Optimization of Soil Aquifer Treatment by Chemical Oxidation with Hydrogen Peroxide Addition

Usman, M[1*]., Waseem, M[2]., Mani, N[3]. and Andiego, N[4].

1. Institute of water resources and water supply, TUHH Hamburg, Germany

2. Faculty of agriculture and environmental sciences, Universität Rostock, Germany

3. Sahasrara Earth services & Resources Ltd, Coimbatore, India

4. Water resources and environmental services department, Nairobi, Kenya

ABSTRACT: Trace organic compounds (TrOCs), mostly found in secondary effluents have a potential impact on the environment including surface water, groundwater and especially aquatic ecosystems. This study focuses on oxidation of five selected TrOCs in column experiments simulating soil aquifer treatment (SAT) integrated with Fenton like reaction using granular ferric hydroxide (GFH) as a catalyst. In order to determine the effectiveness of removing TrOCs by water through this approach, experiments were carried out with ultrapure water containing different target compounds at pH 6 using different dosages of hydrogen peroxide and catalyst. In this study the optimal concentration of hydrogen peroxide for removal of TrOCs was found to be 200 mg/L. However, observed overall removal was low for each target compound. Moreover, little increase in chemical oxidation of micropollutants was observed by increasing dosage of the catalyst. For an optimum concentration of hydrogen peroxide the removal of 33, 34, 28, 29 and 35% were observed for benzotriazole, carbamazepine, phenytoin, primidone and meprobamate, respectively in 5h with a hydraulic retention time of 3h, respectively. Therefore, this treatment scheme might not be a promising option for oxidation of secondary effluents. Thus, other treatment options, such as decrease of pH, recirculation of effluent through columns to increase the hydraulic retention times, other types of catalyst and higher dosage of hydrogen peroxide need to be considered for more efficient removal of TrOCs within SAT integrated with Fenton-like.

Keyword: Chemical oxidation, Fenton-like reaction, Trace organic compounds, Soil aquifer treatment. Removal.

INTRODUCTION

Urbanization is raising domestic, agricultural, and industrial water demands, while shrinking available water resources. Urbanization and industrial expansion may exert severe anthropogenic environmental impact on surface water, leading to contamination with a wide range of trace organic compounds (TrOCs) (Schmidt et al., 2007). Furthermore, population growth and higher living standards throughout the world is raising the demand for freshwater resources. As a result, more weight has been placed on planned reuse of wastewater treatment plants (WWTPs) effluents (Snyder et al., 2004). TrOCs includes

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pharmaceuticals and personal care products (PPCPs), flame retardants, pesticides, and endocrine disrupting compounds (EDCs). Conventional wastewater treatment processes are not capable enough to completely remove TrOCs from water, entering a treatment facility (Daughton and Ternes, 1999). Effluents from WWTPs are major source of TrOCs, especially PPCPs in environment including surface and groundwater due to their incomplete removal with unspecific treatment methods (Bartelt-Hunt et al., 2009; Jurado et al., 2012; Eggen and Vogelsang, 2015 and Ávila and García, 2015). Jelic et al., (2011) mentioned that even the WWTPs, which meet the regulatory requirements for wastewater treatment (Directive 91/271/EEC), have limited efficiency concerning removal of pharmaceutical compounds. TrOCs compounds induce aquatic toxicity even at very low concentrations (Daughton and Ternes, 1999). Among TrOCs, PPCPs are considered as an emerging environmental problem due to their continuous input and persistence in the aquatic ecosystem even at low concentrations (Mohapatra et al., 2014). In addition, conventionally-treated wastewater, usually known as secondary effluent, has been used for irrigation purposes that alter the physicochemical and microbiological properties of the soil and/or introduce and contribute to the accumulation of chemical and biological contaminants in soil which pose serious threats to the human and environmental health (Becerra-Castro et al., 2015). Therefore, it is needed to reclaim wastewater while meeting environmental quality standards.

