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PAHs contaminated soils remediation by ozone oxidation

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ABSTRACT

Remediation of PAHs contaminated soils by means of chemical oxidation is considered an attractive option because of its effectiveness in the removal of PAHs from polluted environmental matrices. In recent years, the use of ozone has gained increasing interest since this technology can be successfully implemented both in situ and ex situ as well as remediation time is fast compared to other options. Moreover, the use of gaseous ozone can provide several advantages over aqueous oxidants, such as Fenton's reagent or permanganate, as a consequence of its easier spread into unsaturated porous media. In this paper, after an introduction of PAHs properties and their environmental fate, and a short overview of the remediation technologies for the treatment of PAHs contaminated soils, the use of ozonation process for the removal of PAHs from contaminated soils is reviewed. In particular, PAHs degradation kinetics by ozonation, factors effecting ozonation efficiency, formation of oxidation intermediates and toxicity are tackled.

Keywords: Biological treatments; Chemical oxidation; Physical treatments; Thermal treatments; Oxidation intermediates; Toxicity

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic compounds which major sources are correlated to petroleum products and to the incomplete burning of fossil fuels [1–3]. The increasing interest on PAHs contaminated soil is due to the toxicity, persistency and occurrence of these compounds [4–7]. Indeed, 16 PAHs have been selected as priority pollutants by the United States Environmental Protection Agency [8].

Two approaches are typically used for the remediation of PAHs contaminated soils: (i) control or immobilization of hazardous material, (ii) treatment of the contaminated soil up to achieve an residual concentration which results in an acceptable risk to public health [6].

Ozone based technologies are considered as an attractive option for the remediation of PAHs contaminated soils because of its effectiveness demonstrated on environmental matrices contaminated by recalcitrant PAHs [9]. Moreover, chemical oxidation by ozone can also be integrated with biological treatments. Several papers [3,9–11] suggest that ozonation pre–treatment can enhance the biodegradability of PAHs which became more available for further biological oxidation [12].

In the present paper remediation of PAHs contaminated soils by means of ozone based technologies is reviewed. After an overview on PAHs properties, their fate into the environment, and the remediation techniques used, the factors effecting the efficiency of PAHs treatment by ozonation in the soil are discussed.

2. Properties and environmental fate of PAHs

PAHs are a group of chemical compounds that are formed during the incomplete combustion or pyrolisis [13–15] of coal, oil, gas, wood, garbage, or other organic

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substances [5,16–17]. Natural sources include the release from forest fires, volcanic eruptions or petroleum products [15]. However, anthropogenic sources have now become the major route of entry of PAHs into the environment [18,19].

PAHs are relatively neutral and stable molecules consisting of two or more fused benzene rings which physico-chemical properties vary widely. In general, PAHs are characterized by high molecular weights, low solubility, low volatility and low biodegradability and tend to strongly adsorb to natural soil organic matter [9,20–23]. The low molecular weight (LMW) PAHs are known to be much more water soluble and volatile than the high molecular weight (HMW) ones, while the HMW PAHs show higher hydrophobicity [1,5]. Since PAHs are strongly adsorbed to the organic matter, they tend to be relatively unavailable for degradation processes. As a result, the range of half-lives for PAHs in soil is quite large and, depending on the compound, it can vary from 2 mon to 2 y or 8–28 y [24]. Therefore, PAHs are regarded as persistent organic pollutants (POP) and their environmental behaviours are largely determined by their physical-chemical properties [5–19]. It is well known that the transfer and the turnover are more rapid for LMW PAHs than for the heavier PAHs [20] since the persistence of such compounds increases with ring number and condensation degree [14]. Furthermore, it has been shown that the degradability and extractability of organic compounds in soil decreases with the time they have been in contact with the soil. This phenomenon is regarded as ‘aging’ or ‘weathering’. The processes of adsorption and aging have a double effect on the fate of PAHs. On one hand, they limit the degradability of the contaminants and, on the other hand, these processes reduce the toxicity of the soil contaminants by lowering the fraction available for uptake by living organisms [5].

Table 1 shows chemical and physical properties of the 16 PAHs included in priority pollutants list by the US—environmental protection agency (EPA).

Although PAHs are considered one of the most important atmospheric pollutants, due to their chemical-physical characteristics the main environmental delivery is the soil (95%) as opposed to air (0.2%) [1]. Deposition from atmosphere is regarded as one of the main sources of PAHs in soil [19], hence soil contamination with PAHs increases considerably in industrial and urban areas [2,14,15]. The background concentrations found in European and North American soils extend from 50 to 500 μg/kg [14] and, as expected, the higher concentrations have been found in urban soils and roadside soils [1,2]. Contaminated sites, on the other hand, can be characterized by much higher concentrations (>10,000 mg/kg soil) [20]. Recently the features and the behaviour of PAHs in agricultural soils is gaining increasing attention since an excessive accumulation of these compounds may not only result in environmental contamination but also in a high uptake of PAHs by crops, which may effect the quality and safety of food [18]. Atmospheric deposition is considered to be also a significant source of PAHs for

Table 1
Properties of the 16 PAHs listed by USEPA as priority pollutants [25]

