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Decomposition of dissolved organic contaminants by combining a boron-doped diamond electrode, zero-valent iron and ultraviolet radiation

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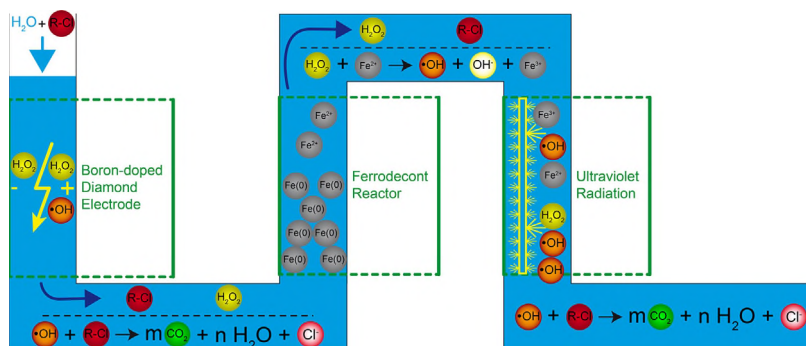
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GRAPHICAL ABSTRACT



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1. Introduction

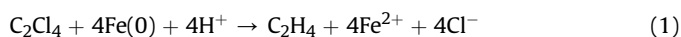
Contaminated sites are areas that are known to pose considerable risks to the health of human beings or the environment due to contaminations in soil and groundwater bodies. These contaminations are caused by various types of substances. Apart from inorganic substances, e.g., heavy metals, organic substances are of great concern as some of them show high environmental persistence and are not readily degradable. Local pollution of the underground mainly derives from (former) industrial-, waste disposal- or military sites, etc.

Panagos et al. (2013) revealed a total number of 342,000 contaminated sites and 2.5 million potentially contaminated sites in Europe, from which the majority affects the groundwater. Approximately 50% of these sites are polluted with heavy metals and mineral oil. Remaining 50% contain benzene, toluene, ethylbenzene and xylene (BTEX), chlorinated hydrocarbons, polycyclic aromatic hydrocarbons, phenols, cyanides and others.

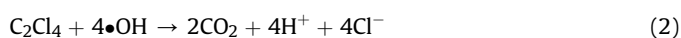
This research project deals with the mineralization of dissolved organic contaminants, i.e., methyl *tert*-butyl ether (MTBE, C₅H₁₂O), the chlorinated hydrocarbon tetrachloroethene (C₂Cl₄) and the pesticide clopyralid (C₆H₃Cl₂NO₂) by using three different water processing techniques (boron-doped diamond electrodes (BDD), zero valent iron (Fe(0)) in a fluidized bed reactor and ultraviolet (UV) radiation).

Thresholds for organic substances in groundwater differ from country to country. According to the drinking water ordinance of Austria ([Bundesminister für soziale Sicherheit und Generationen, 2001](#)), the threshold for clopyralid in the groundwater is 0.1 and 10 µg L⁻¹ for the sum of tri- and tetrachloroethene. The working group on the determination of insignificance thresholds for groundwater of the federal states on water issues (Germany) suggests a threshold of 10 µg L⁻¹ for the sum of tri- and tetrachloroethene in the groundwater as well and 15 µg L⁻¹ for MTBE ([Altmayer et al., 2004](#)). According to the Austrian risk assessment for contaminated sites ([ÖNORMS 2088-1](#)), the threshold for further testing of MTBE in groundwater is 5 and 6 µg L⁻¹ for tri- and tetrachloroethene.

Organic pollutants in waters can be decomposed by reduction and oxidation processes. An example for reductive decomposition (dechlorination) is the reaction of Fe(0) with tetrachloroethene (Eq. (1)), a common solvent which is one of the most abundant pollutants in contaminated sites ([Zhang, 2003](#); [Baumann, 2010](#)).



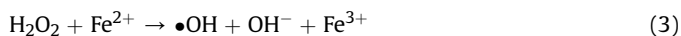
Using Fe(0) as an electron donor for reductive decomposition of the organic contaminant is known to be an effective treatment method. Moreover, oxidative processes, e.g., advanced oxidation processes (AOPs), are chemical treatment procedures which are commonly used in the field of water treatment for the mineralization of organic molecules, involving radical production ([Glaze, 1987](#); [Aieta et al., 1988](#); [Deng and Zhao, 2015](#); [Ikehata et al., 2016](#)). Because of their high reactivity and nonselective oxidation, hydroxyl radical (•OH)-based AOPs are prevalently applied. In case of a complete degradation, reaction products are carbon dioxide, water and/or inorganic compounds, as shown representatively for tetrachloroethene ([Andreozzi, 1999](#); [Miao et al., 2015](#)):



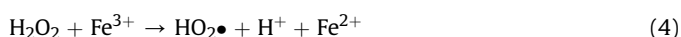
It is well known that intermediate products (metabolites) such as formic and acetic acid are produced during the reaction of C₂Cl₄ with •OH, but these products are also known to immediately react

with present •OH ([Leung et al., 1992](#); [Pignatello et al., 2006](#)).

