Remediation Technologies for PAH contaminated soils

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1 Introduction

Different treatment processes are available for polycyclic aromatic hydrocarbons (PAHs) polluted sites such as confinement, chemical oxidation or biological and thermal treatments. Nevertheless the adequate treatment will be chosen depending on PAHs concentrations in soils.

Thereby, the treatments of soils polluted by high concentrations of PAHs are essentially based on thermal processes. These include incineration for total hydrocarbon concentrations greater than 40,000 to 45,000 mg/kg, and thermal desorption for concentrations of the order of 15,000 to 40,000 mg/kg (UK Environment Agency, 2004; ADEME, 2009). Treatments by chemical oxidation or biological treatments have recently been used for lower PAHs concentrations (Colombano et al., 2010).

At the present time, in France, management of PAHs polluted sites is often, for financial reasons, is carried out using confinement/encapsulation or by land disposal (ADEME, 2009; Basias, 2010; Basol, 2010). This approach is however not sustainable, and does not in fact remove the pollution but simply postpones the problems.

A state of the art on PAHs treatments as mentioned above is presented in the following chapters. This note mainly refers to laboratory and pilot scale experimentations on PAHs removal techniques. Some case studies on PAHs remediation are also referred to.
PAHs are hydrophobic compounds which have a tendency to sorb preferably to soil organic matter. This hydrophobic behaviour tends to make pollutants less available in solution and makes their remediation using chemical or biological techniques less suitable. However, once adsorbed by soil particles, PAHs can be extracted using appropriate solvents. The extraction process is carried out in two steps. The first step consists of desorbing the PAHs from the soil. The second step consists of leaching the desorbed pollutants within the extracted fluid. Two parameters can influence on the process extraction efficiency: the nature of the solvent used for the extraction, and the mass of contaminated soil versus the volume of solvent added ratio (Silva et al., 2005; Gan et al., 2009). These parameters will also vary depending on which pollutant is being considered, the nature of the soil, and the length of time during which solvents and contaminated soils are in contact.

Numerous research projects have been committed to testing pure solvents or solvents mixtures for PAHs extractions. The results showed that up to 95% of the PAH from contaminated soils can be efficiently removed using solvents such as ethanol, 2-propanol, acetone, 1-pentanol and using ternary mixtures of solvents such as water/1-pentanol/ethanol, water/1-pentanol/2-propanol and acetone/ethyl acetate/water. Contact time between soil and solvent during the experiments went from 3 x 1hour to up to 24hours (Khodadoust et al., 2000; Silva et al., 2005; Gan et al., 2009).

In order to improve soil washing results, the following techniques have been tested:

- Enhanced soil washings using surfactants
- Enhanced soil washing using chelating compounds
- Enhanced soil washings using vegetable oils
- Enhanced soil washings using supercritical water or using Subcritical water

### 2.1 Enhanced soil washings using surfactants

Surfactants are usually used in soil washing techniques to counter balance PAHs low solubility in water. They help enhance extraction efficiency.

Numerous R&D studies have been conducted considering anionic and non-ionic surfactants for enhancing the washing capacity of a heavily contaminated soil with phenanthrene. Results show that extraction efficiency ranged from 33.9 to 84% (Deshpande et al., 1999; Ahn et al., 2008; Rodriguez-Escales et al., 2012). Tested non-ionic surfactants were: Tween 40, Tween 80, Brij 30, Brij 35, T-Maz 80, T-MAZ 20, CA 620 and TerraSurf 80. Tested anionic surfactants were Dowfax 8390, sodium dodecyl benzene sulfonate, sodium dodecyl sulphate and Steol 330. It has to be noted however, that several authors have brought to light the surfactant capacity to sorb onto soil particles. Such process leads to a capture of PAHs by non-mobile surfactants and results into an enhanced adsorption of PAHs onto soil particles (Ahn et al., 2008; Zhou and Zhu, 2007).

