

Review

# Polycyclic aromatic hydrocarbons sorbed on soils: A short review of chemical oxidation based treatments

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## Abstract

A brief review is completed on the chemical oxidation of PAHs contaminated soils. Previously, the adsorption and extraction processes are also documented and discussed. The tree main technologies reported in the specialised literature include the use of ozone, hydrogen peroxide (with or without ferrous iron addition) and high temperature pressurized water (both in sub- and super-critical conditions) in the presence of an added oxidant like hydrogen peroxide, oxygen, persulfate, etc. Each process is detailed by the influence of the main operating variables reported in the literature (i.e. presence of organic matter, soil type, reagents dosage, etc.), the kinetics and the description of integrated treatments (i.e. chemical oxidation + biodegradation).

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds that consist of two or more fused benzene rings. They are the by-products of incomplete combustion or pyrolysis of virtually all organic matter. PAHs are considered to be the most widely distributed class of potent human carcinogens present in the environment, and a number of them are catalogued as potential carcinogens by various international agencies [1]. Additionally, other non-cancer-causing effects have not been deeply investigated yet. In aquatic systems, PAHs increase their toxicity with the increasing molecular weight. Although the rate of uptake from the environment is variable among species, bioaccumulation tends to be rapid [2].

PAHs are characterized by their palpable hydrophobic nature. Consequently, these species tend to be adsorbed on solid particulates, especially on the organic fraction of the solids [3]. Accordingly, developing techniques intended to remediate contaminated soils has to consider all the features associated to the adsorption–desorption stages and availability of PAHs to added chemicals.

## 2. The sorption stage

The sorption of hydrophobic organic compounds (as in the case of PAHs) onto soils has been widely investigated by a number of authors [4–11].

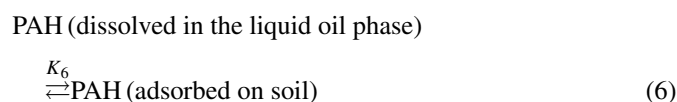
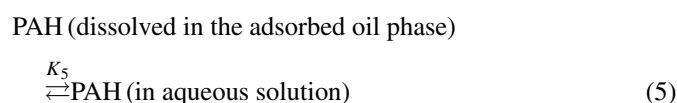
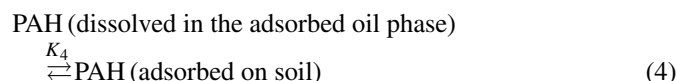
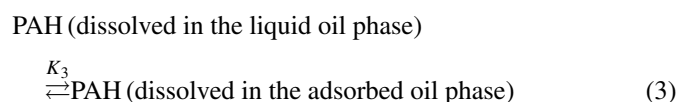
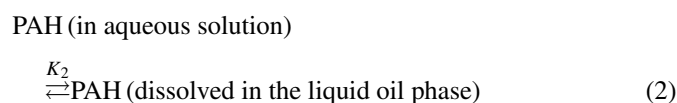
Broadly speaking the most influencing parameters affecting PAHs sorption onto soils are the solubility of the different PAHs and their organic fraction. Other potential factors exerting some influence on the adsorption stage like temperature, salinity or the presence of dissolved organic matter are in fact variables which influence the solubility of the aromatic compounds.

Intimately related to the adsorption process is the sequestration phenomenon. The sequestration is an aging stage in which hydrophobic adsorbed substances show a declining availability to both bioremediation and chemical extraction. The occurrence of sequestration is of significant importance since the toxicity values of sequestered molecules are, obviously, quite different from those assigned to dissolved substances or weakly adsorbed molecules. Physically this phenomenon consists in a migration of adsorbed substances into condensed organic matter and inaccessible micropores present in the geosorbent [7]. Luthy et al. [12] suggested the interaction of several surfaces and matrixes with hydrophobic substances in the sequestration process. Thus, these authors suggest accounting for the presence of inorganic micropores, organic matter in the solid, combustion carbon particulates and spilled organic liquids (i.e. oils). The presence of sub-phases in the solid involves a complex mechanism of mass transfer phenomena that are normally studied at the macroscopic scale by means of static or dynamic experiments [9]. In the majority of cases the adsorption of PAHs on soils follows a linear isotherm [8], i.e., the sorption stage is similar to the partition of non-ionic substances between a hydrophobic and a hydrophilic phase. Nevertheless, non-linear behaviour has also been reported [13]. Luthy et al. [12] give some general rules of thumb to account for the experimental isotherm shapes. These

authors differentiate between five sorption mechanism hypotheses, however, in natural processes more than one case might simultaneously occur, consequently mixing the expected macroscopic results. The five potential cases reported were:

- A. Sorption into amorphous organic matter or non-aqueous phase liquids. Characterized by fast kinetics, linear isotherm, low activation energy and sorption heat with a high chemical extractability.
- B. Sorption into condensed organic polymeric matter or combustion residues. The kinetics is slow showing hysteresis in the adsorption–desorption curves. Upon reaching equilibrium conditions, the isotherm is linear. The activation energy is usually high as well as the heat of sorption. The solvent extractability is catalogued as low.
- C. Adsorption onto water wet organic surfaces. Is a fast process showing non-linear isotherm shapes and low activation energy and low to high (depending on contaminant hydrophobicity) sorption heat. The sorbate can be easily extracted by the adequate solvent.
- D. Adsorption to water wet inorganic surfaces. Characterized by fast kinetics and linear isotherm. The thermodynamic parameters are quite similar to the previous case.
- E. Adsorption into the microporous structure of the solid. This situation is similar to case B with analogous characteristics.

Other authors, however, only consider the soil particulate as a whole entity (organic and inorganic fractions of the soil are taken as a unique entity). Other components not being part of the soil (i.e. oils, dissolved organic matter, etc.) and influencing the adsorption process can also be adsorbed or not onto the solid. Thus, Walter et al. [9] propose a lumped model to account for the transference of PAHs in a three phase system according to



Brion and Pelletier [7] propose a three compartment thermodynamic system organized by the water side dissolved PAHs, the fraction of PAHs chemically extractable at mild conditions (adsorbed phase) and finally the fraction of PAHs strongly adsorbed onto the solid due to the sequestration process (sequestered phase). Accordingly, PAHs can be found dissolved in water following a simple first order adsorption kinetics:

$$-\frac{C_{\text{PAHs}_{\text{dissolved}}}}{dt} = k_1 C_{\text{PAHs}_{\text{dissolved}}} \quad (7)$$

Adsorbed on the solid but easily extracted by a *mild* solvent:

$$-\frac{C_{\text{PAHs}_{\text{adsorbed}}}}{dt} = k_1 C_{\text{PAHs}_{\text{dissolved}}} - k_2 C_{\text{PAHs}_{\text{adsorbed}}} \quad (8)$$

and sequestered into the deep structure of the solid:

$$\frac{C_{\text{PAHs}_{\text{sequestered}}}}{dt} = k_2 C_{\text{PAHs}_{\text{adsorbed}}} \quad (9)$$

The adsorption of PAHs is favoured by an increase in salinity or a decrease in temperature while the presence of humic substances has no appreciable influence on the adsorption extent. In general, the distribution coefficient normalized to the carbon content of the soil ( $K_{\text{OC}}$ ) is independent of the soil properties and can be acceptably correlated to the hydrophobic characteristics of the PAHs investigated (i.e.  $K_{\text{OW}}$  coefficient). Thus, Walter et al. [9] propose the following Eq. (10) after 40 experiments carried out with nine PAHs:

$$\log K_{\text{OC}} = 0.62 \log K_{\text{OW}} + 0.70 \quad (10)$$

where  $K_{\text{OC}}$  is the normalized distribution coefficient defined in Eq. (11) and  $K_{\text{OW}}$  is the octanol/water partition coefficient:

$$K_{\text{OC}} = \frac{K_{\text{D}}}{f_{\text{C}}} = \frac{C_{\text{PAH}_{\text{adsorbed}}}/C_{\text{PAH}_{\text{dissolved}}}}{f_{\text{C}}} \quad (11)$$

$C_{\text{PAH}_{\text{adsorbed}}}$  and  $C_{\text{PAH}_{\text{dissolved}}}$  are the PAH concentration on the soil (in  $\mu\text{g g}^{-1}$ ) and in the aqueous phase (in ppm) at equilibrium conditions, respectively, while  $f_{\text{C}}$  is the organic fraction of soils in  $\text{g g}^{-1}$ . Eq. (10) can, therefore, be utilized to predict the sorption equilibrium from characteristic properties of contaminants and soils.

Previously, He et al. [8] based on the work of Means et al. [14] checked the reported expression by the latter authors by using  $f_{\text{C}}$  as percentage and  $\text{ng g}^{-1}$  and  $\text{ng mL}^{-1}$  for PAH concentrations:

$$\log K_{\text{OC}} = \log K_{\text{OW}} - 2.317 \quad (12)$$

Similarly, a correlation of  $K_{\text{OC}}$  with the solubility ( $S_{\text{W}}$ ) was used by He et al. [8] based on the works of Means et al. [14]:

$$\log K_{\text{OC}} = 2.273 - \log S_{\text{W}} \quad (13)$$

Contrarily to the global adsorption process, the sequestration stage shows a disparity of trends. Nam et al. [15] report a direct relationship between sequestration extent and organic carbon content of soils with values above 2% of this parameter. As reported by Chung and Alexander [16] after the sorption of phenanthrene and atrazine onto 16 different soils, the kinet-

ics and progress of sequestration is apparently a function of the soil nature. In this sense, some correlations of sequestration extent and hydrophobic properties can be found in the literature. Wilcock et al. [17] reported the feasibility of correlations between PAH persistence and properties such as molecular weight, molecular volume, etc. However, Kottler and Alexander [18] found no correlations at all between extractability with *n*-butanol and typical hydrophobic properties like  $K_{\text{OW}}$ , molecular length, etc. Additionally, Brion and Pelletier [7] reported a negligible effect of grain size, organic carbon content and mineral composition on sequestration (although they did influence the first adsorption stage previous to sequestration).