Soil aquifer treatment (SAT) is an advanced wastewater treatment process, both natural and sustainable, which moves as the secondary WWTP effluent through the soil and the aquifer. It can go through significant quality improvements via physical, chemical, and biological processes, which are initially aerobic and subsequently anoxic. SAT is significant potential to remove organic

matter, present in WWTP effluent with a final concentration of 1 mg/L of total organic carbon (TOC) and also has a tendency to remove EDTA (Drewes et al., 2003). It is capable of removing TrOCs such as pesticide, UV blocker, and PPCPs, existing in domestic wastewater, though its performance is compound-specific, wherein some compounds, especially atenolol, cimetidine, and tri-phosphate (TCPP), are more effectively attenuated over time in laboratory experiments (Teerlink et al., 2012). Nham et al., (2015) reported that even TrOCs, so far mostly described as persistent in the literature, i.e., diazepam and primidone attenuated during SAT. Most TrOCs are effectively attenuated during SAT, via biodegradation, sorption, or a combination of these (Quanrud et al., 2003), but the increasing load of TrOCs such as PPCPs in waste and surface waters poses a significant problem for SAT, since some of these compounds are refractory during their subsurface passage. Maeng et al., (2011) studied removal of PPCPs via managed aquifer recharge, and showed that among the target compounds, analysed, carbamazepine (an anticonvulsant) was the most persistent compound, not influenced by the characteristics of different types of organic matter. Different studies reported that carbamazepine is persistent in the environment, and its removal efficiency has been found to be less than 10% in most wastewater treatment plants.

Among the advanced treatment technologies, advanced oxidation processes (AOPs) have been proven most efficient to remove trace concentrations of pharmaceuticals (Michael et al., 2013). In last few decades, AOPs have led to efficient methods for oxidation of natural organic matter and organic pollutant in waters (Sillanpää and Matilainen, 2015). They are categorized by their generation of powerful reactive chemical species, such as hydroxyl radical ($^\bullet$OH), which degrade even the most refractory molecules into biodegradable

compounds or completely mineralize into CO_2 and H_2O (Gogate and Pandit, 2004). AOPs constitute a promising technology for the treatment of wastewaters with non-easily removable organic compounds (Pera-Titus et al., 2004). Among the AOPs, the following techniques have been studied: processes based on hydrogen peroxide (H_2O_2+UV, Fenton, photo-Fenton, and Fenton-like processes), photolysis, photocatalysis, and processes based on ozone (O_3, O_3+UV, and O_3+catalyst). There has been significant interest in the use of AOPs for the treatment of water and wastewater contaminants. The hydroxyl radical has been described to oxidise a range of organic compounds significantly faster than well-established ozonation (Fukushima et al., 2001).

Fenton-based processes, both Fenton and Fenton-like oxidation, are capable of generating reactive radicals, responsible for transformation of organic contaminants, by means of hydrogen peroxide (H_2O_2) and iron salts (Fe^{2+} or/ and Fe^{3+}) directly in the water through chemical transformation. A Fenton-like process that uses solid catalysts, capable of producing oxidants capable of decomposing refractory organic contaminants, provides a favourable alternative for oxidative treatment of polluted water (Xu and Wang, 2012). In this present work, the fate of WWTP effluents during SAT incorporated with Fenton-like process was studied at pH 6 with the main objective to optimize SAT by chemical oxidation of TrOCs which are frequently detected in wastewater affected streams. The lab-scale experiments are carried out with Milli-Q water as an influent, spiked with different target compounds. In this process hydroxyl ($\cdot$OH) radicals are generated through decomposition of hydrogen peroxide in the presence of granular ferric oxide (GFH) as catalyst.

MATERIALS AND METHODS

Five target compounds, namely meprobamate, carbamazepine, primidone, phenytoin, and benzotriazole that are commonly detected in WWTP effluents, were selected in this study. All laboratory experiments were conducted using Milli Q-water mixed with TrOCs and variable concentration of H_2O_2. The objective of this study was to improve the SAT efficiency with regard to TrOC removal, thus ultrapure water with constant concentrations of TrOCs was spiked to eliminate the extra complexity of water matrix, including bacteria, scavengers, and promoters, as all of these parameters may either affect oxidation or induce biodegradation. These target compounds were chosen to spike into the Milli Q-water at a pre-determined concentration of 23 µg/L for each compound. To avoid any biotransformation of target compounds in influent and effluent, all samples were stored in refrigerator (<4 °C).