### 2.2 Enhanced soil washings using cyclodextrin

Cyclodextrin is used as an alternative to organic solvents and surfactants because of its nontoxic and biodegradability characteristics. Cyclodextrin can greatly enhance contaminant
desorption by complexing with PAHs. This phenomenon decreases PAHs adsorption to the solid phase (Brusseau et al., 1997; Ko et al., 1999). Researchs have shown that using cyclodextrin increases considerably naphthalene and anthracene solubility (Wang et al., 1997; Viglianti et al., 2006). The most effective cyclodextrin used for solubilizing PAHs is methyl-β-cyclodextrin.

2.3 Enhanced soil washings using vegetable oils

Vegetable oils are a powerful sorption agent to extract hydrophobic compounds such as PAHs. Recent researchs have put forward the use of vegetable oils (e.g., sunflower, groundnut, etc.) as non-toxic, cost-effective and biodegradable extractants for decontamination of PAHs-contaminated soil. Results from laboratory-column experiments have shown extraction efficiency is up to 80-100% (Pannu et al., 2004; Gong et al., 2005; Gong et al., 2006).

2.4 Enhanced soil washings using supercritical water or using Subcritical water, followed by oxidation

2.4.1 Extraction using supercritical water

Thanks to its low viscosity and high diffusivity, a fluid under supercritical conditions can facilitate extraction of PAHs from soil particles. Supercritical carbon dioxide is often used to extract PAHs (Schleussinger et al., 1996; Hawthorne et al., 2001; Librando et al., 2003). The authors have demonstrated that extraction efficiency can rise up to 90% and even more in some cases. This efficiency is strongly dependent on soil moisture. The desorption technique is particularly efficient when applied to high molecular weight PAHs.

2.4.2 Extraction using subcritical water (Hot water under pressure)

Subcritical water is more hydrophobic than water under normal conditions (temperature and pressure). When subcritical water and PAHs get into contact, attraction of PAHs to the subcritical water is increased leading to a miscibility of the light PAHs.

Numerous research studies have shown significant results on the removal of PAHs by subcritical water extraction techniques under pilot and laboratory scale experiments (Lagadec et al., 2000; Kronholm et al., 2002). Maximum Extraction efficiency rates (around 80%) were obtained for temperatures between 275 and 300°C and treatment times of 20 minutes (Kronholm et al., 2002), 35 minutes (Lagadec et al., 2000) or up to 20 hours (Kronholm et al., 2002).

Some remediation processes for PAHs polluted sediments were set up on an industrial scale. Amongst these numerous processes, the Zimpro process has been carried out, using oxidation, a water heated between 175 and 320°C and a pressure of 20 MPa for a removal of PAHs up to almost 99% (Abramovitch et al., 1999).
It has to be noted that soil washings treatment techniques require subsequent treatment of the aqueous waste containing solvents. The techniques described in the following chapter present in situ and ex situ treatment of PAHs.
3 In situ and ex situ PAHs biological treatments

Bioremediation techniques are usually categorised under in situ techniques (degradation of the contaminant occurring under natural condition) and ex situ techniques (contaminated soil excavated and treated on another site).

3.1 In situ Bioremediation

In situ biodegradation is one of many techniques available for remediation of soils contaminated by PAHs. However, natural attenuation of PAHs is limited by (i) the PAHs adsorption onto soil organic matter and (ii) low PAHs concentration remaining in solution (i.e. their concentrations are not important enough to maintain a biodegradation processus) (Allan et al., 2007). In addition, increasing contaminant-soil contact times and weathering processes significantly affect bioremediation effectiveness by decreasing the contaminant fraction that would be available to microorganisms (Allan et al., 2007, Sponza and Gok, 2011). However, there are several means to improve biodegradation:

- Biostimulation of PAHs using additional nutriments, electron acceptors, etc.
- Minimising the microbial factor using in situ microbial inoculate. However, the high contaminant fraction adsorbed onto soil organic matter remains an issue;
- Increasing PAHs solubility by adding specific agents.

3.1.1 Biostimulation (external nutrients supplementation)

The presence of electron acceptors such as nitrates and sulphates seem to encourage PAHs biodegradation (Mihelcic and Luthy, 1988; Coates et al., 1996). However their use is limited due to their high diffusivity in soils.

The use of iron (III) oxide has been studied as an alternative but there has been so far no conclusive results (Lovley et al., 1994 ; Li and Wrenn, 2004 ; Li et al., 2010).

