenaphthene			Phenanthrene			Anthracene			Fluoranthene		
	C_{Ac_0} (ppm)	τ (s)	K/C_0 (%)	C_{Ph_0} (ppm)	τ (s)	K/C_0 (%)	C_{An_0} (ppm)	τ (s)	K/C_0 (%)	C_{Fl_0} (ppm)	τ (s)	K/C_0 (%)
100	1.57	436	0.7	0.21	537	5.9	2.11×10^{-2}	397	56.4	8.20×10^{-2}	632	13.2
120	1.61	92	2.6	0.19	112	9.8	6.51×10^{-3}	111	15.0	4.12×10^{-2}	237	34.8
120 ^a	1.21	183	3.5	0.18	275	17.1	7.65×10^{-3}	275	18.1	6.49×10^{-2}	280	41.4
120 ^b	1.06	155	3.5	0.15	250	23.2	6.00×10^{-3}	250	23.4	4.68×10^{-2}	350	60.3
140	2.21	676	0.05	0.37	763	5.8	1.14×10^{-2}	625	8.9	7.76×10^{-2}	1269	18.9
150	2.03	730	0.5	0.37	909	0.5	1.27×10^{-2}	658	7.3	8.59×10^{-2}	1230	15.5

Parameter fitting of individual PAHs to Eq. (10). *Experimental conditions:* $V=0.350$ L, $P_T=50$ bars, pH 6.0, $C_{H_2O_2}=0.01$ M.

^a $C_{H_2O_2}=0.005$ M.

^b $C_{H_2O_2}=0.02$ M.

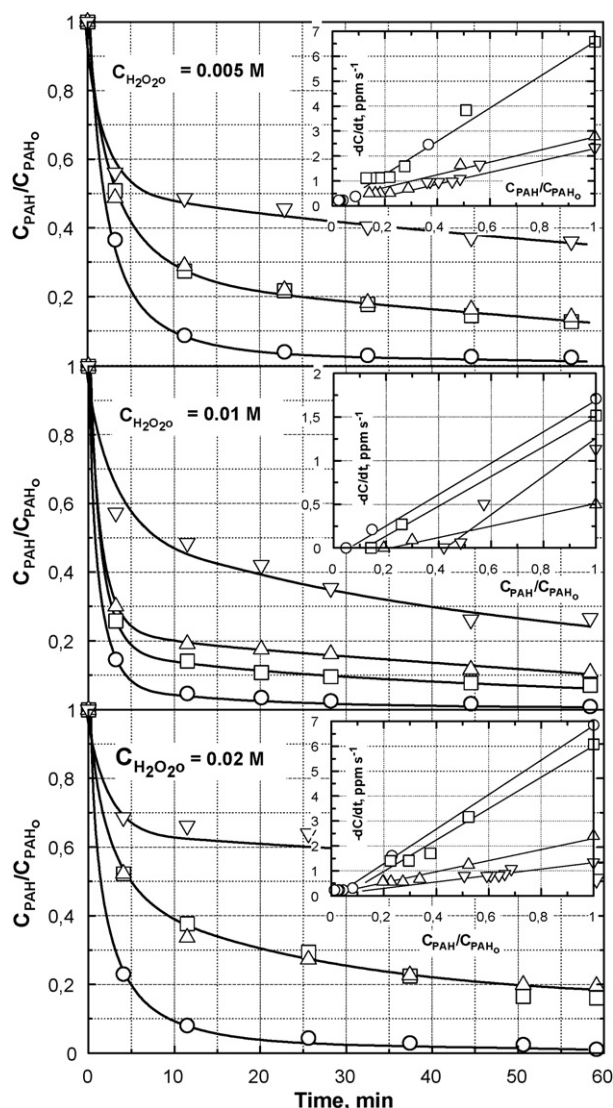


Fig. 4. Wet peroxide oxidation treatment of PAHs. *Experimental conditions:* $V=0.350$ L, $P_T=50$ bars, pH 6.0, $C_{AC_0}=1.29 \pm 0.32$ ppm, $C_{Ph_0}=0.17 \pm 0.02$ ppm, $C_{An_0}=6.72 \pm 0.95 \times 10^{-3}$ ppm, $C_{Fl_0}=5.09 \pm 1.40 \times 10^{-2}$ ppm (average values). Initial concentration of PAHs are detailed in Table 1. ○, Acenaphthene; □, phenanthrene; △, anthracene; ▽, fluoranthene.

calculated for the rest of experiments conducted at different temperatures.

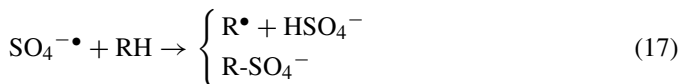
To assess the possibility of H_2O_2 being used at optimum conditions, two more experiments were carried out at 0.005 and 0.02 M, above and below the concentration used in the temperature series.

