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Degradation of landfill leachate compounds by persulfate for groundwater remediation

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Abstract

In this study, batch and column experiments were conducted to evaluate the feasibility of using persulfate oxidation to treat groundwater contaminated by landfill leachate (CGW). In batch experiments, persulfate was compared with H_2O_2, and permanganate for oxidation of organic compounds in CGW. It was also compared with the potential of biodegradation for contaminant removal from CGW. Persulfate was observed to be superior to H_2O_2 and permanganate for degradation of total organic carbon (TOC) in the CGW. Conversely, biodegradation caused only partial removal of TOC in CGW. In contrast, persulfate caused complete degradation of the TOC in the CGW or aged CGW, showing no selectivity limitation to the contaminants. Magnetite (Fe_3O_4) enhanced degradation of leachate compounds in both CGW and aged CGW with limited increase in persulfate consumption and sulfate production. Under dynamic flow condition in 1-D column experiments, both biodegradation and persulfate oxidation of TOC were enhanced by Fe_3O_4. The enhancement, however, was significantly greater for persulfate oxidation. In both batch and column experiments, Fe_3O_4 by itself caused minimal consumption of persulfate and production of sulfate, indicating that magnetite is a good persulfate activator for treating CGW in heterogeneous systems The results of the study show that the persulfate-based in-situ chemical oxidation (ISCO) method has great potential to treat the groundwater contaminated by landfill leachate.

Keywords

Persulfate oxidation; Magnetite; Biodegradation; Landfill leachate; Contaminated groundwater

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1. Introduction

Rapid worldwide economic development in recent years has caused massive generation of industrial and municipal solid waste (MSW). Landfill disposal is currently the most used method for municipal and industrial solid waste management [1, 2]. A main disadvantage of this method is leachate generation, which occurs through rainfall percolation and a series of physicochemical and biological processes in the solid waste [3]. Landfill leachate typically contains a wide variety of organic and inorganic constituents [4]. Landfill leachate can be categorized into young leachate (typically ≤2 years since generation) and mature leachate (typically ≥5 years since generation), depending on the fraction of the organic compounds that are refractory to biodegradation [5]. Due to these refractory compounds, landfill leachate can be a source of long term contamination for soil and groundwater [3, 6, 7]. Different methods, including biological, physical and chemical oxidation processes, have been reported for leachate treatment [8-12].

Advanced oxidation processes (AOPs) such as Fenton oxidation [13, 14], Fenton-like oxidation [15], ozone oxidation [16], photocatalytic oxidation [17], and electrochemical oxidation [5] have been extensively tested for the treatment of landfill leachate. Even though these processes are effective for landfill leachate treatment, their potential application for soil and groundwater remediation poses challenges. Photocatalytic oxidation and electrochemical treatment are not applicable to in situ remediation. While Fenton reagent (Fe-activated hydrogen peroxide) has been used for in situ chemical oxidation (ISCO), hydrogen peroxide suffers from rapid decomposition in the subsurface, resulting in the generation of heat and gas, causing a series of issues, including safety, relatively short radius of influence, and low remediation efficiency [18]. In addition, due to the limited aqueous solubility and inefficient dispersion of ozone gas in heterogeneous subsurface environments, as well as the requirement of on-site generation systems, the application of ozone remediation has also been hindered [19]. Persulfate (PS, $S_2O_8^{2-}$) has been used successfully for in-situ chemical oxidation (ISCO) treatment of groundwater contaminated by organic compounds [20-23]. Persulfate is relatively safe to handle, as it is stable under normal conditions. Furthermore, persulfate is highly soluble in water, it can be conveniently used to mix with soil or injected at high concentrations [21]. In addition, it is more persistent than hydrogen peroxide and thus has a larger radius of influence in the subsurface [22]. Persulfate is a strong oxidant with a high redox potential of 2.01 V. When activated, persulfate produces $SO_4^{\bullet -}$ and HO• radicals which are even more powerful for contaminant degradation (standard redox potentials are 2.6 V and 2.8 V, respectively [23]). Importantly, persulfate is effective for a wide range of compounds including many that are refectory to other treatment methods.