Since only aged material usually exists at contaminated sites, treatments intended to PAHs elimination from soils must consider the extractability of the contaminants. This variable is of paramount importance due to the following reasons: (1) strong sorption of the aromatic compounds into the microporous structure of particulates may impede the fast penetration of the oxidising agents rendering, therefore, a slow diffusion controlled process; (2) as stated previously, sequestered PAHs may not represent a threat to environment. For instance, sequestration is often measured by the extent of mineralization achieved by added microorganisms [15]. Hawthorne et al. [19] highlight the need of extracting only environmentally relevant molecules, i.e., not tightly bound to solid particles. The latter point raises some controversy and can be questioned; more discussion is needed about this particular concept.

### 3. The extraction stage

Several methodologies have been used to extract PAHs from solid matrixes. Basically, they can be classified into two sub-categories: (a) processes using pressurized fluids and (b) processes carried out at atmospheric pressure.

The following extraction technologies are included within the first group:

- *Pressurized liquid extraction (accelerated solvent extraction)*. Accelerated solvent extraction (ASE) is a relatively new extraction technique, in which typical organic solvents are used under moderately elevated temperatures and pressures [19]. ASE allows for a faster extraction time and less solvent volume than classic extraction techniques, such as a Soxhlet extraction. Broadly speaking, the extraction efficiency of ASE is affected by both extraction pressure and temperature, which are the operation parameters of ASE. In addition, sample matrix also exerts some influence on the extraction efficiency.
- *Supercritical fluid extraction*. Supercritical fluid extraction (SFE) has been catalogued as an alternative to the conventional extraction techniques. A supercritical fluid (SCF) is any compound at a temperature and pressure above the critical values (above critical point). In the supercritical environment only one phase exists. The fluid, as it is termed, is neither a gas nor a liquid and is best described as intermediate to the two extremes. This phase retains solvent power approximating liquids as well as the transport properties common to

gases. The behaviour of a fluid in the supercritical state can be described as that of a very mobile liquid. The solubility behaviour approaches that of the liquid phase while penetration into a solid matrix is facilitated by the gas-like transport properties. As a consequence, the rates of extraction and phase separation can be significantly faster than for conventional extraction processes. Furthermore, the extraction conditions can be controlled to effect a selective separation. Supercritical fluid extraction is known to be dependent on the density of the fluid that in turn can be manipulated through control of the system pressure and temperature. In practical terms a SCF can be used to extract a solute from a feed matrix as in conventional liquid extraction. However, unlike conventional extraction, once the conditions are returned to ambient, the quantity of residual solvent in the extracted material is negligible.

Carbon dioxide is the most commonly used SCF [20], due primarily to its low critical parameters (31.1 °C, 73.8 bars), low cost and non-toxicity. However, several other SCFs have been used in both commercial and development processes (ethane, ethylene, propane, etc.).

- **Subcritical water extraction.** The process is based on the liquid water polarity shift as temperature is increased from room values to values below the critical temperature (374 °C). To maintain water in the liquid state the system has to be pressurized with typical pressure values from 50 to 200 bars. Thus, raising the temperature to values above 200 °C involves a decrease in the water dielectric constant comparable to the dielectric constant of typical HPLC solvents like acetonitrile or methanol. Similarly, temperature exerts an analogous effect on other two important parameters like surface tension and viscosity [21]. Taking advantages of the heated water properties, the solubility of some PAHs has been demonstrated to increase up to five orders of magnitude [22]. Fig. 1 illustrates the significant variation of some important water properties with temperature and pressure [23].

The second group of extraction techniques include:

- **Soxhlet extraction.** The method described by Soxhlet in 1879 is the most commonly used example of a semi-continuous method applied to extraction of hydrophobic substances from

soils. This technique is meant to deal with small samples for analytical purposes rather than being a method of realistic environmental applications.

- **Solvent washing.** This technique uses non-extreme conditions to recover PAHs by means of a mixture of water and water miscible co-solvents [24,25]. The potential scaling up of the process relies on solvent recovery and recycling.
- **Surfactant promoted extraction.** A surfactant is a molecule showing two different structural parts in terms of polarity. The polar moiety presents some affinity for polar substances while the non-polar moiety shows the typical hydrophobic properties of this type of compounds. As a consequence, above the critical micelle concentration, non-polar surfactant sides associate each other forming geometrical configurations capable of embedding hydrophobic contaminants inside their structure. Simultaneously, the polar face of micelles is directed towards the solvent (water) so two different micro-environment can be considered in the liquid phase, the hydrophilic and the hydrophobic environments. The critical micelle concentration depends on surfactant chemistry, temperature, ionic strength, presence of organic additives, etc. [26].
- **Extraction by vegetable oils.** Because of the environmental concern raised by the use of common organic solvents or surfactants, alternative non-toxic extracting agents are recently being investigated. Vegetable oils are an economic and environmentally friendly solvent capable of solubilizing PAHs to a similar extent than other more common solvents do (i.e. acetone, dichloromethane, etc.) [27].
- **Extraction by cyclodextrins.** Similarly to the previous strategy, cyclodextrins are used as additive in water washing of soils to facilitate the desorption process of PAHs from the solid [28]. Cyclodextrins are cyclic oligosaccharides of glucopyranose units with a lipophilic cavity in the centre (see Fig. 2). They are produced by the action of a group of enzymes called cyclodextrin glycosyltransferases on starch. The natural product consists of a mixture of the various cyclodextrins, mainly  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin and  $\gamma$ -cyclodextrin, which consist of six, seven, and eight glucopyranose units, respectively. Cyclodextrins are capable of forming inclusion complexes with contaminants by taking up a whole contaminant molecule, or some part of it, into the cavity. Cyclodextrins

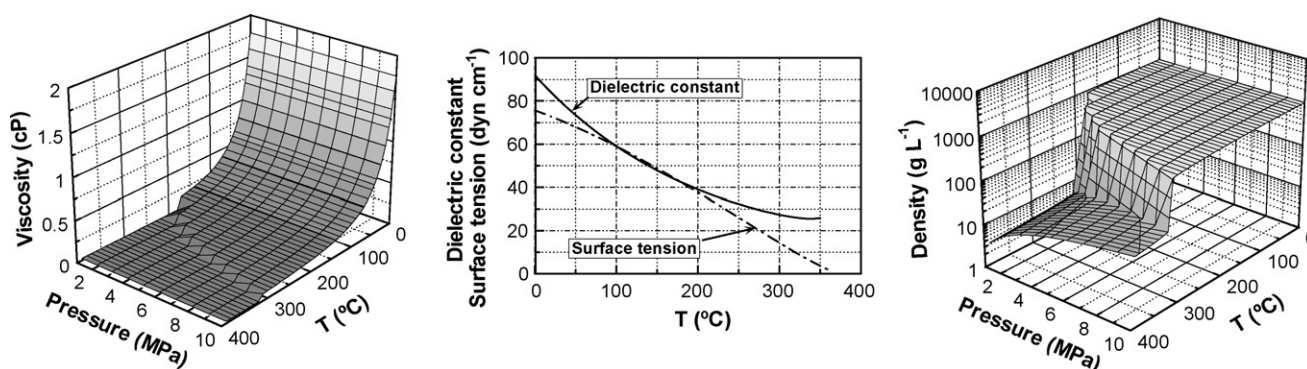


Fig. 1. Evolution of water and steam properties with temperature and pressure.

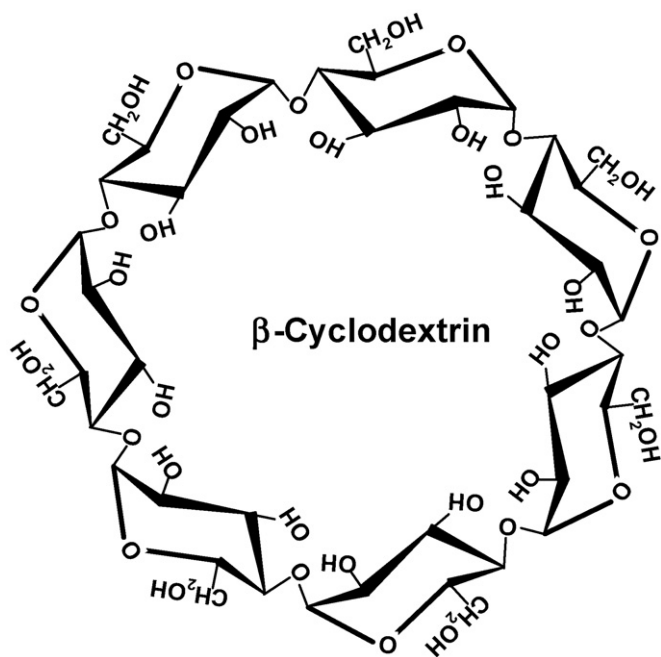


Fig. 2. Structure of cyclodextrins.

offer some advantages over organic solvents like their non-toxic nature and biodegradability.

All the above extraction schemes, except the Soxhlet technique meant for analytical purposes and simple solvent washing due to the excessive time consuming procedure [29], can be considered as suitable technologies showing their own advantages and drawbacks at the time of scaling up to real applications.

Thus, Hawthorne et al. [19], using a contaminated soil from a former manufactured gas plant, reported minor differences in extraction efficiency when utilizing the Soxhlet (for 18 h) extraction, the pressurized  $\text{CH}_2\text{Cl}_2$ –acetone extraction (70 bars,  $100^\circ\text{C}$ , 50 min), supercritical  $\text{CO}_2$  extraction (1 h at  $150^\circ\text{C}$ ) or subcritical water extraction (1 h at  $250^\circ\text{C}$  or 30 min at  $300^\circ\text{C}$ , 100 bars). However, they experienced a significant change in extract quality depending on the methodology followed. Hence, organic solvent based extractions showed no selectivity between PAHs and the rest of organic matter content of the soil. Although to a lesser extent, a similar behaviour was reported for the case of subcritical water extraction while supercritical carbon dioxide removed only 8% of the bulk organic matrix. The extraction selectivity depends on matrix composition. For instance, subcritical water does selectively extract PAHs in a mixture of adsorbed alkanes and PAHs, while supercritical  $\text{CO}_2$  led to a better extraction of alkanes and a poor efficiency of PAHs recovery. According to the previous experimental facts, it cannot be asserted that supercritical carbon dioxide is better or worse than subcritical water, it will depend on soil organic nature. Likely a combination of both would eventually lead to the best results.

