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Optimizing Modern Oxidation Processes for Effective Water and Soil Decontamination

Debaraj Pani[1], Prof. Sanam Sarita Tripathy[2]
Biju Patnaik, University of Technology, Odisha(2023-2025)

Abstract: The present research is focused on deepening the knowledge and practical application of advanced oxidation processes (AOPs) for cleaning up polluted water and soil. AOPs are a modern set of treatment techniques that work by generating highly reactive oxidizing agents, mainly hydroxyl radicals (•OH), directly at the site of contamination. These powerful species are effective in breaking down stubborn organic pollutants commonly found in Indian environmental conditions. In this study, the effectiveness of various AOP methods—including Fenton, photo-Fenton, hydrogen peroxide with UV light (H_2O_2/UV), ozone (O_3), ozone with hydrogen peroxide (O_3/H_2O_2), ozone with UV (O_3/UV), and a combination of ozone, hydrogen peroxide, and UV (O_3/H_2O_2/UV)—was assessed by determining the reaction rates for the removal of nitro-phenols. The primary aim was to optimise these processes for better pollutant removal, making them suitable for large-scale implementation in Indian scenarios.

Experimental results demonstrated that ozonation induced the formation of quinone-based intermediates, while the mineralization of organically bound nitrogen to nitrate ranged from 50% to 100%, contingent upon the applied treatment conditions. The AOPs substantially enhanced the biodegradability of nitrophenol-laden waters and concurrently reduced their toxicity, thereby establishing their efficacy as effective pre-treatment methods preceding conventional biological filtration processes. Moreover, the application of AOPs, particularly ozonation and Fenton-based treatments, achieved effective remediation of recalcitrant contaminants such as nitrophenols, polycyclic aromatic hydrocarbons (PAHs), diesel, shale oil, and transformer oil within soil matrices. Treatment outcomes exhibited dependency on soil composition; sandy soils facilitated higher contaminant removal efficiencies relative to peat soils, which exhibited enhanced chemical retention and consequent reduction in treatment efficacy. Notably, Fenton-like reactions were operable at native soil pH levels, wherein endogenous iron content catalyzed hydrogen peroxide decomposition without necessitating exogenous ferrous ion supplementation.

Critically, synergistic treatment strategies combining chemical oxidation (via ozonation or Fenton chemistry) with biological remediation—employing low-dose oxidants to stimulate microbial degradation—yielded superior contaminant removal compared to either approach employed independently. Economic analyses identified Fenton treatment as the most cost-effective modality for integrated water purification and soil remediation.

Collectively, these findings provide a robust scientific and economic framework to support the broader adoption of advanced oxidation technologies in India, fostering environmental remediation solutions that align with sustainability goals and are amenable to large-scale application.

I. INTRODUCTION

Water pollution resulting from the discharge of hazardous and partially biodegradable organic compounds is a growing environmental challenge, especially in developing countries like India. Conventional biological wastewater treatment systems often struggle to eliminate such pollutants due to their toxic nature and resistance to microbial degradation. Therefore, it is imperative to adopt advanced treatment technologies capable of transforming these contaminants into less harmful forms or achieving their complete mineralisation. Among the emerging technologies, Advanced Oxidation Processes (AOPs) have received considerable attention due to their ability to generate highly reactive oxidants such as hydroxyl radicals (•OH) in situ. These oxidants exhibit strong, non-selective oxidative potential, enabling them to degrade a broad spectrum of organic pollutants in both aqueous and atmospheric environments. As reported by Glaze et al. (1987), AOPs can substantially reduce contaminant levels from parts per million to parts per billion, positioning them as cutting-edge solutions for environmental remediation.

One of the key classes of pollutants is nitrophenols (NPs), which are widely used in industrial applications such as explosives, pesticides, herbicides, and wood preservatives. These compounds often find their way into the environment through accidental spills, industrial effluents, and pesticide runoff. Additionally, secondary formation of NPs has been observed in the atmosphere through photochemical reactions involving nitrogen oxides and aromatic hydrocarbons.

Due to their toxicological significance, compounds such as 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, and 4,6-dinitro-o-cresol have been listed as priority pollutants by international and national regulatory agencies.

Scientific studies have demonstrated that nitrophenols are capable of accumulating in the tissues of warm-blooded organisms and may cause severe health effects, including damage to the liver, kidneys, central nervous system, and blood functions. Exposure routes include ingestion, inhalation, and dermal contact. Despite their known toxicity, limited research is available on the degradation of NPs through ozonation and AOPs, particularly under Indian environmental conditions. While studies have examined the kinetics of 2-NP, 4-NP, 2,4-DNP, and 2,6-DNP under Fenton's reagent, UV/H_2O_2, and photo-Fenton treatment, the degradation of other NPs such as 2,5-DNP and 4,6-DN-o-CR remains underexplored. Likewise, investigations into the combined ozone-based AOP systems such as O_3/H_2O_2 and O_3/H_2O_2/UV are scarce. Some preliminary findings indicate that AOPs can enhance the biodegradability and reduce the toxicity of these compounds, but comprehensive kinetic and toxicity studies are still needed.

In parallel with water contamination, soil pollution is also a major concern in the Indian context, particularly in areas surrounding industrial estates, thermal power plants, and oil-handling facilities. The remediation of contaminated soils traditionally involves methods such as excavation and pump-and-treat techniques. However, these approaches are often economically unviable and environmentally disruptive. Recent developments suggest that in situ chemical oxidation using AOPs—such as ozonation and Fenton-like reactions—could offer a more sustainable, cost-effective, and technically feasible alternative for soil remediation.

These processes are particularly suitable for Indian field conditions, where varying soil types (from sand to organic-rich peat) and limited infrastructure call for low-waste, rapid, and site-specific interventions. The ability of AOPs to improve biodegradability also enables the integration of biological treatment, creating a synergistic approach that enhances overall efficiency. This hybrid model is particularly useful in treating soils contaminated with recalcitrant compounds such as polycyclic aromatic hydrocarbons (PAHs), diesel, transformer oil, and shale oil.

PAHs, commonly accurse the incomplete combustion of organic matter and fossil fuel processing, are widespread in industrial emissions, vehicular exhaust, and accidental spills. In India, significant PAH contamination has been reported near thermal power stations, petroleum refineries, and urban hotspots. These compounds are known to be persistent and carcinogenic, and several of them have been classified as priority pollutants by international regulatory bodies.

Similarly, petroleum derivatives such as diesel, transformer oil, and shale oil are potent soil contaminants. Diesel pollution often results from leaks in underground storage tanks or during transport operations. Used transformer oil can enter the soil through leakages during disposal or recovery processes, while shale oil—a concern in certain global regions—is produced from liquefaction of oil shale. These oils can percolate through soil layers and eventually contaminate groundwater, owing to their content of harmful constituents such as PAHs, phenols, and polychlorinated biphenyls (PCBs).

Despite their environmental significance, little research has been conducted through ozonation or Fenton-like oxidation. Existing studies on PAH degradation using AOPs have shown that such treatments can enhance biodegradability and reduce overall toxicity. Diesel-contaminated soils have also been treated with AOPs followed by biological treatment, which yielded promising results. However, much of this research has been limited to soils with low organic matter content and does not adequately represent diverse Indian soil types.

Recent findings also support the potential of using native microbial populations in conjunction with chemical pre-treatment, avoiding the ecological disruptions that can arise from introducing foreign microbial strains. This integrated approach aligns with the principles of sustainable remediation and holds promise for practical field-level applications across India.

II. OBJECTIVES OF THE STUDY

The objective of this research was to broaden scientific insight and improve the practical use of Advanced Oxidation Processes (AOPs) for effectively treating water and soil contaminated with persistent pollutants. The study primarily focused on the removal of nitrophenolic compounds, which are well-known for their resistance to degradation and harmful effects on the environment. Different AOP techniques were tested—such as ozonation in combination with hydrogen peroxide and/or ultraviolet (UV) light, the use of Fenton's reagent, the photo-Fenton approach, and hydrogen peroxide-based photolysis. The performance of these processes was evaluated based on their ability to degrade nitrophenols, with the aim of determining the most efficient method and identifying the best operational conditions for maximum contaminant removal, especially under conditions relevant to India.

In the water treatment segment of the study, a selection of nitrophenolic compounds—including 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), 2,5-dinitrophenol (2,5-DNP), 2,6-dinitrophenol (2,6-DNP), 4,6-dinitro-o-cresol (4,6-DN-o-CR), and 2,6-dinitro-p-cresol (2,6-DN-p-CR)—were chosen as model pollutants owing to their widespread occurrence, recalcitrance, and toxicity in aquatic environments.

Batch reactor experiments were conducted under controlled laboratory conditions across a spectrum of pH values (typically acidic to near-neutral ranges) to evaluate the comparative degradation efficiencies of standalone ozonation, advanced oxidation processes (AOPs) combining ozone with hydrogen peroxide, and hydrogen peroxide photolysis under ultraviolet (UV) irradiation.

To optimize Fenton and photo-Fenton processes, the study systematically varied hydrogen peroxide dosage levels, both in the absence and presence of ferrous ions (Fe^{2+}) as a homogeneous catalyst, to elucidate their roles in generating hydroxyl radicals (•OH) and accelerating contaminant degradation.

Reaction kinetics were monitored by periodically sampling the reaction mixtures and analyzing residual concentrations of nitrophenols via high-performance liquid chromatography (HPLC). Comprehensive evaluation of treatment efficacy involved measurement of mineralization extent through total organic carbon (TOC) analysis and quantification of aromatic carbon content via ultraviolet-visible (UV-Vis) spectroscopy. Additionally, the mineralization of organically bound nitrogen was assessed by monitoring nitrate formation using ion chromatography (IC).

Toxicity reduction was quantified through bioassays employing standardized microbial or aquatic test organisms to determine improvements in effluent biodegradability and environmental safety. To assess the ecological safety of treated water, Daphnia magna bioassays were employed for toxicity evaluation. Notably, the formation of specific by-products was recorded a comparative cost analysis of AOP variants was also conducted to identify the most economically viable method for the degradation of nitrophenol-contaminated water.

To enhance the sustainability and cost-efficiency of remediation, the study incorporated a hybrid approach that combined chemical oxidation with biological treatment. This included evaluating the influence of chemical pre-treatment on subsequent microbial degradation using native microbial populations. Optimal concentrations of chemical oxidants were identified to ensure minimal toxicity and maximal biodegradability, thereby facilitating effective bioremediation.

Furthermore, the investigation evaluated the influence of soil matrix characteristics—comparing mineral-rich sand and organic-rich peat—on treatment efficacy. Special attention was given to understanding how natural organic matter influences the degradation of PAHs, diesel, transformer oil, and shale oil during both chemical and combined chemical-biological treatments.

In addition to pollutant degradation, ancillary analyses were conducted to monitor the removal of aliphatic hydrocarbons (alkanes) and the reduction in absorbance at 254 nm, indicative of aromatic carbon content in petroleum-contaminated soils. Finally, a cost analysis was undertaken to compare the treatment expenses associated with ozonation (with low-dose chemical oxidants), Fenton, and Fenton-like processes for large-scale soil remediation.

The findings of this study are expected to serve as a scientific and practical foundation for implementing cost-effective, efficient, and scalable treatment strategies for soil and water decontamination, particularly under Indian environmental and infrastructural conditions.

III. LITERATURE REVIEW

A. Water Purification Via Advance Oxidation Process

Advanced Oxidation Processes (AOPs) have emerged as a significant class of water and wastewater treatment technologies in recent years due to their ability to effectively degrade complex and resistant organic pollutants. These processes have garnered considerable interest globally and in the Indian context, particularly for addressing pollution caused by industrial effluents, municipal wastewater, and agricultural runoff.

The concept of AOPs was initially introduced by Glaze et al. in 1987, who defined them as treatment techniques involving the generation of sufficient quantities of hydroxyl radicals (•OH), which are among the most potent and non-selective oxidants. These radicals have the capacity to react rapidly with a wide range of organic compounds, leading to their partial or complete mineralisation.

AOPs encompass a wide array of treatment systems that utilise strong oxidising agents such as ozone (O_3), hydrogen peroxide (H_2O_2), and advanced irradiation methods including ultraviolet (UV) light, ultrasound (US), and electron beams. Additionally, catalysts such as ferrous ions (Fe^{2+}), titanium dioxide (TiO_2), and other transition metal ions are often used to enhance radical generation. A general classification of commonly employed AOP systems is shown in Table 3.1, based on whether they are photochemical or non-photochemical in nature (Huang et al., 1993).

Table 3. 1. List of typical AOP systems (Huang et al., 1993)

Non-photochemical	Photochemical
O3/H_2O_2	O_3/UV
O_3 /GAC	H_2O_2/TiO_2/UV
O_3/OH^-	H_2O_2/UV
O_3/US	H_2O_2/Fe^{2+} (photo-Fenton)
Fe^{2+}/H_2O_2 (Fenton system)	UV/TiO_2
Electro-Fenton	UV/US
Electron beam irradiation	O_2/TiO_2/UV
Ultrasound (US)	O_3/H_2O_2/UV
H_2O_2/US	
O_3/CAT	

The major advantages of AOPs include their high oxidation efficiency, adaptability to varying water quality, and relatively compact equipment requirements. However, their application may be constrained by higher operational costs and specific safety considerations, especially when handling reactive chemicals and high-energy radiation sources (Kochany and Bolton, 1992).

Several commercial-scale AOP technologies have already been developed and trademarked, such as ULTROX, RAYOX, WEDECO, UVOX, ECOCLEAR, and BioQuint. These systems are designed for treating industrial effluents and other complex waste streams.

Among all oxidising agents used in AOPs, the hydroxyl radical (•OH) exhibits one of the highest oxidation potentials (2.80 eV), surpassed only by elemental fluorine. Table 3.2 summarises the oxidation potentials of various oxidising species (Ullmann’s, 1991).

Table 3. 2. Standard Reduction Potentials and Oxidation Strength of Selected Oxidizing Agents

Oxidizing Agents	Oxidation potential, eV
F	3.061
HClO	1.491
Cl	1.363
H_2O_2	1.76
O_3	2.08
HO_2	1.71
HO	2.81
O	2.43

Ozone-based AOPs can function through two primary mechanisms: direct oxidation by molecular ozone and indirect oxidation via reactive radical species (such as •OH and HO_2•) generated through ozone decomposition in aqueous environments. While hydroxyl radicals react rapidly and indiscriminately with most organic substances, their high reactivity may also lead to side reactions with background matrix components such as bicarbonates and carbonates, thereby reducing treatment efficiency (Langlais et al., 1991; Haberl et al., 1993).

In contrast, molecular ozone demonstrates greater selectivity in its reactivity, predominantly targeting compounds featuring multiple bonds such as carbon–carbon double bonds (C=C) and molecules containing nucleophilic or electronegative heteroatoms including nitrogen, sulfur, oxygen, and phosphorus. The rate constants for these ozonation reactions span several orders of magnitude—from as low as 10^{-5} to as high as 10^9 $M^{-1}s^{-1}$—depending on the specific substrate involved (Hoigné and Bader, 1983a, 1983b; Hoigné et al., 1985). This broad range of reactivity enables the selective oxidation of particular contaminants, thereby minimizing overall ozone consumption and enhancing treatment efficiency.

Ultimately, the dominant oxidation pathway during ozonation depends on the chemical composition of the water and operational parameters such as pH, temperature, and the presence of catalysts or radical scavengers. By carefully tuning these factors, one can shift the reaction mechanism to either direct molecular ozone action or radical-mediated oxidation (Hoigné, 1988; Hoigné and Bader, 1976).

1) Common Reactor Setups for Chemical Oxidation in Water Treatment

- Commo reactor used for the Fenton oxidation

A typical batch Fenton system features a non-pressurized reactor vessel fitted with mechanical stirring to provide uniform mixing throughout the process. It includes precise dosing pumps that add acid, base, ferrous sulfate catalyst, and concentrated hydrogen peroxide (typically between 35% and 50%) to the reaction mixture. Because the Fenton reagent combines strong oxidizers and acids, all wetted components must be fabricated from materials with high chemical-corrosion resistance. Therefore, the inner surfaces of the reactor vessel are generally lined with acid-resistant coatings or materials to ensure durability and operational safety.

The sequence of reagent introduction plays a vital role in ensuring the effectiveness of the reaction. Initially, the wastewater is introduced into the reactor, followed by the addition of diluted sulphuric acid to maintain the desired acidic pH—typically in the range of 2.5 to 4.0. Subsequently, the ferrous ion catalyst is added under acidic conditions. If pH adjustments are required during the process, either acid or base may be incrementally dosed, ensuring that the temperature and reaction kinetics are adequately maintained throughout.

After the primary oxidation reaction, the treated effluent is transferred to a neutralisation tank to bring the pH to a safe discharge level. This is followed by passage through a flocculation unit, where destabilised particles aggregate, and then a solid-liquid separation unit to reduce the Total Dissolved Solids (TDS) in the final effluent stream.

Figure 3.1 presents a simplified schematic of the Fenton oxidation process, illustrating the main operational steps and the movement of materials within the system.

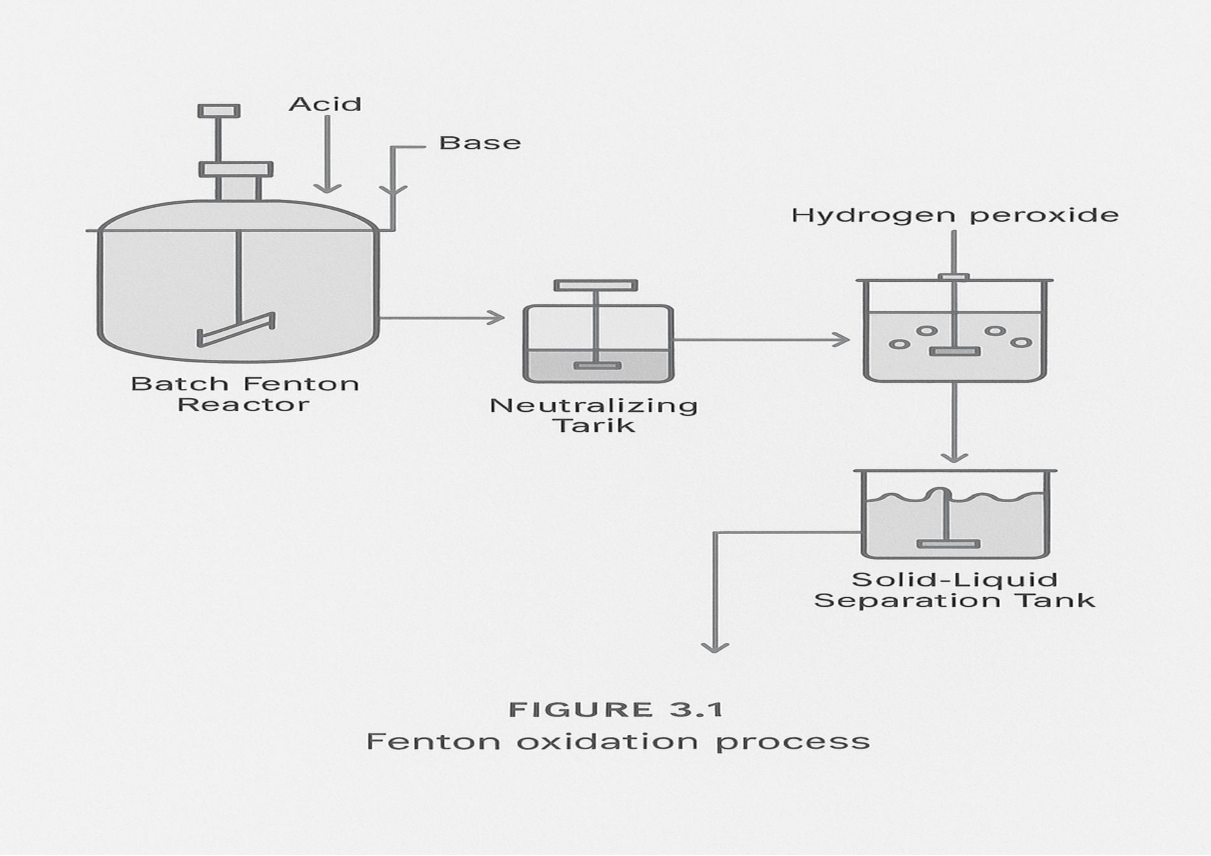


Figure 3.1. Scheme of the Fenton oxidation treatment

- *Reactor Configurations for Ozone Transfer*

The efficacy of ozonation processes in water and wastewater treatment is critically dependent on the mass transfer efficiency of ozone from the gas phase into the aqueous phase. Various gas-liquid contactor technologies are utilized to maximize this transfer, including jet ejectors, packed columns, plate columns, counter-current bubble columns, static-mixers, and mechanically agitated contactors. These contactors vary in their hydrodynamic configurations, interfacial surface area for gas-liquid exchange, bubble size distribution, and turbulence generation, all of which influence ozone transfer rates and mass transfer coefficients (k_La). The selection of an appropriate ozone contactor system is therefore contingent upon specific operational parameters such as ozone dosage requirements, flow rates, treatment volume, and process scalability. To enhance the overall efficiency of ozone dissolution, two major operational strategies are employed:

1. Increasing the interfacial surface area—which can be achieved by reducing bubble size using micro-bubble diffusers made from porous materials such as sintered glass, ceramic membranes, or porous disks (Ledakowicz et al., 2001; Ciardelli et al., 2001).
2. Prolonging contact time between ozone gas and the wastewater stream—by designing deeper contact chambers, typically with depths ranging between 3.7 to 5.5 metres.

