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The fate of H_2O_2 during managed aquifer recharge: a residual from advanced oxidation processes for drinking water production

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ABSTRACT

The fate of H_2O_2 residual from advanced oxidation process (AOP) preceding managed aquifer recharge (MAR) is of concern because H_2O_2 could lead to undesired effects on organisms in the MAR aquatic and soil ecosystem. The objective of this study was to distinguish between factors affecting H_2O_2 decomposition in MAR systems, simulated in batch reactors with synthetic MAR water and slow sand filter sand. The results showed that pure sand and soil organic matter had no considerable effect on H_2O_2 decomposition, whereas naturally occurring inorganic substances on the surface of sand grains and microbial biomass are the two main factors accelerating H_2O_2 decomposition in MAR systems. Additionally, the results showed that the H_2O_2 decompositions with different initial concentrations fitted first-order kinetics in 2-6 hours in a mixture of slow sand filter sand (as a substitute for sand from a MAR system) and synthetic MAR water with high bacterial population. An estimation indicated that low concentrations of H_2O_2 (<3 mg/L) could decompose to the provisional

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standard of 0.25 mg/L in the first centimeters of MAR systems with the influent water containing high microbial biomass 38 ng ATP/mL.

Keywords: Managed aquifer recharge, Advanced oxidation process, H_2O_2 residual, H_2O_2 decomposition factors, Drinking water production

1. Introduction

Managed aquifer recharge (MAR), such as river bank filtration, dune infiltration and artificial recharge, is a natural water treatment process that induces surface water to flow through soil/sediment and into a vertical or horizontal well (Maeng et al., 2011; Tufenkji et al., 2002). This treatment process is robust and cost-effective and is frequently applied in Europe (Van der Hoek et al., 2014). For example, in the Netherlands and Germany, water utilities using MAR as a water treatment process supply drinking water without chlorination as disinfection process (Lekkerkerker, 2012; Maeng, 2010). Previous research demonstrated that the combination of advanced oxidation process (AOP) and subsequent MAR is a potential treatment system to remove various organic micropollutants (OMPs) during drinking water production (Lekkerkerker-Teunissen et al., 2012; Lekkerkerker et al., 2009; Oller et al., 2011). A disadvantage of applying AOP with O_3 is the formation of bromate during oxidation of bromide containing waters. In order to reduce the formation of bromate which has been designated as carcinogenic to humans (Kurokawa et al., 1990), H_2O_2 should be dosed excessively (Knol, 2012; Von Gunten and Oliveras, 1998; Wert et al., 2007). Consequently, the MAR infiltration water may contain residual concentrations of H_2O_2.

A number of studies about H_2O_2 decomposition in aquatic ecosystems and soil ecosystems have focused on biotic factors, such as bacteria (Richard et al., 2007; Zappi et al., 2000) and other microorganisms (Cooper and Lean, 1989; Richard et al., 2007) and abiotic factors, such as iron (Moffett and Zafiriou, 1993; Wilson et al., 2000), manganese (Do et al., 2009; Häkkinen et al., 2004; Russo et al., 2013), transition metals (Lousada and Jonsson, 2010; Moreno et al., 2011), lanthanide oxides (Lousada et al., 2013) and iodide (Wong and Zhang, 2008). H_2O_2 decomposition in water also has been reported (Cooper and Lean, 1989; Moffett and Zafiriou, 1993; Richard et al., 2007; Wilson et al., 2000). The results of Schumb (1949) showed that manganese and iron were extremely reactive with concentrated H_2O_2 solutions. Also, H_2O_2 decomposition studies have been conducted in metal- or DOC-rich waters (Chiritã, 2009; Wilson et al., 2000). Previous research found that a large fraction of H_2O_2 loss in both a fresh water system and soil was attributable to biotic mechanisms. Richard et al. (2007) found that biologically based reactions (i.e., catalase) were the primary mechanism for H_2O_2 decomposition in a shallow fresh water system in New Zealand. It was observed from the literature of Zappi et al. (2000) that the first-order rate constant of biotic reactions was always much higher than that of abiotic reactions for H_2O_2 decomposition in various soils with different calcium, iron, manganese, TOC and phosphorus contents. It is clear that the fate of H_2O_2 in aquatic systems has been investigated comprehensively, and a few studies focused on the reactions of H_2O_2 with natural-occurring constituents in soil (Bissey et al., 2006; Miller and Valentine, 1999). These publications investigated the stability of H_2O_2 as the oxygen source for bioremediation activities in soil, because of several potential interactions of H_2O_2 with various soil constituents and its potentially fast decomposition. Studies of Morgan and Watkinson (1992) and Schumb (1949) reported reaction of H_2O_2 with naturally occurring stabilizers, such as tripolyphosphate, MnO_4^- and Cu^{2+} within soils. Bissey et al. (2006) investigated the interactions between catalyzed H_2O_2 propagations and soil organic matter (SOM) within surface soil and reported that the H_2O_2 decomposition rate decreased with the increase of SOM at neutral pH. Miller and Valentine (1999) examined mechanisms and kinetics of abiotic H_2O_2 decomposition in the presence of sand collected from an aquifer and a riverbed. However, more understanding is needed to determine the fate of H_2O_2 in MAR systems specifically. High concentrations of H_2O_2 can cause damage to cell membranes and have deleterious effects on biological systems (Ananthaswamy and Eisenstark, 1976; Collén and Pedersén, 1996; Wong et al., 2003). Schmidt et al. (2006) concluded that H_2O_2 minimum inhibitory concentration (MIC) to the most sensitive bacteria species *Psedomonas aeruginosa* was 5.1 mg/L. The study of Urfer (1998) demonstrated that the continuous presence of around 1 mg/L H_2O_2 did not lead to a major inhibition of the biological removal of acetate and formate in a lab-scale sand drinking water biofilter. Knol (2012) stated that even very low concentrations of H_2O_2 could lead to undesired destruction of organisms in MAR infiltration ponds and he mentioned a provisional standard of 0.25 mg/L H_2O_2 for MAR infiltration water. Consequently, an improved understanding of the fate of H_2O_2 in MAR systems would be essential to see whether this provisional standard or lower concentrations can be reached.