As observed from Fig. 4 and Table 1, it seems that the optimum value for H_2O_2 concentration at 120°C is located around 0.01 M. From the kinetic point of view, once more fluoranthene is the most recalcitrant hydrocarbon while acenaphthene is the most reactive.

3.2.2. Monopersulfate promoted wet air oxidation

3.2.2.1. Influence of temperature. As inferred from Eq. (8), addition of monopersulfate to the reaction matrix might induce the formation of both, sulfate and hydroxyl radicals.

Accordingly, contaminants can be eliminated by two potential routes, namely radical attack or, alternatively, direct attack of the monopersulfate molecule:

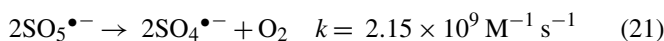
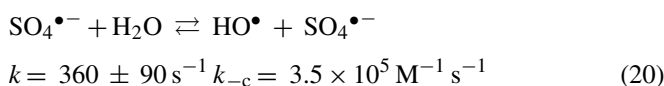
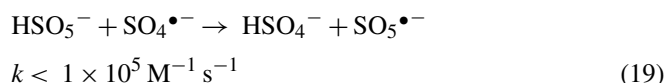


Sulfate radicals are claimed to be stronger oxidising agents than hydroxyl radicals and participate in a complex reaction mechanism [9]:

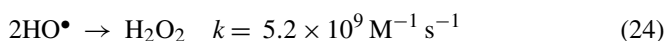
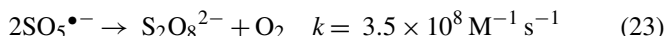
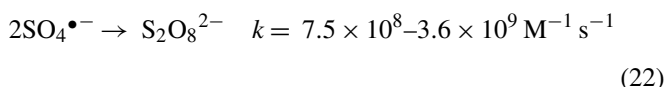
Initiation:



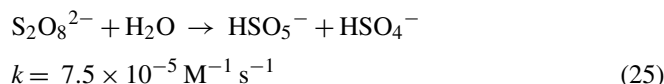
Propagation:



Termination:



Additional reactions:



Consequently, it was decided to check for the capability of this promoter to remove PAHs under WAO conditions. A series of experiments at different temperatures in the range 80 – 150°C was conducted by keeping the rest of operating variables constant. As seen in Fig. 5, temperatures as low as 80°C are sufficient to decompose OXONE[®] and further oxidise the PAHs present in solution. Decomposition of monopersulfate at mild conditions has been previously reported [9]. Thus, with a pre-exponential factor of $3.6 \times 10^{15} \text{ min}^{-1}$ and an activation energy of $13,380 \times R$ (R is the universal gas constant), the first order OXONE[®] decomposition occurs with a rate constant of roughly 0.12 min^{-1} at 80°C . For instance, almost 90% of the initially present monopersulfate should be decomposed in approximately 18 min of reaction, coinciding with the initial fast removal of

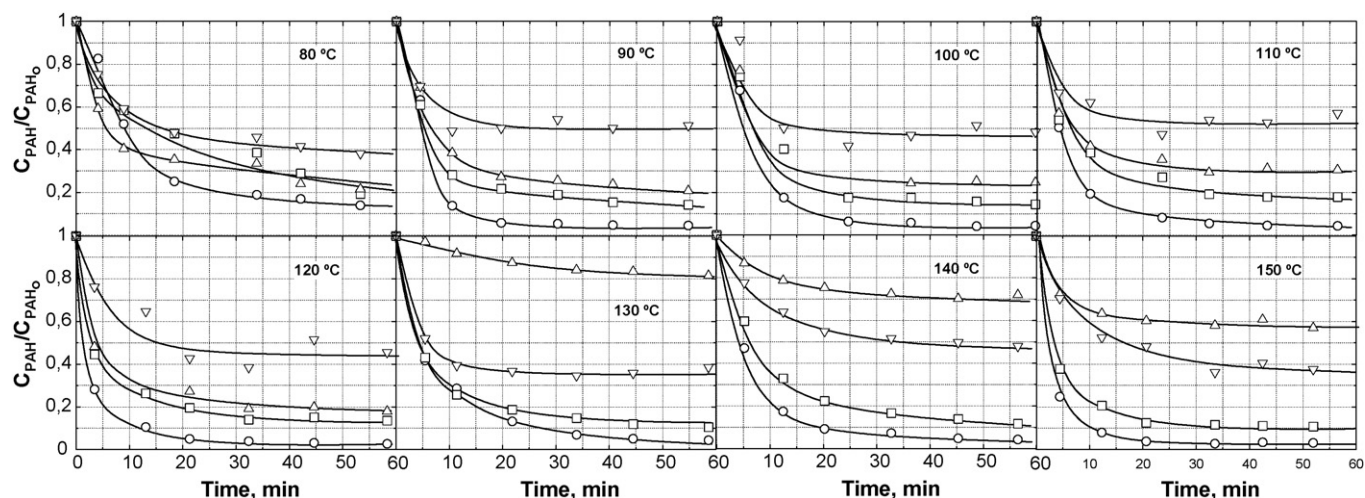
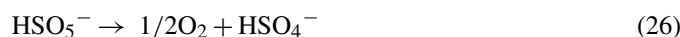