Side-stream injection systems, known for their high mixing efficiency and resistance to gas channelling, can also be used for ozone transfer. These systems operate with a favourable gas-to-liquid flow ratio and are particularly effective for partial stream treatment. However, they present certain limitations such as corrosion risks, operational disturbances like bumping, and relatively shorter gas-liquid contact durations.

Static mixers have attracted increasing interest for their effective performance in large-scale water treatment applications. While their role in water disinfection is well established, their use is progressively expanding into wastewater treatment due to their capability to enhance ozone solubility and mass transfer. Although static mixers may induce higher pressure drops—particularly when treating effluent streams rich in suspended solids or with complex physicochemical characteristics—recent design improvements have significantly improved ozone transfer efficiency under these challenging conditions. Given the greater complexity of effluent streams compared to water containing only microorganisms, the adoption of static mixers in full-scale wastewater treatment processes continues to grow.

- Reactor Configurations for Hydrogen Peroxide Oxidation

The controlled addition of H_2O_2 is a critical step in advanced oxidation processes due to its chemical instability and rapid reactivity. The timing of H_2O_2 introduction into the waste stream is largely influenced by the reaction kinetics between the pollutant and the oxidant. While early addition may ensure extended residence time and better exposure, practical challenges such as inadequate mixing and operational constraints often limit the effectiveness of inline injection. In such cases, an auxiliary holding tank may be required to maintain sufficient contact time. Several process parameters affect the efficiency of hydrogen peroxide utilisation, including temperature, catalyst presence (such as ferrous ions in Fenton's reaction), and the injection rate. Among the various delivery techniques, **gravity feed systems** are considered simple, cost-effective, and quick to implement. However, **pump-based feeding mechanisms**, though offering greater control, require regular maintenance and operational oversight.

A more recent advancement in this field is the **multistage injection system**, where hydrogen peroxide is introduced at multiple points along a treatment train consisting of reactors arranged in series (Shishida et al., 1999; Furukawa et al., 1997). This approach allows for dose adjustment based on the pollutant load and intermediate oxidation products, offering a more flexible and efficient treatment regime.

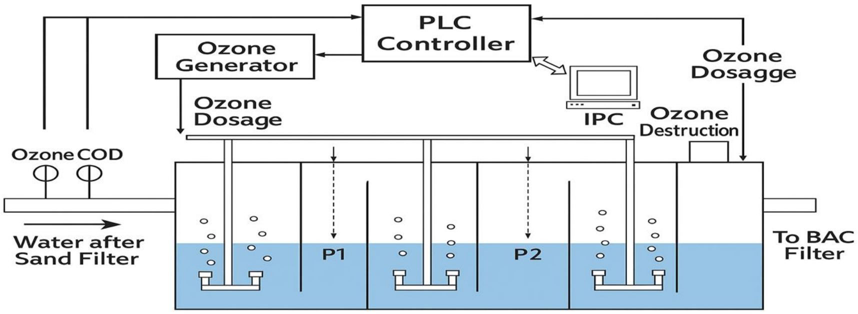


Figure 3.2: Schematic of Equipment Used for Ozonation

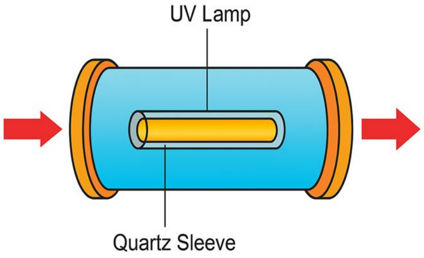
- Design Considerations for UV Reactors

The Ultraviolet (UV) reactors used in AOP systems are primarily classified into two types: open-channel reactors and closed-vessel reactors. A schematic of a typical closed-vessel UV reactor is illustrated in Figure 3.3. The reactor design must carefully account for several hydrodynamic parameters, including flow rate, residence time distribution (RTD), effective reactor volume, turbulence, and dispersion characteristics (EPA US, 1996).

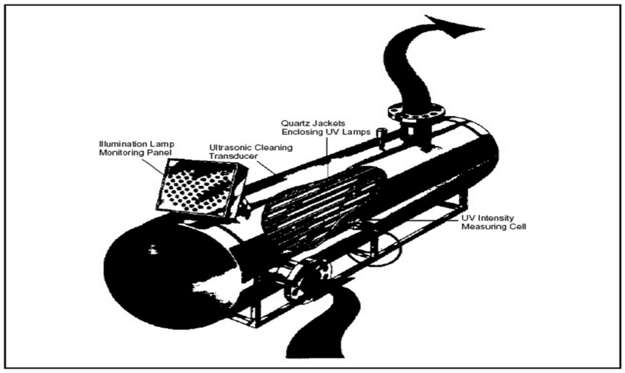
Dispersion in this context refers to the spatial spreading of water constituents within the reactor. An ideal UV reactor would follow a plug flow model, where each parcel of water remains in the reactor for the same duration, entering and exiting in the same sequence. Such conditions are approximated in long, narrow reactors with a high length-to-width ratio and minimal internal dispersion.

To avoid dead zones and enhance treatment uniformity, UV reactors are designed to promote radial turbulence in the direction of flow. While turbulence improves mixing and energy distribution, it also introduces axial dispersion, thereby deviating from ideal plug flow behavior. Innovative designs—such as misaligned inlet and outlet ports and the incorporation of perforated stilling plates—have been adopted to strike a balance between plug flow and turbulent mixing (EPA US, 1996).

The UV lamps themselves are powered electrically and may operate under either low-pressure or medium-pressure configurations. Low-pressure lamps emit at a narrow wavelength centered around 253.7 nm, ideal for germicidal action. Medium-pressure lamps, in contrast, produce a broader spectrum of radiation (180–1370 nm) and are significantly more intense, thus enhancing pollutant breakdown. To protect the lamp from direct water contact, quartz sleeves are typically used, allowing over 95% UV transmittance. **Teflon sleeves** may be used as alternatives but are less efficient, absorbing up to 35% of UV radiation.



Closed-Vessel Ultraviolet Reactor



B. *Chemical Oxidation of Contaminated Soil*

Traditional methods such as excavation followed by landfilling or incineration have long been employed for remediating contaminated soils. However, these approaches are increasingly being reconsidered due to their environmental and practical limitations. For instance, incineration can lead to the formation of toxic secondary pollutants, such as polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxins (Fox, 1996). Similarly, excavation and landfilling only transfer the contaminants from one location to another without actually achieving their destruction. In this context, chemical oxidation technologies have emerged as promising alternatives that are environmentally sound, commercially viable, and technically feasible for soil remediation.

Numerous studies have shown that advanced oxidation techniques—particularly ozonation and Fenton-based treatments—are highly effective at breaking down organic contaminants in soil(Nam & Kukor, 2000; Lee & Hosomi, 2001).

These methods can be deployed both on-site and in situ, allowing for immediate intervention during emergency spill incidents to mitigate soil and groundwater contamination. In such cases, in situ chemical oxidation is particularly advantageous as a rapid-response technology for "hot spot" treatment, offering efficient pollutant degradation while minimising ecological disturbance.

When compared to conventional remediation techniques, in situ chemical oxidation (ISCO) presents several benefits. Employing oxidants like hydrogen peroxide and ozone incurs relatively modest chemical costs, particularly when compared to energy-intensive approaches such as in-situ thermal remediation or surfactant and co-solvent flushing (In Situ Oxidation, 1999). Additionally, ISCO generally requires shorter treatment durations and produces minimal secondary waste, thereby simplifying post-treatment disposal requirements (Technical/Regulatory Guidelines, 2001).

From a reaction kinetics standpoint, chemical oxidation often yields faster results than both biological remediation and thermal or vapour recovery techniques, due to the instantaneous nature of redox reactions involved in the process. However, it is important to note that ISCO is not a one-size-fits-all solution. Certain site-specific limitations—such as incompatible geochemistry, subsurface permeability constraints, or the presence of competing natural attenuation processes—may affect treatment efficacy.

For instance, applying strong oxidants may temporarily disrupt beneficial microbial processes such as natural reductive dehalogenation in sites undergoing monitored natural attenuation (Technical/Regulatory Guidelines, 2001).

One of the key motivations for employing oxidation technologies is to enhance the biodegradability of pollutants that are otherwise recalcitrant or only marginally biodegradable. While bioremediation remains a widely adopted and environmentally benign treatment method, it is slower in cold climates and less effective against biorefractory contaminants. In such cases, integrated treatment approaches that combine chemical oxidation as a pre-treatment with biological remediation offer a strategic advantage by improving overall degradation efficiency.

The success of in situ chemical oxidation also depends on factors such as oxidant–pollutant compatibility, delivery mechanism, and site-specific hydrogeological conditions. Achieving optimal contact between the oxidant and target contaminant is essential. Challenges such as low permeability soils (e.g., clay layers), pollutant entrapment in soil matrices, or migration into fractured bedrock may hinder the uniform distribution and reactivity of the oxidants (Technical/Regulatory Guidelines, 2001; EPA US, 1998; In Situ Oxidation, 1999). Therefore, detailed site characterization and screening are imperative before selecting and deploying a suitable oxidation strategy.

Among the various chemical oxidants employed for environmental remediation, hydrogen peroxide and ozone are the most commonly chosen for in situ soil treatment.

This study concentrates on assessing these two advanced oxidation approaches—namely, ozonation and Fenton-based treatment—to determine their effectiveness and suitability for treating polluted soils, particularly under conditions prevalent in India.

- Hydrogen peroxide treatment

Fenton's reagent can be applied in a number of commercial and patented ways. Geo-Cleanse®, ISOTECTM, and Clean-OxR (In Situ Oxidation, 1999; Chemical Oxidation, 1998) are a few of these that have been effectively used for full-scale soil, such as hydrocarbons and chlorinated solvents.

In commercial applications, Fenton's reagent usually consists of a solution with about 35–50% hydrogen peroxide (H_2O_2 by weight). The starting amounts of hydrogen peroxide and ferrous ions (Fe^{2+}) are selected according to the level of contamination, properties of the subsurface, soil type, and the ideal proportions determined from laboratory research. To increase contact time between reagents and contaminants, additional additives known as stabilizers may be introduced to address medium heterogeneity and control the decomposition rate of H_2O_2 (Baciocchi et al., 2003. Monobasic potassium phosphate (KH_2PO_4), serving both as an organic stabilizer and a microbial nutrient, is commonly incorporated in bioremediation formulations (Hinchee et al., 1990). Prior to the application of Fenton's reagent, acidic amendments may be injected into the subsurface to lower the pH if natural conditions are not conducive to efficient hydroxyl radical formation, as optimal radical formation typically occurs in acidic environments (Technical/Regulatory Guidelines, 2001). According to Baciocchi et al. (2003), pH adjustment is particularly effective in reducing the rate of H_2O_2 decomposition, thereby enhancing treatment efficacy.

Applying hydrogen peroxide (H_2O_2) at concentrations below 35%, such as 10%, offers several advantages. Lower concentrations reduce the risk of excessive heat generation and gas evolution, as well as minimize the potential for contaminant volatilization, Additionally, the overuse of H_2O_2 can be economically inefficient due to unfavorable side reactions, including scavenging interactions between H_2O_2 and hydroxyl radicals (Walling, 1975). Nevertheless, using 10% H_2O_2 may necessitate increased on-site chemical handling and dilution procedures, given that bulk H_2O_2 is typically supplied at concentrations of 35% or 50% (Technical/Regulatory Guidelines, 2001). One approach is to first confirm that the site can handle the desired liquid flow rate before beginning chemical dosing. After achieving the required flow, both ferrous ions and a 35% hydrogen peroxide (H_2O_2) solution are introduced together at the same point to ensure effective mixing in the targeted treatment area. As per established technical guidelines, the injection system used in this method is specially designed to prevent the chemicals from mixing prematurely within the delivery lines. Another distinct approach entails the initial injection of ferrous ion catalysts in a more mobile and organically complexed form into the subsurface. This procedure enables the soil to stabilize, achieving the right pH, sufficient iron presence, and other conditions that favour the Fenton process. Afterward, 50% hydrogen peroxide (H_2O_2) is injected under pressure, which then reacts with naturally present iron in the subsurface to produce hydroxyl radicals. Another technique involves the use of a direct-push probe, which delivers a mixture containing up to 5% hydrogen peroxide, an iron catalyst, and special additives—all in a single injection. As the probe advances, it releases the oxidant solution, softening the soil and making manual probe insertion easier. Figure 3.4 depicts a vertical injection well setup for delivering hydrogen peroxide into both unsaturated (vadose) and saturated soil layers.

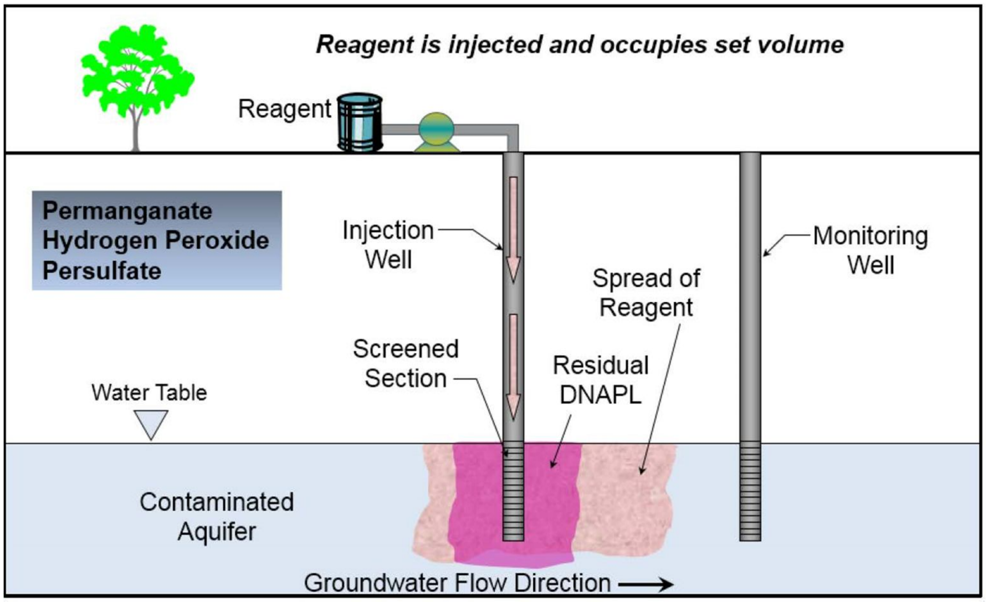


Figure 3. 2. Figure 3.4 provides a schematic overview of how hydrogen peroxideis applied directly in the field for treating contaminated soil and groundwater.

Site remediation may involve a single pressurized injection, multiple reinjections spaced over time, or continuous injection combined with recirculation of treated water. Under controlled pressure, an aqueous mixture of oxidants and any necessary catalysts is delivered through either permanent or temporary injection wells. Key design parameters that influence both the cost and efficacy of the treatment include the concentration of oxidants and catalysts, the target pH of the treatment zone, the number of injection events, injection pressure, and the spatial arrangement of injection wells, specifically the radius of influence around each well (In Situ Oxidation, 1999). Compared to alternative soil remediation methods, Fenton's reagent treatment offers several notable advantages. The process typically requires only days to weeks to achieve effective contaminant degradation. In situ application transforms pollutants into benign or naturally occurring end products such as water (H_2O), carbon dioxide (CO_2), oxygen (O_2), and halide ions. A key benefit of Fenton's treatment over other remediation technologies is its ability to react directly with contaminants in place, minimizing the risk of contaminant migration caused by injection processes themselves (Technical/Regulatory Guidelines, 2001). Additionally, when substantial amounts of reagent are applied, the oxygen generated through hydrogen peroxide decomposition can enhance aerobic biodegradation of residual pollutants. The economic viability and effectiveness of Fenton's reagent treatment can be further improved if hydrogen peroxide is produced on-site, for example, via electrochemical methods.

Recent research has demonstrated that naturally occurring soil iron oxides—including hematite (α-Fe_2O_3), goethite (α-FeOOH), magnetite (Fe_3O_4), and ferrihydrite—can catalyze the oxidation of organic contaminants by hydrogen peroxide, effectively functioning as intrinsic Fenton catalysts. Consequently, in situ Fenton-type treatments can often leverage these native iron minerals, reducing or eliminating the need for exogenous soluble iron catalysts. Nonetheless, certain limitations exist. The process frequently requires pH adjustment to maintain optimal radical generation, and managing the exothermic reactions that produce heat and gas in situ poses operational challenges (In Situ Oxidation, 1999). Additional constraints include low soil permeability, poor delineation of contaminated zones, subsurface heterogeneities, and alkaline soil conditions where carbonate ions may scavenge hydroxyl radicals, diminishing treatment efficacy (Technical/Regulatory Guidelines, 2001).

- Application of Ozone in Environmental Remediation

One of the most effective oxidizing agents used for in situ remediation of contaminated soils is ozone. Similar to its action in water treatment, ozone can degrade organic contaminants either directly through molecular oxidation or indirectly by generating highly reactive hydroxyl radicals (OH•). Studies have demonstrated that metal oxides commonly found on soil and sand surfaces, for example, iron oxyhydroxide (α-FeOOH), manganese oxide (MnO), and aluminium oxide (Al_2O_3), enhance ozone decomposition via heterogeneous catalytic reactions, subsequently promoting OH• formation, Consequently, both ozone and the generated OH• radicals are capable of reacting extensively with various organic pollutants present in the subsurface environment. Due to this high reactivity, gaseous ozone is particularly promising for remediating unsaturated contaminated soils.

Ozone is an on-site gas produced from compressed oxygen or the atmosphere. Both the gas flow rate and the ozone concentration are fixed within relatively small ranges. When produced from oxygen, the ozone concentrations are around 5% (by weight), while when produced from atmospheric air, they are roughly 1% (Langlais et al., 1991). Mass output is commonly used to express ozone generator capacity. Unlike the batch injection approach commonly utilized with Fenton's reagent, ozone-based in situ oxidation typically operates as a continuous process due to the steady supply of ozone from ozone generators. Calculating the necessary capacity of an ozone generator requires careful consideration of parameters including the total oxidant loading, appropriate gas flow rates for subsurface injection, and the permissible treatment duration (Technical/Regulatory Guidelines, 2001).

Ozone gas is delivered and transported subsurfacely in a fundamentally different way than aqueous-phase oxidants. Where the oxidation events mostly take place, is a component of in situ ozonation. It is possible to inject ozone into either the saturated or vadose zones. The amount of ozone that can be found in aqueous solution is orders of magnitude lower than that found in the gas phase. Compared to water, Ozone remains more stable when present as a gas, whereas its breakdown in water is accelerated in the presence of hydroxyl radicals (OH•).Additionally, compared to aquifers, the vadose zone can achieve higher flow velocities. In both situations—injections into the saturated zone or vadose—flow under changeable saturated conditions must be taken into account. The current moisture conditions and geological heterogeneity have a significant impact on the dispersion of injected ozone gas in the vadose zone. Introducing ozone into the saturated soil layer relies on controlled movement of the gas through the subsurface environment principles analogous to sparging, where the introduced gas displaces groundwater, creating a localized unsaturated zone conducive to gas distribution. In this case, preferred gas flow may result from subsurface heterogeneity, and mass transfer and aqueous-phase diffusion may restrict ozone transport in areas that maintain water saturation (Technical/Regulatory Guidelines, 2001).