PAH	Structural formula	Number of benzene rings	Molecular weight [g/mol]	Water solubility [mg/l]	Vapour pressure [mm Hg]	log k_{ow}
Naphtalene	$C_{10}H_8$	2	128.2	–	–	–
Acenaphthylene	$C_{12}H_8$	3	152.2	1.93	4.47×10^{-3}	3.98
Acenaphtene	$C_{12}H_{10}$	3	154.21	3.93	0.029*	4.07
Fluorene	$C_{10}H_{10}$	3	166.2	1.68–1.98	3.2×10^{-4}*	4.18
Phenantrene	$C_{14}H_{10}$	3	178.2	1.20	6.8×10^{-4}**	4.45
Anthracene	$C_{14}H_{10}$	3	178.2	0.076	1.7×10^{-5}**	4.45
Fluoranthene	$C_{16}H_{10}$	4	202.26	0.20–0.26	5.0×10^{-6}**	4.90
Pyrene	$C_{16}H_{10}$	4	202.3	0.077	2.5×10^{-6}**	4.88
Chrysene	$C_{18}H_{12}$	4	228.3	2.8×10^{-3}	6.3×10^{-7}**	5.16
Benzo[a]anthracene	$C_{18}H_{12}$	5	228.29	0.010	2.2×10^{-8}*	5.61
Benzo[a]pyrene	$C_{20}H_{12}$	5	252.3	2.3×10^{-3}	5.6×10^{-9}	6.06
Benzo[k]fluoranthene	$C_{20}H_{12}$	5	252.3	7.6×10^{-4}	9.59×10^{-11}	6.06
Benzo[b]fluoranthene	$C_{20}H_{12}$	5	252.3	0.0012	5.0×10^{-7}*	6.04
Indeno[1,2,3cd]pyrene	$C_{22}H_{12}$	6	276.3	0.062	10^{-11}–10^{-6}*	6.58
Benzo[g,h,i]perylene	$C_{22}H_{12}$	6	276.34	2.6×10^{-4}**	1.03×10^{-10}**	6.50
Dibenzo[a,h]anthracene	$C_{22}H_{14}$	6	278.35	5×10^{-4}	1.0×10^{10}*	6.84

*20°C; **25°C.

surface waters. In the aquatic systems, the hydrophobic organic pollutants are rapidly entrapped by suspended and bed sediments causing sediment contamination [21]. Investigations on Adriatic Sea sediments showed PAHs concentrations in the range 7.2–797 μg/Kg [22]. Since the bioavailability of PAHs adsorbed to sediments is rather low, the polluted sediments also represent an important source of contamination for freshwater animals [2].

3. Remediation technologies for PAHs contaminated soils

The strategies of PAHs contaminated soil remediation depend on the extent of contamination as well as on the qualitative and quantitative content of contaminants [14,20]. Generally, two different approaches can be considered: the containment/immobilization of the hazardous materials and the treatment of the polluted soil to clean it up to an acceptable level of contamination [6]. Soil remediation can be performed by 'in situ' methods, without removing the soil, or by 'ex situ' methods, involving the excavation of the soil which can be treated on site, or moved to another place ('off site'). The containment actions are aimed to prevent the migration of pollutants in the environment by means of physical, chemical or hydraulic barriers [26]. This option was more practical and popular among technicians but, with the increasing of the environment awareness, the containment methods are considered to simply pass the problem to the next generation [6]. Thus this technique is usually temporarily used while waiting for an appropriate treatment [14].

In Table 2 the qualitative efficiency of the main treatment technologies on the removal of PAHs soils is summarized.

3.1. Thermal treatments

Thermal treatments, such as incineration and thermal desorption, are the most effective and applied techniques, since the soil can be used freely after treatment. However their cost is relatively high because they involve soil excavation, transport and heat processes [14].

3.2. Physical treatments

The removal of non volatile or non soluble compounds can be achieved by means of physical treatments. PAHs can be extracted with the help of solvents or surfactants agents, which enhance their availability, transferring afterwards the contaminant in a liquid phase that is specifically treated [13]. However, the extraction stage as single treatment technology does not seem to be a conclusive solution for the remediation of PAHs contaminated soils [12]. Moreover the use of solvents or surfactants is usually discouraged because of the high solvent concentrations required to achieve good results [27].

Table 2
Treatment technology efficiency on PAHs removal [26]

Treatment technology	Mode	Removal efficiency
Containment	in situ	+
Solidification/stabilization	in situ	+
Thermal		
thermal desorption	in situ	++
thermal desorption	ex situ	++
incineration	ex situ	++
pyrolysis	ex situ	++
Physical		
soil flushing	in situ	+
soil vapour extraction	in situ	–
solvent extraction	ex situ	++
soil washing	ex situ	+
Chemical		
chemical oxidation	in situ	–
chemical oxidation	ex situ	+
Biological		
bioventing	in situ	++
enhanced bioremediation	in situ	++
phytoremediation	in situ	+
composting	ex situ	+
landfarming	ex situ	++
bioslurry	ex situ	++

++ good efficiency; + limited efficiency; – no efficiency.

3.3. Chemical oxidation

Chemical oxidation technique is gaining increasing interest for PAHs contaminated soil cleanup, since this treatment yields a fast removal and is not so sensitive to contaminant type and concentration, so that it can be considered as a promising technology for the degradation of high molecular weight PAHs [9,28]. Chemical oxidation is based on the introduction of strong oxidants into contaminated soil in order to degrade organic pollutants in simpler compounds such as carbon dioxide and water or intermediates which are more soluble then parent compounds [11]. The most commonly oxidants used for the degradation of organic pollutants are hydrogen peroxide/Fenton agents, permanganate, persulfate and ozone [12,13,28,29]. Hydrogen peroxide is a powerful oxidizing agent, but at low concentrations (<0.1%) its kinetic is not fast enough to promote the degradation of many hazardous organic contaminants [30]. Hence, to achieve the desired contaminant reductions in a reasonable time, a metal catalyst is required. The oxidative strength of peroxide is commonly increased by the addition of a ferrous salt (Fe^{2+}) as catalyst [10] and this mixture is known as Fenton's reagent. In order to maximize the available Fe^{2+}, acid conditions are necessary with an optimal range about 3.5–5 [27]. Nevertheless, a low pH can mobilize the naturally occurring and anthropogenic metals present in the soil thus resulting in an increased dissolved metal concentration in the groundwater. This concern represents one on the main drawbacks related to the application of the technology [30].