The objective of this study was to distinguish between different factors affecting H_2O_2 decomposition in MAR systems. The general approach in this study was to divide the aquifer environment into two separate physical compartments (water and sand) that contain naturally existing biological and chemical species that might react with H_2O_2. Batch reactor experiments were conducted to determine the reactions of H_2O_2 with biotic (microbial community in water) and abiotic constituents (pure sand particles, inorganic ions in infiltration water, SOM in MAR sand and naturally occurring inorganic substances coating on sand).

2. Materials and methods

2.1. Materials

The top 0.5-2.0 cm (schmutzdecke) of a slow sand filter (SSF) has diverse microbial communities and greatly contributes to the removal of organic matter by biodegradation processes, so this layer is considered to represent aerobic microbial activity of sand filtration systems (Chekol, 2009; Dizer et al., 2004). The SSF sand in the facilities of drinking water utility Dunea (The Hague, the Netherlands) originated from the dune infiltration area. Consequently, schmutzdecke sand (top of SSF) with natural microbial communities was used in batch reactors as a substitute for the sand in the dune infiltration ponds. As a reference, pure sand (silicon dioxide without any impurities; 1.07711.1000, VWR company) was used. The water for batch reactors was prepared with demineralized water (demi-water) and additive chemicals (33 mg Na_2HPO_4/L, 7.5 mg NaH_2PO_4/L, 22 mg K_2HPO_4/L, 140 mg $CaCl_2$/L, 0.031 mg $FeCl_3$/L, 0.032 mg NH_4Cl/L, 40.75 mg $MgSO_4$/L, 17.823 mg $NaNO_3$/L, 0.00114 mg $MnCl_2$/L, 82 mg CH_3COONa/L) to simulate the water quality at the MAR site of Dunea. The characteristics are presented in Table 1. Based on preliminary experiments, it was found that CH_3COONa (Merck, Germany) was rapidly consumed as the source of DOC in the batch reactors, so 24 mg/L DOC was added in order to have residual DOC in the reactors and avoid bacterial starving conditions. Dosing carbon source to levels exceeding natural MAR systems may lead to higher microbial biomass concentration in batch reactors than in natural MAR systems (Pharand et al., 2014) and enhance the endurance ability to decompose H_2O_2. Therefore, a short inventory was performed based on observed adenosine triphosphate (ATP) concentrations in different waters to estimate the effect of carbon dosage on H_2O_2 decomposition (§ 3.4). The H_2O_2 solutions were prepared from a 30% standard solution (Merck, Germany). All the solutions used in this study were prepared using water from a Millipore Milli-Q system. All chemicals were of AR grade.

Table 1

The quality of MAR influent water in Dunea and synthetic MAR water used in batch reactors.