Soils impacted by petroleum hydrocarbons, benzene, toluene, ethylbenzene, xylene (BTEX), and polycyclic aromatic hydrocarbons (PAHs) have been effectively remediated through the commercially available ozone-based remediation technology known as CSparge™.

Ozone can be injected into the subsurface using either vertical or horizontal injection wells for in situ ozonation. Ozone might be added to unsaturated soils via a vertical injection well, as shown in Fig. 3.5. If required, extraction wells can be utilized to regulate the subsurface ozone flow direction. Ozone could potentially be injected into horizontal wells. According to Nelson (1994), horizontal wells are a more efficient way to introduce ozone into unsaturated soils than vertical wells. When ozone is used in conjunction with sparging technology, horizontal wells are also beneficial. However, even though horizontal wells might have certain benefits, it's unclear if these outweigh the extra expense required to create them.

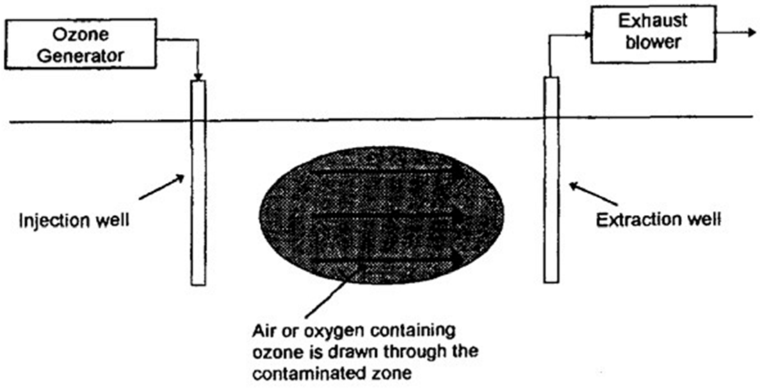


Figure 3. 3. presents a layout of an ozone injection system designed for in situ treatment of polluted soil environments

In situ ozonation has a number of benefits over the other technologies. Ozone can be produced on-site, which removes the handling and storage issues related to other oxidants; 2) it is far simpler to transport ozone to a contaminated area than aqueous oxidants; In situ ozonation frequently results in a rise in hydrophilic chemicals, which are generally more biodegradable and may be broken down more quickly by microbes; This also aid bioremediation by dissolving complicated compounds into simpler, more easily degradable molecules; 5) Ozone can enhance bioremediation by giving the microbial community oxygen as it breaks down, but it must be properly regulated before biotreatment is promoted because it can also be a sterilising agent at large concentrations or for extended periods of time; 6) The mass transfer constraints related to soil venting are avoided since no volatilization of the target compounds is necessary; 7) In situ ozonation would probably be quicker than soil venting or biodegradation, which would cut down on cleanup time and treatment expenses.

IV. MATERIALS AND METHODS

A. *Water Remediation Techniques*

1) Selection of Target Pollutants for Water Purification

The present study examined several nitrophenolic compounds as model pollutants, including 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2-methyl-4,6-dinitrophenol (4,6-DN-o-CR), 2-methyl-2,6-dinitrophenol (2,6-DN-p-CR), 2,4-dinitrophenol (2,4-DNP), 2,5-dinitrophenol (2,5-DNP), and 2,6-dinitrophenol (2,6-DNP). High-purity nitrophenols were sourced from Aldrich Co. For the experiments, a mixture containing 2,4-DNP, 4-NP, 2-NP, and 4,6-DN-o-CR was prepared in double-distilled water. The starting concentration for each individual nitrophenol was maintained at 0.4 mM, while the total concentration in the mixture was set at 2 mM, that is, 0.5 mM of each component. Key chemical and physical properties of these compounds are summarised in Table 1 of Paper II and Table 1 of Paper IV.

2) Advanced Oxidation Techniques Employed

- Application of Fenton's Reagent, Photo-Fenton Process, and Photolytic Methods *Papers I and II*

The kinetics of an individual nitrophenols (NPs) in aqueous solution were investigated under batch conditions employing both Fenton and photo-Fenton treatments. Experiments were performed in a cylindrical glass reactor with a working volume of 0.7 liters containing freshly prepared NP solutions, continuously agitated using magnetic stirring in accordance with standardized protocols. The reaction was quenched by the addition of a 10% aqueous sodium sulfite (Na_2SO_3) solution to halt further oxidation. Additionally, photolysis experiments were conducted under similar conditions, varying hydrogen peroxide (H_2O_2) concentrations to assess their effect on degradation rates. The ultraviolet (UV) irradiation source for hydrogen peroxide photolysis, photo-Fenton, and direct UV photolysis processes was a mercury low-pressure OSRAM lamp operating at 10 W power input. The intensity of UV light at the characteristic wavelength of 253.7 nm (I_0) was quantified using potassium ferric oxalate actinometry and calculated via Equation 2.1, as outlined by Gordon and Ford (1976):

$$I^1\ 0 = \frac{(C_0 - C_n)V}{\varphi T} \qquad (2.1)$$

Here, V refers to the total volume of solution exposed to irradiation (in litres), T is the duration of irradiation (in seconds), ϕ stands for the quantum efficiency (taken as 1.25 at a wavelength of 253.7 nm), C_0 is the starting concentration of Fe^{2+} ions (in mol/L), and C_n is the Fe^{2+} concentration measured after time T. Figure 4.1 provides a schematic illustration of the experimental arrangement used for direct UV photolysis, hydrogen peroxide photolysis, and photo-Fenton experiments. The temperature was regulated throughout by means of a cooling jacket, maintaining a consistent environment at 20 ± 1°C during all experiments.

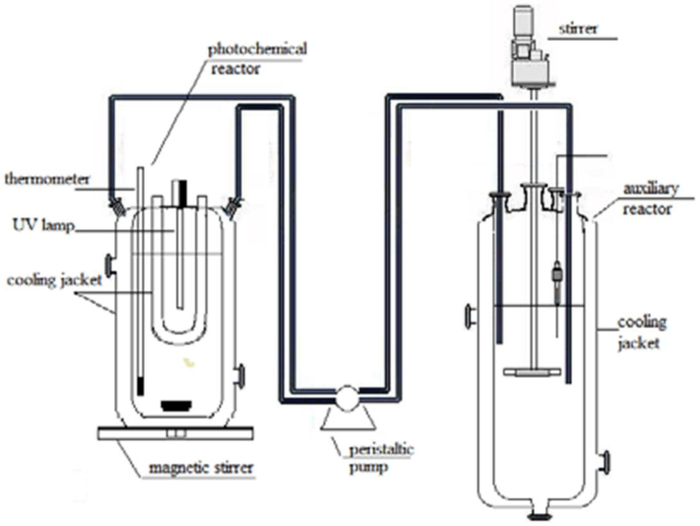


Figure 4. 1. Schematic diagram of the experimental setup used for UV/H_2O_2 oxidation.

- Standalone Ozonation and Use of Peroxides

Papers I and III

Ozone was used to treat nitrophenolic compounds in laboratory-prepared solutions using double-distilled water. These experiments were conducted in a semi-continuous bubble column reactor to study the oxidation process, featuring a height of 18 cm, a diameter of 8.0 cm, and a working volume of 0.8 liters. A schematic diagram of the experimental setup is presented in Figure 4.2.

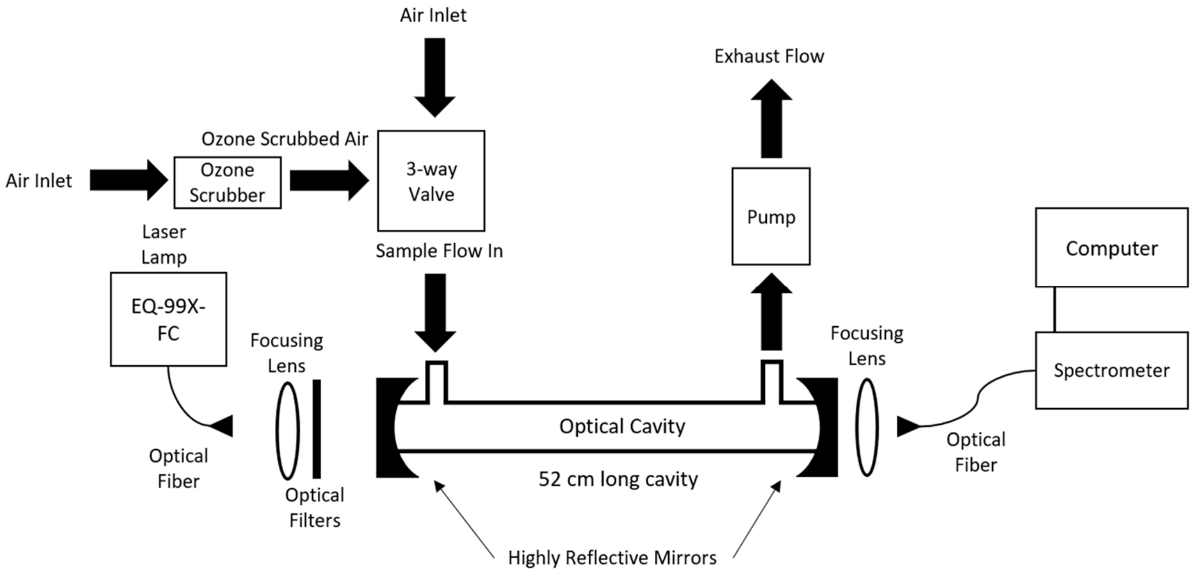


Figure 4. 2. Layout of the experimental apparatus includes: (1) air compressor, (2) ozone generator, (3) gas flow regulator, (4) three-way control valve, (5) bubble column fitted with a water-cooling jacket and ultraviolet lamp, and (6) spectrophotometric analyzer.

A volume of 0.6 L of freshly prepared nitrophenol (NP) solution was introduced into the reactor. Throughout each experiment, the gas flow rate was maintained at 1.0 L min^{-1}, with the ozone concentration in the feed gas controlled at 0.50 ± 0.02 mg L^{-1} (with some tests reaching 1.52 ± 0.02 mg L^{-1}, as reported in Paper I). Experiments involving combined ozone and hydrogen peroxide (O_3/H_2O_2) were conducted under identical conditions, varying the H_2O_2 concentration. Hydrogen peroxide was injected directly into the reactor immediately prior to ozone addition. All tests were performed at ambient temperature, maintained at 20°C).

- Multi-Stage Oxidation: Ozone-Hydrogen Peroxide-UV and Ozone-UV Methods

The same operating parameters used for standalone ozonation were followed when conducting experiments that combined ozone with UV irradiation. The ultraviolet light intensity generated by a low-pressure mercury lamp (58.8 W, DRB 8-1 model, USSR) housed within a quartz tube in the bubble column was determined using potassium ferrioxalate actinometry, yielding a value of 0.749 ± 0.054 µEinstein s^{-1}. Throughout the trials, the temperature was strictly regulated at 20 ± 1°C with the help of a cooling jacket to ensure consistent results.

3) *Consumed O_3 Calculations in water treatment*

The ozone concentration in the feed gas (c_ O_3, mg L^{-1}) during ozonation was determined using Equation 2.2:

$$c_{O3} = 0.15Ext \qquad (2.2)$$

where Ext - extinction (cm).

The inlet dose of ozone (D^{in}, mg L^{-1}) was calculated using Eq. 2.3:

$$D^{in} = \frac{GT c^{in}}{V} \ (2.3) \qquad (2.3)$$

where G is the gas flow rate (L min^{-1}), T is the time duration (min), V is the volume of the solution (L), and c^{in} represents the inlet ozone concentration (mg L^{-1}).

The consumed dose of ozone (d^c, mg L^{-1}) was calculated using Eq. 2.4:

$$d^c = \sum_{n=1}^{n}[(\frac{G\Delta T_n}{V})(C^{in} - \frac{c^{out}\, n-1+ C^{out}\, n)}{2})] \qquad (2.4)$$

where G is the gas flow rate (L min^{-1}), T is the duration of the experiment (min), C^{out} and C^{in} are the outlet and inlet ozone concentrations, respectively (mg L^{-1}), V is the volume of the solution (L), and n denotes the number of experimental data points.

4) *Kinetic studies*

A semi-continuous bubble column reactor was employed to generate degradation curves for nitrophenols (NPs) under different oxidation conditions, ensuring the chemical reaction regime was maintained. According to established principles (Dankwerts, 1973), when specific conditions are satisfied, the influence of mass transfer on reaction rates within a bubble column is effectively negligible, allowing the process to proceed entirely within the kinetic control domain.

$$\frac{D_{O_3}\, X\, k_1}{k_{L^2}} \qquad (2.5)$$

where D_{O_3} represents the ozone diffusion coefficient (m^2 s^{-1}), k_1 is denotes the rate constant for first-order chemical reactions (s^{-1}), and k_L is the mass transfer coefficient for the physical absorption of ozone into the liquid phase (m s^{-1}). The ratio was calculated using an average

k_L alue of 1×10−51 \times 10^{-5}1×10−5 m s^{-1} for popping columns, as reported by Dankwerts (1973), along with a corresponding ozone diffusion coefficient of 1.26×10−91.26 \times 10^{-9}1.26×10−9 m^2 s^{-1} (Münter, 1985):

$$K_1 < \frac{k_L^2}{D_{O_3}} = \frac{(10^{-5})}{1.26 \times 10^{-9}} = 0.079\ s^{-1}$$

Thus, if the first-order rate constant for nitrophenol (NP) degradation is less than 7.9 × 10^{-2} s^{-1}, it is possible to meaningfully compare the breakdown of NPs under various oxidation conditions over time. This benchmark confirms that ozonation primarily takes place in the bulk liquid phase, following kinetic control. This condition was maintained for all ozonation experiments conducted in the present study.

Further, analysis of NP degradation rates revealed that the process followed pseudo-first-order kinetics, as evidenced by regression analysis of concentration versus time data.

$$\frac{dc_{NP}}{dT} = -k_1 c_{NP} \qquad (2.6)$$

As a result, false first-order reaction rate constants were used to compare the rates of degradation of various NPs in aqueous solution in relation to NP concentrations.

Representing the value of as described by Equation 2.7.

$$\text{In}\left(\frac{c_{NP}}{c_{Npo}}\right) = k_1T \qquad (2.7)$$

The amount of time needed for half of the reactant (NP) to vanish is known as the half-life ($T_{1/2}$) was computed for the first-order reaction using Eq. 2.8:

$$\text{In}\left(\frac{c_{NP}}{c_{Npo}}\right) = k_1T \quad \text{and } T_{1/2} = \frac{0.693}{k_1} \qquad (2.8)$$

The 90% conversion time ($T_{90\%}$) refers to the time required to achieve a 90% reduction of the initial nitrophenol concentration. It was calculated using Equation 2.9:

$$\text{In}\left(\frac{c_{NP}}{c_{Npo}}\right) = k_1T_{90\%} \text{ and } T_{90\%} = \frac{2.303}{k_1} \qquad (2.9)$$

Reaction rates were compared by calculating the half-life ($T_{1/2}$) and 90% degradation time ($T_{90\%}$) using equations 2.8 and 2.9. These calculations applied to experimental data from studies employing photolysis combined with hydrogen peroxide, ozonation alone, and ozonation coupled with hydrogen peroxide and/or UV irradiation (Papers I, II, III). Additionally, for evaluating reaction kinetics in experiments using Fenton's reagent and photo-Fenton processes to degrade nitrophenols, The half-life ($T_{1/2}$) and time required for 90% reduction (T_{90}%) were calculated based on the experimental degradation profiles obtained in this study.

5) *Acute toxicity of NPs and Toxicity Reduction Following AOP Treatment*

Papers 1,2,3

The toxicity of nitrophenols (NPs) both before and after advanced oxidation process (AOP) treatment was evaluated using the Daphnia magna bioassay. For these tests, a Daphnia magna clone was sourced specifically for the study. NP solutions were treated to achieve at least 90% degradation of the original compounds. The combined nitrophenol concentration in the test mixture was maintained at 2 mM (0.5 mM of each component), while separate tests for individual NPs used an initial concentration of 0.4 mM. Acute toxicity assessments were conducted over a 24-hour period, following standard protocols to maintain suitable conditions for the Daphnia. The median effective concentration (EC_{50}) and the 95% confidence limits were determined using PROBIT analysis.

6) *Analytical Techniques Employed in Water Treatment*

The analytical methods employed in the water treatment experiments are summarized in Table 4.1.

Table 4.1: Analytical Parameters and Methods Used for Water Treatment Evaluation

Parameter	**Instrument/Equipment**	**Analytical Protocol/Standard**	**Relevant Study Section**
UV absorbance at 254 nm	UV-Vis Spectrophotometer	EPA Method 0415.1	Section III
pH Measurement	Digital pH Meter	Standard Laboratory Practice	Sections I, II, III
Nitrophenol Derivatives	HPLC with UV Detector	Standard HPLC Procedure	Section III
Nitrophenols (NPs)	HPLC with UV Detector	Method by Trapido & Kallas (2000)	Sections I, II, III
Nitrate (NO_3^-)	Ion Chromatograph	Penchuk et al., 1986	Sections I, II, III
Hydrogen Peroxide	UV-Vis Spectrophotometer	Eisenberg Method (1943)	Sections I, II
Total Iron Content	UV-Vis Spectrophotometer	Standard Methods (1994)	Sections I, II
Total Organic Carbon	TOC Analyzer	Standard Methods (1994)	Section III
Chemical Oxygen Demand	Reflux Titration Set-up	Standard Methods (1994)	Sections I, III
BOD & Dissolved Oxygen			

B. *Soil Treatment*

1) *Characterization of soil samples*

The viability of chemical remedies in various soil matrices was tested using sand and peat as models.

Papers IV, V, VI,

Prior to the spiking, the sand was dried at 50 °C after passing through a 0.16–1.0 mm filter. Sand had a pH of 6.7. In addition to 4.52 g kg^{-1} of total iron and 0.27 g kg^{-1} of ion-exchangeable Fe (II), the sand also included 94.36% SiO_2, 4.81% Al_2O_3, and 0.47% organic carbon.

2) *Model compounds in soil treatment*

To ensure the contaminants were evenly distributed and to improve the consistency of subsequent tests, the acetone was continuously mixed and allowed to fully evaporate until the soil was dry. To verify the initial pollutant levels, at least four replicate samples were analyzed.

Paper IV

The mixture of nitrophenols (NPs) used to contaminate the soil included 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), and 4,6-dinitro-o-cresol (4,6-DN-o-CR), all obtained from Aldrich Co. The sand used in these experiments had an initial NP concentration of 685.5 mg per kilogram. Additional chemical and physical properties of these NPs can be found in Table 1 of Paper II and Paper IV.

Paper V

Paper V investigated the degradation of polycyclic aromatic hydrocarbons (PAHs) including phenanthrene, anthracene, fluoranthene, pyrene, and triphenylene, all obtained from Aldrich Co. The study utilized sand samples with total PAH concentrations of 52.46 mg/kg (designated as Sand I) and 66.64 mg/kg (Sand II), alongside peat samples containing 357.8 mg/kg (Peat I), 121.83 mg/kg (Peat II), and 40.21 mg/kg (Peat III) of PAHs.

Paper VI In Paper VI, commercial diesel was used as the target contaminant, with initial concentrations of 12.5 ± 0.4 g/kg in peat and 10.4 ± 0.3 g/kg in sand. Selected chemical and physical properties of the diesel sample are summarized in Table I of Paper VI.

3) *Application of Chemical Remediation Methods*

- Use of Fenton's Reagent for Soil and Water Clean-up

Papers IV, V, VI,

The pollutants in soil slug was studied under batch conditions using Fenton and Fenton-like treatments. Typically, a mixture of contaminated soil and liquid—either DI water with hydrogen peroxide or without added ferrous ions (Fe^{2+})—was placed in a 0.2 L cylindrical glass reactor and vigorously stirred magnetically. Reaction durations varied from 24 hours (Papers IV and V) to 72 hours (Papers V, VI). The treatments were generally conducted at an acidic pH of 3.0 (Papers IV, V, V), although some experiments were performed without pH adjustment (Paper VII). Different chemical dosing strategies were tested, including both gradual and single-step additions of H_2O_2. To terminate the reaction, a 10–20% aqueous sodium sulfite (Na_2SO_3) solution was added. All experiments were maintained at a controlled temperature of 19 ± 2 °C.