Permanganates ($KMnO_4$ and $NaMnO_4$) are strong oxidizing agents with a unique affinity for oxidizing organic compounds containing carbon-carbon double bonds, aldehyde groups, or hydroxyl groups. However permanganates are not effective at oxidizing most aromatic compounds and MnO_2-precipitates can reduce subsurface permeability of the soil [30].

Persulfate is the most recent form of oxidant agent being used for environmental applications [27] and sodium persulfate is the most commonly used salt. The main concerns addressed in the application of persulfate to oxidize organic compounds in soil and groundwater are related to the low pH conditions that may be generated by persulfate decomposition which can mobilize metals present in the soil with the increasing of metal concentrations in the groundwater [30].

Ozone is a gaseous oxidant widely used in wastewater treatment for the oxidation of organic contaminants and successfully applied on PAHs contaminated soil remediation with the purpose of degrade recalcitrant organic pollutants into compounds which are more soluble in aqueous phase [31,32]. In situ ozonation can be carried out by the introduction of gaseous or aqueous ozone by means of injection wells carefully drilled [12,31]. The "ex situ" applications involve the soil excavation and offer a higher remediation efficiency than in situ facilities due to a more exhaustive control over the chemical process [12,33]. The use of ozonation for the remediation of PAHs contaminated soils is the specific aim of the present review and it is discussed in detail in Chapter 4.

3.4. Biological treatments

Bioremediation technologies use the natural capacity of microorganisms to metabolize organic substances into harmless compounds [34,35]. The treatment is achieved by the optimization of process conditions (by aeration, moisture and nutrients addition) in order to accelerate the biological degradation of the contaminants [14]. Biodegradation is one of the most environmentally and cost-effective soil remediation technologies that has been successfully used for the removal of petroleum compounds. Ex situ bioremediation (achieved in a confined and controlled environment) is suitable for the treatment of soils contaminated with LMW PAHs (3–4 aromatic rings), however it often shows limited applicability on degradation of high molecular weight ones (5–6 aromatic rings) that are very recalcitrant due to their low water solubility [28,36]. Anyway, in most cases the kinetics of the process is too slow due to tight bound between contaminant molecules and the soil [12,13].

4. Ozone treatment of PAHs contaminated soils

Ozone is an important oxidant in nature and it is the precursor of transient secondary oxidant species via reactive decomposition in aqueous solutions and sand surface. The detected species include hydroxyl ($OH^\bullet$), perhydroxyl ($HO_2^\bullet$), superoxide ($O_2^{\bullet-}$), ozonide ($O_3^{\bullet-}$) radicals, singlet oxygen (O_2) and hydrogen peroxide (H_2O_2) [37–39]. Ozone is known to react with aromatic compounds leading either to a substitution (atom attack) or to a ring opening (bond attack). The reactivity of PAHs to ozone can be correlated with the atom or bond localization energies of the compounds [40]. The smaller the localization energy and the greater is the reactivity of the compound at a certain position of the aromatic ring [20]. Chemical reactions involved in ozone oxidation process can be divided into two categories: direct oxidation and indirect oxidation [30]. In the first, the oxidation of the targeted chemical is carried out by the parent oxidizer ozone. The typical modes of attack involve the insertion of the ozone molecule into unsaturated carbon-carbon bonds which results in the formation of an ozonide. On the other hand, indirect pathway rely heavily on the hydroxyl radical ($OH^\bullet$) for the oxidation of the contaminant. Hydroxyl radicals are nonselective oxidizers, which rapidly attack organic contaminants and break down their carbon-to-carbon bonds. However, the oxidation pathway of ozone in the soil depends on several factors. Gaseous ozone reacts with PAHs adsorbed onto the soil by means of direct oxidation [41] according to the reaction Eq. (1).

$$O_3 + \text{Soil} - \text{PAH} \rightarrow \text{Soil} - \text{PAH}_{\text{ox}} \ (\text{eventually} + CO_2 + H_2O) \tag{1}$$

Nevertheless gaseous ozone could also decompose on soil active surfaces (i.e., metal oxides, soil organic matter, etc.) [41] to generate hydroxyl radicals according to the reaction Eq. (2).

$$O_3 + \text{Soil} \rightarrow \text{Soil} - HO^\bullet + O_2 \tag{2}$$

In the latter case hydroxyl radicals are responsible of PAHs degradation as reported in the reaction Eq. (3).

$$\text{Soil} - \text{HO}^{\bullet} + \text{Soil} - \text{PAH} \rightarrow \text{Soil} - \text{PAH}_{ox} \text{ (eventually} + CO_2 + H_2O) \qquad (3)$$

In the aqueous phase, the oxidation pathway is mainly effected by pH value; therefore direct ozonation occurs in acid environment while hydroxyl radicals formation is achieved at high pH values [11]. Generally PAH-ozonation in aqueous media can take place by both direct and radical reactions at neutral pH [42]. Moreover, soil ozonation can be achieved in gaseous phase or in aqueous phase [12,29]. Masten and Davies [31] proved that the use of gaseous ozone lead to higher PAHs removal than the one obtained with aqueous ozone solution. Gaseous ozone is characterized by a higher diffusivity that improves the accessibility to contaminants. In addiction, the concentrations of ozone gas are several orders of magnitude higher than those achieved in aqueous phase [12]. It is important to underline that both in gaseous and aqueous phase applications, at the end of the reaction, ozone tends to decompose into oxygen without production of any residues harmful for the environment as conversely happens for other oxidants. It results in a highly aerobic environment that can promote the activity of indigenous bacteria enhancing natural aerobic biodegradation [10]. However, an excess of ozone may have a sterilizing effect on the soil that, dramatically reduce the natural bacterial population [10,43].