Persulfate oxidation has been applied to degrade a variety of contaminants. For example, effective degradation was also reported for petroleum-hydrocarbons [20, 22] chlorinated ethylenes [24-26], chlorinated alkanes [27, 28], dioxane [29, 30], methyl tert-butyl ether (MTBE) [20, 31], polycyclic aromatic hydrocarbons (PAHs) [32-34]. Several studies have reported that persulfate was applied to remove COD and color, and improve biodegradability for landfill leachate in above-ground treatment systems. Deng et al used heat to improve persulfate oxidation for simultaneous removal of refractory organic contaminants and

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ammonia in landfill leachate [4]. Shabiimam and Dikshit used low pH to enhance persulfate oxidation for removing total organic carbon and color from stabilized leachate [35]. Chou et al enhanced persulfate oxidation to treat mature landfill leachate by using microwaves [36].

As noted above, several methods exist for persulfate activation, including heat [37-39], base activation [40-42], ultrasonication [43], UV irradiation [44], electrochemical [45], microwave [36], and transition metals [26, 46, 47]. The majority of these methods are not practical for in-situ applications, with transition metals and base the primary activators employed. Ferrous iron (Fe^{2+}) is commonly used to catalyze persulfate oxidation [48-50]. However, overall oxidation potential is often limited in subsurface systems due to issues related to Fe^{2+} availability. In addition, Fe^{2+} can scavenge $SO_4^{\bullet -}$ at a rate higher than its generation [51]. Zero-valent iron (Fe°) and iron bearing minerals such as geothite, hematite, pyrite, ilmenite, ferrihydrite, lepidocrocite, and magnetite have been studied for heterogeneous persulfate activation [52-58]. Recently, magnetite (Fe_3O_4) was reported to be an effective catalyst as compared to Fe (III) oxides for heterogeneous catalytic oxidation of organic pollutants [55, 59, 60]. Magnetite is a focus due to its ubiquitous presence in the subsurface environment [61, 62]. In addition, application of Fe_3O_4 to persulfate-based chemical oxidation processes for contaminant removal from wastewater has been proven to be successful [63-66]. These results lead to the contention of applying magnetite to persulfate-based ISCO technology for treatment of groundwater contaminated by landfill leachate.

The objective of this study is to investigate the persulfate-based oxidation method for removal of contaminants in landfill leachate contaminated groundwater (CGW), and the potential of persulfate-based ISCO technology for remediation of CGW. The performance of persulfate was compared with two other typical ISCO oxidants (permanganate and H_2O_2). Persulfate-based oxidation was also compared with biodegradation (associated with natural attenuation) for overall evaluation of effectiveness. The use of magnetite (Fe_3O_4) as an activator for enhancing persulfate-based oxidation was also examined. In addition to batch experiments, column experiments were conducted to investigate the performance of the method under dynamic flow conditions.

2. Materials and methods

2.1. Materials

Landfill leachate was collected from the leachate storage tank of Heimifeng landfill (Changsha, Hunan Province, China). The leachate collected was stored in a tinted glass bottle with zero headspace in a refrigerator at 4 °C. Before use, the raw leachate was centrifuged at a rotating speed of 7000 r/min for 20 min, and the supernatant was filtered through a 0.45 μm membrane to remove suspended solids that may interfere with the reactions for dissolved organic matter (DOM) or sample analysis in the following experiments. This is the stock landfill leachate, and the water quality parameters were analyzed and presented in Table 1. Due to a low BOD_5/COD ratio (<0.12) and high NH^{4+}-N concentration, the leachate was classified as mature leachate [67].