Gong et al. [27] reported a similar extraction efficiency of sunflower oil and other more conventional organic solvents.

Strikingly, these authors obtain a better efficacy for the lowest oil:soil ratio used (1:1) than the one obtained by the ratio 2:1. Regeneration of sunflower oil is carried out by activated carbon adsorption. Pannu et al. [30] conducted some experiments focused on the recovery of PAHs from aqueous and soil matrixes. These authors stated that peanut oil is capable of recovering between 88% and 95% of an anthracene artificially contaminated soil regardless of the amount of oil used. However, for a given quantity of oil, an excessive increase in anthracene concentration in soil leads to a notorious decrease of efficiency, likely due to oil saturation. When a mixture of 10 PAHs was treated, temperature exerted a positive effect in the extraction efficiency (from 20 to  $95^\circ\text{C}$ ) as well as agitation time from 3 to 48 h. In any case, a number of concerns is raised in this work. For instance, the amount of oil usage is relatively high (10% of soil weight). Part of oil is retained in the soil bulk. Under some experimental conditions, separation of oil from soil is not an easy task. The latter point is addressed by adding a mixture of polystyrene foam particles and water in slurry mode. These particles retain the most part of the oily phase. Contaminated oil can be further “cleaned” by activated carbon for recycling or alternatively biologically treated and disposed. The whole process seems to be technically feasible but economically unattractive. The authors conceived this process as a potential treatment of PAHs contaminated soils, nevertheless, the extraction stage as a single treatment raises a significant doubt on its feasibility, i.e., the problem (contaminant) is not solved but transferred to a different phase.

Use of surfactants linearly enhances PAHs solubility for surfactant concentrations above the critical micelle concentration [26], however, as stated previously, this technique has to be integrated in a more complex process to degrade contaminants rather than transferring them to a distinct environment.

The thermodynamic and kinetic laws behind the different extraction processes depend on the specific systems investigated (i.e. extraction fluid nature, soil composition and structure, operating conditions, etc.). Kubatova et al. [31] suggest a simple test to assess the limiting stage in extraction processes. Thus, if the limitation step is the desorption kinetics, the extraction fluid flow-rate should not have any appreciable effect on the actual extraction rate. These authors propose a two site kinetic model (a certain fraction of the contaminants,  $F$ , desorbs rapidly ( $k_{\text{FAST}}$ ) while the other fraction desorbs more slowly ( $k_{\text{SLOW}}$ )). The proposal of a two-site model (Eq. (14)) relies on the existence of high and low energy surface sorption sites and/or the existence of external and internal active sites governing the kinetics [32]:

$$\frac{m_{\text{PAH}}}{m_{\text{PAH}_0}} = 1 - [F \exp(-k_{\text{FAST}}t)] - [(1 - F) \exp(-k_{\text{SLOW}}t)] \quad (14)$$

where  $t$  is the time,  $m_{\text{PAH}}$  and  $m_{\text{PAH}_0}$ , the mass of polycyclic aromatic hydrocarbons removed at time  $t$  and initially present in the soil and, finally,  $k_{\text{FAST}}$  and  $k_{\text{SLOW}}$  stand for the rate constants describing the extraction kinetics of the fast desorbing fraction ( $F$ ) and slow desorbing fraction ( $1 - F$ ), respectively. Some authors, however, simplify Eq. (14) to simple first order kinetics [33].

Conversely, if the process is governed by the partition coefficient, the flow-rate of the extracting agent should have a direct effect on the global rate. This effect is accounted for in the following expression:

$$\frac{m'_{\text{PAH}}}{m_{\text{PAH}_0}} = \frac{1 - (m''_{\text{PAH}}/m_{\text{PAH}_0})}{(K_{\text{D}}m_{\text{SOIL}}/(V' - V'')d) + 1} + \frac{m''_{\text{PAH}}}{m_{\text{PAH}_0}} \quad (15)$$

where  $m'_{\text{PAH}}$  and  $m''_{\text{PAH}}$  stand for the cumulative mass of PAHs extracted after flushing the soil with the extractant volumes  $V'$  and  $V''$ , respectively ( $V' > V''$ ),  $K_{\text{D}}$  the partitioning coefficient,  $d$  the extraction fluid density and  $m_{\text{SOIL}}$  is the mass of soil extracted.

Typically, Eq. (14) is best suited for supercritical  $\text{CO}_2$  extraction while expression (15) is better applied to subcritical water processes [30], although, as commented previously, this is just a general rule of thumb and each system shows its particular behaviour. For instance, the two site desorption model was successfully used to simulate the long-term water extraction of PAHs from a manufactured gas plant soil [34]. Yeom et al. [35] extracted phenanthrene from solids by means of non-ionic polyoxyethylene surfactants, they state that the process is not controlled by interfacial film diffusion or partitioning into the micellar phase but rather by matrix diffusion of PAHs molecules within the mixture.

#### 4. The need of an oxidation stage

In any case, the extraction stage as a single treatment technology does not seem to be the definitive solution for PAHs contaminated soils. Degradation of polycyclic aromatic hydrocarbons makes the impression of being of paramount importance.

Biological amendment of contaminated sites might represent an efficient and economically attractive option as a single technology. However, in most of cases the kinetics of the process is too slow due to tight bound of contaminant molecules and soil. Alternatively, bioremediation of soils can be contemplated as a polishing stage after a chemical pre-treatment step [36–41].

Chemical oxidation possesses some advantages over biological soil remediation:

- The time required for “cleaning” of soils is considerably shorter than bioremediation processes.
- Chemical oxidation conditions can be modified (i.e. pressure, temperature, addition of co-solvents, etc.) so unavailable contaminant molecules for biological remediation can actually be accessed by chemical reagents.
- Small mobile units can be constructed to carry out the chemical oxidation “in situ” or “on site” modes.
- Chemical oxidation is relatively insensitive to external disturbances (i.e. contaminant load, temperature changes, presence of biotoxic substances, etc.).
- Chemical oxidation can be combined with the extraction process to conduct the PAH degradation in the extracting fluid.

- Reaction sub-products (if no mineralization is achieved) are usually more biodegradable and soluble than raw materials.

Nevertheless, some drawbacks should also be mentioned:

- This technology is less economic than bioremediation processes.
- If organic solvents are used (i.e. in an extraction stage) these must be carefully handled and recycled.
- If extreme conditions of temperature and, to a lesser extent, pressure are used, wastage of chemical reagents is likely to occur. For instance, sequestered PAHs (which apparently are innocuous from an environmental point of view) can be extracted and oxidised with no need of it.
- Wastage of chemical reagents is also experienced without severe conditions due to the existence of additional organic (and inorganic) harmless oxidisable matter in soils. However, destruction of organic matter might lead to a higher release of sorbed contaminants (a high fraction of PAHs is normally sequestered/adsorbed by the organic segment of soils).
- Sometimes, due to the volume of chemical needed, the process might not be cost effective.

#### 5. The oxidation stage

Chemical oxidation methodologies can be executed in three different modes: “in situ” (by direct injection of chemical into contaminated soils), “on site” (physically carried out at the polluted environs by first removing the soil from the contaminated area) or “off site” (by removing and transferring the contaminated soil to the adequate installations away from the polluted area). The advantages and disadvantages of “in situ” and “on site” cleanups are:

- They are more attractive from an economic point of view.
- “In situ” and “on site” situations are often limited in terms of accessibility. Normally, only the topside of the soil is accessible. Wells are to be drilled, but ultimately the contaminants must struggle gravity and surface tortuosity.

“Off site” technologies are characterized by:

- They normally show a higher remediation efficiency. Off site facilities offer a more exhaustive control over the chemical process. Soil is isolated in a controlled environment, so more caustic chemicals and extreme conditions can be used. Acid leaching can be conducted ex situ without affecting the environment.
- “Off site” technologies remove the bulk of contaminants off site before they can spread further.

The most common chemical oxidation based technologies reported in the specialised literature include the use of ozone, Fenton’s reagent, sub or supercritical water oxidation, permanganate or persulfate. Each one is considered next.

## 5.1. Ozone based technologies

### 5.1.1. General considerations

Ozone soil remediation is an attractive option as this technology can be implemented in any of the three available modes (“in situ”, “on site” and “off site”). Table 1 illustrates some bibliographic references on the use of ozone for the remediation of PAHs contaminated soils.

Additionally, “in situ” ozonation can be carried out by injection of gaseous or aqueous ozone (Fig. 3) [43]. Horizontal or vertical wells can be implemented to introduce the ozone feed stream into soils [44].

Masten and Davies [45] report the advantages of using gaseous ozone ( $O_{3g}$ ) instead of aqueous solutions of this reagent ( $O_{3aq}$ ). Thus, due to the higher diffusivity of  $O_{3g}$ , accessibility of ozone gas to contaminants should theoretically be higher than the accessibility of aqueous ozone. Moreover, the concentrations of ozone gas normally handled are several orders of magnitude higher than those achieved in aqueous phase. The previous statement was corroborated by Goi and Trapido [46] when comparing the three and two phases ozonation of a mixture of 11 PAHs adsorbed on sand or peat. These authors, for instance, reported a roughly 40% of non-reacted PAHs in sand

after three phase ozonation compared to the approximately 20% measured after application of ozone gas. O’Mahony et al. [47] also report a drastic decrease of phenanthrene removal as the water content of soils is increased from 0% to 50%. Kulik et al. [38] confirmed the negative effect of water content by comparing the performance of two and three phase ozonation systems.

If gas ozone is to be used, venting or negative pressure systems may be required (specially if ground surface is paved) to release off-gasses and relieve pressure [48].

The two most critical parameters in ozone soil remediation (and in general in all “in situ” technologies) are the efficient distribution of ozone (oxidant) in the contaminated area and the reactivity of the target compound/s present. This combination requires careful site characterization, screening, and feasibility testing. Regarding ozone distribution, apart of the type of ozone feeding mode (gaseous or dissolved in water), if subsurface heterogeneities or preferential flow paths are not considered an irregular distribution of the oxidant might occur.