Fig. 5. Wet monopersulfate oxidation treatment of PAHs. *Experimental conditions:* $V=0.350$ L, $P_T=50$ bars, $\text{pH } 3.0$, $C_{\text{OXONE}^\circledR}=0.005$ M, $C_{\text{Ac}_o}=1.25 \pm 0.24$ ppm, $C_{\text{Ph}_o}=0.17 \pm 0.04$ ppm, $C_{\text{An}_o}=11.38 \pm 5.34 \times 10^{-3}$ ppm, $C_{\text{Fl}_o}=4.44 \pm 1.52 \times 10^{-2}$ ppm (average values). Initial concentration of PAHs are detailed in Table 2. \circ , Acenaphthene; \square , phenanthrene; \triangle , anthracene; ∇ , fluoranthene.

hydrocarbons. An increase of the working temperature (i.e. increase of OXONE[®] decomposition rate) should lead to the corresponding enhancement of the PAHs oxidation rate, however, the results obtained do not sustain the theory. Thus, in the interval 90–120 °C no significant differences are observed in terms of individual PAH elimination. Perhaps, a slight improvement could be envisaged at 120 °C which is corroborated in Table 2, although the experimental error makes these differences statistically negligible. Nevertheless, a further increase of temperature up to 130 °C involves a considerable reduction in the anthracene depletion rate. In this sense, it is worthy to note that in the interval 80–120 °C, amongst the four PAHs studied, fluoranthene presents the lowest values of conversion rate, however, in the range 130–150 °C, anthracene is the hydrocarbon showing the most recalcitrant character in terms of conversion values. This behaviour seems to be the consequence of an increase in the inefficient decomposition fraction of OXONE[®], leading to species other than active radicals, when temperature is raised:



Observing the trends experienced at 140 and 150 °C, it is noticed a slight enhancement of anthracene conversion if compared to the profile obtained at 130 °C. It is hypothesised that at the higher temperatures oxygen is capable of initiate the oxidation of anthracene.

3.2.2.2. Influence of monopersulfate concentration. Similarly to hydrogen peroxide, an excess of monopersulfate in the reaction media may act as a scavenger of sulfate radicals through reaction (16). Generated persulfate radicals are less reactive than sulfate radicals. The excess of monopersulfate used in the temperature series is comparable to the excess of H₂O₂ previously reported since the stoichiometry is identical for both oxidants:

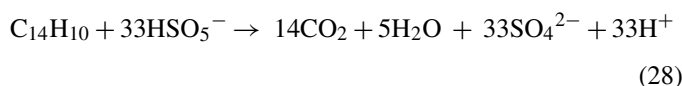
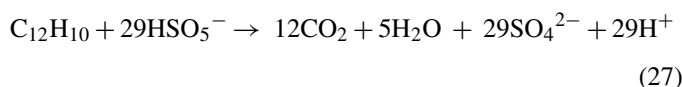


Table 2
Wet monopersulfate oxidation treatment of PAHs

T (°C)	Acenaphthene			Phenanthrene			Anthracene			Fluoranthene		
	C_{Ac_o} (ppm)	τ (s)	K/C_o (%)	C_{Ph_o} (ppm)	τ (s)	K/C_o (%)	C_{An_o} (ppm)	τ (s)	K/C_o (%)	C_{Fl_o} (ppm)	τ (s)	K/C_o (%)
80	1.45	660	12.9	0.22	740	28.2	9.48×10^{-3}	350	27.4	4.89×10^{-2}	390	42.3
90	1.39	395	2.72	0.05	400	15.5	7.36×10^{-3}	406	15.5	4.12×10^{-2}	250	50.2
100	1.27	470	3.3	0.16	619	13.5	6.45×10^{-3}	1100	22.5	4.53×10^{-2}	400	44.3
110	1.26	333	5.0	0.16	400	19.9	8.09×10^{-3}	325	31.5	3.83×10^{-2}	300	53.5
120	1.50	149	4.9	0.21	320	15.7	8.97×10^{-3}	275	20.6	4.69×10^{-2}	450	45.8
120 ^a	1.74	182	8.0	0.32	300	14.5	1.36×10^{-2}	300	12.4	8.50×10^{-2}	300	43.1
130	0.41	400	6.7	0.23	324	13.6	4.33×10^{-3}	1100	80.4	7.19×10^{-2}	270	35.9
140	1.29	375	5.24	0.14	475	14.2	1.96×10^{-2}	475	71.7	5.02×10^{-2}	525	49.6
150	1.47	176	3.86	0.22	225	12.4	2.68×10^{-2}	250	59.5	8.31×10^{-2}	525	39.0

Parameter fitting of individual PAHs to Eq. (10). *Experimental conditions:* $V=0.350$ L, $P_T=50$ bars, $\text{pH } 3.0$, $C_{\text{OXONE}^\circledR}=0.005$ M.