- 3-phase ozonation

Papers IV, V

A semi-continuous bubble column reactor, with a volume of 0.31 L (height: 14.3 cm; diameter: 5.3cm), was utilized to perform three-phase ozonation of soils contaminated with nitrophenols (NPs) (Paper IV) and polycyclic aromatic hydrocarbons (PAHs) (Paper V). In this system, a slurry composed of soil and water was contacted with a gas mixture of ozone and air produced by a laboratory-scale ozone generator. To ensure effective mass transfer and maximize interaction between ozone and contaminants, the slurry was vigorously stirred using a magnetic stirrer.

- Two-phase ozonation

Papers IV, V, VI

In this study (as presented in Papers IV, V, and VI), two-phase ozonation experiments were carried out on dry sand and peat samples using a semi-continuous rising column reactor with a total volume of 0.05 litres (29 cm height, 1.5 cm diameter). Dry soil samples were treated with a blend of ozone and air, produced by a laboratory-scale ozone generator, without making any adjustments to the pH. For tests in Papers IV and V, the concentration of ozone supplied was maintained at 1.00 ± 0.02 mg/L, while for Papers VI and VII, it was kept at 5.00 ± 0.02 mg/L. All runs were performed with a fixed gas flow rate of 1.0 L/min and the temperature was controlled at 20 ± 2°C to ensure consistent treatment conditions throughout.

4) *Calculations of consumed ozone doses in soil treatment*

During ozonation, the ozone concentration in the feed gas (C_{O3}, mg L^{-1}) was calculated using Equation 2.10:

$$c_{O_3} = 0.15Ext \qquad (2.10)$$

where Ext - extinction (cm).

The inlet ozone dose (d^{in}, mg kg^{-1}) was calculated using Equation 2.11:

$$d^{in} = \frac{GTc^{in}}{m} \qquad (2.11)$$

where G is the gas flow rate (L min^{-1}), T is the time duration (min), m is the sample weight (kg), and c^{in} is the inlet ozone concentration (mg L^{-1}).

The consumed dose of ozone (d^c, mg kg^{-1}) was calculated using Eq. 2.12:

$$D^c = \sum_{n=1}^{n}[(\frac{G\Delta T_n}{m})(c^{in} - \frac{(c^{out}\, n{-}1{+}\, c^{out}\, n)}{2})] \qquad (2.12)$$

where C_{out} is the ozone concentration at the outlet (mg L^{-1}), C_{in} is the ozone concentration at the inlet (mg L^{-1}), mmm is the sample weight (kg), n is the number of experimental data points, and G is the gas flow rate (L min^{-1}).

5) Assessment of Biological Remediation in Soil.

Papers IV, V, VI, VII

Following ozonation and Fenton-like pretreatments, soils contaminated with nitrophenols, PAHs, diesel, shale oil, and transformer oil were incubated for aerobic biodegradation. Duplicate sets of treated, untreated, and control samples were maintained at 20 °C in the dark under static, aerobic conditions. For Fenton and Fenton-like treatments (Papers IV–VI), the original sample pH of 3.0 was neutralized to 6.5–7.0 before incubation, whereas transformer- and shale oil-contaminated soils treated with Fenton-like oxidation (Paper VII) were not pH-adjusted. Throughout the incubation period, soil moisture was sustained by periodic additions of sterile doubly distilled water, and no external microbial inocula were introduced..

6) Analyses used for soil treatment

The analytical methods employed in the experiments are summarized in Table 4.2.

Table 4. 1 Analytical Techniques Adopted for Soil Remediation Studies

Analysis	Analytical instrument/Method	Reference	Paper
pH of soil	pH-meter	EPA method 9045C	IV, V, VI, VII
Total iron in soil	AAS	Slight modification from Heron et al., 1994; papers IV, V, VI, VII	IV, V, VI, VII
Ion exchange Fe(II) in soil	AAS	Slight modification from Tessier et al., 1979; papers IV, V, VI,	IV, V, VI
UV-254	UV-Vis Spectrophotometer	EPA method 0415.1	VI, VII
NPs	HPLC-UV	Trapido and Kallas, 2000	IV
PAH	HPLC-FLD	Trapido and Veldre, 1996	V
diesel	Gas Chromatography-MS	Palmroth et al., 2002	VI
alkanes	Gas Chromatography-MS	Palmroth et al., 2002	VI
shale oil	Gas Chromatography-MS	VII	VII
transformer oil	Gas Chromatography-MS	VII	VII
O_3 inlet, outlet	spectrophotometer	IOA Revised Guideline Document, 1998	IV, V, VI, VII

Figures 4.3 through 4.5 present representative chromatographic analyses conducted in this study. Figure 4.3 depicts typical chromatograms of polycyclic aromatic hydrocarbons (PAHs) and nitrophenols obtained using high-performance liquid chromatography with fluorescence detection (HPLC–FLD) and ultraviolet detection (HPLC–UV), respectively.

Figure 4.4 illustrates the gas chromatography–mass spectrometry (GC–MS) profile of the Accustandard DRX-008S multistandard hydrocarbon mixture, which contains 35 n-alkanes ranging from octane to tetracontane.

Lastly, Figure 4.5 displays example GC–MS chromatograms for transformer oil, shale oil, and diesel fuel samples.

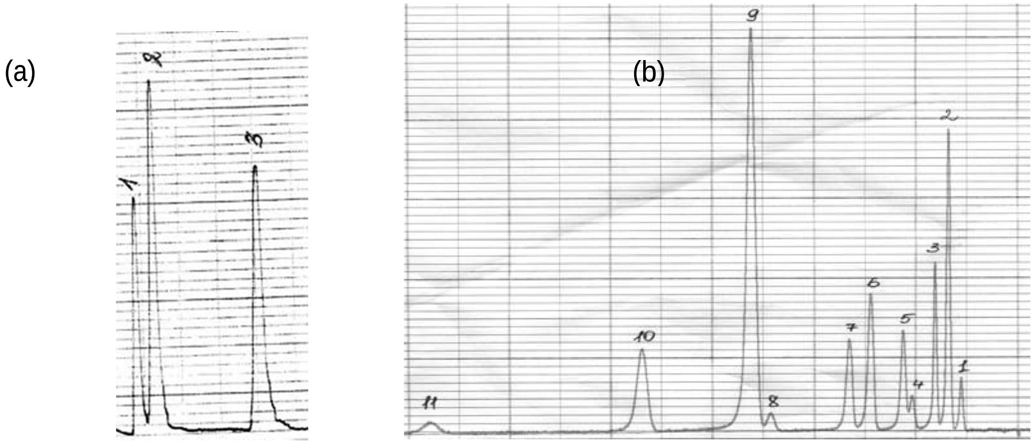


Figure 4. 3. Typical chromatograms of (a) nitrophenols obtained by HPLC-UV detection at 280nm: (1) 4-nitrophenol; (2) 2,4-dinitrophenol; (3) 4,6-dinitro-o-cresol; and (b) polycyclic aromatic hydrocarbons with fluorescence detection at 254 nm

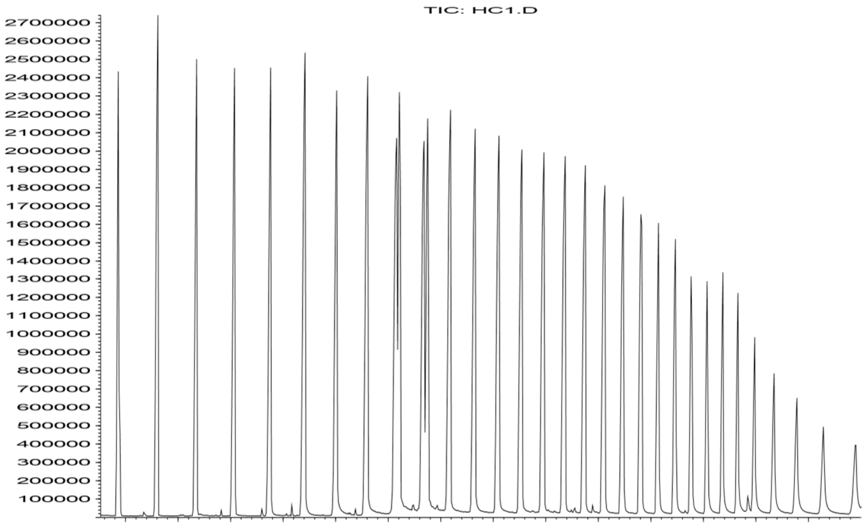


Figure 4. 4. Displays the GC-MS output for a standard mixture of hydrocarbons, used here to establish the detection limits and calibration range for DRX window analysis.

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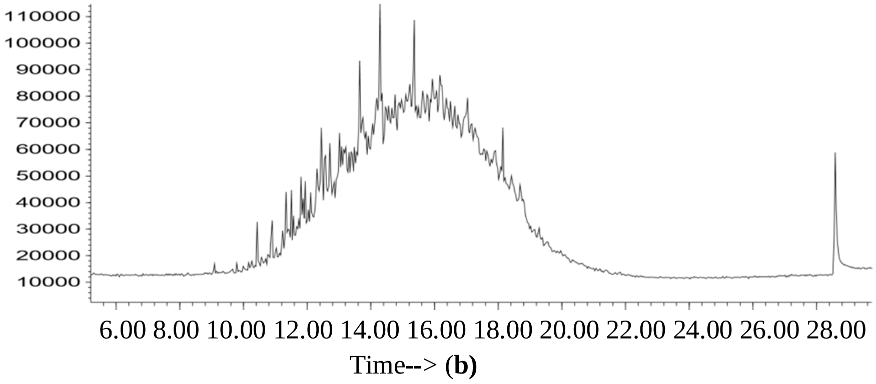

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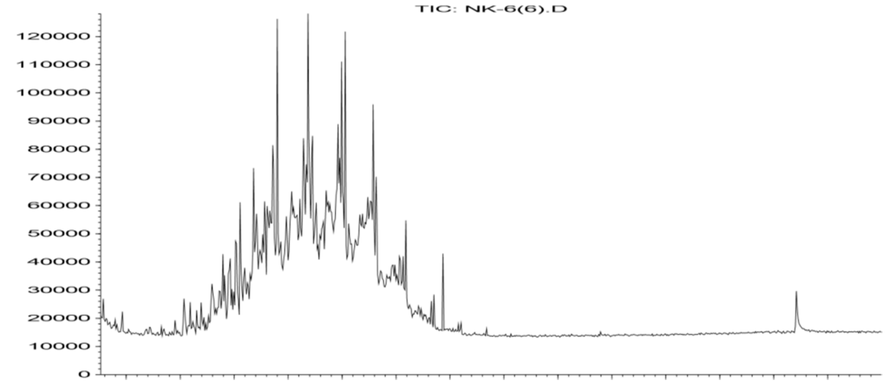

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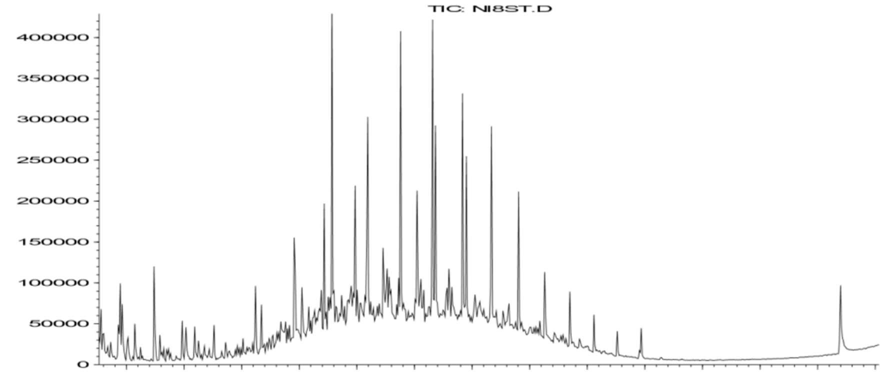

Figure 4. 5. Typical GC-MS chromatograms of (a) transformer oil (tridecane to docosane), (b) shale oil (decane to phytane), and (c) diesel fuel (octane to octacosane) with an internal standard at 28.8 min.

V. RESULT & DISCUSSION

A. Water purification with NP-contaminated

1) AOP for water purification

The present work evaluated the effectiveness of individual ozonation as well as several advanced oxidation processes—including hydrogen peroxide photolysis, Fenton and photo-Fenton methods, ozone combined with UV (O_3/UV), ozone with hydrogen peroxide (O_3/H_2O_2), and the integrated O_3/UV/H_2O_2 system—for breaking down nitrophenolic pollutants in contaminated water.

- Hydrogen peroxide photolysis

Nitrophenols exhibited negligible degradation when mixed with hydrogen peroxide in the absence of UV irradiation, and direct UV photolysis alone yielded very slow pseudo–first-order degradation rates on the order of 10^{-5} s^{-1}, rendering it impractical for field applications (Paper II, Section 5.1). Incorporation of H_2O_2 into the UV treatment markedly accelerated NP removal, with higher peroxide concentrations producing proportionally shorter degradation times (Paper II, Table 2). Mono-substituted nitrophenols degraded more rapidly than di-substituted and methylated dinitrophenols. Within the examined concentration range of 0 to 10 mM hydrogen peroxide, the degradation rates of nitrophenol (NP) were observed to increase linearly in direct proportion to the H_2O_2 concentration (Paper II, Figure 1). This linear relationship is consistent with findings from earlier phenol degradation studies, which similarly reported enhanced removal efficiencies at elevated hydrogen peroxide levels due to increased generation of hydroxyl radicals (Chen et al., 1997). Based on these results, UV/H_2O_2 molar ratios of up to 10:1 were determined to be optimal, balancing effective radical production with efficient reagent use. In addition, the influence of pH on the photo degradation behaviour of 4-nitrophenol and 4,6-dinitro-o-cresol was carefully examined. Unlike earlier studies on other phenolic substances, which reported a strong dependence of photolytic rates on acidic or basic conditions—mainly due to molecular speciation and radical scavenging effects—this research observed that, within the range studied, the degradation of these nitro-substituted phenols did not significantly vary with pH. This indicates that the underlying photochemical pathways for these particular compounds are comparatively less affected by changes in protonation compared to other phenolic derivatives.

- Application of Fenton and Photo-Fenton Processes

To facilitate the degradation of nitrophenols (NPs), both Fenton’s reagent and photo-Fenton processes were applied using varying concentrations of hydrogen peroxide and ferrous ion (Fe^{2+}) catalyst. The initial pH of the reaction solution was maintained at 3.0, a sufficiently acidic condition that ensured solution homogeneity and optimal catalytic activity. As presented in Paper II, Table 3, the degradation kinetics were quantified by calculating the half-life and the time required to achieve 90% conversion of NP, based on the respective degradation curves.

The rate at which nitrophenols broke down during both Fenton and photo-Fenton treatments was found to be strongly influenced by the concentrations of hydrogen peroxide and ferrous ions (Fe^{2+}) used. For example, in the case of 4,6-dinitro-o-cresol, increasing either H_2O_2 or Fe^{2+} led to a noticeable increase in the rate of degradation. This trend was observed for all nitrophenolic compounds tested in this study. These observations are also in agreement with earlier findings for chlorophenols and other substituted phenols, where higher amounts of Fe^{2+} and H_2O_2 resulted in better pollutant removal. The effectiveness of the Fenton process for breaking down 4-nitrophenol at higher reagent levels was also confirmed by previous research, further supporting the utility of this treatment method for nitrophenol remediation.

Mechanistically, the Fenton process relies on the generation of highly reactive hydroxyl radicals (•OH) through the catalytic reaction between Fe^{2+} and H_2O_2. These radicals initiate the oxidative breakdown of nitrophenol molecules by abstracting hydrogen atoms or adding to aromatic rings, leading to ring cleavage and mineralization. In the photo-Fenton process, the presence of UV light enhances the regeneration of Fe^{2+} from Fe^{3+}, thereby sustaining the production of hydroxyl radicals and increasing the overall degradation efficiency. The acceleration of degradation rates with increased Fe^{2+} and H_2O_2 concentrations can thus be attributed to the greater availability of •OH radicals, which promotes more rapid and extensive oxidation of the nitrophenol contaminants.

The findings of the current study demonstrate that UV radiation enhances the activity of the Fenton reagent system, with photo-Fenton treatment accelerating the degradation of all nitrophenols more rapidly than Fenton treatment at equivalent hydrogen peroxide concentrations. Depending on the NP and the concentration of Fenton's reagent used, the enhancement factor varied between 1.3 to 75 for various NPs (paper II, Table 3).

Total breakdown of all the nitrophenol compounds under study was observed when the starting concentration of hydrogen peroxide was maintained at 4 mM or above. At lower peroxide levels—specifically, with $[H_2O_2]_0 = 2$ mM and $[Fe^{2+}]_0 = 0.1$ mM—complete breakdown was still attainable for mono-substituted nitrophenols. However, at hydrogen peroxide concentrations below 1 to 2 mM, neither the Fenton nor the photo-Fenton treatments were able to achieve full mineralization of the nitrophenols, indicating that insufficient oxidant availability limits the extent of degradation under these conditions. In Paper II, Figure 4 illustrates several cases of partial nitrophenol (NP) degradation. Initially, the degradation rate was rapid; however, as the reaction progressed, a clear deceleration occurred, with subsequent degradation proceeding at a much slower pace. Notably, measurements taken immediately after treatment showed that the residual hydrogen peroxide concentration was effectively zero. They discovered that a catalyst ($Fe2+$) added to p-chlorophenol can slow down its breakdown in addition to a low hydrogen peroxide to p-chlorophenol ratio.

Based on the findings of the present study, the optimal chemical ratios for Fenton treatment were determined to be hydrogen peroxide:di-nitrophenol (di-NP) or methyl-dinitrophenol:catalyst (Fe^{2+}) at 10:1:1, and hydrogen peroxide:mono-nitrophenol:Fe^{2+} at 5:1:0.25. In the case of photo-Fenton treatment applied to di-NPs and methyl-dinitrophenols, the required amount of Fe^{2+} catalyst can be reduced, as the catalyst consumed during the reaction is regenerated through irradiation, as described by Equation 3.1 (Yang et al., 1998).

The formula is $Fe(OH)2+ + hv \rightarrow Fe2+ + OH\bullet$ (3.1).

For photo-Fenton treatment, the optimal chemical ratio for methyl-dinitrophenols to Fe^{2+} is approximately 10:1:0.25, or hydrogen peroxide to di-nitrophenol may serve as the ideal proportion. These ratios correspond to the optimal values for Fenton treatment of organic-contaminated water, as recommended by Ruppert et al. (1994) and Tang and Huang (1997).

- Ozone-Driven Treatment Methods and Hybrid Approaches

Ozonation-based removal of organic pollutants from water encompasses intricate mass-transfer dynamics coupled with multiple concurrent chemical reaction pathways. These include direct reactions between the organic molecules and ozone, alongside radical-mediated reactions involving hydroxyl radicals. An aromatic ring substituted with a hydroxyl group displays enhanced reactivity toward electrophilic attack by ozone. Consequently, at pH values below 12, phenolic compounds can be effectively degraded primarily through direct reactions with ozone, with the radical-driven degradation pathway playing a minimal role.

Ozonation trials on the nitrophenol mixture were carried out at two different pH levels, 2.5 and 9.5. The findings indicated that at pH 9.5, the rate of nitrophenol degradation (pseudo-first-order constant) was almost double compared to the acidic condition (pH 2.5), while the amount of ozone consumed dropped by nearly 20%. This supports the well-known principle that phenolic compounds tend to dissociate more at higher pH, forming phenolate ions, which react more rapidly with ozone than their undissociated forms. Thus, alkaline conditions were found to be more suitable for effective ozonation of the nitrophenol mixture.

After treating the nitrophenol mixture with ozone in acidic conditions (pH 2.5), the order of degradation rates for the individual compounds was observed as:

4,6-dinitro-o-cresol > 2-nitrophenol > 4-nitrophenol > 2,4-dinitrophenol.

In contrast, under basic conditions (pH 9.5), the sequence of degradation rates was observed as:

2-NP > 4-NP ≈ 4,6-DN-o-CR > 2,4-DNP.

Many investigations employed an elevated ozone feed-gas concentration of 1.52 ± 0.05 mg L^{-1}. Although increasing the ozone concentration threefold (from 0.5 to 1.5 mg L^{-1}) did not alter the total ozone uptake, it enhanced the 2,4-dinitrophenol (2,4-DNP) degradation rate by approximately threefold (Paper I, Table 3).