3.1.2 Bioaugmentation

Researchers have studied the effects of bioaugmentation (microorganisms injections into contaminated soil) on in situ PAHs degradation. Numerous studies brought to light bacteria and microbial communities that are efficient to degrade PAHs whether they are under aerobic or anaerobic conditions (Wang et al., 1990 ; Otte et al., 1994 ; Hawthorne and Grabanski, 2000 ; Cajthaml et al., 2002 ; Sasek et al., 2003 ; Lamberts et al., 2008 ; Li et al., 2008 ; Leonardi et al., 2007 ; Devi et al., 2011). However, bioaugmentation on its own can have no or little effects on PAHs biodegradation.
3.1.3 Adding specific agents

3.1.3.1 Cyclodextrins
Using cyclodextrins increase the release of PAHs and their availability to microorganisms present in soils and in solutions. Several researchers have demonstrated the positive effects from using both cyclodextrins and PAHs biodegradation processes leading to an extraction efficiency ranging between 14 and 70 % (Wang et al., 1998; Wang et al., 2005; Allan et al., 2007).

3.1.3.2 Surfactants
Several researchers have demonstrated the positive effects from using surfactants for the biodegradation of PAHs (Thiem et al., 1997; Gottfried et al., 2010; Zhu and Aitken, 2010; Bueno-Montes et al., 2011). They have observed that some non-ionic surfactants are more efficient than others to enhance biodegradation and leading to an extraction efficiency up to 62%.

3.1.3.3 Oxygen Release Compounds (ORC)
Solid oxygen sources decompose in the presence of water to produce hydrogen peroxide. They have been investigated as a mean of slowly releasing oxygen into the soil. This technique would improve PAHs biodegradation.

The addition of sodium carbonate peroxhydrate (Na₂CO₃·1.5H₂O₂), commonly referred as sodium percarbonate, has been used to oxygenate saturated soils. However, encapsulation is required because its high water solubility results in rapid release of hydrogen peroxide (Cassidy and Irvine, 2006).

Magnesium peroxide (MgO₂) and CaO₂ are less water-soluble than sodium percarbonate, which allows them to release oxygen over prolonged periods without encapsulation. Magnesium peroxide (MgO₂) and CaO₂ have been studied as they enhance biodegradation of PAHs (Bogan et al., 2003; Kostecki and Mazierski, 2008; Gryzenia et al., 2009; Miksch et al., 2009). Several studies have reported that addition of CaO₂ resulted in increased biodegradation of PAHs ranging between 15 and 83%. The most significant improvement in removal rate (up to 50%) was observed for high-molecular-weight PAHs species (Bogan et al., 2003). Gryzenia et al. (2009) has reported that using 1.9M of CaO₂ catalysed by ethylenediaminetetraacetic acid (EDTA) can treat up to 92% of PAHs. Pilot scale experiments using magnesium peroxide have also shown removal of PAHs up to 98% (EPA, 2001).

3.2 Bioremediation ex situ
Numerous R&D studies have focused on PAHs biodegradation using compost and slurries (landfarming). For example, Wang et al. (1990) have shown that almost all contaminants were eliminated over 12 weeks by a landfarming bioremediation process which consisted of liming, fertilisers and tiling. Another study shows interesting results in contaminant removal by landfarming in a field treatment plot (Hawthorne and Grabanski, 2000). Other studies conducted by Sasek et al. (2003) and Cajthaml et al. (2002) have described removal efficiencies ranging from 35 and up to 80% after 42 days or 100 days of compost being applied onto the contaminated soils (depending on the molecules being considered).
4 Phytoremediation

Several research studies have focused on plants (e.g. ryegrass) as a medium to sustain PAHs remediation in soils. Rezek et al. (2008), Cofield et al. (2008) and Lee et al. (2008) have demonstrated that removal of light PAHs could reach 40 to 99%, with treatment periods just below 3 months and up to 18 months. Heavy PAHs were not affected by the treatment during all the conducted tests.

Others worked on other types of plants (e.g. trees) to sustain PAHs remediation in soils (Liste and Alexander, 2000; Tang et al., 2004; Mueller and Shan, 2006). Liste and Alexander (2000) have observed that within approximately 8 weeks, as much as 74% of pyrene disappeared from vegetated soil.