As discussed beyond, the efficiency of the ozonation treatment depends on several factors including soil moisture, ozone dose, physical chemical properties of the soil, pH values in the soil, physical chemical properties of the contaminant.

4.1. PAHs degradation kinetics during ozonation

Although the number of studies aimed to assess the kinetics of PAHs ozonation in water or oil/water emulsions is relatively large, just a few works have been focused on the reaction kinetics involved in the ozonation of PAHs adsorbed on soils. Generally the latter works are focused on the assessment of ozone decomposition constant instead of PAHs reaction kinetic. PAHs reaction rate in aqueous phase can be described by the following equation, modified from [42].

$$-\frac{dC_{PAH}}{dt} = k_{03} C^{n}{}_{PAH} C_{03}{}^{m} + k_{OH^{\bullet}} C^{n}{}_{PAH} C^{m}{}_{OH^{\bullet}}$$

where n and m are reaction orders, k_{O3} is the reaction rate constant of direct reaction, k_{OH} the reaction rate constant of radical reaction, C_{PAH} the PAH-concentration, C_{O3} the dissolved molecular ozone concentration and C_{OH} the concentration of radicals.

Commonly in water solutions second order kinetic can better describe the reactions [38,44]. Direct reaction rate constants k_{O3} are usually in the range $10–10^3$ $M^{-1}s^{-1}$, while those of the radical reactions k_{OH} are much higher $10^8 - 2 \times 10^9$ M^{-1} s^{-1}. However most of the reaction constants reported in literature refer to both reaction types ($k = k_{O3} + k_{OH}$) [42].

Selective ozonation of highly condensed PAHs in oil/water-emulsions could be described microkinetically by a direct ozone reaction of pseudo-first order (regarding PAHs concentrations). The PAHs mean reaction rate constants are about 1.02 min^{-1} in oil/water-emulsions and are in the upper range compared to those achieved for PAHs dissolved in water [42]. Even in case of PAHs adsorbed on solid matrix (silica particles), the decay of particulate PAH concentrations versus time follows a pseudo-first order kinetic [40,45]. Under this condition, two decay patterns were observed for the reactions of particulate PAHs with ozone. In the first, a total degradation was observed after reaction proving that the oxidation of PAHs by ozone was total. In the second, PAH degradation reached a plateau, which means that PAHs concentrations were becoming stable whatever the increase of reaction time. This suggests that, for some types of particles, the whole quantity of particulate PAHs is not available to the oxidation [40]. In Table 3, the kinetic constant k for the degradation of different PAHs by ozone are summarized.

4.2. Influence of water content of the soil

Several studies demonstrate that soil water content has a great influence on the effectiveness of PAHs oxidation in unsaturated soils, thus the greater the water content of the soil the less effective the ozone treatment. Masten and Davies [31] found out that the efficiency of pyrene removal decreases with the increasing of moisture content in the contaminated soil. As a result, in the air dried soil, the effectiveness of pyrene removal was as high as 63% while in the same soil characterized by an higher moisture content (2.9%) the equivalent ozone mass resulted in a treatment efficiency of 30%. O'Mahony et al. [32] also reported a drastic reduction of phenanthrene removal as the water content of soils increased from 0% to 50%. Luster-Tasely [50] confirmed that, compared to dry soil, wet soils resulted in a lower overall pyrene removal: at pH 6, pyrene removal reached 94.9% in dry soils compared to 55.5 and 33.8% removals obtained in 5 and 10% moisture soils respectively. Similar results were achieved by Zhang et al. [51] who observed that moisture content led to higher anthracene removal (i.e., 51.8%, 55.8% and 59.3% when moisture contents were