These hydroxyl radicals can be produced in various ways, e.g., electrochemically, photochemically and/or through the reaction of H₂O₂ with Fe²⁺, known as the classical homogeneous Fenton reaction (Eq. (3)), which was discovered by Henry John Horstman [Fenton \(1894\)](#).



Later, [Haber and Weiss \(1934\)](#) proposed that •OH are being produced during the reaction, which was revised and elaborated by ([Barb et al. \(1949, 1951a, 1951b\)](#)). Along with the classical homogeneous Fenton reaction (Eq. (3)), a variety of additional reactions are involved in the classical Fenton radical mechanisms, which are discussed in [Deng and Englehardt \(2006\)](#), [Pignatello et al. \(2006\)](#), [Held \(2014\)](#), [Deng and Zhao \(2015\)](#), [Vorontsov \(2018\)](#) and elsewhere. One of these reactions is the Fenton-like reaction (Eq. (4)), yielding Fe(II), hence, Fe can be seen as a catalyst in the classical Fenton radical mechanism. However, due to the low reaction rate, if no additional Fe(II) is provided, Eq. (4) can be the limiting step for Eq. (3).

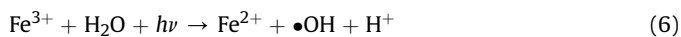


Anyhow, the fundamental step during the water treatment is the production of the desired oxidant (•OH) for degrading the target organic contaminant.

Apart from producing the •OH via the Fenton reaction, it can also be generated photochemically by using UV irradiation. At a wavelength below 400 nm, it is produced by photolysis of H₂O₂ ([Ruppert et al., 1993](#); [Bokare and Choi, 2014](#); [Sirés et al., 2014](#)):



or, depending on the prevailing type of present Fe(III)-bearing complex, through photoreduction of Fe(III) to Fe(II), which is known as the photo-Fenton process ([Ruppert et al., 1993](#); [Feng and Nansheng, 2000](#); [Bokare and Choi, 2014](#); [Mirzaei et al., 2017](#); [Vorontsov, 2018](#)):



Produced Fe(II) can again react with present H₂O₂ according to Eq. (3).

Electrochemical production of •OH for a successful abatement of organic contaminants in aqueous media strongly depends on the electrode material. Suitable materials are Pt, Au, boron-doped diamonds, ebonex[®], stainless steel, Ti/IrO₂-Ta₂O₅ and PbO₂. Anyhow, the highest incineration (oxidation to CO₂) rates were achieved by using BDD ([Scialdone et al., 2008](#)). The potential use of BDD for pollutant removal has been popularized extensively by research groups of Comninellis, Rodrigo and Panizza, e.g. in [Panizza et al. \(2001\)](#), [Brillas et al. \(2004\)](#), [Panizza and Cerisola \(2005\)](#), [Comninellis et al. \(2008\)](#), [Panizza et al. \(2008\)](#) or [Comninellis and Chen \(2010\)](#). During the treatment with a BDD, the anode electrochemically generates •OH, which will readily react with present organic contaminants. Additionally, H₂O₂ is produced at the anode, but also through reduction of molecular O₂ at the cathode ([Kraft et al., 2003](#); [Zhou et al., 2012](#); [Oturán and Aaron, 2014](#)), which will then react with present Fe²⁺ according to the Fenton radical mechanisms as described in Eq. (3) and photochemically to directly produce •OH according to Eq. (5). Besides the desired oxidizing agents, it is known that a variety of metabolites are likewise produced during the treatment of organic contaminated waters with the BDD ([Anglada et al., 2010](#); [Li and Ni, 2012](#); [Bagastyo et al., 2013](#); [Sirés et al., 2014](#)).

In this study, we present a new approach of combining three different treatment methods for the abatement of organic pollutants in aqueous solutions. By exploiting synergy effects, the combination of BDD, Fe(0) in a fluidized bed reactor and UV radiation enhances the treatment efficiency. The substances tetrachloroethene and MTBE, well known to occur in contaminated sites, were chosen for the experiments. Besides, pesticides such as clopyralid are pollutants in the environment. As some of them are sensitive to hydroxyl radical-caused degradation (Westphal et al., 2013) and to electrochemical oxidation (Özcan et al., 2010), we decided to test the potential of the system for the degradation of clopyralid as well. Westphal et al. (2013) performed their experiments in batch glass reactors by adding specific chemicals. Best results were obtained at a pH between 3 and 4. Özcan et al. (2010) used glass cells, equipped with two electrodes. Experiments were conducted at a pH of 3 by applying different currents. The highest abatement rate was achieved by using the highest investigated current of 500 mA. To our knowledge, there has not been published any work reporting the abatement of organic contaminants by using a combination of a BDD, Fe(0) in a fluidized bed reactor and UV radiation.

2. Materials and methods

For the experiments, three different setups were used with three different samples. The goal was to evaluate the efficiency of using the BDD, Fe(0) in a fluidized bed reactor or UV radiation on the degradation of tetrachloroethene, MTBE and clopyralid alone (experiment 1), in any combination of two methods (experiment 2) as well as in combination of all three of them (experiment 3).