Considering the reactivity of PAHs towards ozone, several points have to be addressed. Hence, the reactivity of PAHs is not comparable to the data reported in aqueous phase, these substances do normally react slower adsorbed on soils than they do in water [45]. Also, the reactivity of PAHs regarding the

Table 1  
Bibliographic compilation of ozone soil remediation technologies

Reference	Variables studied	PAHs oxidised	Parameters measured	Notes
[38]	Combination of chemical oxidation + biodegradation	Fluoranthene, phenanthrene, fluorene, pyrene, triphenylene, benz(a)anthracene, chrysene	PAH removal, biodegradability	High molecular weight PAHs are better removed than low molecular weight PAHs for the single ozonation process. The opposite effect is observed in biodegradation experiments
[42]	Feasibility to treat sediments from a freshwater boat slip subjected to coal tar contamination	Naphthalene, phenanthrene, pyrene, benzo(a)pyrene	PAH removal, biodegradability, chemical oxygen demand, by-products	Ozonation for 2 h removes 50–100% of various PAHs in the solid and liquid phases of the sediment. Organic and inorganic content of the sediment are modified by ozonation. Ozonation improves the biodegradability of the contaminants. An integrated chemical–biological system seems to be feasible
[43]	Soil nature, radical scavengers, ozone dose, humic substances	Phenanthrene, benzo(a)pyrene	PAHs removal, ozone uptake	Positive effect of ozone dosage and negative influence of <i>tert</i> -butanol and humic substances. No clear trend in the presence of carbonates
[45]	Presence of organic matter, soil moisture, soil texture	Pyrene, naphthalene, chrysene, phenanthrene	Ozone demand, PAH removal, toxicity	Moisture in soils exerts a higher ozone demand than dried soils. The rate of PAHs ozonation is lower than expected if compared to water experiments
[46]	Two and three phases ozonation, soil nature, PAH molecular weight	Phenanthrene, anthracene, fluoranthene, pyrene, triphenylene, benz(a)anthracene, chrysene, perylene, benzo(e)pyrene, benzo(a)pyrene, benzo(g,h,i)perylene	PAH removal, biodegradability	Two phases ozonation is more effective than three phases ozonation. Ozone plus biodegradation is an effective combined treatment of contaminated soils. PAHs with low number of rings are better eliminated than the congeners of higher molecular weight
[47]	Water content, soil nature, ozone dose	Phenanthrene	PAH removal, biodegradation	Water content exerts a drastic negative effect on ozonation. Ozone is more effective in sandy soils than in clay soils. The combined ozone–biodegradation is effective depending on soil nature and potential of indigenous soil microorganisms
[49]	Soil nature	Naphthalene, fluorene, phenanthrene, anthracene, pyrene, chrysene, benzo(a)pyrene	PAH removal, biodegradation	The order ozone + biodegradation is more efficient than biodegradation + ozonation. Low molecular weight PAHs are better removed than high molecular weight PAHs
[53]	Soil type	Phenanthrene	PAH removal, dehydrogenase activity, ecotoxicological tests	Use of a pre-ozonation stage involves a negative effect in the implementation of a further biodegradation step

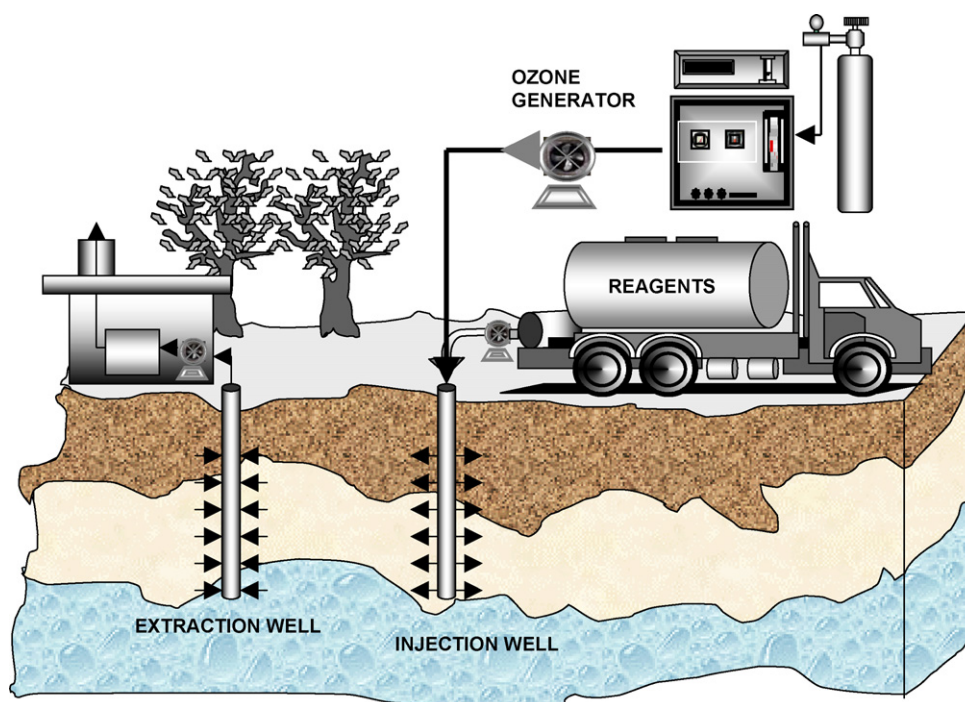


Fig. 3. Scheme of “in situ” soil treatment by direct injection of gaseous ozone or addition of oxidising agent in liquid form (i.e. Fenton’s reagent or ozone dissolved in water).

number of rings is a matter of controversy. In this sense opposite trends have been reported [38,49].

Additionally, ozone can be consumed by the soil organic matter content leading to: (a) wastage of ozone and (b) desorption of sorbed PAHs. The latter effect can be simultaneously considered positive because PAHs are more available for further chemical or biological oxidation and negative if contaminants move to nearby groundwater. Finally, the presence of metal oxides in soils might catalyze the decomposition of ozone into more active hydroxyl radicals, improving therefore, its potential oxidising capability.

The above factors influencing ozone remediation of soils are summarized in Fig. 4.

### 5.1.2. The kinetics

Although the number of studies carried out to assess the kinetics of aqueous ozonation is extremely large, few works have focused on investigating the different kinetic features involved in soil ozonation. Hsu and Masten [50] tried to simulate the removal of phenanthrene adsorbed on soil. These authors carried out some experiments of ozone decomposition in soil water (first order regarding gaseous ozone), ozone decomposition with the soil matrix (second order) and finally they studied the removal of sorbed phenanthrene experiencing the presence of two pseudofirst order kinetic regions. Thereafter, Kim and Choi [51], based on the previous results, developed and tested three different models. Basically the three models were:

- *Equilibrium model.* Ozone in the gas phase dissolves into pore water achieving equilibrium conditions. Accordingly, if

ozone is transported by convection and diffusion in a soil column, the following expressions apply:

- For the ozone gas:

$$\frac{\partial}{\partial t} \left[ \left( 1 + \frac{s_w}{K_H s_a} \right) n s_a C_{O_3g} \right] = \frac{\partial}{\partial z} \left[ \frac{\partial (n s_a C_{O_3g})}{\partial z} D_{O_3g} \right] - v \frac{\partial (n s_a C_{O_3g})}{\partial z} - r_o \quad (16)$$

- For soil organic matter:

$$\frac{\partial (\rho_b C_{OM})}{\partial t} = - \frac{1}{y_{O_3,OM} K_H} n s_w k_{OM,w} C_{OM} C_{O_3g} - \frac{1}{y_{O_3,OM}} f_{OM} n s_a k_{OM,a} C_{OM} C_{O_3g} \quad (17)$$

- For phenanthrene:

$$\frac{\partial (\rho_b C_{PAH})}{\partial t} = - \frac{1}{y_{O_3,PAH} K_H} n s_w k_{PAH,w} C_{PAH} C_{O_3g} - \frac{1}{y_{O_3,PAH}} f_{PAH} n s_a k_{PAH,a} C_{PAH} C_{O_3g} \quad (18)$$

where the notation used was  $t$ : time,  $K_H$ : Henry’s constant,  $s_w$ : water saturation,  $s_a$ : gas saturation,  $n$ : porosity,  $C_{O_3g}$ : ozone gas concentration,  $z$ : spatial variable,  $D_{O_3g}$ : the hydrodynamic dispersion coefficient of gaseous ozone defined as the addition of the effective diffusion coefficient in soil plus the product gas phase dispersivity multiplied by the pore gas velocity,  $v$ : pore gas velocity,  $r_o$ : all reaction rates involving gas ozone consumption,  $\rho_b$ : soil bulk density,  $C_i$ : concentration of species  $i$ ,  $y_{i,j}$ :



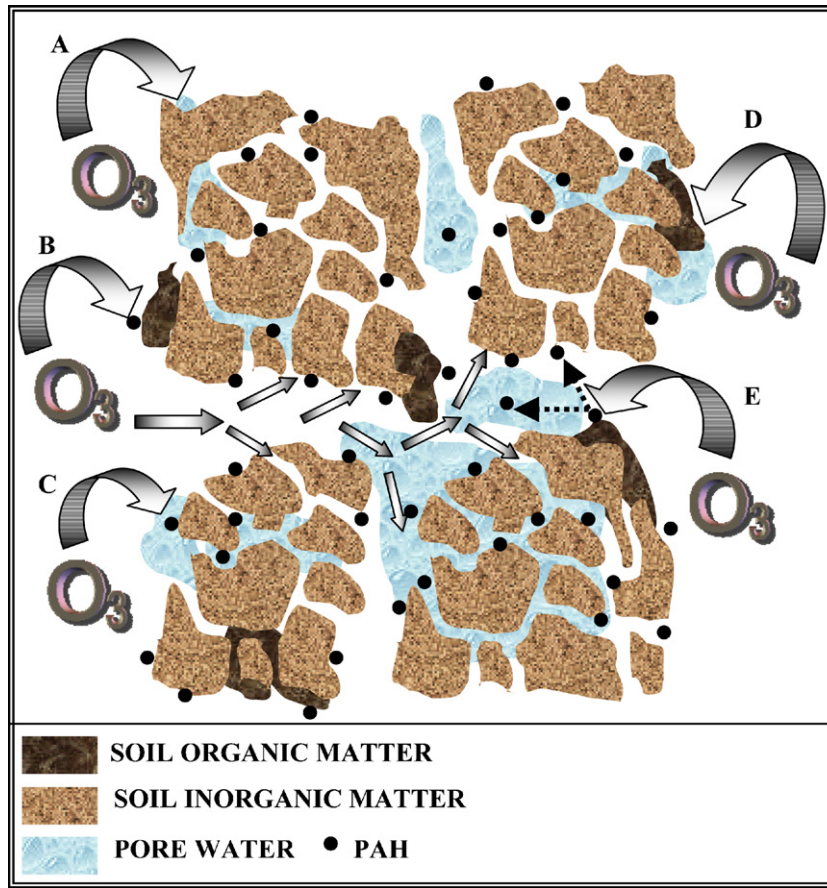


Fig. 4. Potential routes of ozone consumption in soils. (A) Ozone decomposition on mineral surfaces (leading to  $\text{HO}^\bullet$  or ineffective decomposition to oxygen and further deactivation of radicals). (B) Ozone attack to PAHs sorbed onto soil organic matter. (C) Dissolution of ozone into pore water and further reaction with PAHs. (D) Ozone wastage with soil organic matter or non-target compounds dissolved in pore water. (E) Solubilization of sorbed PAHs due to destruction of soil organic matter.