Using 2,4-DNP as a model compound, we conducted a comparative assessment of simple ozonation versus ozone-based advanced oxidation processes (O_3/UV, O_3/H_2O_2, and O_3/UV/H_2O_2). Because the pseudo–first-order rate constant for NP decomposition remained below 7.9×10^{-2} s^{-1} (Paper I, Table 2; Section 2.1.4), ozonation occurred predominantly within the liquid bulk under kinetic control. Accordingly, NP degradation profiles were interpreted to compare reaction rates across the various ozone oxidation regimes (Section 4.1.4).

It is well established that the pKa of a phenolic compound plays a critical role in how pH influences its degradation rate (Langlais et al., 1991). Phenols with higher pKa values tend to exist predominantly in their dissociated form at elevated pH levels, resulting in faster reaction rates compared to conditions where the pH is below the pKa (pH < pKa). When the pH is significantly higher than the pKa (pH >> pKa), the degradation rate generally becomes independent of pH. However, within the intermediate pH range—where pH values transition from below to above the pKa—the reaction rate increases with rising pH. This behavior is exemplified by 2,4-dinitrophenol (2,4-DNP), which has a pKa of 4.03; its degradation rate showed a moderate increase within the intermediate pH range of 2 to 5 during ozonation without additional reagents (Paper I, Figure 3). Beyond this range, further increases in pH had minimal impact on the 2,4-DNP degradation rate (Paper I, Figure 3).

Figure 2 in Paper I illustrates the inlet and outlet ozone concentrations alongside the solution pH evolution during the ozonation of 2,4-dinitrophenol in an initially alkaline medium. The formation of numerous acidic by-products during the ozonation process caused the solution's pH to decrease by approximately 5.9 units (Paper I, Figure 2). Similarly, when a mixture of nitrophenols was subjected to ozonation at pH 9.5, a comparable pH reduction of 6.5 units was observed in the treated solution.

The degradation rates of 2,4-dinitrophenol under O_3/UV treatment were slightly higher at pH 2.5 and closely matched the rates observed during ozonation at pH 9.5 (Paper I, Table 2). This phenomenon may be attributed to the strong UV absorbance of di-nitrophenols at 254 nm, which reduces the amount of UV radiation available to ozone, thereby limiting the production of hydroxyl radicals (•OH). Furthermore, ozone consumption showed no significant differences between standalone ozonation and O_3/UV treatment at either pH level. These results are in agreement with previous studies on 2,4-dichlorophenol degradation.

The addition of hydrogen peroxide to the ozonation process enabled a reduction in ozone consumption while accelerating the degradation of 2,4-dinitrophenol (2,4-DNP). However, beyond a certain concentration of hydrogen peroxide, no further improvement in treatment efficiency was observed. In acidic conditions, the presence of 1–4 mM H_2O_2 significantly enhanced the degradation rate compared to ozonation alone at the same pH. At an initial pH of 9.5, only a 1 mM H_2O_2 dosage contributed to a modest acceleration of 2,4-DNP breakdown. Conversely, increasing the hydrogen peroxide concentration to 2–4 mM at pH 9.5 did not improve degradation rates and instead caused a noticeable inhibition relative to ozonation alone (Paper I, Table 2 and Figure 4). This inhibitory effect is attributed to excessive H_2O_2 acting as a hydroxyl radical scavenger, thereby reducing the availability of reactive radicals for the target compound's oxidation. Compared to standalone ozonation, the combined O_3/H_2O_2 treatment achieved a 40–50% reduction in ozone-specific consumption under acidic conditions and approximately a 10% decrease in basic media (Paper I, Table 2). The simultaneous application of O_3, H_2O_2, and UV light markedly accelerated the degradation of 2,4-dinitrophenol (2,4-DNP). Both the solution's initial pH and the hydrogen peroxide dosage were critical determinants of treatment efficacy under O_3/H_2O_2/UV conditions (Paper I, Figure 4), with the greatest improvements observed under acidic conditions (Paper I, Table 2). Elevating the H_2O_2 concentration enhanced 2,4-DNP removal rates in both acidic and alkaline media. Notably, when 8 mM H_2O_2 was employed, ozone consumption dropped to roughly 1 mmol of O_3 per mmol of 2,4-DNP degraded, the lowest specific ozone usage of all methods tested (Paper I, Table 2).

2) Biodegradability

The effects of ozonation and advanced oxidation process (AOP) treatments on the biodegradability of nitrophenols (NPs) were evaluated using the BOD_7/COD ratio (see Paper I, Table 4; Paper III, Table 1). Findings show that the by-products generated after both AOP and ozonation treatments were significantly more biodegradable than the original NPs. Although the chemical oxygen demand (COD) removal ranged from 24% to 80%—which is lower than the corresponding NP removal efficiency of 77% to 100%—the overall biodegradability of the treated solutions increased markedly.

The biodegradability of reaction by-products formed during ozonation was found to be strongly influenced by the solution pH (Paper III, Table 1). Specifically, the biodegradability of 4,6-dinitro-o-cresol (4,6-DN-o-CR) ozonation by-products was markedly enhanced in acidic media compared to the parent compound. Likewise, ozonation of 4,6-DN-o-CR in basic medium resulted in a substantial improvement in biodegradability. Complete biodegradability was observed for the ozonation by-products of 2,4-dinitrophenol formed in both basic (pH_i 9.5) and neutral (pH 7.0) media, as well as for 4-nitrophenol (4-NP) ozonated under acidic conditions (Paper I, Table 4). These findings align with Wang's (1990) report demonstrating that, at equivalent ozone dosages, 2,4-DNP ozonation products generated in alkaline conditions exhibit greater biodegradability than those formed under acidic conditions.

Ozonation of nitrophenol mixtures similarly enhanced biodegradability (Paper III, Table 1), while treatment with advanced oxidation process (AOP) combinations such as UV/H_2O_2, Fenton, and O_3/UV further improved biodegradability, as exemplified by 2,4-DNP (Paper I, Table 4). Ma et al. (2000) also documented improved biodegradability of 4-NP following Fenton treatment. This increased biodegradability supports the use of ozonation and AOPs as pre-treatment methods to enhance the effectiveness of conventional biological processes in degrading otherwise persistent nitrophenols.

The enhanced biodegradability of treated nitrophenol by-products compared to their parent compounds can be attributed to several key transformations, including nitrogen mineralization, ring hydroxylation, and ring-opening reactions that convert aromatic structures into more biodegradable aliphatic forms, along with reductions in toxicity. These mechanisms were considered in the present study to explain the observed improvements in biodegradability.

3) Nitrogen mineralization

During the breakdown of NPs, the nitro-group was cleaved from the aromatic ring and transformed into nitrate. Nitrate was the most common inorganic nitrogen species. Nitrite, which was only present in the reaction media in very minute amounts during the first stage of the treatment, was oxidized to produce nitrate. Since nitrated aliphatic intermediates were most likely created during treatment, the measured nitrate concentration was almost always lower than the theoretically estimated value.

Following the ozonation of individual nitrophenols (NPs) with 77–100% conversion, the extent of nitrogen mineralization ranged from 66% to 100% at pH 2.5 and 38% to 87% at pH 9.5 (Paper III, Table 1). During the initial 35–40% degradation of nitrophenols, nitrate production progressed slowly; however, as ozonation advanced, the rate of nitrate formation increased markedly in the later stages. When ozonating an NP mixture at pH 2.5, a higher degree of nitrogen mineralization was observed compared to pH 9.5 (Paper III, Figure 4). Under UV/H_2O_2 treatment, 50–60% nitrogen mineralization was achieved at pH 3.0 following approximately 90% NP conversion (Paper II, Section 5.1). This degree of mineralization notably exceeds the organically bound chlorine to chloride conversion ratios of 30–39% reported by Trapido et al. (1997) during photolysis of chlorophenols under similar acidic conditions.

Nitrogen mineralization during Fenton treatment exhibited a similar trend to ozonation: it remained minimal until 60–70% NP degradation was attained, after which it accelerated (Paper II, Figure 6). Upon reaching 90% NP degradation via the Fenton process, 51–67% of organically bound nitrogen was converted to nitrate. Photo-Fenton treatment further enhanced nitrogen mineralization, achieving 85–90% conversion of organically bound nitrogen to nitrate (Paper II, Section 5.2).

Following the degradation of nitrophenols (NPs) by various advanced oxidation processes (AOPs) such as standalone ozonation, O_3/H_2O_2, $O_3/UV/H_2O_2$, and UV/H_2O_2 treatments, nitrate ions were consistently formed as mineralization products. The Fenton and photo-Fenton processes were also evaluated using 2,4-dinitrophenol (2,4-DNP) degradation as a representative case. Nitrogen mineralization during these AOPs generally proceeded slowly during the initial stages of treatment and accelerated toward the later stages of 2,4-DNP degradation (Paper I, Figure 5).

4) Mineralization of Total Organic Carbon and Reduction of Aromatic Carbon

During the ozonation of nitrophenols (NPs), both the absorbance at 254 nm (UV_{254}nm) and total organic carbon (TOC) removal were monitored to assess carbon mineral. Under the experimental conditions, carbon mineralization progressed at a notably slow rate during NP degradation. In comparison to the extent of nitrogen mineralization (Paper III, Table 1), the degree of carbon mineralization was substantially lower.

UV_{254}nm absorbance, which serves as an indicator of aromatic carbon content, exhibited a modest decrease throughout the ozonation process (Paper III). This decrease mainly reflects both NP degradation and the cleavage of aromatic rings into aliphatic intermediates. Although these aliphatic fragments are less amenable to full mineralization than their original aromatic structures, they typically exhibit greater susceptibility to biodegradation (Langlais et al., 1991). This chemical transformation pathway thereby contributes to the observed improvement in the biodegradability of the treated solutions.

5) By-products

Analysis of acetylated fractions by GC–MS identified a suite of hydroxylated intermediates produced during the oxidative transformation of 4-nitrophenol and 2,4-dinitrophenol. Beltrán et al. (1992, 1999a) have shown that, at pH values below 12, ozonation of phenolic substrates proceeds predominantly via direct electrophilic attack by molecular ozone rather than through radical-mediated mechanisms. The electrophilic attack by ozone preferentially targets the ortho and para positions on the aromatic ring when electron-donating groups such as hydroxyl (-OH) are present. In nitrophenols bearing electron-withdrawing nitro groups ($–NO_2$), molecular ozone preferentially attacks the meta position (Langlais et al., 1991), accounting for the range of electrophilic ozonation by-products observed.

Electrophilic ozonation of 4-nitrophenol and 2,4-dinitrophenol notably produced 4-nitrocatechol as a primary intermediate (Paper III, Table 3). Concurrent aromatic nuclear hydroxylation also yielded hydroquinone via nitro-group cleavage, which was further oxidized to p-quinone. At pH 9.5, several degradation pathways for 4-nitrophenol were delineated (Paper III, Figure 7). After the initial ozone attack, ring opening proceeded through a 1,3-dipolar cycloaddition, generating unsaturated intermediates. Subsequent oxidative transformations led to a suite of oxygenated products, including carboxylic acids, alcohols, aldehydes, and quinone-derived ketones. The marked decline in solution pH during ozonisation corroborates the formation of acidic by-products. Although the specific carboxylic acids were not characterized, the generation of these low–molecular-weight compounds likely underpins the enhanced biodegradability observed post-ozonation.

6) Toxicity

Acute toxicity of both individual nitrophenols (NPs) and their mixtures was assessed via the *Daphnia magna* assay , With the exception of 2-nitrophenol (2-NP), all single NPs and mixed formulations produced very low EC_{50} values, signifying pronounced toxicity toward *D. magna* (Paper II, Table 5; Paper III, Table 2). Among the substances tested, 2,4-dinitrophenol (2,4-DNP) and 4,6-dinitro-o-cresol (4,6-DN-o-CR) exhibited the highest toxicity, in agreement with Sax (1984), who reported comparable LC_{50} values for these compounds in murine models.

All treatment methods evaluated—including ozonation, hydrogen peroxide photolysis, and Fenton oxidation—effectively eliminated the toxicity of nitrophenol (NP) solutions. Complete detoxification occurred after roughly 90 % of the parent nitrophenol had been degraded. Furthermore, ozonation effectively eliminated the residual toxicity arising from degradation by-products of both individual and mixed NP solutions. This detoxification occurred regardless of the initial solution pH, provided that over 90% of the target compounds were degraded (Paper III, Table 2). These findings highlight that AOPs are effective not only in degrading NPs but also play a critical role in detoxifying their aqueous solutions.

Pollutant detoxification occurred through processes such as hydroxylation, nitrogen mineralization, and the breakdown of aromatic structures. During the ozonation of nitrophenols, quinones—identified as particularly hazardous intermediates—were formed (see Paper III, Table 3, and Figure 7). For example, the Daphnia magna assay determined an EC50 of 0.18 mg L^{-1} (95% CI: 0.15–0.22 mg L^{-1}) for p-quinone, highlighting its acuete toxicity. However, quinones were not detected in solution during the later stages of treatment, as they were rapidly oxidized during continued ozonation (Paper III).

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7) Comparative Assessment of the Efficiency of the Investigated Processes for Nitrophenol Degradation

The degradation efficiency of nitrophenols was evaluated using 2,4-dinitrophenol (2,4-DNP) as a model compound under various treatment methods, including standalone ozonation, combined ozonation with UV and/or hydrogen peroxide, hydrogen peroxide photolysis, as well as Fenton and photo-Fenton processes (refer to Figure 5.1). Among the peroxide-based treatments—namely, Fenton, photo-Fenton, UV/H_2O_2, O_3/H_2O_2, and $O_3/H_2O_2/UV$—the presence of hydrogen peroxide proved critical for effective nitrophenol removal. Therefore, the most effective 2,4-DNP degradation processes identified in Paper I were chosen for detailed comparative analysis.

The catalyst dosage in photo-Fenton treatment can be reduced because the irradiation facilitates the regeneration of consumed Fe^{2+} ions. However, since Fenton's reagent treatment was able to degrade over 90% of the nitrophenols within a timeframe suitable for practical applications, employing the more complex and consequently costlier photo-Fenton process may not be justified (Paper II, Table 3).

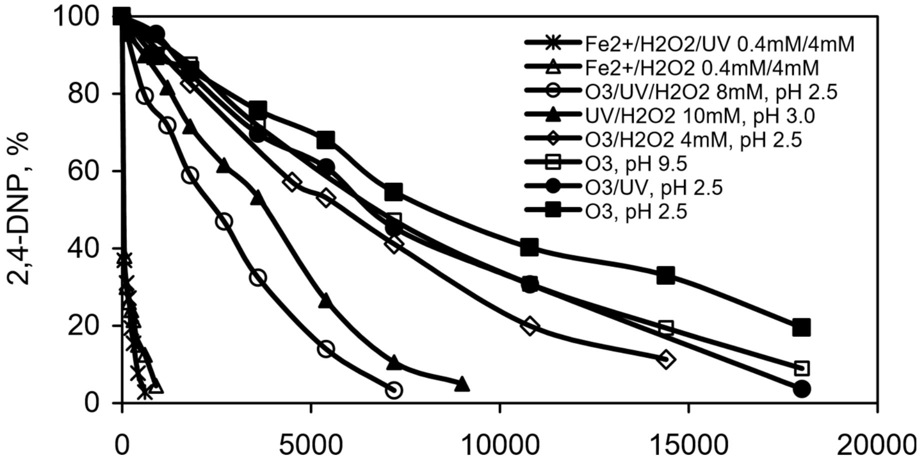


Figure 5. 1. 2,4-DNP Degradation under Various Treatment Methods

Alkalization of the solution can be used to eliminate any remaining iron following the Fenton procedure. At pH ≥ 9.0, iron precipitated as Fe(OH)3 and was extracted as a sludge. After 90 % NP degradation, total iron levels measured post-alkalization and filtration ranged from 0.3 % to 3.2 % of the initial concentration (Paper II, Section 3.2). Following Fenton reagent treatment, residual hydrogen peroxide levels decreased by 4–12% relative to their initial concentration (Paper II, Section 5.2). However, despite its high toxicit the residual concentration of hydrogen peroxide does not cause any problems because it is an environmentally friendly oxidant that is used concurrently in this process, producing only water and oxygen as degradation by-products.

Despite all evaluated methods achieving nitrophenol degradation, Fenton's reagent emerged as the most effective treatment for purifying NP-contaminated water.

8) Treatment Costs of Advanced Oxidation Processes for the Purification of Nitrophenol-Contaminated Water

This data included the costs associated with UV radiation and ozone generation, as well as the consumption of chemicals such as hydrogen peroxide and ferrous sulfate heptahydrate ($FeSO_4·7H_2O$). The calculations were based on 2,4-dinitrophenol (2,4-DNP) as a representative compound, with the summarized results presented in Table 5.1.

The cost analysis utilized the following unit prices: hydrogen peroxide at $0.86 per kilogram, $FeSO_4•7H_2O$ at $0.12 per kilogram, and electricity for both UV irradiation and ozone generation at $0.07 per kilowatt-hour (based on 2001 rates). For ozonation, costs were determined by factoring in that generating 1 kilogram of ozone requires approximately 28 kWh of electricity.

expenses compared to UV/H_2O_2 alone. Among the processes evaluated, Fenton treatment exhibited the lowest cost for 2,4-DNP removal.

Treatment expenses required to achieve 90 % degradation of additional nitrophenols—specifically 4,6-dinitro-o-cresol, 2,6-dinitrophenol, and 4-nitrophenol were applying the optimal reagent ratios, the Fenton process consistently incurred the lowest costs among all AOPs evaluated, mirroring the cost advantages observed for 2,4-DNP removal.

As shown in Table 5.1, the treatment cost for 2,4-dinitrophenol (2,4-DNP) using O_3/H_2O_2 with a low hydrogen peroxide dosage (1–2 mM) was found to be nearly the same as that of ozonation alone.

However, the expenses increased moderately with higher H_2O_2 concentrations of 4 mM and 10 mM. Among the processes evaluated, O_3/UV treatment was relatively expensive compared to other methods such as direct UV photolysis. Incorporating hydrogen peroxide into the O_3/UV system slightly reduced the treatment costs (Table 5.1). Notably, increasing H_2O_2 concentration further decreased the cost of 2,4-DNP removal by $O_3/UV/H_2O_2$. Notably, supplementing the O_3/UV process with 8 mM H_2O_2 reduced treatment expenses by approximately 2.8-fold (from \$5.79 to \$2.10 per m^3) at pH 2.5 and 2.7-fold (from \$6.09 to \$2.28 per m^3) at pH 9.5.

Conversely, lower H_2O_2 dosages (2 mM and 4 mM) in $O_3/UV/H_2O_2$ treatments resulted in increased costs compared to higher dosages (Table 5.1), primarily due to longer treatment durations required to achieve 90% degradation of 2,4-DNP, which in turn elevated the energy consumption for UV generation.

Table 5. 1. Treatment costs for 90% reduction of 2,4-DNP initial concentration (0.4 mM)

Treatment process	$[H_2O_2]_0$, mM	$[Fe^{2+}]_0$, mM	Energy required for O_3, kWh m^{-3}	Energy required for UV, kWh m^{-3}	Cost of energy for UV, \$ m^{-3}	Cost of energy for O_3, \$ m^{-3}	Chemicals (H_2O_2 + $FeSO_4 \times 7H_2O$) cost, \$ m^{-3}	Total cost, \$ m^{-3}
UV, pH 3.0	0	0	0	810	56.8	0	0	56.8
UV/H_2O_2, pH 3.0	11	0	0	28.7	2.10	0	0.30	2.30
UV/H_2O_2, pH 3.0	4.1	0	0	72.91	5.10	0	0.13	5.23
Fenton, pH 3.0	4.1	0.41	0	0	0	0	0.14	0.14
photo-Fenton, pH 3.0	4.1	0.40	0	1.50	0.10	0	0.14	0.25
O_3, pH 2.5	0	0	1.97	0	0	0.15	0	0.15
O_3, pH 9.5	0	0	1.58	0	0	0.12	0	0.12
O_3/UV, pH 2.5	0	0	1.82	81.11	5.69	0.14	0	5.82
O_3/UV, pH 9.5	0	0	1.56	85.51	5.99	0.10	0	6.10
O_3/H_2O_2, pH 2.5	1.1	0	1.08	0	0	0.09	0.04	0.12
O_3/H_2O_2, pH 9.5	1.1	0	1.37	0	0	0.09	0.04	0.13
O_3/H_2O_2, pH 2.5	2.1	0	1.25	0	0	0.08	0.07	0.16
O_3/H_2O_2, pH 9.5	2.1	0	1.40	0	0	0.11	0.07	0.17
O_3/H_2O_2, pH 2.5	4.1	0	0.91	0	0	0.07	0.13	0.19
O_3/H_2O_2, pH 9.5	4.1	0	1.41	0	0	0.11	0.13	0.23
O_3/H_2O_2, pH 2.5	10.1	0	1.02	0	0	0.08	0.29	0.37
$O_3/UV/H_2O_2$, pH 2.5	2.1	0	0.77	51.40	3.61	0.06	0.07	3.71
$O_3/UV/H_2O_2$, pH 9.5	2.1	0	1.11	60.21	4.20	0.09	0.07	4.36
$O_3/UV/H_2O_2$, pH 2.5	4.1	0	0.73	40.51	2.84	0.06	0.13	3.02
$O_3/UV/H_2O_2$, pH 9.5	4.1	0	1.12	45.6	3.20	0.09	0.13	3.40
$O_3/UV/H_2O_2$, pH 2.5	8.1	0	0.54	26.1	1.83	0.05	0.25	2.11
$O_3/UV/H_2O_2$, pH 9.5	8.1	0	0.79	28.41	1.98	0.06	0.25	2.29

The costs of standalone ozonation and O_3/H_2O_2 treatments were comparable to those of the Fenton process. However, ozone-based methods face limitations in competing economically with the Fenton treatment due to the substantial capital investment required for ozone generation equipment. Therefore, it was discovered that the Fenton treatment was the most economical method of purifying NP-contaminated water in addition to being the most successful in terms of NPs destruction.