2.1. Sample description

In this study, three different samples were used. Sample 1 and 2 were original groundwater samples, taken from contaminated sites in Austria and were supposed to contain tetrachloroethene or MTBE, respectively. Analyses of the samples by the time of the beginning of the experiments revealed that the contaminant concentrations were too low for realistic experimental conditions (tetrachloroethene: $<3.33 \mu\text{g L}^{-1}$ and MTBE: $<0.288 \mu\text{g L}^{-1}$). Hence, it was decided to artificially spike the two original waters by using tetrachloroethene ($\geq 99.5\%$ for synthesis) and MTBE (tert-butylmethylether $\geq 99.5\%$ for synthesis) obtained from Carl Roth GmbH + Co KG. In both groundwater samples, the dominant anions were sulfate and carbonate with minor amounts of chloride. Experiments 1 and 3 (described below) were conducted prior to experiment 2. After experiments 1 and 3 were performed, the original groundwater samples from the contaminated sites were spent, consequently, local laboratory tap water (region: Niklasdorf, Styria, Austria) was spiked for experiment 2. Major anion in solution is carbonate, followed by sulfate and chloride.

For the experiments with clopyralid (sample 3), no original contaminated groundwater sample was available, hence, clopyralid (Pestanal, analytical standard, Sigma-Aldrich) was dissolved in the local tap water (described above) for all experiments.

Incomplete dissolution, sorption processes etc. presumably led to divergences between the calculated and measured concentrations at the beginning of the experiments. Therefore, the decrease in concentration of the contaminant was calculated by normalizing the measured concentrations in the samples during the experiments (C) to the measured initial concentration (C_0). Measured initial concentrations are provided in the corresponding captions of the data graphs.

2.2. Treatment methods

2.2.1. Boron-doped diamond electrode

During the experiments, a flow through cell (provided by pro aqua GmbH) was used which contained seven BDD electrodes and two Ir/Ru coated titanium contact electrodes. The two Ir/Ru coated titanium electrodes generate an electrical field within this flow through cell. In this setup, the BDD electrodes are operated bi-polar because they are installed in the generated electrical field within the flow through cell. All electrodes have a distance of 2 mm to one another and a surface area of 42 cm^2 . The required energy is 800 W with a current of 4.2 A, causing a current density of 100 mA cm^{-2} on each electrode.

2.2.2. Ferrodecont process

The second treatment method used in this study is known as the Ferrodecont process and is described in detail in Müller et al. (2014). For this process, Fe(0) granules ($d = 4\text{--}6 \text{ mm}$) are placed in a cascade of reactors. Contaminated water is pumped into the reactors from the bottom to the top, causing a fluidization of the Fe(0) granule bed. In our experiments, a total of 1000 g of Fe(0) was used in two reactors. Due to the fluidization of the granules and resulting turbulences, the granules physically interact with each other, leading to an abrasion of the oxidized and passivated surface layer. Consequently, an unreacted Fe(0) surface is constantly provided, either for direct reductive degradation or as an additional Fe source for the described Fe-catalyzed Fenton radical mechanisms.

2.2.3. UV irradiation

The UV irradiation is performed by using a PURION 2500 90W PRO (Purion, 2018a), equipped with a PURION UV Lampe 90 W (Purion, 2018b). The rod-like mercury low pressure lamp emits UV radiation with 90 W at a wavelength of $\lambda = 254 \text{ nm}$ and is installed in a cylindrical stainless steel case. This assemblage yields a distance from the lamp to inner case surface of 2 mm.

2.3. Experimental setup

The experimental setup consisted of a sample tank, a pump and the treatment devices, which were, depending on the experiment, included or omitted while pumping the sample in cycles. An experiment duration of 60 min was chosen with a (starting) sample volume of 10 L and a pump rate of 600 L h^{-1} . Experimental conditions, such as the pump rate and the applied current for the BDD, result from specific operating properties of the installed treatment devices that are provided by manufacturers. A relatively high pump rate of 600 L h^{-1} is required to cause a fluidization of the Fe(0) granule bed, but also for cooling purposes of the BDD flow through cell. Subsamples were taken after 10, 30 and 60 min of treatment, except for experiment 2, where the time was shortened to 30 min with sampling after 5, 15 and 30 min.

2.3.1. Experiment 1

During experiment 1, the ability to decompose the contaminants by using the different treatment methods independently was tested. The experimental setup and sampling times were the same as described above with two exceptions: no sampling occurred after 10 min of treating the clopyralid sample with the BDD, and the MTBE sample was not treated by using the BDD.

Two additional experiments were performed in this campaign. The first one was conducted to evaluate the efficiency of removing the contaminants by shaking 1 L of the local tap water (see chapter 2.1) together with 100 g of Fe(0) granules and H_2O_2 (1%, Wasserstoffperoxid TR 30% K10L, Brenntag) in an overhead shaker. The pH was set to 5 by adding HCl (30%, techn., Carl Roth GmbH + Co KG).