The biological processes discussed below require long period of treatment. In order to alleviate this constraint, PAHs get oxidised by chemical reactions.
5 PAHS chemical oxidation

The main technologies used for the chemical oxidation of PAHs principally consist of using hydrogen peroxide, persulfate and to a less extent ozone and potassium permanganate can be used alternatively.

5.1 Fenton

5.1.1 Conventional Fenton and Modified Fenton Treatment Processes

In a conventional Fenton reaction, dissolved hydrogen peroxide (H$_2$O$_2$) react with ferrous ion (Fe$^{2+}$) to generate hydroxyl radicals (OH•). This primary radical (OH•) will in turn oxide PAHs (Yap et al., 2011). The oxidation reaction requires acid condition (down to pH<5) in order to regenerate Fe (II) from Fe (III).

The efficiency of the Fenton treatment on PAHs contaminated soils has been well demonstrated in laboratory-scale experiments, showing PAHs removal rates ranging from 8.8 and up to 92%, using H$_2$O$_2$ concentration between 0,3 and 7,8 M (Kawahara et al., 1995; Bogan and Trbovic, 2003; Goi and Trapido, 2004; Jonnson et al., 2006; Jonnson et al., 2007; Silva et al., 2009; Valderrama et al., 2009; Andreottola et al., 2010; Yap et al., 2011; Laurent et al., 2012). However, a case has been described by Flotron et al. (2005) where PAHs degradation did not overcome 8%. The important variation in removal rates is due (i) to differences observed amongst individual PAH properties, (ii) to the way experiments are being conducted, (iii) to the nature of the soil and (iv) to the sorption of PAHs as contaminant-soil contact times are longer and weathering processes occur that is known to inhibit PAHs availability Low-molecular-weight PAHs (3-ring PAH) are usually degraded more efficiently than high-molecular-weight PAHs (4-, 5- ring PAH).

On the field or during pilot-scale experiments, removal rates can range from 70 and up to 100% (Liu et al., 1999; Pradhan et al., 1997; Brown, 1997; Lingle et al., 2001).

Some authors have shown that PAHs degradation in contaminated soils remains possible without Fe$^{2+}$ addition due to the presence of iron oxides in the solid matrices. However, it is noted that the kinetic of the reaction remains slow during the experiment (Watts et al., 2002; Flotron et al., 2005; Kulik et al., 2006).

pH for an optimal Fenton treatment should be between 2 and 4. These conditions should allow a regeneration of the catalyst (Di Palma, 2005; Langwaldt, 2005). Increase in pH prevents the regeneration of the OH• radical because of Fe$^{2+}$ precipitation and H$_2$O$_2$ decomposition are occurring (Di Palma, 2005; Langwaldt, 2005). Low pH used in Fenton reactions imply a negative impact on the soil properties, making the soil often incompatible with a re-vegetation or a biodegradation process (Sahl and Munakata-Marr, 2006; Sirguey et al., 2008; Laurent et al., 2012).

The conventional Fenton reaction has been modified so it can be adapted using a pH in line with natural soil conditions (neutral). Treatments using chelating agents (organic compounds resisting to oxidation) to avoid iron precipitation have been proposed (Nadarajah et al., 2002; Lindsey et al., 2003; Ferrarese et al., 2008; Nam et al., 2001; Georgi et al., 2007; Li et al., 2007; Rastogi et al., 2009; Venny et al., 2012a). Chelating agents which have proven to be effective when used in combination with a Fenton treatment are for example, EDTA, oxalic acid, sodium citrate, gallic acid, catechol and cyclodextrins. However, a recent study
has described the possibility of using an inorganic chelating agent - pyrophosphate de sodium - in combination with a Fenton oxidation, a process which would more likely result in more efficient removal rates than when conventional chelating agents are being used (Venny et al., 2012b).

Surfactants or vegetable oils have been brought to light as enhancing Fenton type treatments as they can encourage PAHs desorption from the soil medium and therefore making the contaminants more readily available (Bogan et al., 2002; Kyin et al., 2009).