coefficient for the reaction of species  $i$  and  $j$ ,  $f_i$ : factor accounting for the reaction of species  $i$  with ozone gas depending on water saturation,  $k_{i,w}$ : second order rate constant for the reaction of species  $i$  and dissolved ozone, and  $k_{i,a}$ : second order rate constant for the reaction of species  $i$  and gaseous ozone.

- **Kinetic model.** There is no equilibrium between gas and aqueous ozone. Ozone gas is transferred into pore water due to the driving force. The mass transfer coefficient is the important parameter in the global transference rate. The following equations are used:

- For the ozone gas:

$$\begin{aligned} \frac{\partial}{\partial t} [ns_a C_{O_3g}] &= \frac{\partial}{\partial z} \left[ \frac{\partial (ns_a C_{O_3g})}{\partial z} D_{O_3g} \right] - v \frac{\partial (ns_a C_{O_3g})}{\partial z} \\ &\quad - ns_a k_{La} (C_{O_3g} - K_H C_{O_3}) - ns_a C_{O_3g} (k_{d,a} \\ &\quad + f_{OM} k_{OM,a} C_{OM} + f_{PAH} k_{PAH,a} C_{PAH}) \end{aligned} \quad (19)$$

- For the aqueous ozone:

$$\begin{aligned} \frac{\partial}{\partial t} [ns_w C_{O_3}] &= ns_a k_{La} (C_{O_3g} - K_H C_{O_3}) - ns_w C_{O_3} (k_{d,w} \\ &\quad + f_{OM} k_{OM,w} C_{OM} + f_{PAH} k_{PAH,w} C_{PAH}) \end{aligned} \quad (20)$$

For the soil organic matter and contaminant the expressions are (17) and (18).  $C_{O_3}$  stands for dissolved ozone,  $k_{La}$  the overall mass transfer coefficient,  $k_{d,a}$  and  $k_{d,w}$  are the ozone self-decomposition in the gas and aqueous phases, respectively.

- **Lumped model.** This model assumes that ozone dissolution into pore water can be neglected and only gas phase reactions occur. The equations of this model are:

- For the ozone gas:

$$\begin{aligned} \frac{\partial}{\partial t} [ns_a C_{O_3g}] &= \frac{\partial}{\partial z} \left[ \frac{\partial (ns_a C_{O_3g})}{\partial z} D_{O_3g} \right] - v \frac{\partial (ns_a C_{O_3g})}{\partial z} \\ &\quad - ns_a C_{O_3g} (k_{d,a} + f_{OM} k_{OM,a} C_{OM} + k_{PAH,a} C_{PAH}) \end{aligned} \quad (21)$$

- For soil organic matter:

$$\frac{\partial (\rho_b C_{OM})}{\partial t} = - \frac{1}{y_{O_3,OM}} ns_a k_{OM,a} C_{OM} C_{O_3g} \quad (22)$$

- For phenanthrene:

$$\frac{\partial(\rho_b C_{\text{PAH}})}{\partial t} = -\frac{1}{Y_{\text{O}_3, \text{PAH}}} n_{s,a} k_{\text{PAH},a} C_{\text{PAH}} C_{\text{O}_3g} \quad (23)$$

Kim and Choi [51] tested the three models by optimizing the unknown parameters. The main conclusion reported by these authors indicated that the reaction of the soil organic matter was one of the most important factors to take into account.

The optimized parameters in the previous models are specific for each situation and cannot be easily extrapolated to real situations (i.e. in a real case there is not a column containing the polluted soil). Likely, simpler empirical models are better suited for this type of systems.

### 5.1.3. Integrated treatments

Chemical oxidation based technologies can be considered as a stand-alone remediation process or, alternatively, they can be integrated into a strategy of two or more sequential remediation approaches. The use of ozone offers several possibilities:

- *Integrated extraction–ozonation.* As commented previously, the reaction rate of adsorbed PAHs with ozone might be drastically decreased if compared to reaction rates experienced in the aqueous phase. Consequently, a wise strategy to increase the efficiency of ozonation processes would consider the extraction of contaminants prior to the oxidation either in water or in a less polar solvent. Solvents with low toxicity capable of dissolving high amounts of ozone are a suitable selection [52]. As reported in the extraction section, several approaches can be considered (subcritical water, accelerated solvent extraction, etc.), the appropriate option will depend on a number of factors like the amount and nature of soil organic matter, presence of contaminants other than PAHs,

etc. The ozonation stage applied after the extraction is meant not only for PAHs oxidation but also for solvent recovery and recycling.

This integrated system is mainly intended to be carried out in “on site” or “off site” modes (Fig. 5).

- *Integrated ozonation–biodegradation.* This combination is based on the capability of ozone to: (a) transform PAHs, rendering them into more biodegradable intermediates and (b) oxidise the soil organic material releasing adsorbed contaminants so they are more biologically available. This integrated process has been studied by a number of authors [38,46,47,49,53]. Different and opposite results have been reported on the potential of this combination [47].

Thus, Goi and Trapido [46] claim the positive effect of the combined ozonation–biodegradation of soils if compared to single biodegradation, however, the initial PAH load in both systems are different, so no valuable conclusions can be drawn. In any case, single biodegradation is capable of reducing the PAH content a 30% (from 100% to roughly 70%) while biodegradation after ozonation is more effective (from roughly 55% to 10%). Kulik et al. [38] state a positive influence of the combined ozone–biodegradation in a creosote contaminated soil, although opposite results were experienced by substituting the chemical oxidation stage by the Fenton’s process.

Contrarily, Stehr et al. [53] reported a slower biological degradation of phenanthrene by *Sphingomonas Yanoikuyae* when the soil was ozone pre-treated. Moreover, these authors claimed an increase in dehydrogenase activity in a real PAH contaminated soil when increasing the ozone dose applied.

The positive effect found in the literature is sustained by the following hypothesis:

- The pre-ozonation stage converts PAHs into more soluble oxygenated molecules which, consequently, are more available to microorganisms.

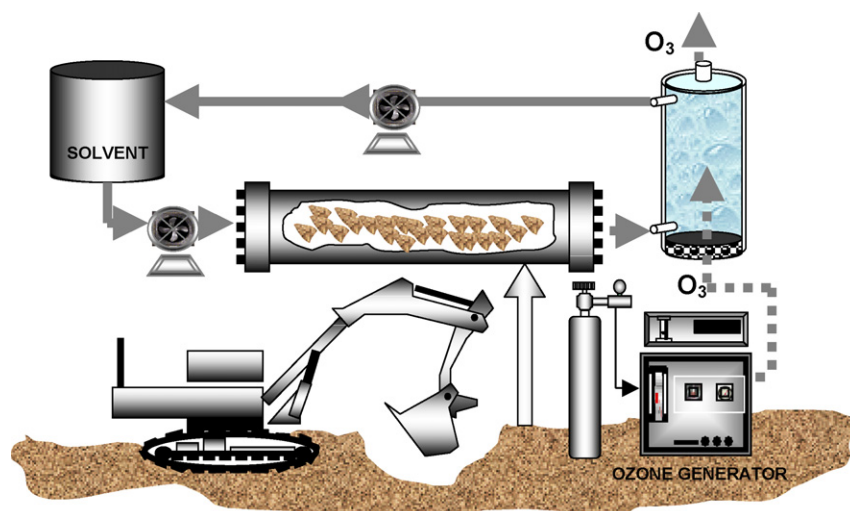


Fig. 5. “On site” or “off site” combination of extraction + solvent recycling. PAHs are oxidised by ozone which is catalogued as an environmentally friendly oxidising agent. Extraction is carried out with hot water or a harmless solvent if possible.

- b. Oxidation by-products are normally more biodegradable than the parent compounds.
- c. Chemical oxidation is capable of attacking organic matter present in soil, releasing therefore adsorbed PAHs from the active sites.

In the opposite direction, the following hypotheses can be considered:

- a. Oxidation intermediates might show a higher toxicity than parent compounds.
- b. Ozone can also destroy the indigenous microbial population of soils which eventually may help to artificially inoculated strains to biodegrade PAHs.
- c. Ozone might break the same PAH chemical bonds used by microorganisms, so the latter can miss their biochemical pathways to generate energy.