Two bottles were prepared and shaken for 5 and 15 min. The second one, a reference experiment, shall provide information about the decrease in contaminant concentration through degassing, sorption processes etc., by storing 1 L of sample in a HDPE bucket which was kept at ambient conditions with contact to the atmosphere. After 1 h, a sample was taken and analyzed.

2.3.2. Experiment 2

The second experiment was conducted by using all possible combinations of two treatment methods. As mentioned earlier, this campaign was carried out after performing experiments 1 and 3 by using spiked local tap water and shorter experiment durations. Hydrogen peroxide (1%) was also added to the solution at the beginning of the treatment.

Additionally, the effect of solely applying H_2O_2 (1%) on the abatement of tetrachloroethene and MTBE has been investigated in this campaign. The sample was pumped in the same cycle as for the other experiments but all treatment aggregates were bypassed.

2.3.3. Experiment 3

In experiment 3, the combination of all three treatment methods was tested, which means the contaminated water is pumped in cycles when it passes the BDD flow through cell, the Fe(0)-containing reactors and the UV light. This setup is labeled "Combination" in the following. Treatment times were chosen as described above. Furthermore, the effect of H_2O_2 (1%) and $\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$ (1% and pH 3) addition was investigated.

2.4. Analytical methods

Samples were taken throughout the experiments according to ISO 5667-3: free of air bubbles in either glass stoppered wide neck glass bottles (MTBE) or in Duran glass bottles with a PTFE lid (tetrachloroethene and clopyralid). To avoid an enhanced degassing of the contaminant during sampling, turbulences were prevented as good as possible. Prior to sampling, bottles for tetrachloroethene and MTBE containing samples were rinsed with sample solution, but not the bottles for the clopyralid containing sample. After sampling, all samples were cooled, protected against light and transported to the laboratory, where the contaminant was extracted/stabilized and measured.

Tetrachloroethene was analyzed according to ISO 10301 by using a gas chromatography system Clarus 500 of Perkin Elmer, equipped with two capillary columns, two ECD detectors, a Turbomatrix 110 headspace autosampler of Perkin Elmer and nitrogen 5.0 as carrier gas. For separation and confirmation, two capillary columns were used, a Restek RTX-Volatiles (60 m, 0.32 mm ID, 3.0 μm df) and a HP-624 (60 m, 0.32 mm ID, 1.8 μm df). Additionally, the concentrations of trichloroethene, cis 1,2-dichloroethene, trichloromethane, tetrachloromethane, bromdichloromethane, dibromchloromethane, tribrommethane, 1,1-dichloroethene, dichloromethane, trans-1,2-dichloroethene, 1,1-dichloroethane, 1,1,1-trichloroethane, 1,2-dichloroethane, 1,2-dichloropropane, cis-1,3-dichloropropane, trans-1,3-dichloropropane, 1,1,2-trichloroethane were measured simultaneously by this method.

Concentrations of MTBE were determined after DIN 38407-09 with a gas chromatography system Thermo Finnigan Trace GC in combination with a Thermo Finnigan Trace DSQ mass spectrometry system. Helium 5.0 was used as the carrier gas, with a headspace autosampler, TurboMatrix 110 of Perkin Elmer and a Restek RTX-VMS (60 m, 0.32 mm ID, 1.8 μm df) capillary column.

The clopyralid concentrations were quantified following DIN 38407-35 with a Shimadzu Nexera U-HPLC system, equipped with a DGU-20A degasser, two LC-30AD pumps and a CTO-20AC column oven. A mass-selective detector (Shimadzu LCMS 8040)

was used with argon as the collision-induced dissociation (CID) gas and an ESI interface for ionization. A Parker LCMS30 generator provided nitrogen and separation was performed by a Shimadzu Shim-pack XR-ODS II column (3 mm \times 100 mm, 2.2 μm). Further information about the analytical method is provided by Mann et al. (2016).

3. Results and discussion

3.1. Tetrachloroethene

The degradation of tetrachloroethene by using the described treatment methods alone and in various combinations was tested in experiments 1 to 3; results are shown in Fig. 1. The background colors represent the different concentration ranges in the experiments.

After 1 h, 60% of the original concentration was present in the reference sample (Fig. 1a) revealing a concentration decrease, probably through degassing and/or sorption processes. Shaking the sample in the overhead shaker with Fe(0) and H_2O_2 leads to a concentration decrease of around 30% within 5 min. A significant further decrease within the next 10 min was not observed. Since the reaction of dissolved Fe, H_2O_2 and the contaminant still proceeded