All experiments were conducted in lab-scale columns, with inner diameters of 2 cm and lengths of 35 cm. All experiments were performed with sand, with 30% of porosity and 0.02 to 0.2 mm in size. A defined amount of sand and GFH as iron oxide mineral was mixed thoroughly before packing the columns, meaning that packed column studies had been conducted. The base of each column was well equipped with a screen to avoid loss of sand media and clogging of effluent line.

A peristaltic pump was used to pump feed water continuously to the system through silicon tubing. Experiments were run in down flow mode. Initially the system was operated for 24 h with a hydraulic loading rate of 15 mL/h to achieve the breakthrough point for all selected micro-pollutants. In order to accomplish breakthrough point, the concentration of each TrOC in influent was pre-set as 23 µg/L. The breakthrough point for all selected micro-pollutants occurred at almost 3.14 Bed Volume (BV_T). Once the breakthrough was achieved, H_2O_2 was introduced into the system with influent micro-pollutants. As aforementioned, four
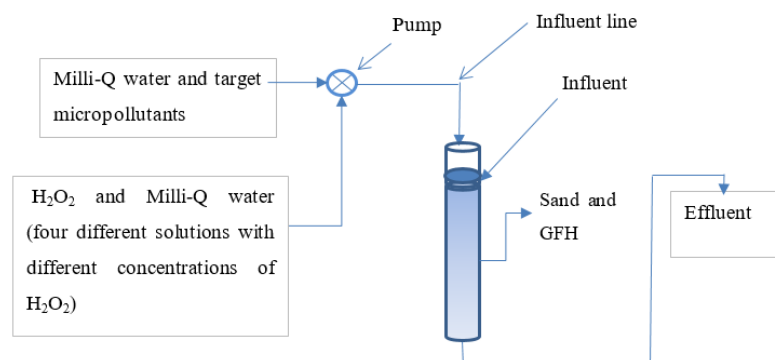
Fig. 1. Configuration of column studies for experiments after achieving a breakthrough

different concentrations of H_2O_2 along with one control/reference without H_2O_2 were selected to check the optimum concentration of H_2O_2 for selected TrOCs. These four concentrations were prepared with deionized water in four different containers and all selected TrOCs in one separate container. In this case, the influent was a combination of different H_2O_2 concentrations and TrOCs. Hence, the concentration of each TrOC was reduced from 23 µg/L to 11.5 µg/L after dilution with four different H_2O_2 solutions. Figure 1 shows the experimental setup. Afterwards, the system was run again for a treatment time of 5 h. Hydraulic loading rate was kept constant, equal to 15 mL/h. Each experiment was conducted in triplicate, using four different columns operating in parallel. All experiments were conducted under saturated conditions. The same procedure was adopted to investigate the effect of GFH dosage with the exception of BVT. It was increased from 3.14 to 7.86 to achieve the breakthrough point for all selected micro-pollutants at higher dosages of GFH; however, the breakthrough point was not achieved for benzotriazole.

The transition metal iron (Fe) has been widely studied in the form of single or supported metal oxide, showing its ability to improve total organic carbon removal by promoting hydroxyl radical's formation. In the present study, GFH (GEH), supplied by Wasserchemie Germany, was used as a heterogeneous catalyst. Heterogeneous Fenton processes attract much attention, because most of the used iron, leftovers in the solid phase, can be reused (Sable et al., 2015).

Four different feed water qualities with different H_2O_2 concentrations were chosen for TrOCs oxidation experiments. Each feed water, comprised of Milli-Q water, target compounds, and chosen concentration of hydrogen peroxide (Table 1), was prepared by pipetting required amount of H_2O_2 and pouring into a container. For comparison purposes, reference column (To) was fed with the solution which contained no H_2O_2 to quantify the effects of sorption and biodegradation and remaining (T_1, T_2, and T_3) was fed with the solution having different concentration of H_2O_2.