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Ultrapure water was used to represent groundwater for dilution of landfill leachate to produce CGW due to the very high salt concentrations in the leachate (the salt concentrations in CGW were significantly higher than those in typical groundwater) (dilution factor was 50). The organic compounds in the CGW were analyzed using gas chromatography-mass spectrometry (Shimadzu GCMS-QP2010, Japan) (Fig. S1, SI). The total organic carbon (TOC) was determined by TOC analyzer (Shimadzu TOC-VCPH, Japan). Details for GC-MS and TOC analysis are presented in Analytical Methods (Section 2.5). The results show that the major species detected by the GC-MS were low molecular weight hydrocarbons and oxygenated hydrocarbon derivatives (Table 2). Some of the compounds, such as trans-2-Dodecen-1-ol, trifluoroacetate and diethyl phthalate, are refractory compounds that have long life times in the environment. The TOC in CGW was measured to be 68 mg/L.

The aged CGW was produced by aging CGW to remove the degradable compounds. Briefly, CGW in a 4-L flask was placed in an incubation chamber at 25 °C until TOC in the CGW stabilized (~15 days). The incubation continued for another 20 days to obtain the aged CGW. The DOM in the aged CGW typically consists of compounds refractory to biodegradation, such as fulvic acid [68].

Sodium persulfate ($Na_2S_2O_8$, ≥98.0%) and hydrogen peroxide (H_2O_2, 30%) were purchased from Sinopharm Chemical Reagent, Shanghai, China. Potassium Permanganate ($KMnO_4$, ≥99.5%) was from Kaixin Chemical Reagent (Hengyang, China). The magnetite (Fe_3O_4, 99%) was obtained from Aladdin Industrial Corporation (Shanghai, China) and was characterized by electron scanning microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) (Image shown in Fig. S10, SI). The particle size of the Fe_3O_4 solids is ~1 μm. The other chemicals were of reagent grade and obtained from Hengxing Chemical Preparation Corporation Co., Ltd (Tianjin, China). All solutions were prepared using ultra-pure water produced by UPT-II-40 (Ulupure, Chengdu, China) with an electrical resistivity of 18.3 MΩ·cm.

The quartz sand used for the column experiments was obtained from Zhilei Building Co. Ltd (Guangzhou, China). The sand was ultrasonically cleaned, air-dried and then screened. The segment with the size of 100-120 mesh (0.125-0.147 mm) was used in the experiments.

2.2. Batch degradation experiments

Persulfate was first compared with permanganate and H_2O_2 (not Fenton reagent) for oxidative degradation of the organic compounds in CGW. 40-mL borosilicate vials were used as the reactors for this experiment. 20 mL of oxidant solution at concentration of 86 mM and 20 ml of CGW were mixed in a vial, and the vial was closed using a cap with polytetrafluoroethylene lined septa. Multiple vials were placed in a thermostat water bath (25 ± 1 °C) with a lid, which maintained the reaction in the dark. At predetermined time intervals, three vials as replicates were sacrificed for sample analysis. These vials were first transferred to an ice-water bath to quench oxidation reactions, and then the solution was immediately analyzed for TOC, oxidant concentration, and pH. In the experiment in which persulfate was used as the oxidant, sulfate concentration was also measured.

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A complementary experiment was conducted to examine the impact of biodegradation (natural attenuation) on TOC. The experiment was conducted by following the same procedures as used in the oxidative degradation experiment except that the 20 mL of oxidant solution was replaced by ultrapure water. TOC and pH in the samples were measured at predetermined time intervals.

A control experiment was conducted to test for possible loss of organic compounds due to adsorption to vials, photochemical decomposition, or other unidentified physicochemical processes during the course of the experiment. For this test, 1 g/L of sodium azide (a bactericide) solution was used in place of the oxidation solution, which was used to inhibit microbial activity.