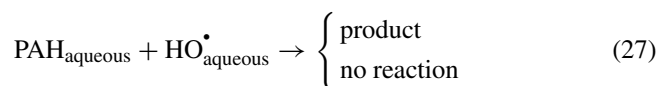
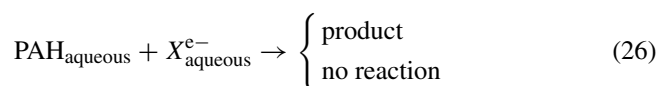
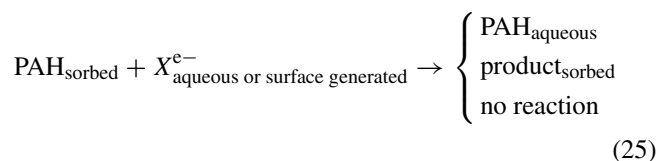
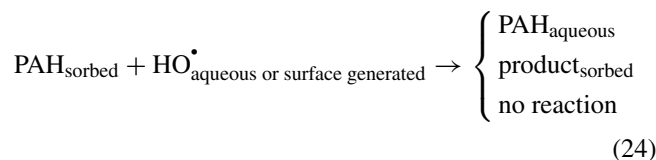
## 5.2. Fenton's based technologies

### 5.2.1. General considerations

This method is by far the most studied chemical oxidation technology in soil remediation. Table 2 depicts some references focusing in the optimization of Fenton's operation conditions for PAHs contaminated soil treatment. Due to the simplicity of implementation, the system can be applied "in situ", "on site" and "off site" (see Fig. 3).  $H_2O_2$  is injected in concentrations ranging from 3% to 35% by weight at normal or high pressure [48]. Some of the particular characteristics of this system include:

- Hydrogen peroxide, by means of an iron salt (normally Fe(II)) artificially added is decomposed into highly active species (hydroxyl radicals or high valence iron species like Fe(IV) or Fe(V)). Alternatively, the presence of iron oxides into the inorganic components of soils can play the same role than dissolved iron. Thus, Flotron et al. [54] showed that iron oxides present in the solid matrix were capable of decomposing hydrogen peroxide so contaminant molecules located in the vicinity could effectively be removed. The Fenton mechanism can be initiated by goethite, hematite and magnetite but not by ferrihydrite [58]. Additionally Kawahara et al. [59] support a different hypothesis. Hence, iron on the internal surfaces of the soil structure undergoes a red-ox cycle by an electron transfer between iron and the organics. As a consequence, the contaminants are better extracted and oxidised. In any case, one hypothesis does not preclude the possibility of the other.
- If iron is needed, this species can be co-injected with  $H_2O_2$  and mixed at the end of the well or, contrarily it can be delivered after  $H_2O_2$  feeding. Hydrogen peroxide decomposition is an exothermic reaction and, consequently, all the possible effects of heat release should be taken into consideration when implementing this technology (i.e. stripping of volatile contaminants, encouragement of thermal oxidation, safety factors, etc.).

- The role of soil organic matter is controversial. Most of investigations underline the negative effect exerted due to scavenging of active species. However, humic and fulvic substances are capable of acting as electron shuttles so they can facilitate the regeneration of Fe(II) from Fe(III). Additionally, some authors have reported that contaminated soils with less than 5% of organic matter tend to adsorb PAH into their microporous structure (if it exists) impeding, therefore, the appropriate contact between contaminants and reagents. Apparently, the negative effect of sorption can be partially overcome by using high doses of hydrogen peroxide. Bogan and Trbovic [60] investigated these aspects. These authors used six different soils artificially contaminated with coal tar. For soils with a carbon content below 5% degradation efficiency was inversely correlated to the organic material (mainly humic and fulvic acids) while an opposite trend was experienced for soils with high values of organic carbon content. The effect of sequestration was more pronounced in low organic content soils. Also, low molecular weight PAHs were "entrapped" more easily than high molecular weight PAHs. According to these authors a dual adsorption mechanism takes place to account for the previous results, the adsorption on humic and fulvic acids and sequestration onto the microporous structure of humin.
- Use of high hydrogen peroxide concentration is recommended to face PAHs adsorbed onto non-aqueous phase liquids. The reason seems to rely on the appearance of an alternative reductive pathway capable of degrading organics resistant to the action of hydroxyl radicals [61]. The general mechanism under vigorous Fenton's conditions could be interpreted as follows:



where  $X^{e-}$  stands for typical reductant species generated in Fenton's mechanism (superoxide and hydroperoxide anions, quinones, electrons, etc.). Under normal circumstances, aqueous PAHs should react with hydroxyl radicals, so reaction (27) would eventually lead to oxidised products. The pathway for the rest of reactions will depend on the nature of species involved, the type of sorption, etc.

Table 2  
Bibliographic compilation of Fenton soil remediation technologies

Reference	Variables studied	PAHs oxidised	Parameters measured	Notes
[38]	Reagents dose	Fluoranthene, phenanthrene, fluorene, pyrene, triphenylene, benz( <i>a</i> )anthracene, chrysene	PAH removal, biodegradability	Oxidation of PAHs is achieved by hydrogen peroxide in the presence and absence of added Fe(II), however, the conversion is higher if Fe(II) is added. Fenton's oxidation significantly enhances biodegradation in sand but has an opposite effect in peat
[46]	Step-wise addition of H <sub>2</sub> O <sub>2</sub> , reagents dose, soil nature, PAH molecular weight	Phenanthrene, anthracene, fluoranthene, pyrene, triphenylene, benz( <i>a</i> )anthracene, chrysene, perylene, benzo( <i>e</i> )pyrene, benzo( <i>a</i> )pyrene, benzo( <i>g,h,i</i> )perylene	PAH removal, biodegradability	Step-wise addition of H <sub>2</sub> O <sub>2</sub> results in better PAH removal efficiency in sand than a single addition. The oxidation can be performed with no artificially added Fe(II)
[54]	PAHs reactivity in water, soil type, effect of aging	Benzo( <i>a</i> )pyrene, benzo( <i>b</i> )fluoranthene, fluoranthene	PAHs removal, intermediates, kinetics	Oxidation of native PAHs occurs at the surface. The PAHs load of soils favours the oxidation. There is no need of Fe(II) addition
[55]	Use of surfactants	Anthracene, phenanthrene, and fluoranthene	PAH removal	Extraction is carried out before oxidation. Surfactants and organic matter in soils exert a scavenging effect on hydroxyl radicals
[56]	Goethite addition, pH, H <sub>2</sub> O <sub>2</sub> dose, soil organic matter, bicarbonate concentration	Phenanthrene	PAH removal, intermediates, mineralization	Bicarbonates and organic matter in soils exert a scavenging effect on hydroxyl radicals. Hydrogen peroxide decomposition is almost completed in the first 30 min of reaction. Neutral pH can be used
[57]	Goethite, H <sub>2</sub> O <sub>2</sub> dose, bicarbonate, pH	Phenanthrene, anthracene, pyrene	PAH removal, intermediates	The kinetics of PAHs degradation is investigated. The process can be carried out at neutral pH
[58]	H <sub>2</sub> O <sub>2</sub> dose, slurry volume, pH, Fe(II) dose	Benzo( <i>a</i> )pyrene	PAH removal, mineralization	High doses of H <sub>2</sub> O <sub>2</sub> are required to face the presence of NAPL. The stoichiometric factor of H <sub>2</sub> O <sub>2</sub> consumed per PAH mineralized is higher than in aqueous phase. Dissolved Fe(II) exerts a negative effect. The vigorous Fenton like system is a two-stage process with desorption and oxidation/reduction of contaminants
[59]	Extractability	Acenaphthylene, naphthalene, 2-methylnaphthalene, benzo( <i>a</i> )pyrene, dibenzofuran, chrysene, benzo( <i>b</i> )fluoranthene, benzo( <i>a</i> )anthracene, pyrene, fluorene, acenaphthene, fluoranthene, phenanthrene, anthracene	PAHs concentration	The extractability of PAHs increases in the first hour of treatment. Thereafter, they are oxidised/degraded
[60]	Soil nature, effect of aging, effect of porosity, distribution of soil organic matter	Indeno( <i>c,d</i> )pyrene, benzo( <i>g,h,i</i> )perylene, dibenzo( <i>a,h</i> )anthracene, benzo( <i>a</i> )pyrene, benzo( <i>k</i> )fluoranthene, chrysene, benzo( <i>b</i> )fluoranthene, benzo( <i>a</i> )anthracene, pyrene, fluoranthene, phenanthrene, anthracene	Sequestration degree, PAHs removal	Soil organic matter mainly composed of humin has a detrimental effect on oxidation when subjected to aging. This is especially observable for low molecular weight PAHs. Soils with a high content of fulvic and humic substances show no sequestration features, however they negatively influence the oxidation stage
[62]	Addition of ethanol, surfactant addition, H <sub>2</sub> O <sub>2</sub> dose, Fe(II) dose	Benzo( <i>a</i> )anthracene	PAHs removal, biodegradability, intermediates	Addition of ethanol increases the efficacy of chemical oxidation. No appreciable effect was experienced after surfactant addition. Intermediate biodegradability is higher than the parent compound
[63]	Oil addition	Indeno( <i>c,d</i> )pyrene, benzo( <i>g,h,i</i> )perylene, dibenzo( <i>a,h</i> )anthracene, benzo( <i>a</i> )pyrene, benzo( <i>k</i> )fluoranthene, chrysene, benzo( <i>b</i> )fluoranthene, benzo( <i>a</i> )anthracene, pyrene, fluoranthene, phenanthrene, anthracene	PAH removal	Addition of vegetable oils significantly enhances the efficacy of Fenton's treatment, particularly regarding to high molecular weight PAHs
[64]	pH, H <sub>2</sub> O <sub>2</sub> dose, Fe(II) dose	Anthracene, benzo( <i>a</i> )pyrene	PAHs removal, biodegradation	Non-ionic surfactants improve the PAHs oxidation conversion. The effect of surfactants on biodegradation depends on the PAH nature
[66]	Reagents dose, addition of Fe(III) chelating agents	Naphthalene, fluorene, phenanthrene, anthracene, pyrene, chrysene, benzo( <i>a</i> )pyrene	PAHs removal, biodegradation, mineralization	Use of chelating agents allows for the implementation of Fenton's reaction at circumneutral conditions. The combination of biodegradation + modified Fenton leads to better results than the reverse order

Table 2 (Continued)

Reference	Variables studied	PAHs oxidised	Parameters measured	Notes
[67]	Addition of ethanol, H <sub>2</sub> O <sub>2</sub> dose, Fe(II) dose	Benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene	Reaction rate, PAH removal, intermediates	Addition of ethanol drastically enhances the efficiency of the process. The other important parameter is H <sub>2</sub> O <sub>2</sub> concentration. Reaction rate is similar or even higher in soil than in pure ethanol
[68]	Reagents dose, surfactant addition	Phenanthrene, pyrene, benzo(a)pyrene	Mineralization	Fenton's oxidation increases the mineralization achieved by indigenous microbes. No positive effect is observed after surfactant addition

- Use of co-solvents might lead to significant improvements of the process. Lee and Hosomi [62] showed a spectacular increase of oxidation efficacy of sorbed benz(a)anthracene when increasing ethanol dosages from 0.5 to 1.5 mL (1 g soil + 0.2 mL 0.5 M Fe(II) + 0.3 mL H<sub>2</sub>O<sub>2</sub>). Thus, if no ethanol was added, no appreciable removal of PAH was experienced while 1 mL of ethanol led to a 97% of benz(a)anthracene oxidation. Additionally, Bogan et al. [63] demonstrated the beneficial effects exerted by vegetable oils addition to the reaction system. These researchers used vegetable oil to extract the PAH fraction more tightly sorbed to soils and recalcitrant to oxidation (i.e. high molecular weight PAHs), carrying out thereafter the oxidation stage.
- Use of surfactants [64] or chelating agents like cyclodextrins [65] or gallic acid and catechol [66] has also been reported to enhance in one or another way the possibilities of Fenton's oxidation.