Parameter	O_2 (mg/L)	pH	NH_4^+-N (mg/L)	NO_3^--N (mg/L)	SO_4^{2-} (mg/L)	Fe^{3+} (mg/L)	Mn^{2+} (mg/L)	DOC (mg/L)
MAR influent water	10.4±1.2	7.9±0.2	0.00997	3.7±0.1	48±2	0.0106	0.001	3.9±0.7
Synthetic MAR water	9±1.0	7.8±0.3	0.00847	2.9±0.1	30.6±2	0.0106	0.0005	22±2

2.2. Batch experimental setup

Batch experiments were performed with 39 glass batch reactors with a volume of 1 L for around 3 months. Batch reactors were filled with 100 g SSF sand and 500 mL synthetic MAR water to simulate MAR systems (Lekkerkerker, 2012; Maeng, 2010). In addition, reference batch reactors were prepared with 100 g pure sand silicon dioxide and 500 mL synthetic MAR water. All batch reactors were placed in a dark room, either temperature controlled (12±0.5 ℃) or ambient temperature (23-27 ℃), depending on the experiment. Batch reactors were uncovered so that air could enter batch reactors to maintain oxic conditions. To avoid anaerobic conditions, the batch reactors were slightly shaken daily without disturbing the biofilm that had developed on the sand.

2.3. Experiments

To divide the aquifer environment into two separate physical compartments (water and sand) that contain naturally existing biological and chemical species that might react with H_2O_2, this study used an experimental set-up as shown in Fig. 1, providing an overview of batch reactors' conditions used in the experiments. All batch reactors were prepared and sampled in triplicate. The performed experiments were divided into:

a) Abiotic: H_2O_2 decomposition under autoclaved conditions (with/without sand)

b) Effect of sand: H_2O_2 decomposition with 200 g, 100 g, and 50 g autoclaved SSF sand

c) Effect of biomass: H_2O_2 decomposition with microbial biomass, 2.74, 1.17, 0.75 and 0 ng ATP/mL

d) Effect of initial H_2O_2 concentrations: H_2O_2 decomposition with 5.0, 3.0, 1.0 and 0.5 mg/L

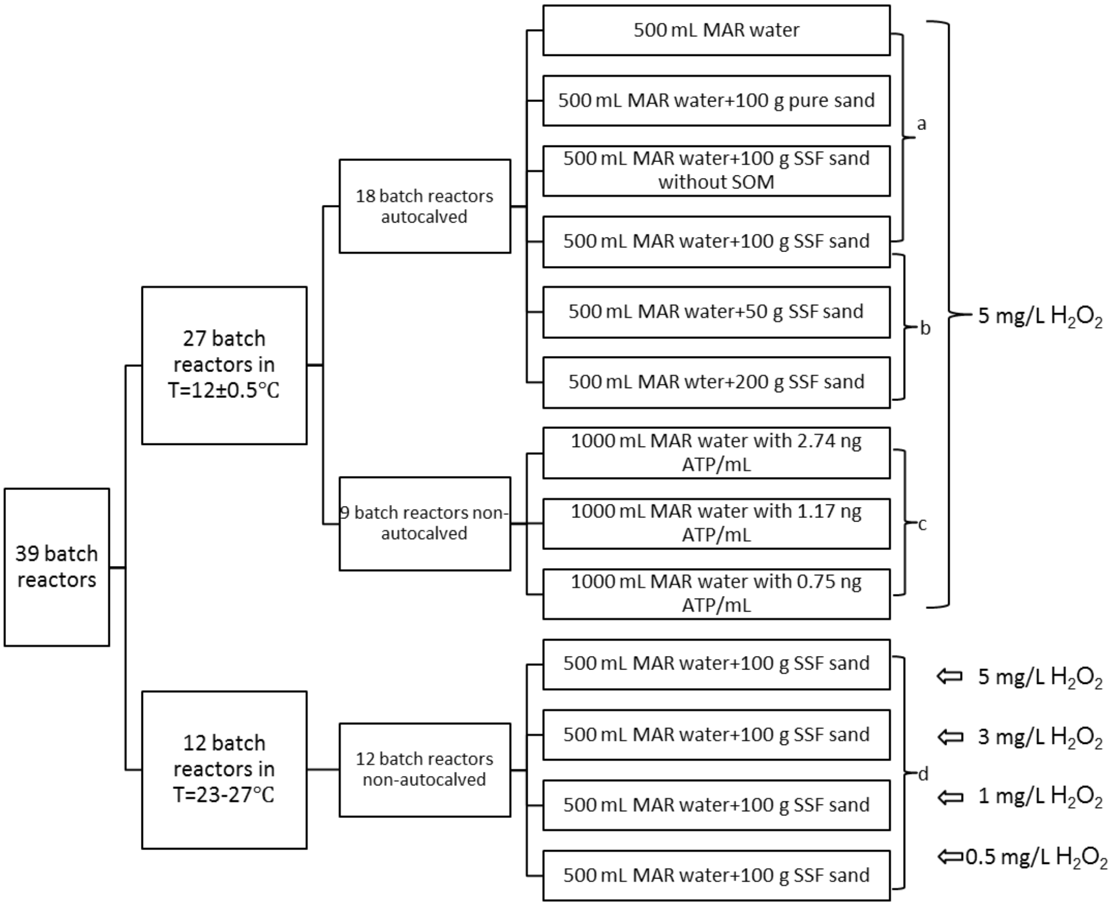

Fig. 1. Batch reactors in triplicate with different treatments (non-autoclaved or autoclaved, 23-27 ℃ or 12±0.5 ℃, 5 mg/L, 3 mg/L, 1 mg/L or 0.5 mg/L dosage).