Table 3
Reaction constant *k* of PAH degradation with ozone in several matrices

PAH	Matrix	Co	Operating conditions	k_{PAH}	Order	Ref.
Phenanthrene	Water	$4.04\ 10^{-6}$ M	Semi-batch, stirred reactor, V_L 4.6 L, pH 7, T 20°C	$4.4 \times 10^{-3}\ s^{-1}$	II	[44]
Naphtalene	Water	$0.4 - 0.7 \times 10^{-5}$ M	Semi-batch, bubble column, V_L3 L, pH 5.6, T 1°C	$5.5 \times 10^{2}\ M^{-1}s^{-1}$	II	[46]
Fluoranthene	Water	$2.0 - 4.1{\times}10^{-6}$ M	Semi-batch, bubble column, V_L1,5 L, pH 6.5, T 20°C	$4.2 \times 10^{3}\ M^{-1}s^{-1}$	II	[47]
Phenanthrene		$1.3 - 5.5 \times 10^{-6}$ M		$1.0 \times 10^{4}\ M^{-1}s^{-1}$	II	
Pyrene		$0.13 - 0.3{\times}10^{-6}$ M		$3.6 \times 10^{4}\ M^{-1}s^{-1}$	II	
Benzo[a]pyrene		$0.05 - 1{\times}10^{-8}$ M		$5.3 \times 10^{4}\ M^{-1}s^{-1}$	II	
Benzo[e]pyrene	Oli/water emulsion	$1.1 - 5 \times 10^{-6}$ M	Semi-batch, stirred reactor, V_L 3 L, pH 6.7, T 30°C, dodecane 750 mg L^{-1}	1.01 min^{-1}	I	[42]
Benzo[k]fluoranthene		6.3×10^{-6} M		1.03 min^{-1}	I	
Phenanthrene	Silica particles	500 µg/g	Reactor cells containing particles deposited on glass fibre filter	$1 - 4 \times 10^{-3}\ s^{-1}$	I	[40]
Anthracene		500 µg/g		$4.5 - 10 \times 10^{-3}\ s^{-1}$	I	
Fluoranthene		500 µg/g		$1.5 - 4.5 \times 10^{-3}\ s^{-1}$	I	
Pyrene		500 µg/g		$1.5 - 5 \times 10^{-3}\ s^{-1}$	I	
Benz[a]anthracene		500 µg/g		$1.5 - 5.5 \times 10^{-3}\ s^{-1}$	I	
Chrysene		500 µg/g		$1.5 - 2.5 \times 10^{-3}\ s^{-1}$	I	
Benzo[k]fluoranthene		500 µg/g		$2.5 - 15 \times 10^{-3}\ s^{-1}$	I	
Benzo[e]pyrene		500 µg/g		$1 - 4 \times 10^{-3}\ s^{-1}$	I	
Benzo[a]pyrene		500 µg/g		$1.5 - 4.5 \times 10^{-3}\ s^{-1}$	I	
Indeno[1,2,3cd]pyrene		500 µg/g		$1 - 4 \times 10^{-3}\ s^{-1}$	I	
Benzo[ghi]perylene		500 µg/g		$1 - 4 \times 10^{-3}\ s^{-1}$	I	
Coronene		500 µg/g		$5 \times 10^{-3}\ s^{-1}$	I	
Dibenzo[a,l]pyrene		500 µg/g		$1 - 4 \times 10^{-3}\ s^{-1}$	I	
Anthracene	Silica particles	500 µg/g	Reactor cells containing particles deposited on glass fibre filter	0.63 min^{-1} (I)	I	[45]
Phenanthrene		500 µg/g		2.9 min^{-1} (I)	I	
Pyrene	Silica particles	500 µg/g	Soild phase ozonation. Mixture of Pyrene, 1-hydroxypyrene and 1-nitropyrene.	$5.5 - 15.5 \times 10^{-3}\ s^{-1}$	I	[48]
Phenanthrene	Spiked soil	212 mg/kg	Soild phase ozonation. SOM 2800 mg/kg	$1.42 \times 10^{-4}\ s^{-1}$ (*)	II	[49]

I: first order (s^{-1}).

II: second order ($M^{-1}s^{-1}$).

*Value adapted by [23].

9.1%, 4.8% and 0%, respectively). The decrease of ozone efficiency with the increase of soil water content may be due to the fact that PAHs become less accessible to ozone in the presence of water. The latter leads to a reduced contact time of ozone and decreases pore space in the soils hindering the transport of gaseous ozone through the solid matrix [32]. Moreover, moisture increases ozone demand [31] since the presence of water promotes the dissolution of natural soil organic carbon [32]. As a consequence, the observations reported above suggest that higher ozone concentrations would be needed to remediate moist contaminated soils [50].

4.3. Influence of pH values

Ozonation efficiency on PAHs removal is strongly affected by pH values as literature data suggest.

Kornmuller et al. [36] determined the influence of pH on the ozonation treatment of PAHs in oil/water emulsion. Authors observed that the rate of the oxidative reaction of PAHs with ozone decreases as pH increases. Faster reaction rate is achieved under acid conditions (pH 2.5) which are correlated with the direct oxidation of the aromatic compounds. At high pH values (10.9) the oxidation rate dramatically decreases probably because of the decomposition reactions of ozone.

Haapea et al. [11] investigated the effect of pH on the mass balances of PAHs remaining in the liquid and solid phases after a slurry phase ozonation. Results showed that the highest overall removal of PAHs was obtained under acidic conditions for each ozone dose applied according to previous works. Conversely, Luster-Tasely et al. [50] found out that the removal of pyrene from air-dried soil increases according to pH . The order for pyrene removal was pH 2 < pH 6 < pH 8. In 5% moistured soils, pyrene removal followed the same order observed for air-dried soil. Oh the other hand, opposite results were obtained increasing soil moisture to 10%. In this case pyrene removal followed the order of pH 2 > pH 6 > pH 8.

According to the results discussed above, it is possible to conclude that when PAHs ozonation is carried out in presence of water (i.e., emulsions, slurry phase, soil with high moisture content) the higher removal efficiency is achieved under acid conditions while in air-dried soils or soils characterized by a low water content (5%) the best PAHs reduction is obtained at high pH values.

4.4. Influence of soil matrix

Physical properties of soil matrix have a great influence on the effectiveness of PAH removal by ozone. O' Mahony et al. [32] compared phenanthrene removal in soils characterized by different physical properties and proved that levels of phenanthrene removal in sandy soils were higher than the ones achieved in clayey soil. Sandy soils have larger pore spaces that facilitate an easier transport of gaseous ozone through the matrix; moreover the metal oxides (such as goethite, MnO, Al_2O_3) contained on sand surface can act as catalytic sites accelerating the decomposition of ozone into OH radicals [37]. It is important to underline that metal oxides were also found to play an important role on the migration velocity of the ozone front which was inversely related to the content of these elements; thus catalytic reactions with metal oxides can potentially slow down ozone transport in soils [33].