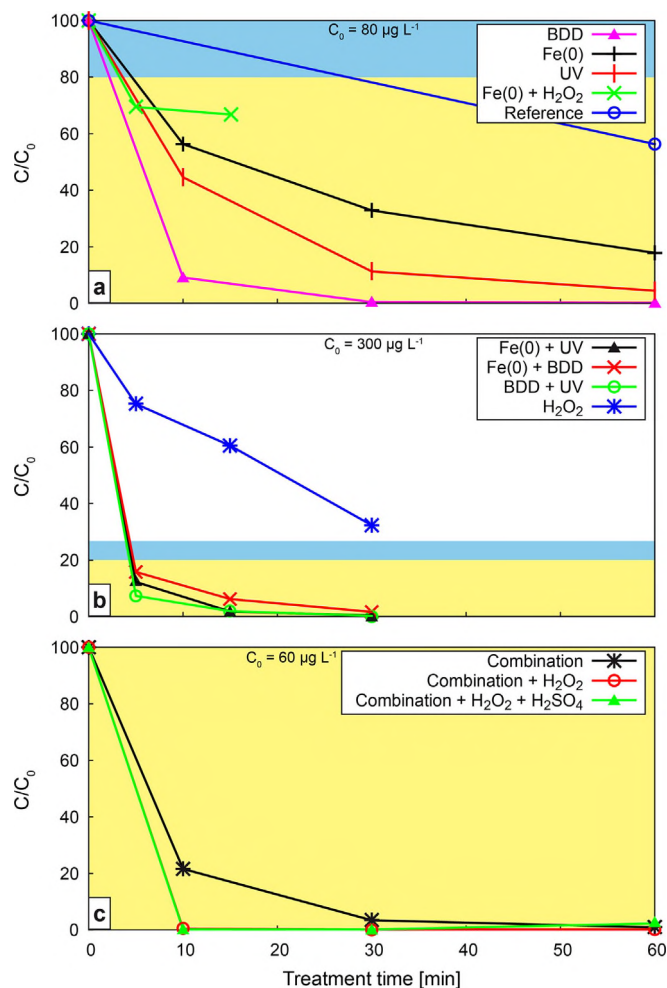


Fig. 1. Degradation of tetrachloroethene during experiment 1 (a; $C_0 \sim 80 \mu\text{g L}^{-1}$), experiment 2 (b; $C_0 \sim 300 \mu\text{g L}^{-1}$) and experiment 3 (c; $C_0 \sim 60 \mu\text{g L}^{-1}$). Different background colors represent concentration ranges (yellow: 0–60 $\mu\text{g L}^{-1}$, blue: 60–80 $\mu\text{g L}^{-1}$ and white: 80–300 $\mu\text{g L}^{-1}$).

after shaking was stopped, the concentration in both samples further decreased until the time of analyses, resulting in almost equal abatement rates.

Applying the BDD, UV radiation or Fe(0) (in the fluidized bed reactors) led to significant concentration decreases, however, using the BDD is the most effective treatment method (Fig. 1a). After 30 min of treatment, approximately 60% of the contaminant was decomposed by using Fe(0), whereas a concentration decrease of almost 100% was achieved by using the BDD. After 1 h of treatment, roughly 80% of the tetrachloroethene was decomposed by Fe(0) and 95% by using the UV irradiation.

By combining two of the treatment methods and by adding H₂O₂, high removal rates were achieved (Fig. 1b). After 5 min of treatment, more than 80% of the originally dissolved amount of tetrachloroethene has been removed by using any possible combination. The highest removal efficiency was reached by combining the BDD with the UV irradiation. After 30 min of treatment, less than 2% of the original concentration was present in solution. Using solely H₂O₂ leads to an almost steady, but relatively slow decrease in concentration. After 30 min, 33% of the initial tetrachloroethene was detected.

After 10 min of treatment by combining all three treatment methods with addition of H₂O₂ and H₂O₂ + H₂SO₄, more than 99% of the tetrachloroethene was removed, however, this high removal efficiency was not achieved by using the combination alone with no further addition of chemicals (Fig. 1c).

The tetrachloroethene treatment samples were additionally analyzed regarding possible metabolite formation (see section 2.4). Trichloromethane, tetrachloromethane, bromdichloromethane, dibromchloromethane and tribrommethane were identified to form during the experiments. By using solely the BDD, the formation of metabolites (especially trichloromethane) occurred, and a removal of the metabolite has not been observed. Contrary, the treatment with the combination of all three methods led to further abatement of these newly formed compounds.

3.2. MTBE

Experiment 1 showed that the removal of MTBE by using the treatment methods alone (Fig. 2a) was not as sufficient as for tetrachloroethene. After 1 h of treatment, approximately 30% of MTBE was removed by using Fe(0) and 40% by using the UV irradiation. The efficiency of Fe(0) + H₂O₂ to remove MTBE in the overhead shaker was similar to tetrachloroethene. The concentration decrease of the reference sample was not as significant as for the tetrachloroethene sample and after 1 h of exposure to the atmosphere, 84% of the contaminant was still present in the sample.

The efficiency of H₂O₂ alone revealed a relatively slow reaction rate: 66% of the initial MTBE concentration was present in solution after 30 min of treatment (Fig. 2b). An efficiency increase was achieved by applying two of the treatment methods and H₂O₂. After 5 min, around 20% or less of the original MTBE concentrations were left in solution and additional 10 min of treatment yielded further MTBE decomposition to less than 1% of the initial concentrations, except for the treatment with Fe(0) + BDD (~10%). Results show a prominent effect of UV irradiation on the degradation of MTBE.

The effect of treating the water with a combination of all three treatment methods on the MTBE concentration was relatively small (26% present after 1 h of treatment), nevertheless, this effect increased significantly by the addition of H₂O₂ and/or H₂O₂ + H₂SO₄ (Fig. 2c).