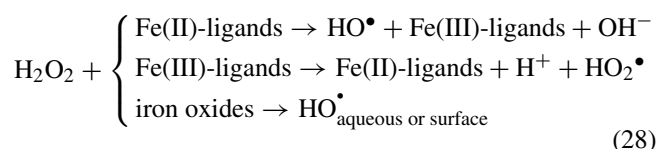
### 5.2.2. The kinetics

Although the number of Fenton kinetic studies accomplished in aqueous solution is extremely high, few works have focused in the assessment of reaction rates for sorbed contaminants. Thus, besides of the assumed mechanism in aqueous solution, the particular features of the soil presence should be accounted for (desorption, surface reactions, diffusion, etc.).

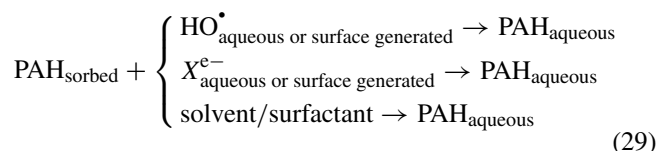
Lee et al. [67] described the process by simple pseudo first order kinetics and compared the rate constant obtained in pure ethanol and soil. These authors reported a similar rate in both milieus for benzo(a)pyrene (0.297 and 0.288 day<sup>-1</sup>, respectively) and dibenz(a,h)anthracene (0.209 and 0.253 day<sup>-1</sup>) and quite different results for benzo(k)fluoranthene, 0.025 day<sup>-1</sup> in ethanol versus 0.104 day<sup>-1</sup> in soils. Kanel et al. [57] also report a pseudofirst order of PAHs removal from sand by hydrogen peroxide decomposition in the presence of goethite. The rate constant found by these authors were in the interval 0.29–1.58 day<sup>-1</sup> for phenanthrene, 0.22–1.30 day<sup>-1</sup> for anthracene and 0.16–1.00 day<sup>-1</sup> for pyrene, depending on the operating conditions.

If a more detailed mechanism is considered the following main reactions should be taken into account. For simplicity reasons, the active oxidising species involved is the hydroxyl radical, although some authors claim the co-existence of other active molecules like high valence iron cations:

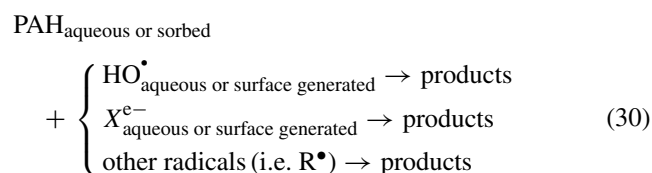
- H<sub>2</sub>O<sub>2</sub> activation:



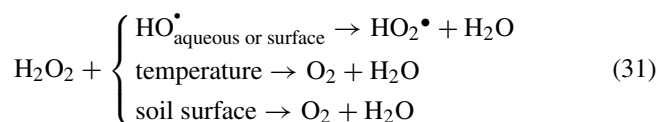
- PAH desorption:



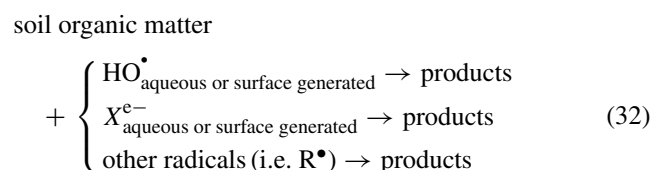
- PAH reaction:



- H<sub>2</sub>O<sub>2</sub> deactivation/scavenging:



- Competing reactions:



The acid–base equilibrium of HO<sub>2</sub><sup>•</sup> and H<sub>2</sub>O<sub>2</sub>, the speciation of iron species with pH and other radical mediated species should be added to reactions (28)–(32).

### 5.2.3. Integrated treatments

Fenton's reagent can also be implemented in conjunction with other complementary technologies. Typically, biodegradation is the preferred process to be combined with the hydrogen peroxide mediated oxidation. The results obtained by this combination are

discordant, although most of them confirm the positive effect of the integrated stages.

Thus, Lee and Hosomi [62] reported the beneficial effect of microbial degradation of benz(*a*)anthracene 7,12-dione (main by-product of benz(*a*)anthracene Fenton's oxidation) after chemical oxidation if compared to control experiments (with no biodegradation). Kulik et al. [38] claimed, after 8 weeks of bioremediation, a further 20.5% and 16.5% of PAHs elimination in a creosote contaminated sand when applying a pre-Fenton's stage with and without Fe(II) addition, respectively. These authors point out the release of oxygen and generation of less recalcitrant compounds as the probable reasons for the enhanced aerobic process. However, in the same work, opposite results are observed when pre-oxidising creosote contaminated peat. Moreover, non-catalytic oxidation by H<sub>2</sub>O<sub>2</sub> followed by biodegradation led to poorer PAHs conversion than bioremediation alone. Un-reacted hydrogen peroxide seems to be the cause of the negative effect observed. Goi and Trapido [46] did not experience such a negative effect when pre-treating peat contaminated with a mixture of 3, 4 and 5 ring PAHs. Piskonen and Itävaara [68] also stated a significant improvement by using a pre-Fenton step of the mineralization of phenanthrene and pyrene by indigenous soil microorganisms. Nadarajah et al. [64] reported an increase from 30–50% to 60–80% of benzo(*a*)pyrene removal when comparing bioremediation and combined Fenton-bioremediation processes, respectively. Nam et al. [66] overcame the drawback of using low pH's in Fenton's pre-stages by using Fe(II) chelating agents, these authors claimed a 98% conversion of 2 and 3 ring PAHs and 70–85% conversion of 4 and 5 ring PAHs by combining the modified Fenton's treatment and biodegradation.

### 5.3. Sub- and super-critical water based technologies

#### 5.3.1. General considerations

As stated in the extraction section, water at high temperatures behaves and shows the same properties than common organic solvents. Accordingly processes like wet air oxidation

(WAO) or supercritical water air oxidation (SWAO) can, *a priori*, combine the extracting capacity of water at these conditions with the oxidation capacity of dissolved oxygen (or other oxidants) at high temperature. These technologies, if applied to contaminated soils, can be implemented "on site" or "off site". Although the option of using other solvents different from water can be considered, WAO and SWAO do not necessitate of non-environmentally friendly substances (only water and oxygen are used). Accordingly, these processes can be included in the so called "green chemistry" [69].

Oxidation of PAHs can be conducted simultaneously to the extraction or after extracting the target compounds. In the first case, oxidants might eventually attack organics species deposited onto the soils (not extracted). Since some PAHs are not easily extracted, this can represent an advantage. However, some oxidant wastage can also be experienced by reactions with non-target compounds or radical deactivation against soil surfaces. Most of studies reported in the recent literature follow the second scheme, i.e., extraction is carried out in a first stage and thereafter the oxidation takes place by addition of the corresponding oxidising agent (Table 3). Fig. 6 illustrates the experimental equipment used by Kronholm et al. [69–71]. These authors reported the optimum conditions for extraction + supercritical oxidation of a mixture of PAHs deposited onto sea sand and previously dissolved in toluene [69]. In their study, extraction time did not show any significant influence on PAHs recovery, although results for toluene were clearly influenced by this parameter. Contrarily, temperature exerted a clear positive effect in the extraction of high molecular weigh PAHs with significant differences found at 200 and 300 °C. The second step (oxidation) was highly conditioned by the oxidant dosage (hydrogen peroxide) and reaction time. Temperature effect was difficult to evaluate due to changes in reaction time, inefficient decomposition of H<sub>2</sub>O<sub>2</sub>, etc. In a similar work, however, the same authors [71] claimed a positive effect of reaction temperature on PAHs conversion when treating a real soil sample from a decommissioned coal gasification plant in Husarviken, Stockholm (Sweden). Additionally, if subcritical

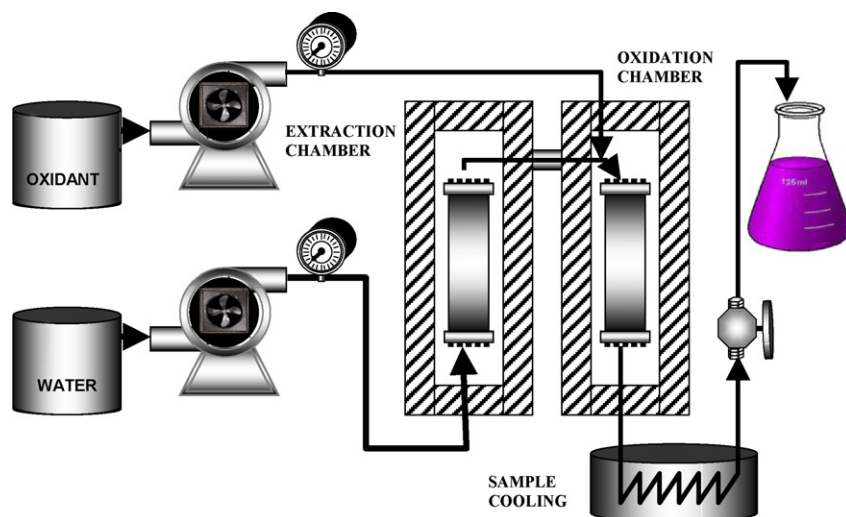


Fig. 6. Experimental setup to conduct high temperature high pressure experiments on contaminated soils. Water is fed to the extraction chamber. The extract is oxidised in the oxidation chamber, cooled and further depressurized to collect samples.