B. Soil Treatment

1) O_3 treatment of soil

- Effects of soil matrix in O_3 treatment

The composition of the soil matrix plays a critical role in determining the effectiveness of ozone-based remediation, with distinct differences observed between sand and peat substrates. In this study, sand was selected as a representative mineral soil, while peat was used to model organic-rich soils. The results indicate that the efficiency of ozone treatment is significantly impacted by the type of soil present. For instance, during two-phase ozonation of polycyclic aromatic hydrocarbons (PAHs), diesel, shale oil, and transformer oil adsorbed onto the soil matrix, removal efficiencies were noticeably lower in peat than in sand. Achieving comparable levels of contaminant removal in peat required substantially higher doses of ozone (see Paper V, Figure 2; Paper VI, Figure 1; Paper

VII, Figures 3 and 4). This suggests that the presence of high organic content in peat not only reduces the treatment efficiency but also increases the ozone demand.

Similarly, three-phase ozonation experiments carried out on PAH-contaminated sand and peat reaffirmed this matrix-dependent effect on treatment outcomes (refer to Paper V, Figures 1 and 2). In these experiments, sand consistently exhibited greater removal rates and required lower amounts of ozone compared to peat.

The observed reduction in treatment efficacy for peat can largely be attributed to two factors: slower desorption rates of contaminants from the organic matrix and the high organic matter content itself. Organic matter in peat can act as a significant ozone sink, consuming large amounts of ozone that would otherwise be available for contaminant oxidation, thus limiting the overall efficiency of the process.

Further supporting this, ozonation experiments conducted on uncontaminated soils revealed that peat exhibited a much greater intrinsic ozone demand than sand—requiring 1.29 grams of ozone per kilogram of peat, compared to just 0.26 grams per kilogram for sand. This marked difference highlights the need to account for soil organic content and matrix characteristics when designing and optimizing ozone-based soil remediation strategies, as organic-rich soils will generally require higher ozone dosages and may yield lower contaminant removal efficiencies.

- Effect of soil water content in ozone treatment

The effect of water content on soil ozonation was examined using nitrophenols (NPs) (Paper IV) and polycyclic aromatic hydrocarbons (PAHs) (Paper V) as model contaminants. Introducing water diminished PAH removal (Paper V, Table 2). In both sand and peat, two-phase ozonation outperformed three-phase treatment in PAH degradation and ozone efficiency—a consequence of PAHs' low solubility and high octanol–water partitioning and of ozone loss via self-decomposition and dissolution in pore water. By contrast, NPs (which are highly water-soluble) exhibited enhanced desorption from soil pores in three-phase systems, yielding higher removal rates and increased ozone uptake compared to two-phase ozonation (Paper IV, Table 1; Figures 1–2).

2) The Fenton/Fenton-like treatment of soil

- Effect of soil matrix in the Fenton treatment

Similar to the observations in ozonation studies, the soil matrix significantly influenced the effectiveness of Fenton treatment. Compared to sand, peat required a higher dosage of hydrogen peroxide to achieve effective pollutant degradation through Fenton-like reactions. As illustrated in Figure 5.2, under identical treatment conditions and equivalent H_2O_2-to-contaminant weight ratios, sand facilitated greater contaminant removal than peat for pollutants such as diesel, shale oil, and transformer oil.

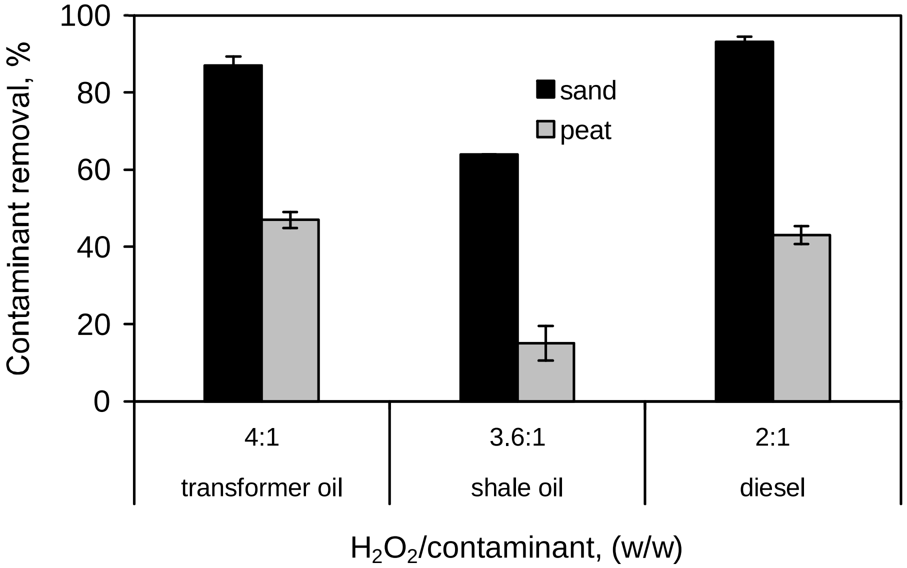


Figure 5. 2. Comparison of removal efficiencies for transformer oil, shale oil, and diesel following a 72-hour Fenton-like treatment with daily additions of hydrogen peroxide at 0, 24, and 48 hours, conducted in sand and peat soil matrices (Papers VI, VII).

When applying Fenton treatment to polycyclic aromatic hydrocarbons (PAHs), a three-step daily addition of hydrogen peroxide (1 day/3 additions) achieved approximately 80% PAH removal in sand, compared to 61% removal in peat (Paper V, Figure 1). In contrast, a single batch addition of hydrogen peroxide resulted in around 60% PAH removal in both sand and peat matrices. Excess hydrogen peroxide can inhibit degradation by quenching hydroxyl radicals (•OH) through reactions with hydrogen peroxide itself and hydroperoxyl radicals.

Soil organic matter content significantly governs the rate of H_2O_2 decomposition and subsequent •OH radical generation, which in turn controls demonstrated that hydroxyl radical generation from H_2O_2 decomposition was substantial in soils with low organic matter content, but considerably lower in soils rich in organic matter. This phenomenon likely contributes to the observed higher contaminant removal in sand compared to peat under moderate hydrogen peroxide dosing conditions.

- *Effect of hydrogen peroxide and catalyst addition and treatment time in fenton/fenton-like treatment*

It was found that the elimination of contaminants during Fenton and Fenton-like treatments of soil was influenced by multiple factors, including the weight ratios of H_2O_2 to soil and Fe^{2+} to soil, the treatment duration impact of these treatment parameters varied considerably between different soil matrices—sand and peat—and across contaminant types, such as nitrophenols (NPs), polycyclic aromatic hydrocarbons (PAHs), diesel, transformer oil, and shale oil.

Paper VI

As the H_2O_2/diesel/Fe^{2+} weight ratio rose, so did the amount of diesel removed from the sand, until the ideal level of contamination removal was achieved (paper VI, Figure 2). Diesel degradation in sand was not improved by further raising the H2O2/diesel/Fe2+ weight ratio; in fact, it led to a decrease in diesel removal (paper VI, Figure 2). In order to remove diesel from sand, the ideal weight ratio of H2O2/diesel/Fe2+ in a 72-hour Fenton treatment (with a daily injection of H2O2) was determined to be 0.3:1:0.05.

NPs degradation was observed even with the sole addition of H_2O_2 (Paper IV, Figure 3). This effect can be attributed to the catalytic activity of various transition metals naturally present in soil—such as manganese, copper, cobalt, and zinc—along with the bioavailable fraction of total iron, which can activate hydrogen peroxide without the need for externally added Fe^{2+}. Moreover, hydrogen peroxide addition likely enhanced iron availability by promoting the generation of additional Fe^{2+} species, thereby facilitating further catalytic pathways for NP degradation.

Paper VII

In the Fenton-like treatment of transformer oil-contaminated sand, increasing the H_2O_2:oil ratio from 0.04:1 to 4:1—a 100-fold rise—did not lead to a marked improvement in removal efficiency (see Paper VII, Figure 1). A comparable trend was observed with shale oil (Paper VII, Figure 2), where elevating the H_2O_2:oil ratio occasionally even resulted in reduced degradation. These results indicate that excessively high doses of hydrogen peroxide do not enhance remediation performance; instead, moderate H_2O_2 levels (such as 0.06:1 to 0.24:1 for shale oil) are adequate for effective Fenton-like treatment..

Unlike the results observed with sand, increasing the H_2O_2-to-transformer oil weight ratio in peat improved transformer oil removal up to an optimal point (see Paper VII, Figure 1). According to Walling (1975), excessive hydrogen peroxide concentrations can lead to competition between H_2O_2 and organic molecules for hydroxyl radicals (•OH), thereby diminishing the efficiency of organic oxidation. This finding is consistent with the observations of Petigara et al. (2002), who noted that efficient •OH generation occurs at lower H_2O_2 concentrations in soils. Thus, an optimal H_2O_2-to-contaminant ratio exists for effective oxidation, which depends on the specific reactivity of the organic compounds toward hydroxyl radicals.

In this study, the optimal H_2O_2-to-transformer oil ratio for a 72-hour Fenton-like treatment in peat (with daily H_2O_2 additions) was identified as 4:1 (w/w) (Paper VII, Figure 1). A similar trend was found for shale oil, where the highest removal in peat was achieved at an H_2O_2-to-oil ratio of 0.24:1 (w/w); higher peroxide dosages did not further enhance—and occasionally reduced—removal efficiency (Paper VII, Figure 2). These results indicate that incremental, low-concentration dosing of hydrogen peroxide optimizes Fenton and Fenton-like treatment performance in soils. This approach not only reduces reagent costs but also prevents excessive heat and gas production, both of which can hinder effective contaminant degradation.

- Effect of soil pH on the Fenton treatment

The effect of pH on the performance of Fenton and Fenton-like treatments in soil remediation was also evaluated. Acidic conditions, particularly within the pH range of 2.0 to 4.0, proved optimal for reducing nitrophenols (NPs), polycyclic aromatic hydrocarbons (PAHs), and diesel contaminants in soil (Papers IV, V, VI). This preference is attributed to the enhanced decomposition rate of hydrogen peroxide under acidic conditions, as previously documented by Huang et al. (1993).

The gradual hydrolysis of ferric ions (Fe^{3+}) under these conditions generates a catalytically active surface that facilitates interaction with hydrogen peroxide, while ferrous ions (Fe^{2+}) accelerate the production of hydroxyl radicals (•OH), the primary oxidants driving contaminant degradation.

Furthermore, the applicability of Fenton and Fenton-like treatments at natural soil pH levels was evaluated for the remediation of transformer oil and shale oil-contaminated soils without pH adjustment (Paper VII). Although acidic conditions (pH 3.0) combined with optimal H_2O_2-to-contaminant ratios yielded somewhat higher contaminant removal, treatment at native soil pH also demonstrated effective remediation performance (Paper VII, Figures 1 and 2)

Generally speaking, acids may be introduced to the subsurface to lower its pH before applying Fenton's reagent if the contaminated zone's natural pH is too high for effective hydroxyl radical formation. When emergency reaction measures need to be performed within a few hours of contamination and for soil cleanup in situ, lowering the pH will be highly helpful. However, the inability to remediate the deeper layers due to technological limitations and the challenge of mixing large amounts of soil will make pH adjustment of the soil for in situ application more challenging. As a result, the treatment is less economical. Additionally, abrupt changes in soil pH might negatively impact the soil microbial community, which will delay the biodegradation of leftover pollutants or their oxidation byproducts. Therefore, the Fenton technology's use for in situ remediation of polluted soil requires a thorough examination, and the particular instance will determine how best to optimize it.

3) Biodegradation of Soil Contaminants Before and After Chemical Pre-Treatment

The effectiveness of combining chemical pre-treatment—such as Fenton oxidation or ozonation—with subsequent biodegradation by introduced microorganisms has been previously. It is important to distinguish between remediation approaches that rely on chemical pre-treatment followed by biodegradation using native microbial populations versus those that employ bioaugmentation with externally introduced microorganisms. Chemical pre-treatment requires the right amount of chemicals (ozone, hydrogen peroxide) to remove contaminants and sustain microbial activity for subsequent biodegradation. When compared to soil rehabilitation using chemical treatment alone, remediation strategies that combine chemical treatment with biodegradation by native microorganisms are more environmentally sound.

Although standalone chemical oxidation (Papers IV–VII) achieved substantial contaminant removal in soil, we subsequently evaluated integrated chemical–biological remediation strategies. Moderate doses of oxidants—either ozone or hydrogen peroxide—were employed as Fenton-like or ozonation pretreatments, followed by biodegradation. The most effective yet conservative oxidant dosages were identified from the current studies (Papers IV–VII) to maximize subsequent microbial degradation. The efficacy of these combined treatment regimens is summarized in Figures 5.3–5.6.

When there was no chemical pre-oxidation, the biodegradation of pollutants in soil proceeded slowly. The biotreatment duration cannot be competitive, even though biodegradation occasionally produced a little better elimination of pollutants. Furthermore, pollutants in soil were more successfully removed by a combination of chemical and biotreatment than by either method alone (diesel breakdown in peat is the only instance). The findings also showed that the soil matrix had a significant impact on the removal of diesel fuel, shale oil, PAH and transformer oil using a combination of chemical and biological treatment.

While diesel fuel removal was more effective in peat, the combined ozonation and biodegradation approach achieved superior overall removal of polycyclic aromatic hydrocarbons (PAHs) and shale oil in sand (Figures 5.3 and 5.4). Although ozonation alone enhanced transformer oil removal in sand, the combined ozonation and biodegradation treatment yielded comparable transformer oil removal efficiencies in both soil matrices (Figures 5.3 and 5.4). Additionally, it is important to account for the relatively higher ozone consumption observed during peat remediation compared to sand when evaluating pollutant removal efficiencies across different soil types using combined ozonation and biodegradation methods.

Soil composition markedly influenced contaminant removal under Fenton-based remediation (Figures 5.5 and 5.6). When Fenton-like oxidation was combined with biodegradation, removal efficiencies for PAHs, transformer oil, and shale oil in peat exceeded those achieved by biodegradation alone; however, absolute removal in peat remained lower than in sand. Notably, both matrices were treated with identical H_2O_2-to-contaminant ratios, underscoring the matrix-dependent variability in treatment performance. Notably, despite higher hydrogen peroxide additions, the Fenton-like treatment exhibited reduced efficiency in removing diesel from peat compared to sand (Figures 5.5 and 5.6).

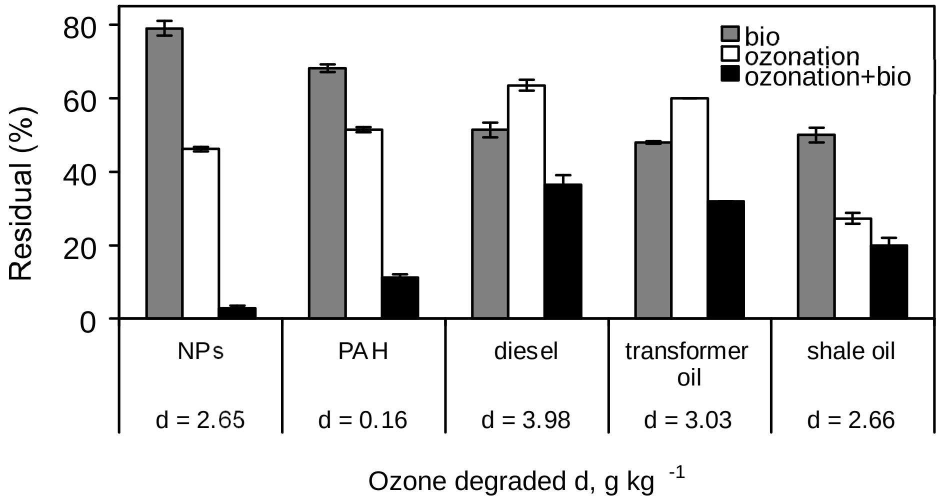


Figure 5. 3. Biodegradation of Residual concentrations (%) of NPs, diesel, transformer oil, shale oil & PAHs in sand after 28–56 days

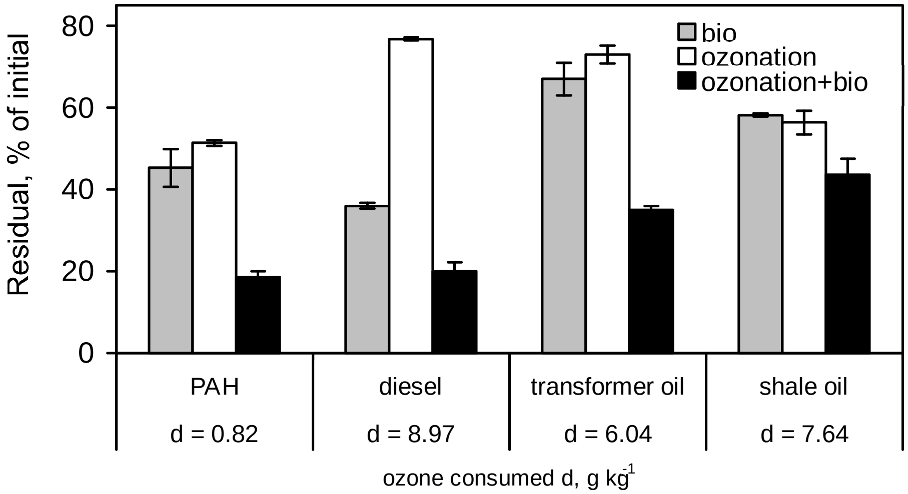
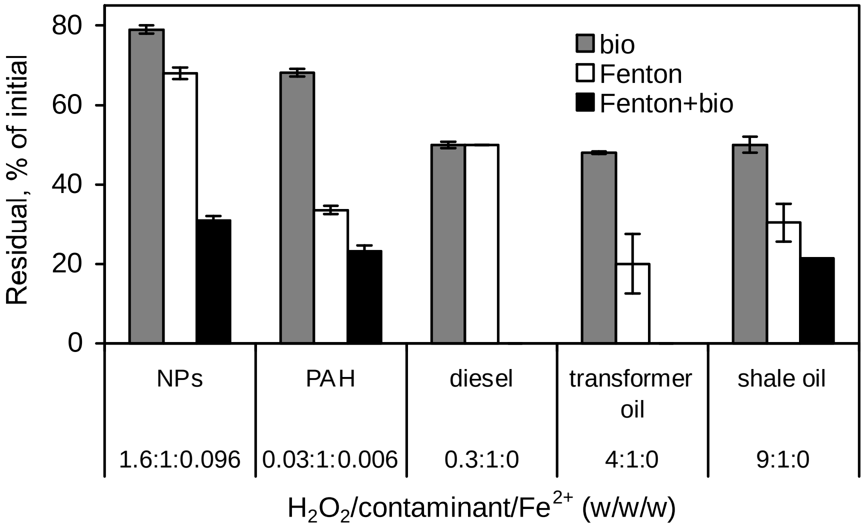


Figure 5. 4. Residual (%) of PAHs, diesel, transformer, and shale oils in peat after biodegradation, ozonation, and combined treatments.