Table 1. Experiments with constant GFH in each column with varying H_2O_2 concentrations

Treatments	Column filling by sand and GFH	Influent	
		H_2O_2 (mg/L)	TrOC
T_0 (reference)	Each column filled with 90 % sand and 10 % GFH up to 35 cm height.	0	Spiked concentration of each target compound was 23 µg/L. The concentration of each TrOC was reduced from 23 µg/L to 11.5 µg/L after introduction of H_2O_2 solution.
T_1 (50 mg/L H_2O_2)		50	
T_2 (100 mg/L H_2O_2)		100	
T_3 (200 mg/L H_2O_2)		200	

Table 2. Experiments with variable amounts of GFH in each column with constant H_2O_2 concentration of 100 mg/L and 200 mg/L

Treatments	Amount of GFH in column (%)	H_2O_2 (mg/L)	Influent TrOC
T_0 (reference)	0	100/200	Spiked concentration of each target
T_1	10	100/200	compound was 23 µg/L. The
T_2	30	100/200	concentration of each TrOC was
T_3	50	100/200	reduced from 23 µg/L to 11.5 µg/L after introduction of H_2O_2 solution.

To investigate the effect of different GFH dosages on removal efficiency and/or fate of TrOCs, experiments with varying dosage of GFH and constant concentration of H_2O_2 in each column was carried out with the reference column having no GFH (To), as shown in Table 2.

Time-composite samples were taken from the effluent of all four columns and stored at 4 °C in plastic sampling bottles. Five samples from each column effluent were regularly taken every 30 min during the entire treatment time of 3 h to 5 h and one influent sample was taken for each column. To minimize any potential losses due to degradation in the storage container, the stock solution of each TrOC was kept at 4° C.

The quantification of TrOCs compounds was performed, using liquid chromatography with tandem mass spectrometry (LC-MS/MS), similar to the method described by (Trenholm et al., 2009). This analytical technique combines physical separation capabilities of liquid chromatography with mass analysis and separation capabilities of tandem mass spectrometry, having very high sensitivity and selectivity. An Ultra-High-Performance Liquid Chromatography (UHPLC) system (PLATINblue UHPLC, Knauer Wissenschaftliche Geräte GmbH), coupled with an AB Sciex QTRAP 5500 mass spectrometer (MS) (Applied Biosystems), was used for compound quantification. The chromatographic column was an ACQUITY UPLC HSS T3 1.8µm 2.1x30mm (Waters®). All selected compounds were measured in positive electrospray ionization (ESI) mode.

Approximately 100 µl/ml of all target compounds internal standards were added to the eluate and used for quantification. Mobile phases for measurements in ESI positive mode were 4 mM ammonium formate in water containing 0.1 % formic acid and 4 mM ammonium formate in acetonitrile containing 0.1 % formic acid. In ESI positive mode a gradient method was used to deliver the mobile phases.

H_2O_2 concentration in influents and effluents was measured by I_3^- method, described by Klassen et al. (1994). Concentration of H_2O_2, being as low as 1 µM, can be measured conveniently by this method, which is based on spectrophotometric determination of I_3^- formed when H_2O_2 is added to a concentrated solution of iodine. Both potassium iodide (KI) buffer (Solution A), consisted of KI, sodium hydroxide (NaOH), and ammonium molybdate, and potassium hydrogen phthalate buffer (Solution B), consisted of potassium hydrogen phthalate, were prepared. Solutions A and B got mixed in equal volumes. Afterwards sampled H_2O_2 was added to this mixture and the solution samples got diluted to achieve an absorbance reading of ~0.9 by photometer.

RESULTS AND DISCUSSION

The effect of H_2O_2 concentration on the rate of oxidation of TrOCs ([TrOC] = 11.5 µg/l) by Fe(III)/H_2O_2 was investigated over a wide range of concentrations of H_2O_2 (1.47 mM – 0.587 mM or 50-200 mg/L), at pH = 6.0 so that optimum H_2O_2 concentration could be detected for this

process. In this experiment, all four columns operated at loading rates of 15 mL/h for a treatment time of 5 h, which involved a hydraulic retention of 3 h.