Additional co-solvents facilitate PAHs desorption and increase their availability for treatment. Ethanol is a polar solvent commonly used for soil pre-treatment before a Fenton oxidation actually takes place. Soil pre-treatment times vary between 3 hours and 24 hours and optimal ethanol concentrations range between 0.75 mg/L and 5 mg/L (Lee et al., 1998; Lee and Hosomi, 1999; Lee and Hosomi, 2000; Lee and Hosomi, 2001a; Lee and Hosomi, 2001b; Lee et al., 2002; Lundstedt et al., 2006). Studies have shown that the more contact time there is between the soil and the contaminant, the more ethanol will be needed. Removal efficiency can vary between 73 and 99.5% (depending on the considered PAH) (Lee and Hosomi, 2001a; Lee et al., 2002). On the contrary, Lundstedt and al (2006) have observed a small enhancement, i.e. between 11 and 28 % when using a combined Ethanol/Fenton treatment.

When pH is higher than 4, salt stabilizers are used to prevent any H2O2 degradation. Potassium dihydrogen phosphate has been used as a stabiliser by Valderrama et al. (2009) and Karkala and Watts (1997) to improve treatment performances of combined oxidation and biodegradation for the removal of PAHs. An alternative method is to use calcium peroxide or magnesium peroxide as they encourage the release of H2O2 by dissolution of calcium and magnesium in water when pH conditions are neutral (Bogan et al., 2003; Ndjou’ou and Cassidy, 2006; Gryzenia et al., 2009).

5.1.2 Fenton-Like Treatment Process

Low pH used in Fenton reactions imply a negative impact on the soil properties (Sahl and Munakata-Marr, 2006; Sirguey et al., 2008; Laurent et al., 2012).

Iron (III) oxides are used as a catalyst source to counterbalance low pH. Reactions which are not using Fe2+ as a catalyst in homogeneous conditions are considered as Fenton-Like Treatments. Fenton-Like reactions allow treatments to take place without acidifying the soil.

Oxides that are capable of catalysing H2O2 in soils are goethite (FeOOH), hematite (Fe2O3), magnetite (Fe3O4) and ferrihydrite (Fe10O15:9H2O) (Tyre et al., 1991; Watts et al., 2002; Kanel et al., 2003; Yap et al., 2011; Usmann et al., 2012). Fenton-like reactions catalysed by Goethite have revealed a good capacity in PAHs degradation (Watts et al., 2002; Kanel et al., 2003; Kanel et al., 2004).

In laboratory-scale experiment, removal rate went up from 55 to 89%, using H2O2 concentrations from 5 M to 15 M and using 25 mg/kg to 34 g/kg of oxides (Watts et al., 2002; Kanel et al., 2003; Kanel et al., 2004).

5.1.3 Influence of the solid phase (soil)

Bogan and Trbovic (2003), Goi and Trapido (2004) and Flotron et al. (2005) have demonstrated that Fenton treatment success is dependent on the solid phase properties
(e.g. organic content) and on the PAHs availability. This availability is dependent on the age and concentration of contamination.

Bogan and Trbovic (2003) have been particularly interested on how the fraction of organic content influences PAHs removal rates following a conventional Fenton treatment. Their studies showed an optimal PAHs treatment efficiency for soils characterised with 5% organic content. When fractions of organic content are higher, PAH adsorption becomes an issue. Several authors advise on using high concentrations of $\text{H}_2\text{O}_2$ (> 7.5M) to counterbalance this problem (Goi and Trapido, 2004 ; Jonnson et al., 2006).

5.1.4 Influence of operational parameters

Numerous research studies have highlighted the influence of operational parameters in the effective oxidation processes within laboratory-scale experiments. Such operational parameters are pH, reaction time, UV radiation, hydrogen peroxide concentration, Fe (II) amendment, and the $\text{H}_2\text{O}_2$/soil mass ratio (Kulik et al., 2006 ; Silva et al., 2009). It is noted that the most important factor is reaction time.

Some authors suggest using oxidation in several stages. Goi and Trapido (2004) have described that a several stages oxidation is more efficient than a one stage oxidation.