3.3. Clopyralid

Almost the same concentration of clopyralid was detected in the reference sample after 1 h of exposure to the atmosphere (Fig. 3a),

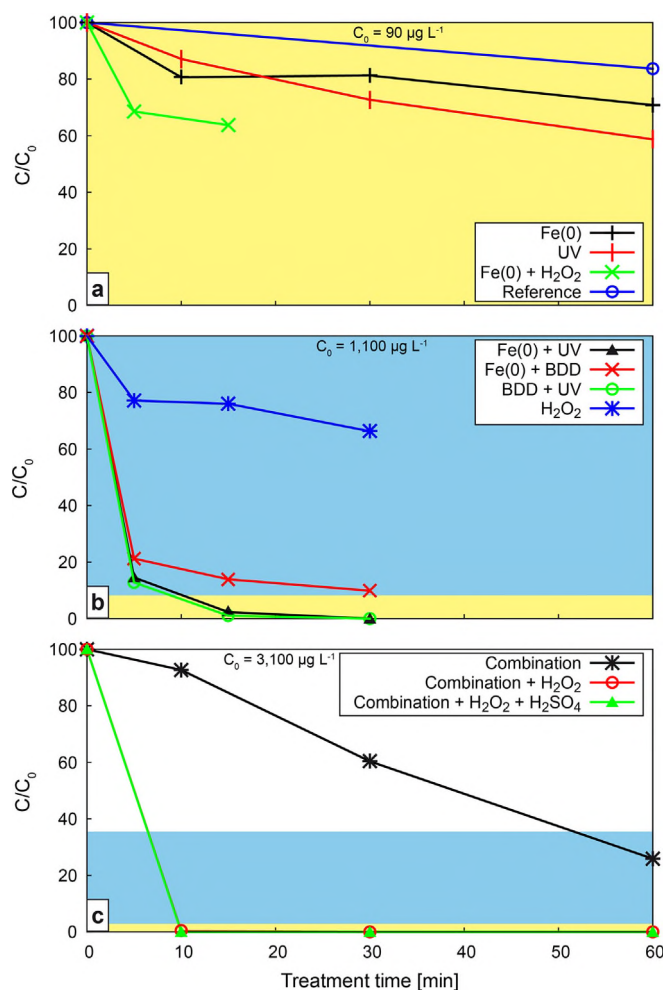


Fig. 2. Degradation of MTBE during experiment 1 (a; $C_0 \sim 90 \mu\text{g L}^{-1}$), experiment 2 (b; $C_0 \sim 1100 \mu\text{g L}^{-1}$) and experiment 3 (c; $C_0 \sim 3100 \mu\text{g L}^{-1}$). Different background colors represent concentration ranges (yellow: $0\text{--}90 \mu\text{g L}^{-1}$, blue: $90\text{--}1100 \mu\text{g L}^{-1}$ and white: $1100\text{--}3100 \mu\text{g L}^{-1}$).

and 31% were decomposed by treatment with Fe(0) and H₂O₂ for 15 min in the overhead shaker. Treating the clopyralid containing solution with the BDD led to a concentration decrease of 87% within 60 min and 42% within 30 min by using UV irradiation. The concentration decreased to 57% of the initial concentration after 10 min of treatment with Fe(0), however, a slight increase was detected until the end of the experiment. The reason for this is not known until now, however, it could be due to adsorption and later desorption of clopyralid during the experiment or more likely due to inaccuracy of the measurements.

By using a combination of Fe(0), BDD and H₂O₂ a steady decrease to 82% of the initial concentration was achieved within 30 min of treatment (Fig. 3b). By using the other combinations, the efficiency was increased significantly and after 30 min of treatment, less than 5% of the initial concentration was present in solution.

Fig. 3c shows the results of applying all three treatment methods simultaneously on the clopyralid containing solution. The concentration decrease can be described by an exponential decay; however, the efficiency is increased again through the addition of H₂O₂ and H₂O₂ + H₂SO₄ as observed for the other contaminants before. Nevertheless, the efficiency was much higher at lower pH, which might be related to the rather complex aromatic chemical