Table 3  
Bibliographic compilation of high pressure/temperature soil remediation technologies

Reference	Variables studied	PAHs oxidised	Parameters measured	Notes
[69]	Extraction time, extraction temperature, oxidation time, oxidation temperature, H <sub>2</sub> O <sub>2</sub> dose	Naphtalene, fluorene, anthracene, phenathrene, pyrene, chrysene, perylene	PAHs concentration, intermediates	The process used is a combination of consecutive extraction + supercritical hydrogen peroxide oxidation. Temperature increases extraction efficiency but not the oxidation stage. PAHs dissolved in toluene, most of H <sub>2</sub> O <sub>2</sub> is consumed to degrade toluene
[70]	Extraction vessel diameter, flow direction, flow-rate	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno-1,2,3,(c,d)pyrene	PAHs concentration, by-products, TOC	The process used is a combination of consecutive extraction + subcritical persulfate oxidation. Temperature shows an optimum value around 300 °C in oxidation efficiency. Similarly, increasing oxidant dosages exert a positive effect
[71]	Soil nature	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, perylene, benzo(g,h,i)perylene, indeno-1,2,3,(c,d)pyrene	PAHs concentration, by-products, TOC	The process used is a combination of consecutive extraction + supercritical hydrogen peroxide oxidation. Temperature positively influences the extraction stage. Pressure effect is not investigated
[72]	Water flow-rate, extraction temperature, scaling up, comparison to bioremediation and SFE with CO <sub>2</sub>	Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, acenaphthene, fluorine, phenathrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b,k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3,c,d)pyrene, benzo(g,h,i)operylene	PAHs concentration, fertility, toxicity	At 275 °C (1 mL min <sup>-1</sup> , 8 g of soil) all PAHs are extracted from a real soil. Studies are conducted at laboratory and pilot plant scale. Extracted water shows a brownish aspect. Natural flocculation of water occurs overnight with subsequent removal of PAHs. No oxidation data are reported
[73]	Temperature extraction, soil nature, oxidising agent	Acenaphthene, phenathrene, fluoranthene, chrysene, benzo(a)pyrene, pyrene	PAHs concentration	The process used is a combination of simultaneous extraction + wet air oxidation (oxidising agent is air, oxygen or hydrogen peroxide). Temperature exerts a positive effect on extraction. Hydrogen peroxide is the best oxidant

wet persulfate oxidation is used [70] an optimum in temperature is also experienced mainly due to opposite effects, i.e., higher organics oxidation rate and higher inefficient persulfate decomposition rate.

Lagadec et al. [72] attempted to scale up the subcritical water remediation of PAHs contaminated soils. These authors carried out experiments in both lab and pilot plant scale and compared their results. In the first case, a temperature of 275 °C was sufficient to remove all PAHs of a historically contaminated soil below the detection limit of the analytical procedure followed. When extrapolating the experimental conditions to a pilot scale, the extraction of high molecular weight PAHs was somewhat delayed, probably due to a slower soil heating if compared to the laboratory experiment.

Dadkhah and Akgerman [73] carried out some assays on artificially contaminated soils and naturally polluted soils from a railroad tie manufacturing plant. They completed the simultaneous extraction–subcritical oxidation of PAHs in batch mode in the presence of air, oxygen or hydrogen peroxide. For spiked soils, extraction under inert atmosphere of nitrogen was almost complete at 270 °C, a fraction of the heavier PAHs remained in the soil after extraction. However, use of an oxidising agent was capable of achieving values above 99% of PAHs removal from soils, even when the combined process was conducted at a lower temperature than the single extraction process in the pres-

ence of nitrogen (250 °C versus 270 °C, respectively). Analysis of PAHs in water confirmed the oxidation of these compounds to levels close to zero. The oxidation extent varied depending on the PAH considered and the oxidising agent used. Conversion values oscillated between 91% for phenanthrene in the presence of air to almost 100% for anthracene in the presence of oxygen or hydrogen peroxide. The efficiency of the oxidants followed the order air < oxygen < hydrogen peroxide. When using the real soil, the previous results were confirmed experiencing even better conversions due to lower PAH concentration in the latter matrix if compared to the spiked soil.

### 5.3.2. The kinetics

No kinetic studies are reported on the wet oxidation of PAHs dissolved in soils. Lagadec et al. [72] illustrated the evolution of PAHs extraction with time at bench scale; however, the investigations published to the present moment only give information on the final PAHs degradation/removal with no attention paid to the velocity of the process. Basically the stages involved in the mechanism would be similar to those reported for the Fenton system. In this case, if hydrogen peroxide is used as the oxidising agent, its activation would be accomplished by simple thermal scission:



If oxygen is employed, the dissolution of this species into water should be taken into account:

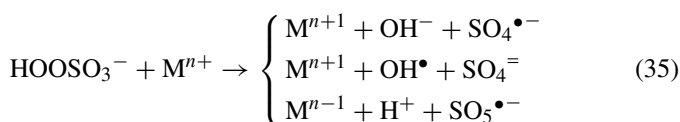
$$\frac{dC_{O_2}}{dt} = k_L a (C_{O_2}^* - C_{O_2}) \quad (34)$$

where  $k_L a$  is the global mass transfer coefficient and  $C_{O_2}^*$  indicates oxygen concentration in equilibrium for a given temperature and pressure. Normally, wet air oxidation processes are carried out in an excess of oxygen so its concentration can be considered constant throughout the whole oxidation period.

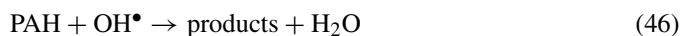
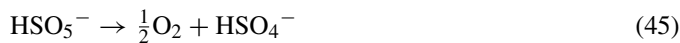
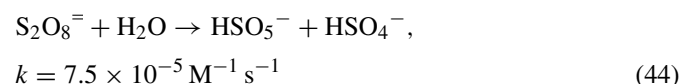
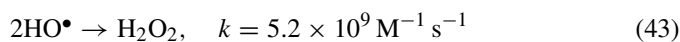
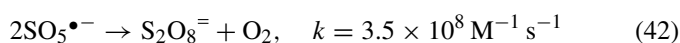
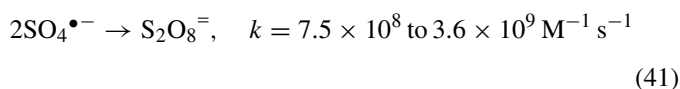
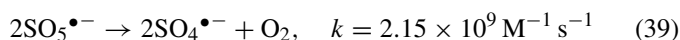
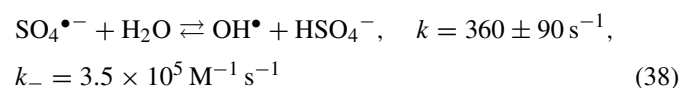
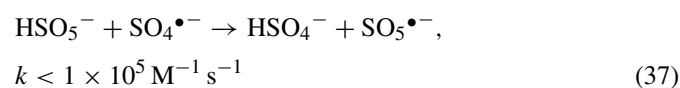
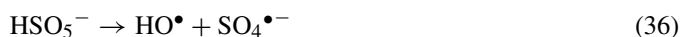
### 5.3.3. Integrated processes

Similarly to the kinetic studies, there is a lack of investigations dealing with the combination of high pressure high temperature remediation of PAHs with other technologies, especially biodegradation processes. The advantages that other oxidation technologies offer for a further polishing stage based on conventional biodegradation processes are, in this case, improved due to the extraction capacity of hot water.

Use of co-solvents would likely improve the extraction efficiency achieved allowing for the use of milder conditions. These milder conditions would eventually permit the implementation of other oxidising agents like ozone, persulfate, etc. Addition of monopersulfate is a recent alternative in wet oxidation processes [74]. Commercialized under the name of OXONE<sup>®</sup>, this salt is capable of generating sulfate radicals with a higher oxidising capability than hydroxyl radicals. Although OXONE<sup>®</sup> is normally used at room conditions in the presence of a metallic catalyst ( $M^{n+}$ ):



under high temperature conditions the monopersulfate molecule decomposes to initiate a radical mechanism similar to the one reported for the wet air oxidation [74]:



## 6. Final considerations

The crucial factors when considering chemical oxidation as the remediation technology of contaminated soils are the oxidant capability of the reagents used and their effective feeding into the contaminated soil. The latter problem can, however, be minimised if “on site” or “off site” procedures are applied. If “in situ” technologies are to be used, surface heterogeneities and preferential flow paths can lead to the presence of untreated areas once the oxidation has taken place. Another feature to be accounted for is the attack of oxidants to natural organic matter and the subsequent release of sorbed PAHs to groundwater (especially in permeable soils). Knowledge of the soil nature and physico-chemical characteristics is of paramount importance at the time of considering any chemical oxidation system. Additionally hydro geological factors have also to be taken into account if “in situ” processes are to be implemented. The Interstate Technology and Research Council [48] recommends the measurements of the following geological and chemical data:

- *Hydrogeologic.* The parameters included in this section consider the hydraulic conductivity/permeability, particle size distribution, soil porosity, and fluid flow direction and gradient. The latter property is of paramount importance to assess the potential migration of released contaminants/by-products.
- *Chemical data.* Chemical characterization of contaminants sorbed on soils is crucial to check for PAHs preferential locations and to assess the efficiency of the treatment. Also, the presence of other contaminants or reducing agents different from PAHs should be evaluated. The data would actually help to properly dose the oxidising reagents. The oxidant demand is usually delineated by measuring the oxidisable matter of a soil.

Also, depending on the chemical technology adopted, additional data should be necessary (i.e. the presence of iron species, the media pH, carbonates, moisture content, etc.).

A significant lack of kinetic data is experienced when surveying the related literature. Kinetic data help to reactor design and scaling up as well as reagent’s dosing. Also, more pilot plant studies are required to properly assess the potential use of the different technologies at the time of scaling up.

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