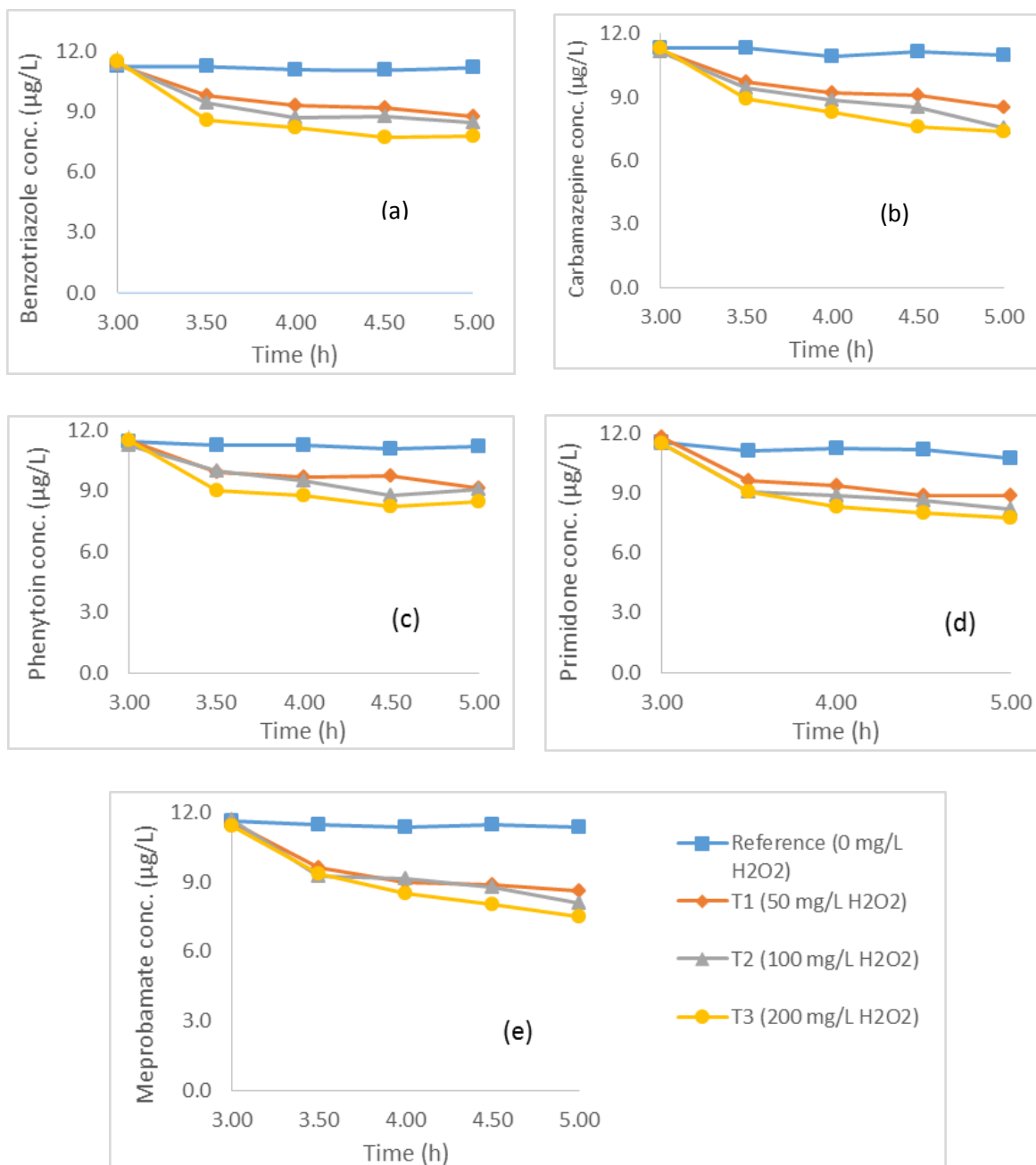Figure 2 shows the results of TrOCs concentration in treated water, measured periodically.

Fig. 2. Effluent concentration of (a) benzotriazole, (b) carbamazepine, (c) phenytoin, (d) primidone, and (e) meprobamate over time with H_2O_2 concentrations of 0, 50, 100, and 200 mg/L. The average effluent concentration was measured for 3 h (as the hydraulic retention time) until the completion for all experiments with constant GFH in each column and varying H_2O_2 concentrations, for which the average was used from triplicate experiments (n=3).