2.3.1. Abiotic experiments

To distinguish abiotic reactions from biotic reactions of H_2O_2 in MAR, sand (SSF sand, pure sand) and synthetic MAR water were autoclaved at 121 ℃ for 40 minutes to eliminate biological activity. Based on previous study, the enzymatic activity within soil will be completely deactivated by autoclaving (Aggarwal et al., 1991). In this study, ATP was measured in batch autoclaved reactors and was present in the range of 0.04-0.06 ng/mL during the whole experimental process, which indicated that bacteria and enzyme existing in cells and released to water were inactivated by autoclaving. The SOM in SSF sand was removed by heating at 500 ℃ for 2 hours. To further distinguish between the different abiotic decomposition factors of H_2O_2, 500 mL MAR water, 500 mL MAR water+100 g pure sand, 500 mL MAR water+100 g SSF sand without SOM and 500 mL MAR water+100 g SSF sand were put in 12 batch reactors respectively (Fig. 1 series a). 5 mg/L H_2O_2 was dosed into these batch reactors, and H_2O_2 concentration was measured at nine different time points (T=0 h, 1 h, 2 h, 4h, 8 h, 24 h, 48 h, 72 h and 144 h). To further investigate to what extent inorganic content (e.g., metal oxides) on SSF sand impacted H_2O_2 decomposition, the experiment was repeated with different amounts of autoclaved SSF sand (50 g, 100 g and 200 g) and 500 mL MAR water (Fig. 1 series b). 5 mg/L H_2O_2 was dosed into these 9 batch reactors. H_2O_2 concentration was measured at six different time points (T=0 h, 2 h, 8 h, 24 h, 72 h, 144 h). All 18 abiotic batch reactors were placed in a temperature controlled room (12±0.5 ℃).

2.3.2. Biotic experiments

To investigate the relationship of microbial population and H_2O_2 decomposition rate, 5 mg/L H_2O_2 was dosed into 9 batch reactors with different initial microbial population (Fig. 1, series c). MAR water with microorganisms was collected from effluent water of a batch reactor with 500 mL MAR water and 100 g SSF sand in ambient temperature 23-27 ℃. Batch reactors with 2.74 ng ATP/mL contained the effluent above without dilution. Batch reactors with 1.17 ng ATP/mL and 0.75 ng ATP/mL were prepared by dilution with 500 mL and 725 mL demi-water respectively. H_2O_2 concentrations were measured at nine different time points (T=0 h, 4 h, 7 h, 23 h, 30 h, 45 h). The experiments were conducted in a temperature controlled room (12±0.5 ℃).

2.3.3. Different concentrations of H_2O_2

12 batch reactors filled with 500 mL MAR water and 100 g SSF sand were placed in ambient temperature (23-27 ℃) (Fig. 1, series d). Adaptation of the microbial communities on the SSF to the

laboratory conditions was achieved by refreshing water every five days until steady state conditions were reached with respect to DOC removal (Lekkerkerker-Teunissen et al., 2012; Maeng, 2010). Steady state conditions (85% DOC removal) were achieved after two months.

After ripening the reactors, H_2O_2 spiking experiments started. To evaluate H_2O_2 fate, different concentrations of H_2O_2 (5 mg/L, 3 mg/L, 1 mg/L, 0.5 mg/L) were dosed to batch reactors one day after water refreshing. The research of Lekkerkerker (2012) and Knol (2012) showed that 6 mg/L H_2O_2 dosage was enough to form sufficient OH radicals for oxidation in the AOP, so the residual H_2O_2 concentration in effluent water of AOP (being the MAR influent water) will not exceed 6 mg/L. Hence, 0-5 mg/L H_2O_2 was dosed into batch reactors in this experiment. H_2O_2 concentrations were measured at five different time points (T=0 h, 1 h, 2 h, 4 h and 6 h).

2.4. Analysis and measurements

DOC was measured with a Shimadzu TOC analyzer. All samples (30 mL) were measured at constant temperature (20 ℃) after being filtered through 0.45 µm filters (SPARTAN^{TM}, Whatman, Germany) which had been flushed twice with demi-water. Samples were acidified by adding 1.6 mL 2 mol/L HCl (Sigma-Aldrich).