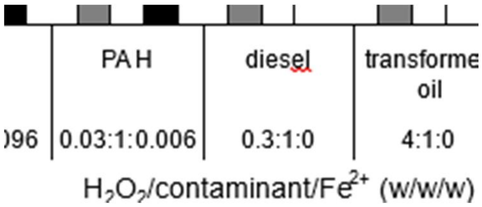


Figure 5. 5. Residual (%) of NPs, PAHs, diesel, transformer oil, and shale oil in sand after biodegradation (28–56 days), Fenton/Fenton-like treatment, and combined Fenton/Fenton-like + biotreatment (Papers IV–VII).

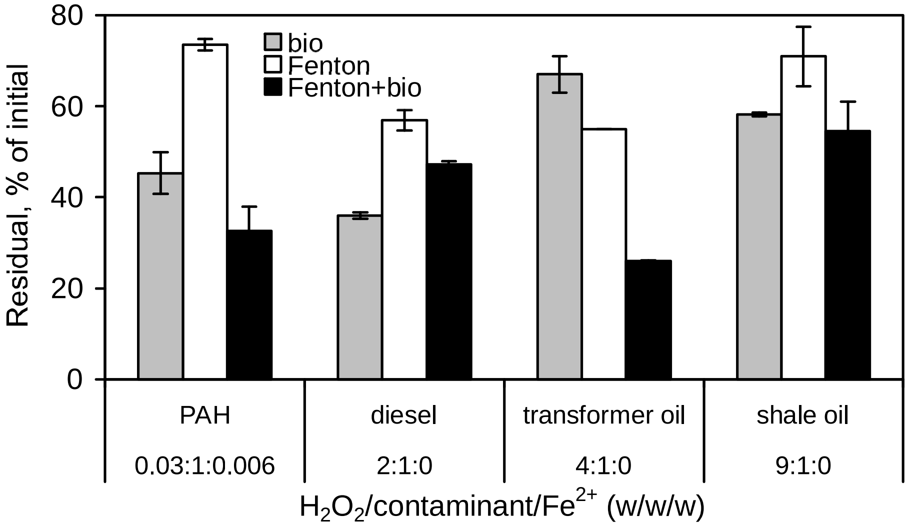


Figure 5. 6. Residual (%) of PAHs, diesel, transformer oil, and shale oil in peat after biodegradation (28–63 days)

A comparative evaluation of remediation strategies revealed that combining biodegradation with Fenton-like oxidation yielded the highest removal efficiencies for diesel-contaminated sand. In contrast, the integration of biodegradation with ozone pretreatment was found to be the most effective approach for remediating peat soils. For soils contaminated with transformer oil, sequential application of Fenton-like oxidation followed by microbial degradation produced the best results.

When comparing Fenton pretreatment followed by biodegradation with ozonation plus biodegradation, the latter approach resulted in a greater overall elimination of PAHs in soil (Paper V, Figures 5 and 6). Additionally, it was observed that in both chemically treated and untreated soils, 3-ring PAHs degraded more rapidly in both sand and peat matrices than 4-, 5-, or higher-ring PAHs (Article V).

These findings align with the work of Nam et al. (2001) and Nam and Kukor (2000), who reported that low-molecular-weight PAHs are more susceptible to rapid and extensive biodegradation than their high-molecular-weight counterparts.

The biodegradation of nitrophenols (NPs) in sand was significantly improved by pre-treating the soil with either Fenton's reagent or ozonation. Among these, the sequence of ozonation followed by biodegradation resulted in higher NP removal efficiencies in sand than the combination of Fenton pre-treatment and biodegradation (see Figures 3.3 and 3.5). Furthermore, nitrophenols with lower molecular weights, such as 4-nitrophenol (4-NP), exhibited greater biodegradability compared to higher molecular weight compounds like 2,4-dinitrophenol (2,4-DNP) and 4,6-dinitro-o-cresol (4,6-DN-o-CR)

These results indicate that integrating chemical oxidation (either ozonation or Fenton treatment) with subsequent biodegradation outperforms standalone methods, thereby enhancing soil remediation efficiency and offering potential cost savings.

5.2.3.1 Biodegradation of alkanes in diesel-contaminated soil

In situ biodegradation is a complex process influenced by numerous factors, including the microbial community composition, environmental conditions such as temperature, oxygen availability, and moisture, as well as the predominant types of hydrocarbons and their bioavailability. Among these, the molecular composition of the soil pollutants is a primary determinant of biodegradation rates. Complex mixtures like shale oil, transformer oil, and diesel fuel comprise multiple molecular constituents with varying susceptibilities to degradation.

Petroleum hydrocarbons are generally organic substances made up of hydrogen and carbon atoms organized in different structural arrangements.

They fall into two groups in the broadest sense: aromatics (fragrant) and aliphatics (fatty). Alkyl-aromatics, monoaromatics, diaromatics, and polynuclear aromatics can make up as much as 30–40% of diesel fuel (Composition of Petroleum Mixtures, 1998). During the chemical pre-treatment, the aromatic portion was reduced, and then the UV-254 absorbance was removed. Degradation of aromatics through ring cleavage events most likely produced this reduction (paper VI, Figures 1 and 3). Alkanes, alkenes, and cycloalkanes are the three primary classes of aliphatics. Normal, branched, and cyclic alkanes make up 60–90% of most fuels (Composition of Petroleum Mixtures, 1998). Paper VI employed a diesel formulation comprised of 20 % alkanes—66.5 % linear C_{11}–C_{18}, 16 % linear C_{19}–C_{26}, and 17.5 % branched (phytane + prylene)—and systematically evaluated the degradation of each fraction (Paper VI, Figures 4 and 5).

Following chemical oxidation and a 30-day biodegradation period, removal efficiencies for short-chain n-alkanes (C_{11}–C_{18}) exceeded those for long-chain homologues (C_{19}–C_{26}) in both sand and peat matrices contaminated with diesel. This distribution of degradation aligns with trends observed in biodegradation trials of untreated soils (Paper VI, Figures 4 and 5). Additionally, branched alkanes such as pristane and phytane exhibited lower degradation rates than their short-chain linear counterparts. The presence of branching significantly impedes the biodegradation process.

A comparative assessment of treatment methods demonstrated that, for diesel-contaminated sand, the combination of biodegradation with Fenton-like treatment was more effective in alkane removal than combined ozonation and biodegradation. Conversely, in diesel-contaminated peat, the integration of biodegradation with pre-ozonation outperformed the combined Fenton-like and biological treatment in alkane removal.

4) *Treatment costs of soil chemical remediation*

A preliminary assessment of treatment costs was conducted using experimental data on the degradation of target pollutants, factoring in the expenses for ($FeSO_4 \cdot 7H_2O$ and H_2O_2) and the energy required for ozone production. According to 2005 prices, energy was estimated at $0.10 per kWh, $FeSO_4 \cdot 7H_2O$ at $0.12 per kilogram (containing 20% ferrous iron), and hydrogen peroxide at $0.86 per kilogram (100% concentration). The cost of ozonation was determined by assuming that the generation of 1 kilogram of ozone consumes approximately 28 kWh of energy. Given the impracticality of recovering unreacted chemicals efficiently under in situ conditions, cost estimates were based on the total amounts of ozone and hydrogen peroxide applied during treatment.

The integration of chemical and biological treatments for contaminated soil remediation is recommended as a strategy to reduce chemical additive usage and enhance the economic feasibility of chemical processes. Accordingly, Table 5.2 presents estimated treatment costs for Fenton, Fenton-like, and ozonation processes employing moderate chemical dosages (as illustrated in Figures 5.4, 5.5, 5.6, and 5.7).

Costs associated with ozonation and Fenton/Fenton-like remediation of diesel-contaminated soil using low reagent dosages are presented in Paper VI, Table 2. In these treatments, lower hydrogen peroxide dosages proved to be more cost-effective. The inclusion of the ferrous ion catalyst (Fe^{2+}) facilitated reduced hydrogen peroxide requirements, thereby significantly lowering overall treatment expenses. Notably, costs associated with Fenton and Fenton-like treatments were substantially lower than those for ozonation (Paper VI, Table 2).

Economic analysis revealed that treating contaminated sand was more cost-effective than applying ozonation to peat, as Fenton and Fenton-like methods for peat demanded substantially higher reagent doses (Table 5.2; Paper VI, Table 2). Comparative analysis revealed that ozonation incurred significantly greater expenses than Fenton and Fenton-like processes. Additionally, it is important to note that chemical costs typically represent only 15–30% of the total remediation lifecycle costs when evaluating treatment expenses with costs covering both the acquisition of the generation equipment and the associated electricity usage. When these substantial capital investments for ozone production are considered, ozonation becomes an even more expensive option for in situ soil remediation.

This conclusion is supported by various cost assessments from real-world implementations documented in the literature (EPA US Chemical Oxidation, 1998; In Situ Oxidation, 1999; Technical/Regulatory Guidelines, 2001). Therefore, compared to ozonation, Fenton and Fenton-like treatments offer a more economical chemical remediation alternative for contaminated soils.

Table 5. 2. Treatment Costs for Chemical Remediation of NPs-, PAH-, Transformer Oil-, and Shale Oil-Contaminated Soils

Contaminant	Treatment process	H_2O_2/contaminant/ Fe^{2+} (w/w/w), *O_3/contaminant (w/w)	Contaminant removed, %	Energy required for O_3, kWh t^{-1}	Cost of H_2O_2, \$ t^{-1}	Cost of $FeSO_4 \times 7H_2O$, \$ t^{-1}	Total cost, \$ t^{-1}
NP	Fenton	1.5:1:0.097	33	0	0.95	0.05	0.99
	ozonation	*7.4:1.5	55	561	0	0	57
PAH	Fenton	0.3:1.5:0.08	67	0	0.03	0.0003	0.03
	ozonation	*65:1.5	50	111	0	0	11.1
transformer oil	Fenton-like	4:1.5:0	81	0	60	0	60
	ozonation	*2.5:1.5	23	1121	0	0	111
shale oil	Fenton-like	9.5:1.5:1	50	0	43.3	0	43.3
	ozonation	*7.5:1.5	73	1120	0	0	112
PAH	Fenton	0.05:1:0.005	27	0	0.04	0.0005	0.04
	ozonation	*495:1.5	23	1681	0	0	169
transformer oil	Fenton-like	4.5:1.5:1	46	0	65.5	0	65.5
	ozonation	*6.4:1	32	3361	0	0	336
shale oil	Fenton-like	9.2:1.5:1	30	0	42.7	0	42.7
	ozonation	*23:1.5	43	3361	0	0	336

VI. CONCLUSION

The present study demonstrated that enhanced oxidation offers a diverse array of effective methods for degrading aqueous nitrophenols (NPs). Degradation kinetics differed markedly across treatment methods, with Fenton processes achieving a tenfold reduction in NP concentration within minutes, whereas UV photolysis required several hours to reach the same level of removal.

In addition to their effectiveness in degrading nitrophenols (NPs), standalone ozonation and advanced oxidation processes (AOPs) also contribute to the detoxification and enhanced biodegradability of NP-containing wastewater. Key mechanisms underlying these improvements include ring hydroxylation, nitrogen mineralization, and ring-opening reactions that transform aromatic compounds into more biodegradable aliphatic forms, alongside a reduction in overall toxicity. These findings support the application of AOPs and ozonation as valuable pretreatment strategies to improve the efficacy of conventional biological treatments in removing hazardous and recalcitrant NPs. Although combining enhances nanoparticle degradation and reduces ozone consumption, this advanced oxidation process (AOP) becomes less economically competitive compared to standalone ozonation when higher treatment costs are considered. Taking capital expenditures into account, the Fenton treatment emerges as the preferable option, even though operational costs for ozonation and Fenton processes may be similar. This is largely because Fenton treatment requires minimal capital investment, whereas ozone equipment installation involves substantial upfront costs. Consequently, among the AOPs evaluated, Fenton's reagent stands out as the most effective and cost-efficient treatment method. Both chemical treatments (ozonation and Fenton) and combined chemical-biological approaches proved highly effective in remediating soils contaminated with nitrophenols (NPs), polycyclic aromatic hydrocarbons (PAHs), matrix significantly influences treatment efficacy. Contaminant removal was more efficient in sand (mineral soil), whereas peat (organic-rich soil) required higher chemical dosages and achieved lower removal rates. The selection of remediation strategies, whether ex situ or in situ, was determined by the nature of the contamination and the appropriateness of two-phase or three-phase ozonation systems. Hydrogen peroxide effectively degrades contaminants through reactions catalyzed by naturally occurring iron in soils, characteristic of Fenton-like processes. In soil remediation applications employing Fenton and Fenton-like treatments, the use of moderate reagent dosages combined with incremental, stepwise hydrogen peroxide additions was shown to enhance treatment efficacy.

These methods proved effective across a range of pH conditions, including both acidic environments (pH 3.0) and the native pH of the contaminated soils, underscoring their versatility for practical remediation scenarios.

Chemical oxidation methods, such as ozonation and Fenton treatment, achieve a more rapid reduction in contaminant concentrations in polluted soils compared to biodegradation alone. This accelerated contaminant removal is particularly critical when preventing the migration of toxins into deeper soil layers or groundwater. For effective soil rehabilitation, combining chemical oxidation with biological treatment has demonstrated superior performance over either approach used independently. To preserve and enhance the activity of indigenous microorganisms following chemical oxidation, it is advisable to employ moderate concentrations of oxidants—such as hydrogen peroxide or ozone—during Fenton-like or ozonation pretreatments, and subsequently follow with a biodegradation phase.

Cost analysis indicates that the Fenton and Fenton-like treatments represent the most economical chemical remediation methods for contaminated soils. Although chemical oxidation alone can effectively degrade contaminants such as nitrophenols, PAHs, diesel, transformer oil, and shale oil, a strategy that combines moderate chemical pre-treatment with subsequent biological degradation offers superior efficiency and cost-effectiveness compared to either approach used in isolation.

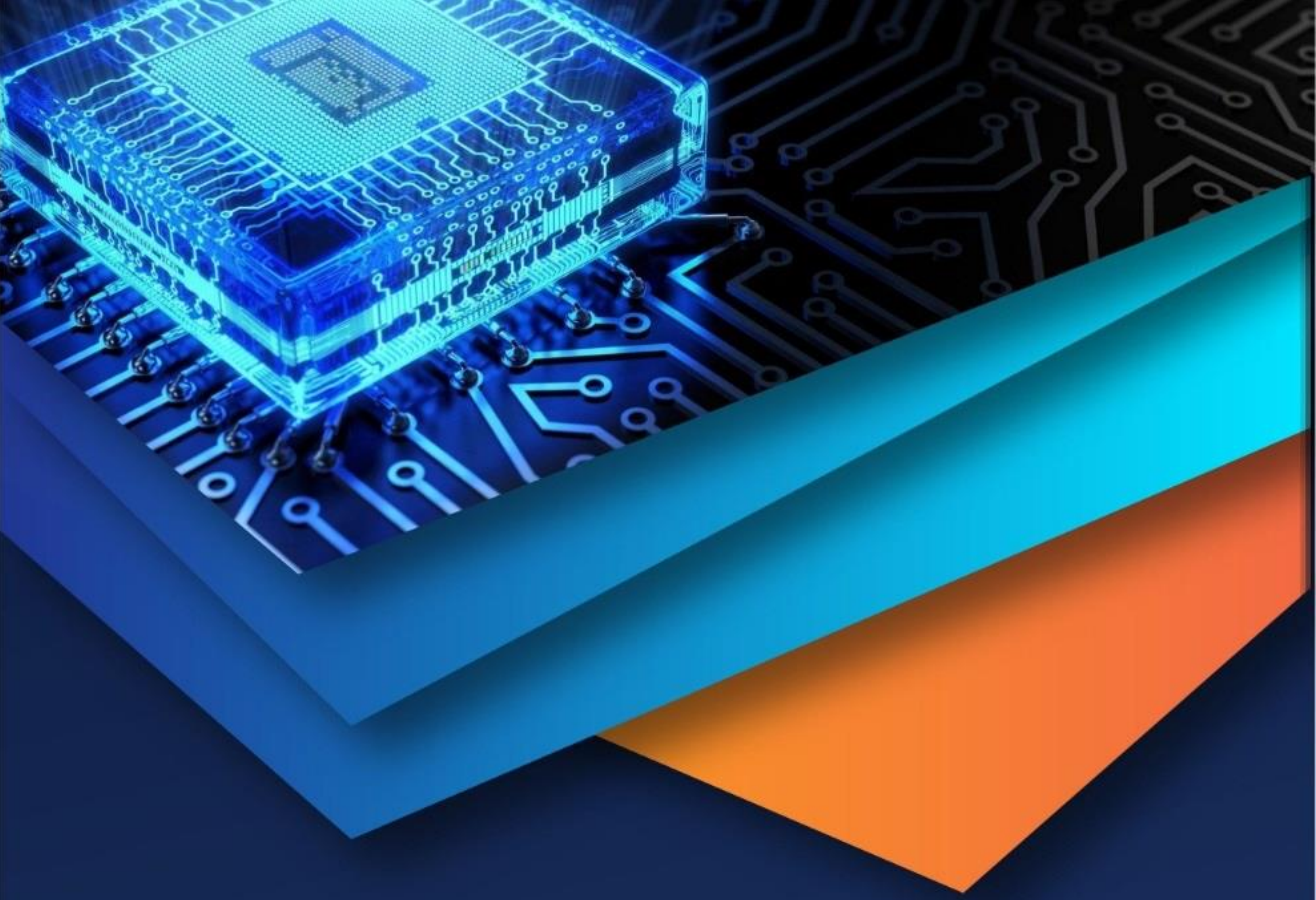
REFERENCEs

[1] Adams, C.D., Cozzens, R.A., Kim, B.J. 1997. Effects of ozonation on the biodegradability of substituted phenols. - Water Research, vol 31, no 10, p 2655-2663. Ahn, Y., Jung, H., Tatavarty, R., Choi, H., Yang, J.-W., Kim, In S. 2005.
[2] Monitoring of petroleum hydrocarbon degradative potential of indigenous microorganisms in ozonated soil. – Biodegradation, vol 16, p 45-46.
[3] ATSDR: Toxicological profile for NPs. Department of Health and Human Services, Public Health Service, Atlanta, GA: U.S., 1992.
[4] Baciocchi, R., Boni, M.R., D'Aprile, L. 2003. Hydrogen peroxide lifetime as an indicator of the efficiency of 3-chlorophenol Fenton's and Fenton-like oxidation in soils. - Journal of Hazardous Materials, vol B96, p 305-329.
[5] Barbeni, M., Minero, C., Pelizzetti, E. 1987. Chemical degradation of chlorophenols with Fenton's reagent (Fe^{2+} + H_2O_2). - Chemosphere, vol 16, nos 10-12, p 2225-2237.
[6] Beltran, F.J., Garcia-Araya, J.F., Alvarez, P.M., Gimeno, O. 1999a. Effects of single and combined ozonation with hydrogen peroxide or UV radiation on the chemical degradation and biodegradability of debittering table olive industrial wastewaters. – Water Research, vol 33, no 3, p 723-732.
[7] Beltran, F.J., Rivas, J., Alvarez, P.M., Alonso, M.A., Acedo, B. 1999b. A kinetic model for advanced oxidation processes of aromatic hydrocarbons in water: application to phenanthrene and nitrobenzene. - Industrial & Engineering Chemistry Research, vol 38, p 4189-4199.
[8] Beltran, F.J., Gomez-Serrano, V., Duran, A. 1992. Degradation kinetics of pnitrophenol ozonation in water. - Water Research, vol 26, no 1, p 9-17.
[9] Benitez, F.J., Beltran-Heredia, J., Acero, J.L., Rubio, F.J. 1999. Chemical decomposition of 2,4,6-trichlorophenol by ozone, Fenton's reagent, and UV radiation. - Industrial & Engineering Chemical Research, vol 38, no 4, p 1341-1349.
[10] Bogan, B.W., Trbovic, V. 2003. Effect of sequestration on PAH degradability with Fenton's reagent: roles of total organic carbon, humin and soil porosity. – Journal of Hazardous Materials, vol B100, p 285-300.
[11] Bowers, A., Netzer, A., Norman, J.D. 1973. Ozonation of wastewater – some technical and economic aspects. – The Canadian Journal of Chemical Engineering, vol 51, no 3, p 332.
[12] Chen, J., Rulkens, W.H., Bruning, H. 1997. Photochemical elimination of phenols and COD in industrial wastewaters. - Water Science and Technology, vol 35, no 4, p 231-238.
[13] Chen, R., Pignatello, J.J. 1997. Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds. - Environmental Science & Technology, vol 31, p 2399-2406.
[14] Choi, H., Lim, H.-N., Kim, J., Cho, J. 2001. Oxidation of polycyclic aromatic hydrocarbons by ozone in the presence of sand. – Water Science and Technology, vol 43, no 5, p 349-356.
[15] Ciardelli, G., Ranieril, N. 2001. The treatment and reuse of wastewater in the textile industry by means of ozonation and electro-flocculation. – Water Research, vol 35, no 2, p 567-572.
[16] Ciardelli, G., Capanneli, G., Bottino, A. 2001. Ozone treatment of textile wastewaters for reuse. - Water Science and Technology, vol 44, no 5, p 61-67.
[17] Combs, R., McGuire, P. 1989. Back to basics – the use of ultraviolet light for microbial control – Ultrapure Water Journal, vol 6, no 4, p 62-68.
[18] Composition of Petroleum Mixtures/W. Weisman (ed.). Total Petroleum
[19] Hydrocarbon Criteria Working Group Series/prepared by T.L. Potter and K.E.
[20] Simmons. U.S.: Amherst Scientific Publishers, 1998. p 52-63.
[21] Cunningham, S.D., Berti, W.R., Huang, J.W. 1995. Phytoremediation of contaminated soils. - Trends Biotechnology, vol 13, p 393-397.
[22] Dabestani, R., Ivanov, J.N. 1999. A compilation of physical, spectroscopic and photophysical properties of polynuclear aromatic hydrocarbons. - Photochemistry and Photobiology, vol 70, no 1, p 10-34.
[23] Danckwerts, P.V. Gas-Liquid Reactions. Mc Graw-Hill Book Co., 1973, p. 266.
[24] Dieckmann, M.S., Gray, K.A. 1996. A comparison of the degradation of 2-nitrophenol via direct and sensitized photocatalysis in TiO_2 slurries. - Water Research, vol 30, no 5, p 1169-1183.
[25] Eisenberg, G.M. 1943. Colorimetric determination of hydrogen peroxide. – Industrial Engineering and Chemical Research, vol 15, no 5, p 327-328.
[26] EPA US Chemical Oxidation, Field Applications of In Situ Remediation
[27] Technologies, Office of Solid Waste and Emergency Response, Technology Innovation Office, Washington, DC 20460, 1998. p 31.
[28] EPA US 1996. Ultraviolet Light Disinfection Technology in Drinking Water Application – An Overview. EPA 811-R96-002, Office Of Ground Water and Drinking Water.

