Innovative Advanced Oxidation Strategies for Efficient Water Purification and Soil Remediation

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Abstract - This study aims to enhance understanding of advanced oxidation processes (AOPs) for the decontamination of soil and water. AOPs represent a powerful class of remediation technologies that rely on the in situ generation of highly reactive oxidants, primarily hydroxyl radicals, to degrade a wide range of organic pollutants. The oxidation rate constants for nitro phenol in various AOP systems—Fenton, photo-Fenton, H_2O_2/UV, O_3, O_3/H_2O_2, O_3/UV, and O_3/H_2O_2/UV—were determined to optimize these processes. Results showed that zonation generated Quinone-type by-products and that the mineralization of organically bound nitrogen to nitrate ranged from 50% to 100%, depending on the treatment system used.AOPs also improved the biodegradability and reduced the toxicity of pollutants, making them suitable as pre-treatment methods for filtering nitro phenol-contaminated water. The study confirmed that substances such as nitro phenols, polycyclic aromatic hydrocarbons, diesel, shale oil, and transformer oil could be effectively removed from soil using zonation and Fenton- based treatments. However, contaminant removal was less effective in peat than in sand matrices, due to the peat's chemical and physical characteristics. Interestingly, the Fenton process was effective at the soil's natural pH, with indigenous iron catalyzing the hydrogen peroxide reaction without the need for added Fe^{2+}.

***Key Words*:** : Advanced Oxidation Processes (AOPs),Fenton Treatment,Ozonation,Nitrophenols,Hydroxyl Radicals,Photo-Fenton,Biodegradability,Soil Remediation, Water Purification, Organic Contaminants, Reaction Rate Constants, Quinone By-products,Mineralization,Hydrogen Peroxide (H_2O_2).

1.INTRODUCTION

A wide variety of substances are released into the water. Some of them are difficult to eliminate in biological wastewater treatment plants because they are both poisonous and partially biodegradable. Effective techniques for the breakdown of organic pollutants—either to less hazardous chemicals or to their full mineralization—are therefore required.

In order to speed up the oxidation and destruction of a variety of organic contaminants in contaminated water and air, sophisticated oxidation procedures (AOP), which generate extremely powerful chemical oxidants like the hydroxyl radical (OH) in situ, have recently gained attention (Glaze et al., 1987). When used properly, AOP offers a good chance of lowering the concentration of contaminants from hundreds of parts per million to fewer than five parts per billion. They are referred to be "the treatment processes of the 21st century" for this reason.

One of the most commonly used industrial organic chemicals is nitro phenol (NP). They are used as explosives, wood preservatives, pesticides, herbicides, and insecticides. NPs can get into the environment through spills, industrial discharges, or even as a byproduct of some insecticides that include NPs (EPA US, 1993). Additionally, NPs have been implicated in the breakdown of pesticides such as nitro fen and parathion (Kiwi et al., 1994). It is frequently inevitable that aqueous wastes will be produced during the formulation, distribution, and field application of pesticides. NPs have been found in cloud and fog water condensates and on airborne particulate matter as secondary pollutants that result from the release of nitrogen oxide and aromatic hydrocarbons through photochemical reactions in the atmosphere (Heretic, 1991). Four NPs have been included to the 129 priority pollutants list by EPA US (2-NP, 4-NP, 2,4-DNP, and 4,6-DN-o-CR) (Keith and Tallied, 1979). NPs are frequently found in soil, ambient freshwater, marine ecosystems, industrial effluents, and the atmosphere.

NPs are extremely harmful substances. They build up in warm-blooded organisms. There have been reports of both acute and long-term impacts on humans and animals. According to epidemiological research, NPs harm the liver, kidney, blood, and central nervous system.

2.1. Materials

2.1.1 Water treatment

Model compounds in water treatment

The compounds under investigation included 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-nitrophenol (2,4-DNP), 2-nitrophenol (2,4-DNP), 2-nitrophenol (2,5-DNP), and 2,6- dinitrophenol (2,6-DNP). Analytical grade nitrophenols (NPs) were acquired from Aldrich Co. The NP mixture included 2,4-DNP, 4-NP, 2-NP, and 4,6DN-o-CR. NPs were dissolved in twice- distilled water to create the samples. A single NP's starting concentration was 0.4 mM, and the mixture's NP concentration was 2 mM (0.5 mM of each NP). Paper II, Table 1, and Paper IV, Table 1 present some of the chemical-physical characteristics of NPs.

AOP applied

The Fenton, photo-Fenton, photolysis

Papers I and II

Individual NPs' rate of deterioration in water-based solutions during the neither Fenton nor photo- Fenton techniques was investigated in a batch setting.