ATP is used in all cells as carrier of free energy and phosphate groups to drive many chemical reactions. ATP plays a key role in metabolic processes in the cells and can therefore be used as a measure for biomass. In this study, ATP was measured as total ATP in the supernatant. ATP was measured using a Quench Gone Aqueous test kit and a LB9509 luminometer (both Aqua tools, France).

Hydrogen peroxide test kits (1.18789.0001, VWR company) with a detection range of 0.015-6.00 mg/L were used for water-phase H_2O_2 measurements because of ease of operation, the rapid decomposition of H_2O_2 and accuracy of results. Since the sand water mixture in this experiment was turbid, 8 mL was pipetted into the reaction cells after being filtered through 0.45 µm filters. After 10 minutes, the sample was transferred to a 10/20 mm rectangular cell and measured in a photometer (Spectroquant NOVA 60).

Based on X-ray diffraction analysis (Department of Materials Science and Engineering, TU Delft), the inorganic constituents of the SSF sand were determined. Table 2 shows the percentages of important metal oxides in SSF sand.

Table 2

The weight percentages of important inorganic constituents other than SiO_2 in SSF sand.

Main inorganic constituents	Weight percentage (%)
Al_2O_3	3.532
Fe_2O_3	0.432
MgO	0.25
TiO_2	0.037
MnO	0.012
ZnO	0.004

3. Results and Discussion

3.1 Abiotic decomposition of H_2O_2 in the presence of SSF sand

Fig. 2 shows the abiotic decomposition of H_2O_2 in the autoclaved batch reactors with and without SSF or pure sand. H_2O_2 in autoclaved MAR water did not decompose in 114 hours (6 days). Also, no H_2O_2 decomposition was observed in the presence of autoclaved pure sand, which implies that pure sand (silicon dioxide) does not adsorb or react with H_2O_2. However, H_2O_2 decomposed by around 64% in both SSF sand groups with and without SOM. There was no significant difference in the H_2O_2 decomposition trend in SSF sand with and without SOM, which indicates that SOM in SSF sand has no effect on H_2O_2 decomposition. These experiments suggest that the reaction of H_2O_2 with naturally occurring inorganic substances on SSF sand (e.g., metal oxides) contributes to H_2O_2 decomposition.

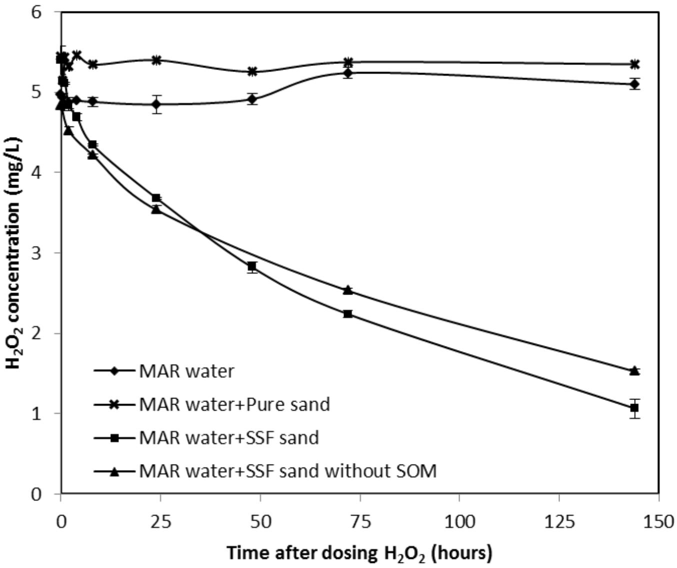

Fig. 2. H_2O_2 decomposition under autoclaved batch reactors at T=12±0.5 ℃ in triplicate (series a Fig. 1).

In contrast to what would be expected, no H_2O_2 decomposition was observed in MAR water only. It has long been known that one of the mechanisms of H_2O_2 decomposition is due to catalytic species, such as Cu^{2+}, Fe^{3+} and Mn^{2+}, which initiate radical-chain reactions and cause H_2O_2 to decompose more quickly in alkaline solution than in neutral or acidic media (Galbács and Csányi, 1983). Possible reasons why H_2O_2 did not decompose in MAR water could be that the low concentrations of metal ions (0.0106 mg Fe^{3+}/L, 0.0005 mg Mn^{2+}/L) could not promote H_2O_2 decomposition, the pH in this experiment was neutral instead of alkaline, and Cl^- and SO_4^{2-} might have inhibited H_2O_2 decomposition (De Laat et al., 2004).

To further investigate to what extent inorganic content (e.g., metal oxides) within SSF sand impacts H_2O_2 decomposition, the experiment was repeated with different amounts of autoclaved SSF sand (50 g, 100 g and 200 g). Fig. 3 presents the decomposition of H_2O_2 in 500 mL MAR water and autoclaved SSF sand, showing an increased removal of H_2O_2 (51%, 64% and 69%) at higher SSF content.