Low levels of phenanthrene removal in ozonated clay soils were generally attributed to a reduced contaminant reactivity when it becomes adsorbed in clay micropores [32].

In addition, ozone oxidation resulted in a higher PAH removal from sand compared to the results achieved in peat soils. Degradation of PAH in peat during ozonation may be limited by the high content of soil organic matter that results in a strong adsorption of PAH as well as it may consume significant amounts of ozone that therefore is less available to react with the contaminant [9,52]. The latter observation is confirmed by Goi et al. [10] which proved that ozone consumption during the ozonation of non-contaminated soil was significantly lower in sand than in peat. As a result, ozonation of PAH adsorbed on sand required lower ozone doses than ozonation of PAH adsorbed on organic soils such as peat. Finally, it's important to notice that at high pH values ozone generate hydroxyl radicals witch are less selective than ozone [9] and tend to react more easily with soil organic matter. However, the reactivity of ozone with soil organic matter can also promote the desorption of PAHs adsorbed on. This effect can be considered both positive, since more PAHs are available for further chemical or biological oxidation, and negative, in case of in situ ozonation, because the contaminant can likely migrate in ground water [41].

4.5. Influence of the structure of the contaminant

The effectiveness of ozone oxidation depends on the chemical-physical proprieties of the target contaminants. Concerning the reactivity of PAH according to the number of benzene rings, opposite trends have been reported [41]. In aqueous solutions, the increases of the number of aromatic rings lead to an enhancement of the aromatic compounds reactivity to ozone. For example, naphtalene reacts 1500 and phenantrene 10,000 times faster than benzene [38]. Kulik et al. [52] investigated the ozonation potential on soils (sand and peat) artificially contaminated by creosote containing a mixture of seven PAHs formed by three and four aromatic rings. In both ozonated soils, four low-molecular weight PAHs (three-ring) were oxidized by ozone more slowly than higher-molecular weight (four-ring) PAHs in aqueous medium. This observation suggests that the reactivity of ozone increases as the number of fused benzene rings raises. This is based on the consideration of bond localization energies of PAHs, since organic compounds having lower bond localization energy are more easily attacked by ozone molecules. Accordingly, anthracene and pyrene are known to be more reactive to ozonation than naphtalene and phenantrene [53]. Similarly, Rivas et al. [12] observed that in artificially contaminated soil the removal of four-rings PAH is higher compared to three-rings PAH under different operating conditions. Opposite results were obtained in slurry phase by Nam et al. [9] who investigated the ozonation on soils artificially contaminated by a mixture of PAH having a different number of benzene rings: naphthalene (two-rings), fluorene, phenantrene and anthracene (three-rings), pyrene and chrysene (four-rings) and benzo(a)pyrene (five-rings). Experimental data suggest that ozonation can be an effective process to remove PAHs present as a mixture in soil, especially for two- and three-ring hydrocarbons. The authors relate these results to the high volatility of low molecular weight PAHs; so it is likely that the air stream delivering ozone volatilized some of them.

Other authors underline the high importance of solubility of PAHs in water that effects the desorption and transfer of PAHs from solid to liquid phase and represents the limiting factor of PAHs ozonation in sewage sludge [44]. On the other hand, Kornmuller et al. [36], who investigated PAHs ozonation in oil/water emulsions, did not observe any dependency of PAHs reactivity on their solubility in water nor on the number of condensed rings. They concluded that reaction efficiencies were primarily affected by the molecular structure of each PAH. However, it is important to notice that the reactivity of PAHs in the soil is not comparable to the data reported in aqueous phase since substances are usually more slowly adsorbed on soils compared to water solutions [31].

4.6. Influence of contamination age

Since PAHs adsorption to soil was found to increase with longer exposure times [5,54] ozone efficiency in PAHs removal from aged soils is expected to decrease. Luster-Tasely [50] investigated the influence of contamination age on the effectiveness of PAHs ozonation. Soils contaminated by pyrene were stored for 6 mon to compare the efficiency of PAHs removal in freshly contaminated soil and aged soils; pyrene removal efficiency by ozone decreased by 3–4 times in the aged soils compared to freshly contaminated one. Taking into account these results, the predictions of remediation yields and reaction kinetics obtained from laboratory ozonation studies using short-term contaminated soil (i.e., spiked soils) result in an overestimation of the ability to remediate soils characterized by long-term contamination.

4.7. Influence of ozone concentration and contact time

Several authors investigated the effect of ozone concentration, contact time and ozone flow-rate on PAHs removal by ozone oxidation. O' Mahony et al. [32] observed that a greater removal of phenanthrene occurred in soils as ozone dose was increased; an higher oxidation was also observed when contact time was increased. Similar results were obtained by Rivas et al. [41] who investigated different factors effecting the oxidation by ozone of four PAHs composed by 3 aromatic rings (acenaphtene, anthracene, phenentrene) and 4 aromatic rings (fluorantene). Ozone concentration positively effected PAHs removal, although the incremental benefits were difficult to appreciate when high ozone concentrations were used. According to the results of Rivas et al. [41] flow-rate seems to have no influence on the process efficiency. Choi et al. [37] proved that higher bezo(a)pyrene and phenantrene removal was achieved as ozone dosage (mg O_3/min) was increased, confirming that the degradation of organic compounds is proportional to the mass of ozone input. These results are in accordance with studies of Luster-Tasely et al. [50] who observed that pyrene removal efficiency in the soil increased with the increasing of ozone dose expressed as MgO_3/ppm of pyrene. On the opposite, when Kornmuller et al. [36] investigated the ozonation process of PAHs in oil/water-emulsions the removal of benzo(e) pyrene and Benzo(k)fluoranthene was found to be independent by ozone concentration. Finally, it is important to take into account that the oxidation of a PAHs mixture requires an ozone dosage that is greater than the one obtained as arithmetic sum of individual dosage to achieve the same levels of removal as that obtained when hydrocarbons were present singly in soil [9].