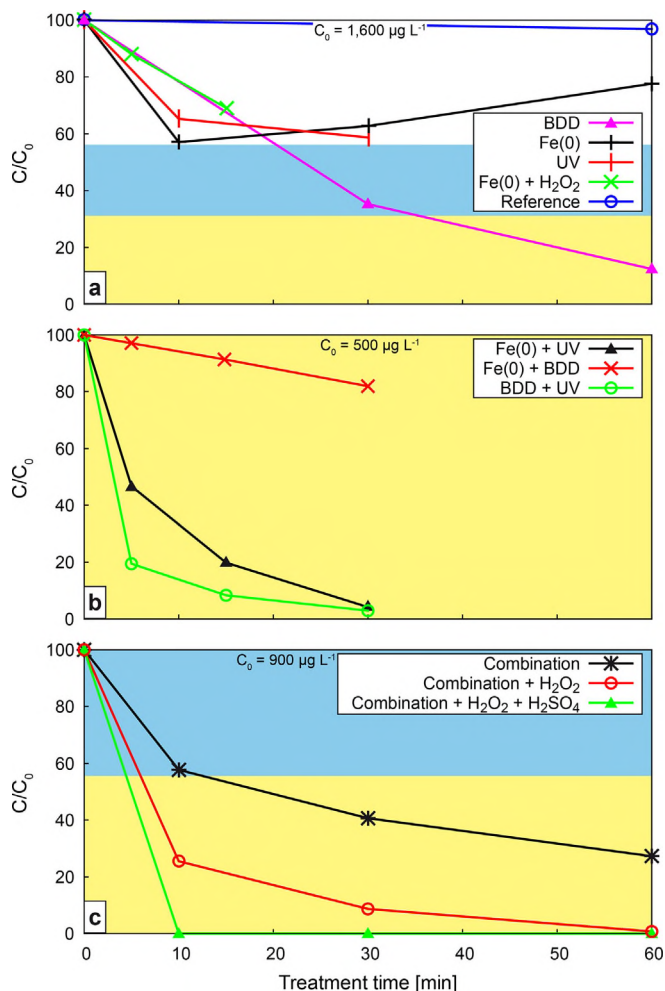


Fig. 3. Degradation of clopyralid during experiment 1 (a; $C_0 \sim 1600 \mu\text{g L}^{-1}$), experiment 2 (b; $C_0 \sim 500 \mu\text{g L}^{-1}$) and experiment 3 (c; $C_0 \sim 900 \mu\text{g L}^{-1}$). Different background colors represent concentration ranges (yellow: 0–500 $\mu\text{g L}^{-1}$, blue: 500–900 $\mu\text{g L}^{-1}$ and white: 900–1600 $\mu\text{g L}^{-1}$).

structure compared to aliphatic tetrachloroethene and MTBE. For clopyralid, part of the degradation mechanism is the oxidative ring opening which is enhanced by adding the H₂SO₄, whereas the oxidative appealing acid H₂SO₄ was not required for the destruction of the chemical structure of tetrachloroethene or MTBE.

3.4. Efficiency evaluation

Most of the concentration curves are characterized by a, more or less, strong concentration degradation at the beginning of the treatment, followed by a stagnation of this decay, consequently, the curves can be described as an exponential decay with different reaction rates. However, some exceptions occurred. By using Fe(0) + BDD for the clopyralid containing water (Fig. 3b), a linear concentration decrease was observed. The decrease of tetrachloroethene and MTBE by using H₂O₂ (Figs. 1b and 2b) seems not to be exponentially, however, predicting the further degradation is not possible due to stopping the experiment after 30 min when the concentrations were still relatively high. The same was also the case for degradation of clopyralid in the overhead shaker with Fe(0) and H₂O₂ (Fig. 3a). By applying the treatment methods alone on the MTBE- and clopyralid-containing sample, the efficiency is rather limited (Figs. 2a and 3a).

Altogether, it was shown that the single treatment methods work, but not very effective. Fe(0) in combination with H₂O₂ in an overhead shaker works to a certain degree, but it is not able to reduce the concentration to a satisfying level. The reductive abatement solely by Fe(0) in the fluidized bed reactors is the least efficient method. The degradation of tetrachloroethene and MTBE by H₂O₂ is also not very efficient.

However, combining two methods and addition of H₂O₂, exploited synergy effects, yielding a significant efficiency enhancement.

The contaminant removal by using the combination of the three treatment methods is not very effective for MTBE and clopyralid, besides, the experiment with tetrachloroethene revealed promising results. The addition of H₂O₂ or H₂O₂ + H₂SO₄ increased the efficiency in any case.

The experiments show that the injection of H₂O₂ has an immense impact on the removal rates of the selected contaminants. These results indicate that the desired production of H₂O₂ by the BDD treatment is not sufficient by using this electrode size and power and the optimum ratio of Fe(II) to H₂O₂ for supporting the Fenton reaction was not achieved without injecting additional H₂O₂ to the system. A change to an acidic pH (H₂SO₄ addition) supports degradation in any case.

In most cases, the treatment methods led to an exponential decrease in contaminant concentration. Consequently, the treatment is much more efficient at higher concentrations. Fig. 4 displays the absolute contaminant abatement for the lowest concentration ranges (yellow background of Figs. 1–3).

In order to compare the different treatment methods in the specific low concentration range, the degradation curves were shifted to the left until they intersect time 0, if they enter the lowest concentration range for a particular contaminant (yellow background of the diagrams). Results are presented in Fig. 4, including relevant thresholds for the contaminants.

By comparing the treatment methods in the low concentration ranges, following conclusions can be drawn: the combination of all three treatment methods with addition of H₂O₂ and H₂SO₄ is most efficient and all concentrations are below the corresponding thresholds. For clopyralid (Fig. 4c), the concentration decreased faster by using the UV irradiation in combination with the BDD or Fe(0) compared to the combination with addition of H₂O₂. However, the threshold (0.1 $\mu\text{g L}^{-1}$) could only be reached with the combination of all methods using H₂O₂ and H₂SO₄.