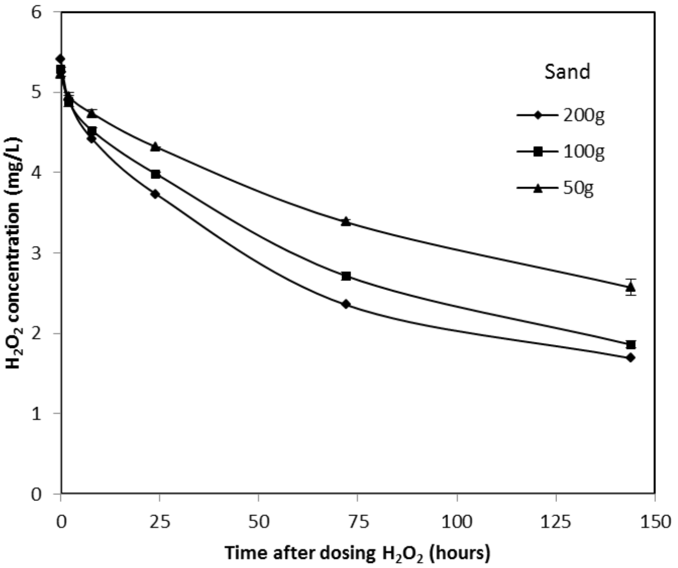

Fig. 3. H_2O_2 decomposition with 200 g, 100 g, and 50 g autoclaved SSF sand in 500 mL synthetic MAR water at T=12±0.5 °C. All batch reactors were in triplicate (series b Fig. 1).

This supports the finding that inorganic surfaces on the SSF sand effects H_2O_2 decomposition. Metal oxides may well be responsible for this observation, as this has also been reported in previous research (Hiroki and LaVerne, 2005; Lousada et al., 2013; Russo et al., 2013) and metal oxides were present in the SSF sand (Table 2). This may also explain why in Fig. 2 the H_2O_2 decomposition was slightly faster without SOM since inorganic content (e.g., metal oxides) coating on SSF without SOM may have more free surface area. This phenomenon is in agreement with results of Bissey et al. (2006) who found that H_2O_2 decomposition was faster in sand with 0.2% SOM than with 1.6% SOM at pH 7. However, the increase of H_2O_2 decomposition with the increase of SSF sand was slow, raising the question whether abiotic H_2O_2 decomposition by the natural sand will sufficiently contribute compared to biotic processes.

3.2. Biotic decomposition of H_2O_2 within MAR water

To investigate the effect of microbial biomass (represented as ATP) on H_2O_2 decomposition, 5 mg/L H_2O_2 was dosed into four synthetic MAR water groups with various levels of microbial biomass, extracted from SSF sand. Fig. 4 shows the H_2O_2 decomposition in MAR water with different bacterial populations, without the addition of sand. It was observed that only the group without living biomass did not show H_2O_2 decomposition while H_2O_2 decomposed in the other groups with biomass. The H_2O_2 decomposition rate considerably increased with the increase of microbial biomass.

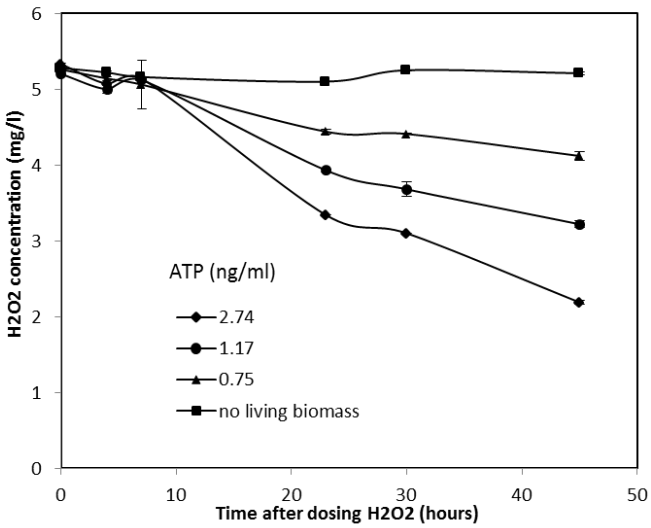

Fig. 4. H_2O_2 decomposition with microbial biomass, 2.74, 1.17, 0.75 and 0 ng ATP/mL at T=12±0.5 °C. All batch reactors were in triplicate (series c Fig. 1).

Even low microbial biomass (0.75-2.74 ng ATP/mL) resulted in considerable H_2O_2 decomposition (22-59%) in synthetic MAR water in only 45 hours. Therefore, microbial biomass is another main factor promoting H_2O_2 decomposition in MAR systems. This result is confirmed by previous studies, such as Sarathy et al. (2011) reported that 10 mg/L H_2O_2 was removed quickly by biologically activated carbon filters with high microbial population, Urfer and Huck (1997) reported that the rapid removal of 1 mg/L H_2O_2 in a biological filter may be attributed to its reaction with biomass.