Results indicate that oxidation occurred in three columns, receiving H_2O_2 as an oxidizing agent, as the reference column did not show any TrOC oxidation. Figure 2 shows that the experiment was incomplete during the 5 hours of the treatment time, yet it was about to get completed, since a steady state effluent concentration can be observed at 5 h, meaning very small oxidation of all selected micro-pollutants from 4.5 h to 5.0 h of the treatment time.

All five target compounds were found in the treated water with variable levels. Figure 2 illustrates the observed average influent and effluent concentration of the selected TrOCs. Although the greatest changes to influent quality are expected to be originated from oxidation with ˙OH radical (Venny et al., 2012), additional removal may be possible along flow paths due to bio-filteration. As a parcel of water moves through the column, the chemical traits of water changes, because the ˙OH radical is a very strong oxidizing agent, as mentioned earlier. Due to the formation of ˙OH radical, there was a significant removal of the selected TrOCs, which can be seen in Figure 3. The removal efficiencies stood higher than 20 to 35% for all selected compounds.
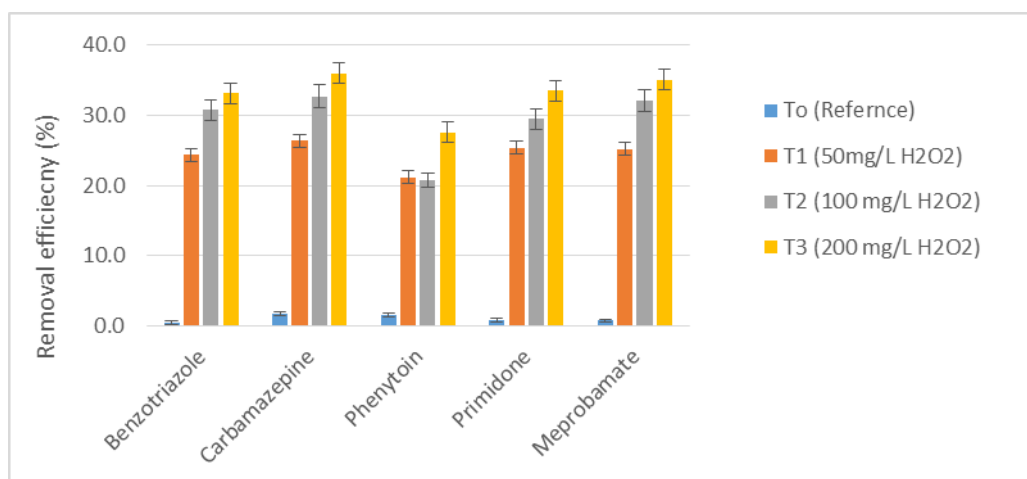

Fig. 3. Removal of all selected TrOCs as a function of different H_2O_2 concentrations (0, 50, 100, and 200 mg/L) at 5 h. The rates are the average from triplicate experiments (n=3).

Among all tested H_2O_2 concentration, 200 mg/L is the one to result in the highest degree of degradation for all selected TrOCs, followed by 100 mg/L and 50 mg/L, respectively. More ˙OH radicals might have been produced at higher H_2O_2 concentrations. Phenytoin (8.46 ± 1.38 μg/L) and primidone (8.18 ± 0.41 μg/L) were detected in the effluents at 5 h with relatively higher concentrations than other target micro-pollutants, whereas benzotriazole (7.78 ± 0.71 μg/L), meprobamate (7.48 ± 0.88 μg/L), and carbamazepine (7.40 ± 0.16 μg/L) had the lowest concentrations. The removal efficiencies for benzotriazole, carbamazepine, phenytoin, primidone, and meprobamate were 33%, 36%, 28%, 33%, and 35%, respectively. The removal efficiencies for carbamazepine and meprobamate turned out to be higher, compared to those of other target micro-pollutants (33% benzotriazole, 28% phenytoin, and 33% primidone). The rate constants for reaction with hydroxyl radicals ($K_{˙OH}$) were as the following: 7.6×109 M^{-1} s^{-1} for benzotriazole at pH = 5.8 (Naik and Moorthy, 1995), $(6.7 \pm 0.2) \times 109$ $M^{-1} \cdot s^{-1}$ for primidone (Real et al., 2009), and 8.8×109 M^{-1} s^{-1} for carbamazepine (Huber et al., 2003). Available literature data showed that carbamazepine, benzotriazole and

primidone are fast reacting compounds; however, these compounds were partially removed. Therefore, their removal was not in line with their rate constants. Up to 35% attenuation of all target compounds were observed at 5 h with optimum H_2O_2 concentration of 200 mg/L, and 10% GFH as catalyst in every column. This removal was due to pure oxidation with ˙OH radical, which could be enhanced by biodegradation if columns were seeded with a secondary effluent to develop the biological activity. As reported by Abel et al., (2013), more than 80% removal efficiency was observed in hydrophobic ionic compounds with the highest biological activity.