5.1.5 Fenton/biodegradation

Several researchers have observed a significant improvement in heavy and light PAHs biodegradation, using a “pre-Fenton type oxidation” stage. For example, they obtained for benzo(a)pyrene removal rate of up to 60-80% (against a rate of 30-50% in the case of a bioremediation on its own) (Lee et al., 2002 ; Nadarajah et al., 2002 ; Piskonen and Itävaara, 2002 ; Valderrama et al., 2009). However, it has to be noted that Kulik et al. (2006) have presented a creosote contaminated site, where a catalytic oxidation by $\text{H}_2\text{O}_2$ followed by a biodegradation leads to a low degradation rate of PAH, compared to when a biodegradation is carried out on its own. Valderrama et al. (2009) have shown that an excess in hydrogen peroxide cause a law biological treatment rate.

Several authors have studied the influence of using surfactants or chelating agents on PAHs degradation within a Fenton/biodegradation treatment process (Nam et al., 2001 ; Piskonen and Itävaara, 2005). Using a chelating agent, they described a degradation rate of up to 98% for 2-, 3- ring PAHs and of up to 70-85% for 4-, 5- ring PAHs. Otherwise, using surfactants did not bring any significant benefit on the Fenton/biodegradation treatment.

5.2 Persulfate

Persulfate is usually used as a salt, mainly sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) that has a higher solubility than others salts (Huling & Pivetz, 2006).

To improve its oxidising capacity, persulfate can be activated to produce sulphate radicals ($\text{SO}_4^{2-}$). This activation can be carried out using several approaches: chemical approach, thermal approach or using a transition metal such as Fe (II) (House, 1962; Balazs et al., 2002).

Within R&D, Andreottola et al. (2010) and Liang and Guo (2010) studies have delivered interesting results on PAHs chemical oxidation using an activated persulfate (by means of a thermal and a chemical approach with FeO). Treatment techniques using activated persulfate can reach a removal rate of up to 68-99 %.
Yet, an activation using Fe (II) is facing a major inconvenient: the conversion of Fe (II) into Fe (III) when Fe (II) is in excess (Buxton et al., 1997). Therefore, in these cases, an optimal catalyst concentration would be required. Another problem when using Fe (II) as a catalyst is Fe (II) low stability. Effectively, Fe (II) is no longer regenerated when pH is higher than 4. Chelating agents can be used to prevent a precipitation from the catalyst onto the solid phase when pH conditions are neutral (Liang et al., 2004; Nadim et al., 2006; Killian et al., 2007; Gryzenia et al., 2009). Such organic chelating agents comprise of EDTA, citrate, polyphosphate, glycolic acid, catechol, nitrotriacetic acid (NTA), and tetrahydroquinine.

Numerous researches focused on combining sodium persulfate and hydrogen peroxide in treatment processes (Block et al., 2004; Cronk & Cartwright, 2006; Thompson et al., 2006; Crimi and Taylor, 2007). In these treatment processes, it is a give and take situation, i.e. hydrogen peroxide can initiate the formation of persulfate radicals and sulphate radicals can stimulate the formation of OH• radicals. In addition, hydrogen peroxide would react with the most active compounds, allowing the oxidation of the less active compounds by sulphate radicals.

The influence of metallic oxides on persulfate reactivity has been studied (Do et al., 2010; Usman et al., 2012b). Results have shown that goethite, hematite, magnetite and manganese oxides can activate persulfate.

### 5.3 Ozone

Two distinct injection methods can be used for in situ ozone treatment of PAHs: injection of gaseous ozone (most advantageous method) and injection of aqueous ozone.

Injection of gaseous ozone is a more effective technique than injection of aqueous ozone (Masten and Davies, 1997; Russo and al, 2010). Indeed, it was observed that 20% of PAHs remain in the soils following gaseous ozone treatment against 40% following an aqueous ozone treatment (Masten and Davies, 1997). This difference is due to a better diffusivity of the gaseous ozone, leading to more contact between contaminants and oxidising agent. This kind of treatment requires a gas venting system being set up in order to retrieve the injected gas.

Zeng and Hong (2002) have shown a PAHs reduction between 50 and 100% using a 2 hours long ozonation period while treating contaminated sediments. Kulik et al. (2006) have demonstrated a more effective ozonation when dealing with high molecular weight PAHs.