In the cylindrical glass reactor, 0.7 L of fresh NP liquid was treated using magnetic stirring as per standard protocol. In these tests, the process was halted by adding a 10% aqueous solution of Na2SO3. Different H2O2 concentrations were used under the same conditions for the process of photolysis in the presence of hydrogen peroxide. The UV source for the hydrogen peroxide photolysis, photo-Fenton, and direct UV photolysis treatments was a mercury low- pressure conditions prevail OSRAM lamp with a 10 W energy input.

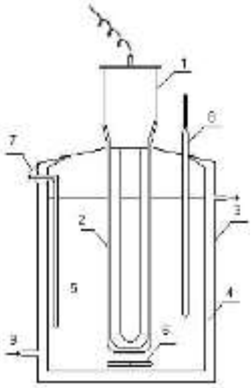


Figure 3. 1. Scheme of experimental apparatus used in UV/H2O2, direct UVphotolysis, and photo-Fenton oxidation processes (1 – UV lamp; 2 – quartz sleeve; 3 – cooling jacket; 4 – reactor; 5 – irradiated solution; 6 – stirrer; 7 – sample intake; 8 – thermometer; 9 – thermostat)

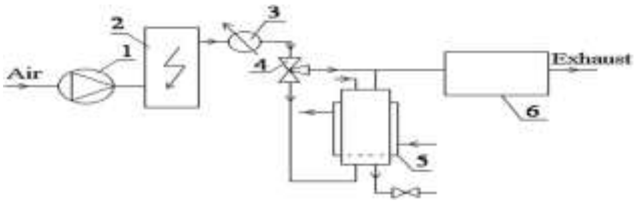
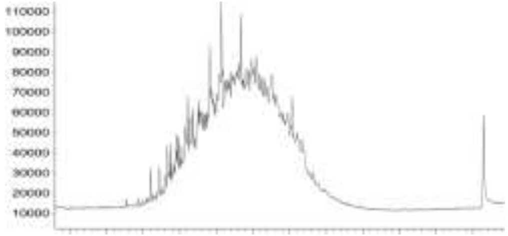


Figure 4. 2. Scheme of the experimental set (1 – compressor; 2 – ozonator; 3 – flow meter; 4 – three-way cock; 5 – bubble column equipped with water jacket and UV- lamp; 6 – spectrophotometer)



4. RESULTS AND DISCUSSION

To assess their capacities to break down the target molecule, non-accompanied ozonation and different AOPs (hydrogen peroxide photolysis, Fenton, photo-Fenton, O3/UV, O3/H2O2, and O3/UV/H2O2) were used in this study to purify NP-contaminated water.

5.1 Hydrogen peroxide photolysis

NPs were not degraded when they were stirred with hydrogen peroxide in the absence of UV light. With a pseudo-first order reaction rate constant of roughly 10-5 s-1, direct UV-photolysis produced NP degradation that was extremely sluggish and unsuitable for real-world use (paper II, chapter 5.1). The addition of hydrogen peroxide to the UV treatment significantly expedited the breakdown of NPs. As the quantity of H2O2 increased, the degradation time was significantly reduced (paper II, Table 2). Mono-NPs significantly increased the rate of degradation more than di-NPs and methyl-dinitrophenols did. In hydrogen peroxide photolysis treatment, the rate of degradation was linearly correlated with the concentration of hydrogen peroxide (for H2O2 concentration range 0-10 mM) (paper II, Figure 1). Chen et al. (1997) found a similar effect of H2O2 concentration on the rate of phenol degradation, showing that a higher hydrogen peroxide concentration significantly increases the efficiency of phenol degradation.

The effect of soil matrix in the Fenton treatment
The soil matrix affected the Fenton treatment's effectiveness, just like in ozonation tests. When compared to the treatment of sand, a greater hydrogen peroxide dose was necessary for the Fenton-like reaction in peat to effectively degrade pollutants. According to Fig. 5.2, sand removed more contaminants than peat under the same treatment circumstances and with the same weight ratios of H2O2/contaminant (diesel, shale oil, and transformer oil).