4.8. Ozonation intermediates and toxicity

The oxidation of organic contaminants, under suitable conditions, may finally result in a total mineralization with the formation of end products such as carbon dioxide, water and other inorganic compounds. However, as shown above for PAHs, chemical degradation processes more often result in a partial oxidation/mineralization with the formation of a large variety of other compounds (named oxidation intermediates) that are resistant to further degradation [20]. Accordingly, the performance of a soil remediation process can be determined not only by measuring the reduction of the contaminant concentration but also by identifying the main intermediates eventually formed and by assessing their fate into the environment. Specifically, ozonation of PAHs can generate several oxidation intermediates such as o-carboxybenzaldehyde and phthalic acid, observed at low ozone dosage, and oxalic and formic acid, observed at higher ozone dosage [3]. In general, ozonation of PAHs adsorbed onto the soil result in the formation of oxidation intermediates which are characterized by a higher biodegradability compared to parent compounds [11,52]. The common intermediates identified for the ozonation of Benzo[a]pyrene in the aqueous phase included ring-opened aldehydes, phthalic derivatives, and aliphatics which likely abound at different stages of ozonation [3]. The degradation of Benzo[a]pyrene in aqueous phase is initiated by electrophilic attack of O_3 resulting in the formation of ring-opening products (i.e., 3-methylchrysene), aldehydes (7-ethyl-8-ethanal-pyrene), and 4-methyl-5-methanal-chrysene. The reactions of intermediates with O_3 or its oxygenated radicals result in the production of other oxygenated intermediates such as acids (i.e., benzoic acids, butanoic acids) and phthalate. The production of alkenes (i.e. hexene, phentene groups) and alkanes (i.e., pentadecane, octadecane, nondecane) occurred in the later stage. Gao et al. [55] investigated the ozonation of benz[a]anthracene absorbed on azelaic acid particles and showed that two degradation pathways took place: one led by the C atom attack (resulting in the formation of hydroxybenz[a]anthrone and benz[a]anthracene-7,12-dione) another led by the C–C double bond attack resulting in the formation of 2-(2-formyl)phenyl-3-naphthoic acid. Compared to the results achieved from the ozonation of PAHs in liquid-phase [56,57], it can be observed that the ozonation of PAHs may undergo to different pathways depending on the phase involved. The ozonation of phenanthrene resulted in the formation of biphenyl compounds as well as a number of mono-aromatic intermediates such as salicylic acid and phthalaldehydic acid were identified [32]. Moreover, the latter intermediates were found to be more biodegradable than the biphenyl which was less biodegradable than phenanthrene itself. Ozonation of acenaphthylene water solutions resulted in oxidation intermediates such as ketones, aldehydes and carboxylic acids which in turn were degraded to low molecular, harmless end products [58]. A research work aimed to identify the pathway for the ozonation of pyrene in acetonitrile/water mixtures concluded that the contaminant reacted with secondary oxidants formed from ozone self-decomposition in water [56]. In this case, the formation of fourteen intermediates including aldehyde and carboxylic acid substituted phenanthrene and biphenyl-type oxidation products were identified. Herner et al. [59] isolated three main byproducts of pyrene ozonation dissolved in acetonitrile/water solution: 4-carboxypenathrene, 4-carboxy-5- phenanthrene carboxaldehyde and an other compound which functional group was not identified.

The ozonolysis of benzo[a]anthracene dissolved in acetonitrile/wate mixture has been described by Yao et al. [57]. The type of intermediates identified was found to depend largely on the reactions pathway. When the mechanism of reaction is the atom attack, the ozonation by-products are the quinone or hydroxyl functional groups, while the bond attack caused ring cleavage, resulting in phenyl-naphthyl type products. Additionally, the results showed that ozonolysis of benzo[a]anthracene in this solvent mixture occurred preferentially by bond attack rather than by the atom attack type of reaction. Primary products of reaction of gas-phase ozone with anthracene and phenanthrene adsorbed on silica particles were identified [45]. Anthraquinone and anthrone were found to be the main intermediates of anthracene and 1,10-biphenyl-2,20-dicarboxaldehyde the main intermediate of phenanthrene.

The partial oxidation/mineralization of organic compounds may result in the formation of oxidation intermediates more toxic than parent compounds. Oxidation intermediates resulted from the ozonation of benzo[a]pyrene in aqueous phase were found to be biodegradable with a measured first-order rate constant of 0.18 d^{-1} and did not result in any acute toxic effect on *Escherichia Coli* bacteria [3]. A non-genotoxic bioassay able to monitors gap junction intercellular communication (GJIC) was investigated to assess the presence of potential tumor promoters after the ozonation of pyrene in acetonitrile/water mixtures [60]. The higher inhibition effect was observed when pyrene reached a removal as high as 50%, showing that the intermediate products increased toxicity. On the other hand, further ozonation resulted in the formation of stable compounds, most of which were found to be not inhibitory to GJIC. These results are consistent with the conclusion of further works [61] that were focused on the toxicity evaluation (luminescent inhibition bioassay) of the intermediates derived from the oxidation of PAHs dissolved in water solutions by means of UV-based technologies.

Other studies [59] concluded that the pyrene as parent compound was a strong inhibitor of GJIC, more than the main individual ozonation by-products (isolated in laboratory). Moreover, considering the relationship between the structure and the toxicity of pyrene ozonation by products, the obtained results suggested that the presence of an aldeyde group in the molecular structure of the intermediates is at least partially responsible of the GJIC inhibition.