Several authors suggest using ozonation in several distinct stages. Goi and Trapido (2004) have shown that a three ozonation-step is more effective than a two ozonation-step.

#### 5.3.1 Ozonation/biodegradation combination

Ozone transforms PAHs into more biodegradable products. It will then consume available organic matter, leading to PAHs desorption and making these PAHs more available for removal.

There are numerous studies looking at treatments combining both ozonation and biodegradation techniques (Nam and Kukor, 2000; Stehr et al., 2001; Goi and Trapido, 2004; Kulik et al., 2006; O'Mahony et al., 2006). Some authors have proved the beneficial use of such combination when treating PAHs, in particular if these results are compared to results of a conventional biodegradation treatment (Nam and Kukor, 2000; Goi and Trapido, 2004; Kulik et al., 2006). Biodegradation treatment following an ozonation treatment would
allow a further 45% removal of the remaining PAHs (Goi and Trapido, 2004). However, Stehr et al. (2001) and O'Mahonny et al. (2006) have reported a much slower PAHs biological degradation when soils underwent an ozone pretreatment phase. This phenomenon can possibly be explained by the release of inhibitors during the ozonation process.

5.4 Potassium permanganate

Potassium permanganate has shown its applicability to reduce PAH contamination in groundwater and soils.

Batch tests at the bench scale, have demonstrated the efficiency of potassium permanganate when oxidising PAHs (Brown et al., 2003; Silva et al., 2009b). The best degradation conditions were obtained using phenanthrene for a KMnO4/PAH weight ratio of 40 and a reaction time of 72 hours (Silva et al., 2009b). The observed soil concentration decrease of benzo (a) pyrene, pyrene phenanthrene and anthracene are 72.1, 64.2, 56.2, and 53.8%, respectively, for a 30 minutes treatment time and a 160 mM oxidant concentration. A decrease of 13.4% and 7.8% were observed by Brown et al., 2003 for fluoranthene and chrysene respectively.
6 Thermal processes

Remediation thermal processes use heat to destroy or mobilise (volatilisation) PAHs. Numerous research works have tested various thermal treatment techniques. For example, an incineration remediation trial lead to removal rates of up to 90%, using temperatures between 870 and 1200°C (Acharya and Ives, 1993); a thermal desorption lead to removal rates between 87.0% and 99.9% depending on the considered PAH and for maximum temperatures ranging between 300 and 350°C (Renoldi et al., 2003; De Franca et al., 2009); and finally venting-thermal desorption (SVTD) was also tested by Harmon et al., 2001.

Thermal remediation techniques have been used to treat PAHs contaminated sediments on an industrial experiment scale (Abramovitch et al., 1999). Results were variable:

- ReTeC's Thermal Desorption Technology (low heat) (PAHs desorption up to 60%)
- SoilTech's Anaerobic Thermal Process Technology
 Abramovitch *et al.* (1999) has studied the decomposition of PAHs in soil using microwave energy. No PAHs remain in the soil after remediation (initial concentration was approx. 0.125 mg/g). These experiments offer a valid model for the in situ remediation of these pollutants from contaminated soil.
8 Polycyclic Aromatic Compounds treatment

Polar PAHs (hetero-PAHs) or Polycyclic Aromatic Compounds (PAC) differ from PAHs because of the presence in their structure of hetero-atoms S, N or O. These imply different physic-chemical properties to hetero-PAHs (NSO-compounds). Hetero-PAHs are more hydrophilic and therefore more soluble in water (Licht et al., 1996). Hetero-PAHs high mobility and persistence can generate significant contaminant plumes. (Pereira et al., 1987; Johansen et al., 1997, Zamfirescu and Grathwohl, 2001; Jarsjö et al., 2005).

Numerous studies on PAHs treatment have been carried out, whether they are following biological, chemical or physical approaches. However, little work has been done on treating specifically hetero-PAHs.

8.1 Biological degradation

Biological degradation of hetero-PAHs has nevertheless been studied in laboratory experiments. Results have shown that nitrogen compounds (N-PAH) and oxygen compounds (O-PAH) degrade more rapidly than sulphur compounds (S-PAH) (Kuhn and Suflita, 1989; Meyer and Steinhart, 2000).