3.3. Abiotic vs biotic H_2O_2 decomposition

The results above indicated that naturally occurring inorganic substances surfacing on sand grains and living biomass would be the two main factors promoting H_2O_2 decomposition during MAR. To further compare the effects of these two main factors, Fig. 5 shows H_2O_2 decomposition trends under abiotic and biotic conditions, with and without SSF sand. The batch reactors with both non-autoclaved SSF sand and MAR water with 38 ng ATP/mL provided the most rapid H_2O_2 decomposition by achieving almost complete removal in 6 hours. However, the slowest decomposition occurred in both autoclaved

MAR water and SSF sand. Comparing the above results, it indicates that the biotic reactions contributed with a large fraction to H_2O_2 decomposition in the reactors with non-autoclaved SSF sand and MAR water with 38 ng ATP/mL. Additionally, H_2O_2 decomposition in non-autoclaved MAR water with 2.74 ng ATP/mL decomposed faster than in the reactors with both autoclaved SSF sand and MAR water, illustrating that the contribution of biotic reactions, in the presence of 2.74 ng ATP/mL, to H_2O_2 decomposition in SSF sand is more than abiotic reactions. However, at lower ATP concentrations (<1.71 ng ATP/mL), abiotic decomposition is faster and should therefore not be neglected.

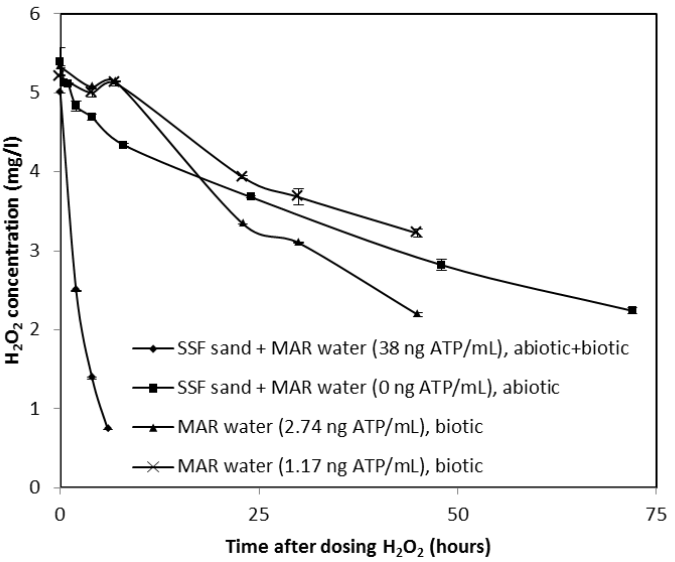

Fig. 5. Biotic and abiotic H_2O_2 decomposition. All batch reactors were in triplicate.

This result is different from previous studies. As was stated in the introduction, the removal of H_2O_2 was greatly attributed to biotic factors instead of abiotic factors in most cases investigated, such as biologically active zones in situ (Bajpai et al., 1994) and biologically active filters (Urfer and Huck, 1997) which contain much higher microbial biomass than natural MAR water. Several researchers investigated the microbial biomass in lakes and rivers, as MAR influent water, and found that ATP concentration range of 0.1-2 ng/mL (Cavari, 1976; Hamilton-Galat and Galat, 1983; Kramer, 2012; Noges, 1996; Pridmore et al., 1989). In practice however, especially in the late spring and in the early summer, ATP increases substantially to values of 2.79 ng/mL in Lake Rotorua (Pridmore et at., 1989) and 2.945 ng/mL in Lake Kinneret (Cavari, 1976). This demonstrates that biotic reactions would be the primary mechanism for H_2O_2 decomposition in MAR systems only when MAR waters contain much higher ATP concentrations than the range of 0-2.74 ng/mL as used in this study.

3.4. H2O2 decomposition at different initial concentrations

So far, previous research has primarily focused on single H_2O_2 concentrations (Häkkinen et al., 2004; Miller and Valentine, 1999; Urfer and Huck, 1997; Zappi et al., 2000), whereas the fate of different H_2O_2 concentrations is important for setting the maximum allowable limit to prevent undesired effects on aquatic and soil ecology. Fig. 6 presents the H_2O_2 decomposition at different initial concentrations in SSF sand and synthetic MAR influent water with a large microorganism content (38 ng ATP/mL). H_2O_2 initial concentrations in the range of 0.5-3 mg/L decomposed to below the detection limit 0.015 mg/L in 2-6 hours and 5 mg/L H_2O_2 decomposed to 0.73 mg/L in 6 hours.