The results of the MTBE treatment (Fig. 4b) were similar to those, obtained with the clopyralid sample. Highest depletion rates were achieved by using all three treatment methods with addition of H₂O₂ and H₂SO₄. The effectivity of treating the water with the combination of all three methods and the addition of H₂O₂ is comparable to treating the water by using the UV irradiation in combination with H₂O₂ and the BDD or Fe(0). Both thresholds (5 and 15 $\mu\text{g L}^{-1}$) were reached by these methods, however, the combination (three methods) with H₂O₂ injection works better at higher concentrations, whereas rather low MTBE concentrations decrease faster by using the UV irradiation in combination with H₂O₂ and the BDD or Fe(0).

Fig. 4a clearly shows that the abatement of tetrachloroethene in the range below 60 $\mu\text{g L}^{-1}$ is more sensitive than for the other contaminants. Both thresholds (6 and 10 $\mu\text{g L}^{-1}$) were reached by using the BDD and UV light alone, in any combination of two treatment methods, as well as by the combination of the three methods alone and with addition of H₂O₂ (and H₂SO₄). As for the other contaminants, the best efficiency was obtained by adding the chemicals H₂O₂ and H₂SO₄ to the treatment with the combination of all three methods, however, the effect of adding H₂SO₄ to the system is not as significant as for the other contaminants.

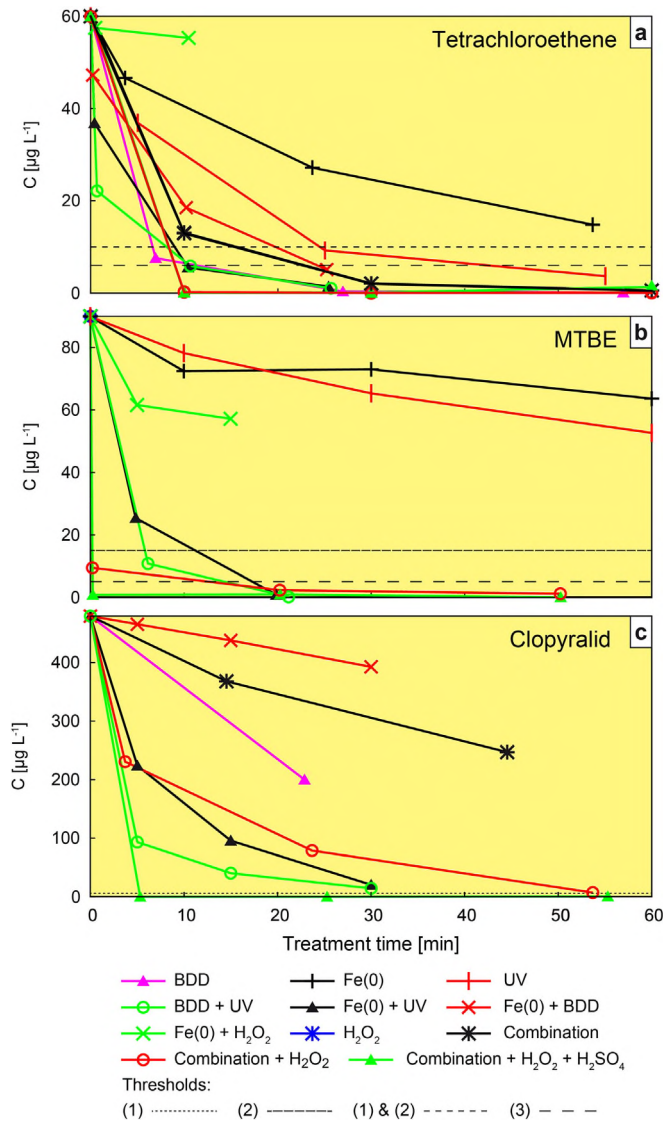


Fig. 4. Absolute concentration decrease curves after the lowest C_0 values of the corresponding contaminant were reached (yellow diagrams of Figs. 1–3). The curves are normalized to time 0 (= shifted to the left). Thresholds: (1): Drinking water ordinance (Bundesminister für soziale Sicherheit und Generationen, 2001), (2): Altmayer et al. (2004) and (3): ÖNORM S 2088-1.

4. Conclusions

The experiments showed that using a combination of the BDD, Fe(0) and UV irradiation with addition of H_2O_2 and H_2SO_4 is a very effective and non-selective treatment method. Given thresholds for tetrachloroethene, MTBE and clopyralid were reached in all samples. Nevertheless, good degradation rates were also obtained without H_2SO_4 addition and also by using UV irradiation in combination with the BDD or Fe(0). Applying the treatment methods alone yielded a decrease in the organic contaminant concentrations, but it was not sufficiently effective except for treating tetrachloroethene by the BDD. In case of clopyralid degradation, a combination of all methods and addition of H_2O_2 (and H_2SO_4) was superior to the sole use of the BDD. These results reveal the high potential of combining the different treatment methods and consequently occurring synergy effects, also with regard to metabolite decomposition.

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