[29] EPA US 1993. Integrated Risk Information System (IRIS) 2,4-DNP. Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati, OH.
[30] EPA US 1986. Health and Environmental Effects Profile for Dinitrocresols, EPA/600/x-86/197. Environmental Criteria and Assessment Office, Office of Research and Development, Cincinnati, OH.
[31] EPA method 9045C. Soil and Waste pH. Available: http://www.epa.gov
[32] EPA method 0415.1 Organic Carbon – Total UV Promoted. Available: http://www.epa.gov
[33] Finnish Standard SFS 5062: Water quality. Determination of the acute toxicity with water flea, Daphnia magna Straus, 1984.
[34] Fox, R.D. 1996. Physical/chemical treatment of organically contaminated soils and sediments. - Journal of Air and Waste Management, vol 46, p 391-413.
[35] Furukawa, S., Yasunaga, N., Kawaai, Y., Hirotsuji, J. 1997. Highly efficient ozonehydrogen peroxide reactor with multiple injection port. In: Proceedings of the 13th Ozone World Congress, vol 1, p 499.
[36] Gates-Anderson, D.D., Siegrist, R.L., Cline, S.R., 2001. Comparison of potassium permanganate and hydrogen peroxide as chemical oxidants for organically contaminated soils. – Journal of Environmental Engineering, vol 127, p 337-347. Glaze, W.H. 1987. Drinking water treatment with ozone. - Environmental Science and Technology, vol 21, no 3, p 224-230.
[37] Glaze, W.H., Kang, J.W. 1988. Advanced oxidation processes for treating groundwater contaminated with TCE and PCE: laboratory studies. Journal AWWA, vol 80, no 5, p 57-63.
[38] Glaze, W.H., Kang, J.W., Chapin, D.H. 1987. The chemistry of water treatment involving ozone, hydrogen peroxide and ultraviolet radiation. - Ozone Science & Engineering, vol 9, no 4, p 335-342.
[39] Gogate, P.R., Pandit, A.B. 2004. A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. - Advances in Environmental Research, vol 8, p 501-505.
[40] Gordon, A.J., Ford, R.A. The Chemist’s Companion. A Handbook of Practical Data, Techniques and References. New York: A Wiley-interscience publication, 1976. 541 p. (in Russian).
[41] Grimmer, G.G. (ed.) Environmental Carcinogens: Polycyclic Aromatic Hydrocarbons. Chemistry, Occurrence, Biochemistry, Carcinogenicity. CRC Press, Inc., Boca Raton, FL. 1983.
[42] Haberl, R., Urban, W., Gehinger, P., Szinovatz, W. 1993. Oxidation of industrial wastewaters containing non-biodegradable constituents by ozone with and without simultaneous irradiation. In: Proceedings of the eleventh ozone world congress, 29 August - 3 September San Francisco, USA, vol 1, p S-10-1 – S-10-12.
[43] Heron, G., Christensen, T.H., Tjell, J.Chr. 1994. Oxidation capacity of aquifer sediments. – Environmental Science and Technology, vol 28, p 153-158.
[44] Herterich, R. 1991. Gas chromatographic determination of nitrophenols in atmospheric liquid water and airborne particulates. – Journal of Chromatography, vol 549, p 313-
[45] 324.
[46] Hinchee, R.E., Downey, D.C., Aggarwal, P.K. 1990. Use of hydrogen peroxide as an oxygen source for in situ biodegradation: Part I. Field studies. – Journal of Hazardous Materials, vol 27, p 287-299.
[47] Hoigné, J. 1988. The chemistry of ozone in water. In: Process Technologies for Water Treatment, Stucki, S. (ed.), New York: Plenum Press, p 121-143.
[48] Hoigné, J., Bader, H., Haag, W.R., Staehelin, J. 1985. Rate constants of reactions of ozone with organic and inorganic compounds in water: III – Inorganic compounds and radicals. - Water Research, vol 19, no 8, p 993-1004.
[49] Hoigné, J., Bader, H. 1983a. Rate constants of reactions of ozone with organic and inorganic compounds in water: I – Non-dissociating organic compounds. - Water Research, vol 17, p 173-183.
[50] Hoigné, J., Bader, H. 1983b. Rate constants of reactions of ozone with organic and inorganic compounds in water: II – Dissociating organic compounds. - Water Research, vol 17, no 2, p 185-194.
[51] Hoigné, J., Bader, H. 1976. The role of hydroxyl radical reactions in ozonation process in aqueous solutions. – Water Research, vol 10, p 377.
[52] Hoigné, J., Bader, H. 1975. Ozonation of water: role of hydrogen radicals as oxidizing intermediates. - Science, vol 190, p 782-784.
[53] Huang, C.P., Dong, C., Tang, Z. 1993. Advanced chemical oxidation: its present role and potential future in hazardous waste treatment. - Waste Management, vol 13, p 361-
[54] 377.
[55] IOA (International Ozone Association EAG) Revised Guideline Document. Ozone
[56] Concentration Measurement and Monitoring in a Concentrated Process Gas by UVabsorption. Masschelein, W.J., Blaich, L., Langlais, B., Thieben, E., Bell, J., Reading, A. In: Ozone Science and Engineering Special Issue on Quality Assurance in Ozone Practice, 1998, vol 20, p 433-487.
[57] In Situ Oxidation 1999. USA: Technology Status Review, performed by ThermoRetec
[58] Consulting Corporation with assistance from HydroGeoLogic, Inc. and Coleman
[59] Research Corporation – Energy & Environmental Group, Environmental Security
[60] Certification Program, November 1999, p. 42.
[61] Janknecht, P., Wilderer, P.A., Picard, C., Labort, A. 2001. Ozone water contacting by ceramic membrane. - Separation and Purification Technology, vol 25, p 341-346. Jans, U., Hoigné, J. 1998. Activated carbon and carbon black catalysed transformation of aqueous ozone into OH-radicals. - Ozone Science & Engineering, vol 20, no 1, p 6790.
[62] Keith, L.N., Telliard, W.A. 1979. Priority pollutants. 1-a perspective view. - Environmental Science and Technology, vol 13, no 4, p 416-423.
[63] Kim, J., Choi, H. 2002. Modelling in situ ozonation for the remediation of non-volatile PAH-contaminated unsaturated soils. – Journal of Contaminant Hydrology, vol 55, p 261-285.
[64] Kiwi, J., Pulgarin, C., Peringer, P. 1994. Effect of Fenton and photo-Fenton reactions on the degradation and biodegradability of 2 and 4-nitrophenols in water treatment. - Applied Catalysis B: Environmental, vol 3, p 335-350.
[65] Kochany, J., Bolton, J.R. 1992. Mechanism of photodegradation of aqueous organic pollutants. 2. Measurement of the primary rate constants for reaction of ${}^{\bullet}$OH radicals with benzene and some halobenzenes using an EPR spin-trapping method following the photolysis of H_2O_2. – Environmental Science and Technology, vol 26, p 262-265.

[66] Kong, S.-H., Watts, R.J., Choi, J.-H. 1998. Treatment of petroleum-contaminated soils using iron mineral catalyzed hydrogen peroxide. - Chemosphere, vol 37, no 8, p 1473-1482.
[67] Ku, Y., Su, W.-J., Shen, Y.-S. 1996. Decomposition of phenols in aqueous solution by a UV/O_3 process. - Ozone Science & Engineering, vol 18, p 443-460.
[68] Kwon, B.G., Lee, D.S., Kang, N., Yoon, J. 1999. Characteristics of p-chlorophenol oxidation by Fenton reagent. - Water Research, vol 33, no 9, p 2110-2118.
[69] Langlais, B., Reckhow, D.A., Brink, D.R. (eds.). Cooperative Research Report: Ozone in water treatment: Application and Engineering. USA: Lewis publishers, Chelsea, 1991. 569 p.
[70] Ledakowicz, S., Maciejewska, R., Perkowski, J., Bin, A. 2001. Ozonation of reactive blue 81 in the bubble column. – Water Science and Technology, vol 44, no 5, p 47-52. Legube, B., Karpel Vel Leitner, N. 1999. Catalytic ozonation: a promising advanced oxidation technology for water treatment. - Catalysis Today, vol 53, p 61-72.
[71] Lee, B.-D., Hosomi, M. 2001. A hybrid Fenton oxidation – microbial treatment for soil highly contaminated with benz(a)anthracene. - Chemosphere, vol 43, p 1127-1132.
[72] Lee, B.-D., Hosomi, M., Murakami, A. 1998. Fenton oxidation with ethanol to degrade anthracene into biodegradable 9,10-anthraquinone: a pretreatment method for anthracene-contaminated soil. - Water Science and Technology, vol 38, p 91-97.
[73] Levin, M.A., Gealt, M.A. Biotreatment of industrial and hazardous waste. New York:
[74] McGraw-Hill, p 4. 1993.
[75] Lipczynska-Kochany, E. 1992. Degradation of nitrobenzene and nitrophenols by means of advanced oxidation processes in a homogeneous phase: photolysis in the presence of hydrogen peroxide versus the Fenton reaction. - Chemosphere, vol 24, no 9, p 1369-1380.
[76] Lipczynska-Kochany, E. 1991. Degradation of aqueous nitrophenols and nitrobenzene by means of the Fenton reaction. - Chemosphere, vol 22, nos 5-6, p 529-536.
[77] Ma, Y.-S., Huang, S.-T., Lin, J.-G. 2000. Degradation of 4-nitrophenol using the Fenton process. – Water Science and Technology, vol 42, nos 3-4, p 155-160.
[78] Mackay, D., Shui, W.Y., Ma, K.C. Illustrated Handbook of Physical-Chemical
[79] Properties and Environmental Fate of Organic Chemicals. FL: Lewis, Boca Raton. 1992.
[80] Masschelein, W.J., Goossens, R. 1984. Nitrophenols as model compounds in the design of ozone contacting and reacting systems. - Ozone Science & Engineering, vol 6, p 143-162.
[81] Masten, S.J. 1991. Ozonation of VOCs in the presence of humic acid and soils. – Ozone Science & Engineering, vol 2, p 287-312.
[82] Masten, S.J., Davies, S.H.R. 1997. Efficacy of in-situ ozonation for the remediation of
[83] PAH contaminated soils. - Journal of Contaminant Hydrology, vol 28, p 327-335. Munter, R., Preis, S., Kamenev, S., Siirde, E. 1993. Methodology of ozone induction into water and wastewater treatment. – Ozone Science & Engineering, vol 15, no 2, p 149-165.
[84] Munter, R. 1985. Ozone decomposition in aqueous solutions. – Soviet Journal of Water Chemical Technology, vol 7, p 16-22 (in Russian).
[85] Nam, K., Rodriguez, W., Kukor, J.J. 2001. Enhanced degradation of polycyclic hydrocarbons by biodegradation combined with a modified Fenton reaction. – Chemosphere, vol 45, p 11-20.
[86] Nam, K., Kukor, J.J. 2000. Combined ozonation and biodegradation for remediation of mixtures of polycyclic aromatic hydrocarbons in soil. - Biodegradation, vol 11, p 1-9. Nelson, C.H., Brown, R.A. 1994. Adapting ozonation for soil and groundwater cleanup. - Environmental Engineering, a Supplement to Chemical Engineering, p EE20EE24.
[87] Palmroth, M.R.T., Pitchel, J., Puhakka, J.A. 2002. Phytoremediation of subarctic soil contaminated with diesel fuel. - Bioresource Technology, vol 84, p 221-228.
[88] Penchuk, Ya.O., Haldna, Yu.L., Kangro, A.V., Margna, L.Yu., Orav, I.P. 1986.
[89] Ionchromatographic determination of drinking water ions. In: Proceedings of Tartu State University, vol 743, p 160-167 (in Russian).
[90] Petigara, B.R., Blough, N.V., Mignerey, A.C. 2002. Mechanisms of hydrogen peroxide decomposition in soils. - Environmental Science and Technology, vol 36, p 639-645.
[91] Pierpoint, A.C., Hapeman, C.J., Torrents, A. 2003. Ozone treatment of soil contaminated with aniline and trifluralin. - Chemosphere, vol 50, p 1025-1034.
[92] Richard, J.Y., Vogel, T.M. 1999. Characterization of a soil bacterial consortium capable of degrading diesel fuel. - International Biodeterioration & Biodegradation, vol
[93] 44, p 93-100.
[94] Ruppert, G., Bauer, R., Heisler, G. 1994. UV-O_3, UV-H_2O_2, UV-TiO_2 and the photoFenton – comparison of advanced oxidation processes for wastewater treatment. - Chemosphere, vol 28, no 8, p 1447-1454.
[95] Sax, N.I. Dangerous Properties of Industrial Materials. USA: Van Nostrand Reinhold Company, Sixth edn., 1984.
[96] Shishida, K., Echigo, S., Yamada, H., Matsui, S. 1999. Study of the development of the high performance ozone/hydrogen peroxide water treatment system for TOC removal: effect of operational parameter. – Journal of Japanese Society of Water Environment, vol 22, p 199.
[97] Standard Methods for the Examination of Water and Wastewater. USA: American
[98] Public Health Association, American Water Work Association, Water Pollution Control
[99] Federation, 17th ed., 1994. 1268 p.
[100] Stehr, J., Müller, T., Svensson, K., Kamnerdpetch, C., Scheper, T. 2001. Basic examinations on chemical pre-oxidation by ozone for enhancing bioremediation of phenanthrene contaminated soils. – Applied Microbiology and Biotechnology, vol 57, p 803-809.
[101] Stover, E.L., Wang, L.-W., Medley, D.R. 1982. Ozone assisted biological treatment of industrial wastewaters containing biorefractory compounds. - Ozone Science & Engineering, vol 4, p 177-194.
[102] Tang, W.Z., Huang, C.P. 1997. Stochiometry of Fenton's reagent in the oxidation of chlorinated aliphatic organic pollutants. - Environmental Technology, vol 18, p 13-23. Technical/Regulatory Guidelines. USA: Technical and Regulatory Guidance for In
[103] Situ Chemical Oxidation of Contaminated Soil and Groundwater. Prepared by Interstate Technology and Regulatory Cooperation Work Group In Situ Chemical Oxidation Work Team, 2001, 25 p.
[104] Teel, A.L., Warberg, C.R., Atkinson, D.A., Watts, R.J. 2001. Comparison of mineral and soluble iron Fenton's catalysts for the treatment of trichloroethylene. - Water Research, vol 35, p 977-984.

[105] Tessier, A., Campbell, P.G.C, Bisson, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. – Analytical Chemistry, vol 51, no 7, p 844851.
[106] Trapido, M., Kallas, J. 2000. Advanced oxidation processes for the degradation and detoxification of 4-nitrophenol. - Environmental Technology, vol 21, p 799-808. Trapido, M., Veressinina, Y., Munter, R. 1998. Advanced oxidation processes for degradation of 2,4-dichloro- and 2,4-dimethylphenol. – Journal of Environmental Engineering, vol 124, no 8, p 690-694.
[107] Trapido, M., Veressinina, Y., Hentunen, J.K., Hirvonen, A. 1997. Ozonation of chlorophenols: kinetics, by-products and toxicity. - Environmental Technology, vol 18, p 325-332.
[108] Trapido, M., Veldre, I. 1996. On polynuclear aromatic hydrocarbons contaminated levels in the ecosystem of Lake Peipsi in the 1970s-1980s. - Hydrobiologia, vol 338, p 185-190.
[109] Ullmann's. Encyclopaedia of industrial chemistry. Germany: VCH Verladsgesellschaft, 5 ed., 1991. p 415-419.
[110] Walling, C. 1975. Fenton's reagent revisited. - Accounts of Chemical Research, vol 8, p 125.
[111] Wang, Y.-T. 1990. Methanogenic degradation of ozonation products of biorefractory or toxic aromatic compounds. - Water Research, vol 24, no 2, p 185-190.
[112] Watts, R.J., Stanton, P.C., Howsawkeng, J., Teel, A.L. 2002. Mineralization of a sorbed polycyclic aromatic hydrocarbon in two soils using catalyzed hydrogen peroxide. - Water Research, vol 36, p 4283-4292.
[113] Watts, R.J., Haller, D.R., Jones, A.P., Teel, A.L. 2000. A foundation for the riskbased treatment of gasoline-contaminated soils using modified Fenton's reactions. - Journal of Hazardous Materials, vol 76(B), p 73-89.
[114] Watts, R.J., Bottenberg, B.C., Hess, T.F., Jensen, M.D., Teel, A.L. 1999a. Role of reductants in the enhanced desorption and transformation of chloraliphatic compounds by modified Fenton's reactions. - Environmental Science and Technology, vol 33, p 3432-3437.
[115] Watts, R.J., Foget, M.K., Kong, S.-H., Teel, A.L. 1999b. – Hydrogen peroxide decomposition in model subsurface systems. - Journal of Hazardous Materials, vol 69(B), p 229-243.
[116] Watts, R.J., Stanton, P.C. 1999. Mineralization of sorbed and napl-phase hexadecane by catalyzed hydrogen peroxide. - Water Research, vol 33, p 1405-1414.
[117] Watts, R.J., Dilly, S.E. 1996. Evaluation of iron catalysts for the Fenton-like remediation of diesel-contaminated soils. - Journal of Hazardous Materials, vol 51, p 209-224.
[118] Watts, R.J., Udell, M.D., Leung, S.W. 1992. Treatment of contaminated soils using catalysed hydrogen peroxide. In: Chemical Oxidation Technologies for the Nineties, W.W. Eckenfeld, A.R. Bowers, J.A. Roth (eds.), A Technomic Publishing Company, INC, Lancaster, USA, 1992, p 37-50.
[119] Yang, M., Hu, J., Ito, K. 1998. Characteristics of Fe^{2+}/H_2O_2/UV oxidation process. -
[120] Environmental Technology, vol 19, p 183-191.
[121] Yu, C.-P., Yu, Y.-H. 2001. Mechanisms of the reaction of ozone with p-nitrophenol. - Ozone Science & Engineering, vol 23, p 303-312.



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