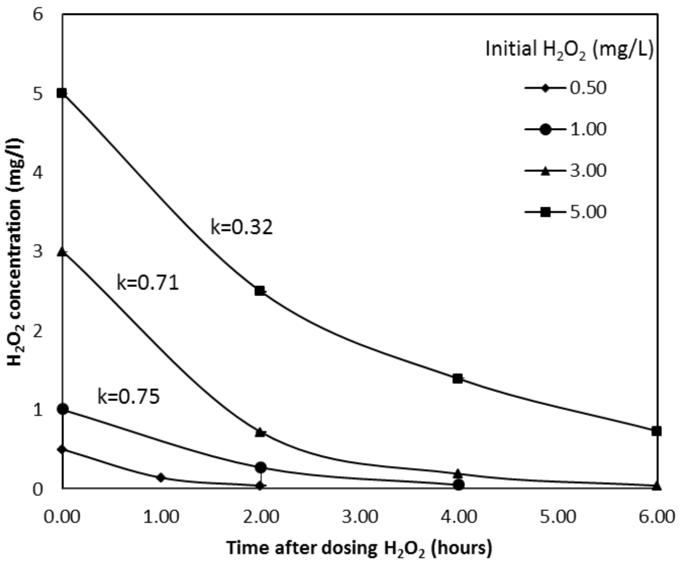

Fig. 6. H_2O_2 decomposition under different initial concentrations, 0.5, 1.0, 3.0 and 5.0 mg/L, in the presence of SSF sand at T=23-27 °C. All batch reactors were in triplicate (series d Fig. 1).

As is shown in Fig. 6, H_2O_2 decompositions followed first-order kinetics in the three H_2O_2 spiking groups (5, 3 and 1 mg/L) in the presence of SSF sand. It is in agreement with previous studies (Miller and Valentine, 1999; Zappi et al., 2000). Interestingly, first-order rate coefficients k values increased with the decrease of H_2O_2 initial concentrations. The same phenomenon was reported in the study of Silhacek and Taake (2005).

It is noteworthy that to maintain the growth of microorganisms in this experiment, DOC was dosed in concentrations higher than in most MAR influent waters, particularly in winter periods. However, the pre-treatment AOP before MAR can increase the degradable organic matter and lead to increased bacterial population in MAR influent water, probably two to three times higher than MAR systems without the pretreatment AOP (Pharand et al., 2014). Also, natural water may contain higher ATP concentrations by themselves, such as 0.07-18 ng/mL in Lake 227 (Canada), 0.07-7.93 ng/mL in St. Lawrence Estuary, 0.03-11.9 ng/mL in Pyramid Lake (NV) (Hamilton-Galat and Galat, 1983). Therefore, microbial biomass in MAR systems after AOPs may reach 38 ng ATP/ml under specific conditions.Assuming a microbial biomass concentration around 38 ng ATP/mL in MAR influent water and H_2O_2 decomposition rate is steady in the surface of MAR sand, the first-order kinetics were applied to predict the decomposition of residual H_2O_2 in MAR systems. Drinking water utility Dunea operates the MAR with an infiltration velocity of 0.042 m/h (1 m/day). An estimation based on the first-order kinetics is that different initial concentrations (5, 3 and 1 mg/L) of H_2O_2 could decompose to the provisional standard, 0.25 mg/L, stated in the introduction within around 9, 4, and 2 hours corresponding to a depth of 36, 17 and 8 cm. However, in practice the microbial activity may not be steady with depths. Previous studies (Das et al., 2013; Haughton et al., 2001) reported that the highest microbial population exists in the top 0-20 cm of soil and the microbial activity decrease a lot below the depth of 20 cm. It could thus be concluded that low concentration of H_2O_2 (<3 mg/L) may be decomposed to 0.25 mg/L in the first centimeters of dune sand in the presence microbial biomass of 38 ng ATP/mL in the MAR infiltration water.

4. Conclusions

This study investigated the fate of H_2O_2 as the residual of AOP during MAR. The main conclusions of this study are:

- No H_2O_2 decomposition was observed in batch reactors with synthetic MAR water only, nor in reactors containing pure sand. In MAR systems, pure sand and MAR water have no effect on H_2O_2 decomposition.
- H_2O_2 decomposed slightly faster in batch reactors with SOM than in batch reactors without SOM, but there was no significant difference in H_2O_2 decomposition between the two groups.
- Naturally occurring inorganic substances on the surface of sand grains and living biomass are the two main factors promoting H_2O_2 decomposition in MAR systems.
- Low concentration (<3 mg/L) of H_2O_2 in MAR influent water may decompose below 0.25 mg/L in the centimeters of MAR systems with water containing high microbial biomass (such as 38 ng ATP/mL).

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