^a $C_{\text{OXONE}^\circledR}=0.0025$ M.

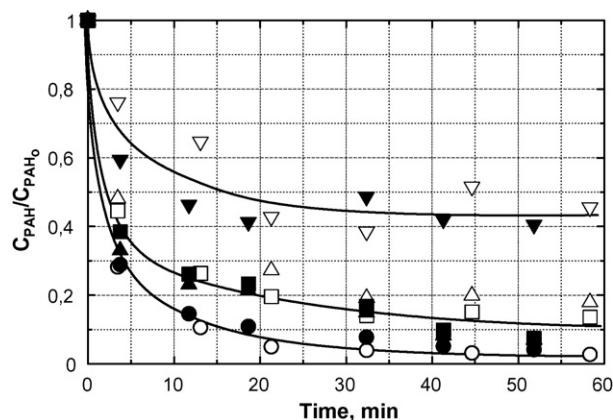
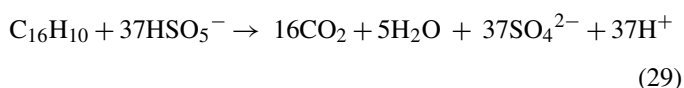


Fig. 6. Wet monopersulfate oxidation treatment of PAHs. *Experimental conditions:* $V = 0.350$ L, $P_T = 50$ bars, pH 3.0, $C_{\text{OXONE}^\circledR} = 0.005$ M (open symbols), $C_{\text{OXONE}^\circledR} = 0.0025$ M (solid symbols), $C_{\text{Ac}_0} = 2.1$ ppm, $C_{\text{Ph}_0} = 0.36$ ppm, $C_{\text{An}_0} = 15.8 \times 10^{-3}$ ppm, $C_{\text{Fl}_0} = 7.5 \times 10^{-2}$ ppm (average values). Initial concentrations of PAHs are detailed in Table 2. \circ ●, Acenaphthene; \square ■, phenanthrene; \triangle ▲, anthracene; ∇ ▼, fluoranthene.

Table 3
Averaged τ and K/C_0 values from H_2O_2 and OXONE^\circledR promoted experiments

		τ	K/C_0
H_2O_2 promoted experiments	Acenaphthene	379 ± 222	1.8 ± 1.3
	Phenanthrene	474 ± 252	10.4 ± 6.7
	Anthracene	386 ± 174	21.5 ± 14.5
	Fluoranthene	666 ± 378	30.7 ± 14.7
OXONE^\circledR promoted experiments	Acenaphthene	349 ± 107	5.8 ± 2.0
	Phenanthrene	423 ± 108	16.4 ± 3.2
	Anthracene	509 ± 223	37.9 ± 16.7
	Fluoranthene	379 ± 69	44.9 ± 3.7

95% confidence interval is calculated by means of $\pm 1.96(\text{S.D.}/N^{1/2})$.



Accordingly, it was decided to run one more experiment by halving the concentration of OXONE^\circledR used in the previous experiments. Fig. 6 illustrates the results obtained. As observed from this plot, no significant differences were observed when lowering the OXONE^\circledR concentration from 5×10^{-3} to 2.5×10^{-3} M, suggesting the possibility of reducing operating costs associated to reagent expenses.

Averaging the values of τ for the H_2O_2 and OXONE^\circledR promoted experiments and calculating the 95% confidence interval, the following figures displayed in Table 3 are obtained. According to this table, no significant differences are experienced in the case of acenaphthene and phenanthrene (perhaps a higher final conversion is obtained in the H_2O_2 promoted runs). Hydrogen peroxide seems to favour anthracene oxidation while in the case of fluoranthene, OXONE^\circledR appears to lead to a faster process but lower final conversions than the system using hydrogen peroxide.

4. Conclusions

From the study presented, the following main conclusions can be derived:

- At 180°C some non-oxidative processes occur leading to a partial disappearance of the target PAHs.
- The presence of oxygen accelerates the hydrocarbons elimination, with a positive effect of temperature in the range 170 – 190°C .
- Addition of free radical promoters (either hydrogen peroxide or monopersulfate) enhances the process by reducing the reaction time and the working temperatures and pressures. An optimum in temperature has to be located to avoid inefficient decomposition of the promoters to species other than free active radicals. Also, an optimum in promoter concentration has to be established to discard the free radical scavenging effect of an excess of the former.

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