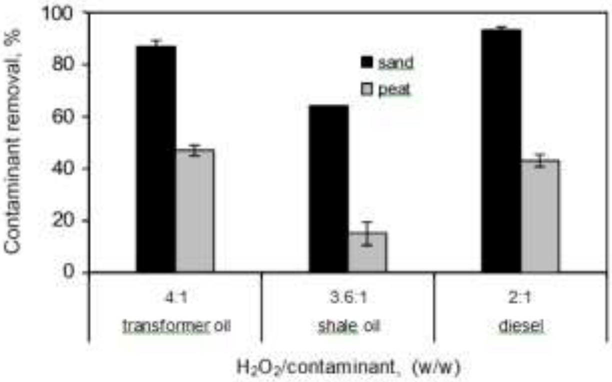
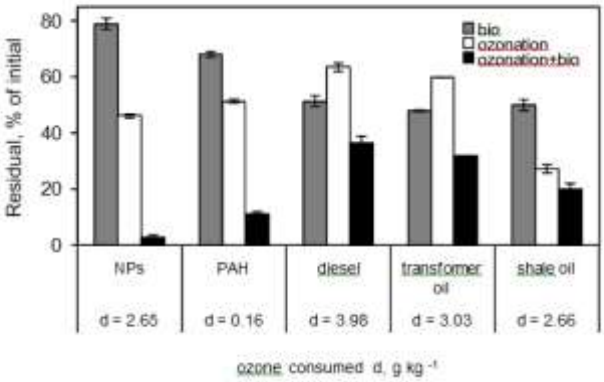


Figure 5. 2. Comparison of contaminants (transformer oil, shale oil and diesel) removal by 72-hours

When applying the Fenton treatment to PAH, the 3-step addition of H2O2 per day (1d/3) resulted in 80% PAH elimination in sand and 61% PAH removal alone in peat (paper V, Figure 1). Both sand and peat had 60% of their PAHs removed when H2O2 was added all at once. In the presence of hydrogen peroxide excess, the quenching of OH• by hydrogen peroxide and hydroperoxyl radicals may restrict degradation.



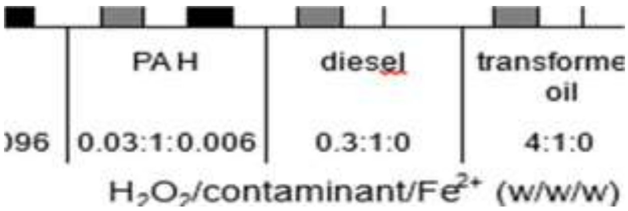


Figure 5. 5. Residual concentrations of NPs, PAH, diesel, transformer oil and shale oil (%) in sand after 30 days biodegradation (diesel, transformer oil, shale oil), 28 days biodegradation (NPs) and 56 days biodegradation (PAH), Fenton/Fenton-like treatment, and combined Fenton/Fenton-like + biotreatment (papers IV, V, VI, VII)

Compared to biodegradation, the use of chemical oxidation (ozonation or the Fenton treatment) for contaminated soil remediation allowed for a quicker decrease in the concentration of contaminants. Therefore, when it's required to prevent toxins from penetrating deeper soil layers or the aquifer, chemical oxidation is essential for quickly reducing their concentration in contaminated soil. For the rehabilitation of polluted soil, integrated chemical and biological processes have proven to be a more successful treatment method than either one alone. To promote bioremediation by the native microorganisms that survived the chemical oxidation, moderate concentrations of chemical oxidants (hydrogen peroxide, ozone) should be used in conjunction with chemical treatment (both Fenton-like or ozonation) and biodegradation.

According to a cost analysis, the least expensive chemical treatment technique for cleaning up polluted soil was the Fenton/Fenton-like treatment. Even though the contaminants under study (NPs, PAH, diesel, transformer oil, and shale oil) were degraded by chemical treatment alone, chemical treatment combined with subsequent biological treatment (using moderate amounts of chemicals) would offer a more effective and economical method of site remediation than either single treatment approach alone.

5. CONCLUSIONS

The present work showed that a wide range of options for the destruction of aqueous NPs are made possible by enhanced oxidation. In these treatments, the rate at which NPs degraded varied by several orders of magnitude, ranging from a few minutes (the Fenton treatment) to several hours (UV-photolysis) needed to reduce the initial concentration of NPs by ten times.

In addition to effectively degrading NPs, non-accompanied ozonation and AOP can also be used to detoxify and increase the biodegradability of wastewater that contains NPs. Ring hydroxylation, nitrogen mineralization, ring opening processes that convert aromatics to aliphatics, and toxicity reduction were taken into consideration as contributing elements to the improvement in biodegradability. The potential application of AOP and ozonation to enhance the ability of traditional biological treatment to eliminate hazardous and weakly biodegradable NPs is supported by the achieved biodegradability enhancement and detoxification of treated NPs.

Even though ozone treatment in conjunction with hydrogen peroxide and/or UV radiation accelerated the degradation of nanoparticles and decreased ozone consumption, such AOP was found to be less competitive than non-accompanied ozonation when a significant increase in treatment costs is taken into account. When capital expenditures for implementing the treatment are considered, the Fenton treatment is better even if the costs of the ozonation and Fenton treatments were determined to be comparable. While the Fenton treatment does not require significant capital costs, the installation of ozone equipment does. Therefore, out of all the AOPs being studied, Fenton's reagent appears to be the most effective treatment approach.

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