The formation of oxidation products by the ozone reaction of pyrene adsorbed on particles was investigated for the first time by Miet et al. [48]. Oxidation products identified for the heterogeneous reaction of ozone with pyrene are 1-hydroxypyrene, phenanthrene-4,5-dicarboxaldehyde and 4-oxapyren-5-one. Stehr et al. [62] investigated the formation of oxidation intermediates

Table 4
Intermediates identified after PAHs ozonation in different matrix

PAH	Media	Co	Operating conditions	Intermediates	Ref
Benzo[a]pyrene	Water	n.s.	Packed column reactor fed by an ozonated water; batch reactor	Alcane: tridecane; pentadecane; octadecane; octadecane; methyl; nondecane; henicosane Alkenes: 1-pentene, 2-isopropyl; 1-hexene, 4,5-dimethyl, 2-ethyl; 2-hextene, 2,3,4,5-tetramethyl; 3-octene, 5-methyl, 3-ethyl; 3-nonene, 6,8-dimethyl¸ 1-hextene, 3,5-dimethyl, 2-isopropyl¸ 3-nonene, 6,8-dimethyl¸ 1-heptene, 6-methyl, 2-isopropyl¸ Aldehyde: 7-ethyl-8-ethanal-pyrene Phthalic derivatives: phthalic anhydride Acids: 1,2-benzenedicarboxylic acid, diisooctyl;, butanoic acid, 5-oxo allyl ester; benzoic acid, ethyl ester	[3]
Pyrene	Water Acetonitrile/water solution (90:10 v/v)	5 mm	Semi-batch, stirred reactor, V_L 100 ml, pH 3.7	Aldehyde and acid functional groups; dialdehyde and diacid functional groups	[56]
Pyrene	Water acetonitrile/water solution (90:10 v/v)	5 mm	Semi-batch, stirred reactor, V_L 200 ml, pH 2	4-carboxypenathrene; 4-carboxy-5-phenanthrene carboxaldehyde;and other compunds	[59]
Benz[a] Anthracene	Water Acetonitrile/water solution (90:10 v/v)	1mm	Semi-batch, stirred reactor, V_L 100 ml, pH 3.9	Phenyl ± naphthyl type ozonation products; Quinone type ozonation products: benz[a] anthraquinone; Lower molecular weight products: s dihydroxy-naphthalene 2-carboxybenzalDehyde, 2-hydroxybenzoic acid; 2-phthalic acid	[57]
Benzo[e]pyrene	Oli/water emulsion	6.2 µm	Semi-batch, stirred reactor, V_L 2L, pH 6.7, T 30°C, dodecane 750 mg l^{-1}	Ozonide; oxepinone	[63]
Pyrene	Azelaic acid particles	n.s	Reaction chamber containing azelaic acid particles generated by the homogeneous nucleation method	4-carboxy-5-phenanthrenecarboxyaldehyde (71%); hydroxypyrene (23%)	[55]
Benz[a] Anthracene				2-(2-formyl)phenyl-3-naphthoic acid (35%); hydroxybenz[a]anthrone (30%); benz[a] anthracene-7,12-dione (18%)	
Anthracene	Silica particles	500 µg/g	Reactor cells containing particles deposited on glass fibre filter	Anthraquinone; anthrone	[45]
Phenanthrene		500 µg/g		1,10-biphenyl-2,20-dicarboxaldehyde	
Pyrene	Silica particles	500 µg/g	Soild phase ozonation. Mixture of Pyrene, 1-hydroxypyrene and 1-nitropyrene	1-hydroxypyrene; 4-oxapyren-5-one¸ phenanthrene-4,5-dicarboxaldehyde	[48]
Anthracene		50 mg/kg	Soil column artificially spiked with PAHs	9,10-Anthraquinon	[51]

n.s.: not specified.

after ozonation of soils contaminated by phenanthrene. The intermediates formed were biodegraded more efficiently by *Sphingomonas yanoikuyae* or mixed cultures when the ozonation process resulted in monoaromatic compounds. On the other hand, primary ozonation products (with biphenylic structures) were found to be not biodegradable. Toxicity assays using *Bacillus subtilis* and garden cress indicated that the ozonated soils show higher toxic or inhibitory effects towards different organisms than the phenanthrene or PAHs itself.

Table 4 summarizes the main oxidation intermediates detected during the ozonation of PAHs.

5. Conclusive remarks

PAHs have been identified as priority pollutants. Accordingly, soils contaminated by PAHs result in a risk to the environment and human health.

Remediation of PAHs contaminated soils by ozone is considered to be an attractive option because of its effectiveness in the remediation of environmental matrices contaminated by recalcitrant PAHs. Results documented in scientific literature show that the efficiency of ozonation treatment in PAHs removal depends on several factors such as the contaminants reactivity, the soils physicochemical properties and the feeding conditions of ozone into the soil matrix. Therefore, in order to limit the influence of soil heterogeneity and to better control the operating factors as well as the formation of dangerous oxidation intermediates, “on site” or “off site” applications should be carefully chosen. Taking into account that (i) PAHs oxidation intermediates adsorbed onto the soil seem to show higher toxicity or inhibitory effects towards different organisms than the parent compounds but (ii) only a few studies have been focused on by-product production and the toxicological effects of PAHs ozonation in the soil, further investigations are necessary. Finally, it is important to underline that, in order to achieve a successful and safe remediation, the ozonation process should be operated taking into account both the removal of the parent compounds and the formation of potentially toxic by-products.

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