In order to study the effect of catalyst loading on oxidation of all target compounds, except benzotriazole, through Fenton-like process, some experiments were carried out, using 100 mg/L and 200 mg/L H_2O_2 as well as different dosages of GFH (10–50% of total sand mass) at room temperature. Figure 4 demonstrates chemical oxidation profiles of these compounds in reaction to both 100 mg/L and 200 mg/L H_2O_2.
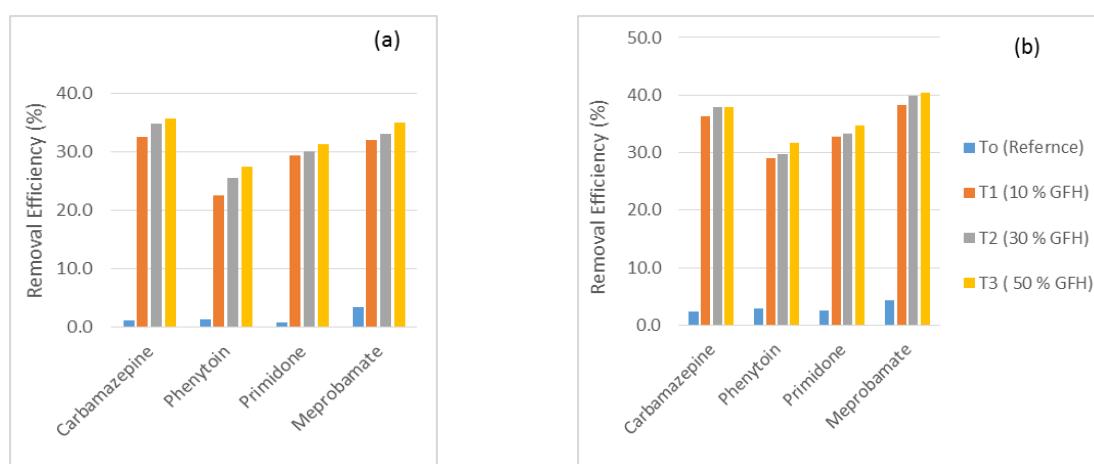

Fig. 4. Effect of different dosages of GFH on chemical oxidation of all selected TrOCs with (a) 100 mg/L H_2O_2 and (b) 200 mg/L H_2O_2, having different amounts of GFH in each column, (n=1)

Even by increasing the concentration of GFH as the catalyst in column sand mass from 10% to 30% and from 10% to 50% with H_2O_2 concentrations of 100 mg/L and 200 mg/L, removal efficiency for all selected micro-pollutants was almost the same as the case wherein GFH was merely 10% of total sand mass in the column. This means that by further increasing the catalyst concentration (to 30% and 50% of total sand mass), there was no further enhancement in TrOCs degradation. From this experiment, it can be stated that H_2O_2 concentration is the limiting parameter for oxidation of all selected micro-pollutants.

Decomposition of H_2O_2 can be catalysed with enzymes. This reaction is very fast, producing water and dissolved oxygen, as shown in the following Equations 1 and 2. This mechanism has been discussed for bioremediation of contaminated soils, with its main problem being the excessive loss of H_2O_2 in the surroundings of injection wells. Coupled with the fact that iron can exist in two different oxidation states, i.e., Fe^{2+} and Fe^{3+}, it allows the catalyst to break the reaction into two different redox steps, each with a lower energy barrier to completion than the non-catalysed reaction:

$$H_2O_2 + 2Fe^{3+} \rightarrow O_2 + 2Fe^{2+} + 2H^+ \tag{1}$$

$$H_2O_2 + 2Fe^{2+} + 2H^+ \rightarrow 2H_2 + 2Fe^{3+} \tag{2}$$
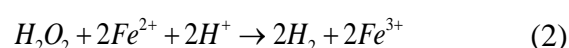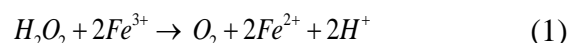
Note that the first step in the catalysed reaction involves reduction of the ferric ion (Fe^{3+}) to the ferrous ion (Fe^{2+}), which is

then re-oxidized to ferric ion in the second step. Hence, on net, the catalyst is not consumed in the course of decomposition. Iron is not the only possible catalyst for this reaction. Since H_2O_2 is biologically harmful, a number of enzymes, large protein molecules that catalyse biologically-important reactions, also catalyse this reaction.

Some solutions of hydrogen peroxide with different concentration were applied to the sand columns, containing TrOCs, and the concentration of hydrogen peroxide was measured in the samples including both influents and effluents of the columns. Under experimental conditions, H_2O_2 partially oxidized the TrOCs (approximately 35%) in sand columns in the presence of GHF as catalyst. Column studies demonstrated that H_2O_2 decomposed very rapidly, while interacting with GFH as an external source of iron mineral. The study underscored the fact that H_2O_2 may react with GHF to produce hydroxyl radical, likely to serve as an oxidizing agent for micro-pollutants. Benzotriazole, carbamazepine, primidone, phenytoin, and meprobamate were used as indicator compounds in this study. Table 3 gives the results of H_2O_2 consumption in the experiments.

Table 3. Measured periodic consumption of H_2O_2 during the experiments for constant dosage of GFH and varying concentration of H_2O_2

Column Nr.	Influent conc. (mg/L)	Effluent concentration of H_2O_2 (mg/L) at				
		E1@ 3:00 h	E2@ 3:30 h	E3@ 4:00 h	E4@ 4:30 h	E5@ 5:00 h
1 (T_o)	0	0	0	0	0	0
2 (T_1)	50	0.8	0.5	0.4	0.3	0.2
3 (T_2)	100	1.0	0.9	1.1	0.6	0.5
4 (T_3)	200	3.2	1.9	1.7	0.6	0.0

CONCLUSION

The study system, SAT integrated with Fenton-like reaction, has the ability to oxidize the selected TrOCs, for no oxidization of all micro-pollutants was observed in all reference columns. All columns receiving H_2O_2 attenuated all target compounds even at low concentrations of H_2O_2. This is due to chemical oxidation with ˙OH radical, as no chemical oxidation was observed in reference columns. However, observed oxidation of selected TrOCs was low even at higher dosage of 200 mg/L H_2O_2. Based on present study, it can be concluded that this system is not a promising technology, for all TrOCs attenuated to up to 35% with H_2O_2 concentration of 200 mg/L and GFH dosage of 10% in 5 h. A parametric study was also conducted, using different dosages of GFH in Fenton-like reaction for degradation of all selected TrOCs; however, higher dosages of GFH proved to be capable of improving the performance a little bit. The removal efficiencies, achieved at H_2O_2 concentration of 100 mg/L and GHF dosage of 50%, was limited to 35.8%, 27.5%, 31.4%, and 35.1% and to 37.9%, 31.6%, 34.8%, and 40.4% at H_2O_2 concentration of 200 mg/L (with the same catalyst dosage), for carbamazepine, phenytoin, primidone, and meprobamate, respectively. Therefore, it can be concluded that H_2O_2 is a limiting parameter for system. The removal efficiency of this system for micro-pollutants might be enhanced by conducting experiments at a lower pH rate, found by different studies to be optimum for Fenton-based reactions. Other possible solutions for higher removal of TrOCs could be an increase of hydraulic retention time via recirculation of column effluent through a series of two to three columns as well as changing the type of the iron source. Generally, SAT provides oxic conditions, followed by anoxic conditions. Many TrOCs, mostly biodegradable compounds, can be reduced to groundwater in the meantime. In this way, all TrOCs, including

both biodegradable and persistent ones, could be removed efficiently and economically. Moreover, this system can be included in a multi-barrier treatment system for removal of TrOCs in water treatment, as part of indirect non-potable reuse schemes.

Acknowledgments

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