Under aerobic conditions, quinoline (N-PAH) is almost entirely degraded whereas dibenzo thiophene (S-PAH) undergo a slow degradation (Mueller et al., 1991; Dyreborg et al., 1997). Cometabolic transformations were reported for sulphur compounds such as thiophene and benzothiophene (Dyreborg et al., 1998; Bressler et al., 1998; Rivas et al., 2003; Mundt et al., 2004). Other researcher groups have described that degradation of two- to five-ring PAHs was inhibited by the presence of hetero-PAHs but some PAHs can also inhibit the hetero-PAHs degradation (Milette et al., 1995; Dyreborg et al., 1996a; Dyreborg et al., 1996b; Licht et al., 1996; Milette et al., 1998; Meyer and Steinhart, 2000).

Under anaerobic conditions, Dyreborg et al. (1997) describe hetero-PAHs persistence to biodegradation (thiophene and benzothiophene) under sulphate-reducing and denitrifying conditions. However, Annweiler et al. (2001) and Mundt et al. (2004) have demonstrated that a cometabolic transformation of PAHs was possible under denitrifying and sulphate-reducing conditions. Other researchers have shown quinolone biodegradation was possible under methanogenic, denitrifying and sulphate-reducing conditions (Kuhn and Suflita, 1989; Godsy et al., 1992; Licht et al., 1996; Rockne and Strandt, 1998).

The table below summarises aerobic and anaerobic conditions which can enhance (or not) biodegradation of individual hetero-PAHs.
Table 1: aerobic and anaerobic conditions which can enhance (or not) biodegradation of individual PACs, (Borke and Husers, 2008)

<table>
<thead>
<tr>
<th>Verbindung</th>
<th>Elektronenakzeptor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Benzo[12]fluorine</td>
<td>+</td>
</tr>
<tr>
<td>Benzo[b]thiophen</td>
<td>+/c</td>
</tr>
<tr>
<td>Carbazol</td>
<td>+</td>
</tr>
<tr>
<td>Chinoln</td>
<td>+</td>
</tr>
<tr>
<td>Chinolinon</td>
<td>+</td>
</tr>
<tr>
<td>Dibenzofuran</td>
<td>+</td>
</tr>
<tr>
<td>Dimethylbenzofuran</td>
<td>+</td>
</tr>
<tr>
<td>Dimethylichinoline</td>
<td>+</td>
</tr>
<tr>
<td>2-Hydroxytriphenyl</td>
<td>+</td>
</tr>
<tr>
<td>Isochinolin</td>
<td>+</td>
</tr>
<tr>
<td>Isochinolinon</td>
<td>+</td>
</tr>
<tr>
<td>Methylbenzofuran</td>
<td>+</td>
</tr>
<tr>
<td>Methylbenzothiophene</td>
<td>+</td>
</tr>
<tr>
<td>Methylchinoline</td>
<td>+</td>
</tr>
<tr>
<td>Methylchinolinone</td>
<td>+</td>
</tr>
</tbody>
</table>

* Transformation nachgewiesen
- Transformation nicht nachgewiesen
+/+ Transformation in wenigen Fallen für einzelne Isomere nachgewiesen
+/ - Transformation nicht immer bzw. nicht für alle Isomere nachgewiesen
- Transformation nicht untersucht
o Transformation nur kometabolisch nachgewiesen

8.2 Chemical oxidation

Usman (2011) has studied the oxidation of fluorenone by Fenton-like treatment and by persulfate oxidation.

Concerning the Fenton like treatment, the author reported that the complete removal of the O-PAH was obtained using magnetite as an iron source. But on the contrary, degradation did not exceed 20% in the cases when (i) H<sub>2</sub>O<sub>2</sub> was used on its own (i.e. without catalyst) and (ii) H<sub>2</sub>O<sub>2</sub> was used with soluble Fe (II) as catalyst.

Concerning the persulfate oxidation, results indicate that degradation of fluorenone resulted in its complete degradation when persulfate was activated by magnetite while removal rate was very low (<20%) by treatment without activation or with ferrous ion catalyst.


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