2.3. Effect of Fe_3O_4 on degradation of leachate compounds by persulfate

15 ml of persulfate solution at concentration of 86 mM and 15 mL CGW were mixed in a 40-ml borosilicate vial. 0.6 g of Fe_3O_4 was added into the mixed solution to yield a solid-liquid ratio of 1:50 (w/w). Then three glass beads with a diameter of 4-5 mm were added into each vial for better agitation during the experiment. These vials were closed using caps with polytetrafluoroethylene lined septa and then placed in a reciprocal water-bath shaker running at 300 rpm (25 ± 1 °C). At predetermined time intervals, three vials were sacrificed for sample analysis. These vials were first transferred to an ice-water bath to quench reaction. Then the samples were filtered through a 0.22-μm glass fiber membrane to remove the Fe_3O_4 solids. The filtrate was immediately analyzed for the concentration of TOC, persulfate, sulfate, ferrous ion and total iron and pH. Control experiments were conducted to examine whether Fe_3O_4 caused biodegradation or adsorption. In the control experiment to see whether Fe_3O_4 caused biodegradation, 1 g/L of sodium azide solution was used in place of the oxidant solution. Using sodium azide was to inhibit activity of microorganisms and thus prevent biodegradation (removing the impact of microbial activity from the reaction). In the other control experiment to see whether Fe_3O_4 caused adsorption, the oxidant solution was replaced with ultrapure water (sodium azide was avoided) and the test lasted for only 2 h.

The degradation of organic compounds in aged CGW by Fe_3O_4-activated persulfate was also investigated following the methods described above.

2.4. Column experiments

The column used in the experiments was 2 cm in inner diameter and 20 cm in length. It was constructed of glass with all connectors constructed of stainless steel. Two column experiments were conducted to test degradation of TOC in CGW. In one experiment the column was packed with the silica sand, and in the other the column was packed sequentially with silica sand (2.5 cm), a mixture of Fe_3O_4 and sand at a mass ratio of 1:9 (15 cm), and silica sand (2.5 cm). The packed columns were flushed with CO_2 to displace air, then vertically oriented and saturated with degassed water using a valveless piston pump (QG-6, Fluid Metering INC, USA), and then oriented horizontally for the experiments.

Before the column experiment, volatility of the leachate compounds in CGW in reservoir (incompletely sealed) was examined. Ultrapure water and CGW at a ratio of 1:1 (v:v) were

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mixed in the reservoir. The reservoir was sampled at predetermined time intervals and TOC were measured. Results demonstrated that volatilization caused minimal loss of TOC from the reservoir (Fig. S5, SI).

In each column experiment, two solutions were used for injection. The first solution was a mixture of ultrapure water and CGW at a ratio of 1:1 (v:v). This was used to test biodegradation in the column. The second solution was a mixture of persulfate solution (86 mM) and CGW at a ratio of 1:1 (v:v), which was used to test oxidative degradation. The solution was injected into the column at a flow rate of 0.05 ml/min, which is equivalent to a mean pore-water velocity of 0.045 cm/min. After 7-8 pore volumes of injection, the influent was switched to water. Effluent samples were collected in glass tubes placed in an ice-water bath so as to quench the reaction during sample collection. The samples were then weighed and analyzed for pH and the concentrations of TOC, persulfate, sulfate, ferrous ion, and total iron. The concentrations of TOC and persulfate in the reservoir were measured before, during, and after each experiment. These measured values were used as the reservoir concentrations (C_0) correspondingly for the effluent samples collected at different times. Between injection of the two solutions, the column was flushed with degassed water for at least 10 pore volumes.

An additional set of experiments was conducted to test degradation of aged CGW by persulfate in the Fe_3O_4 column. The injection solution was prepared by mixing persulfate solution (86 mM) and aged CGW at a ratio of 1:1 (v:v). The procedure of the experiment was identical as that used for the column experiment for CGW treatment.

2.5. Analytical methods

The organic compounds in the CGW were analyzed using gas chromatography-mass spectrometry (Shimadzu GCMS-QP2010, Japan) equipped with a DB-5ms capillary column (50 m × 0.25 mm ID × 0.25 μm). The temperature for the GC-MS interface and ion source were 250 °C and 220 °C, respectively. The mass spectrometer was operated in the electron ionization (EI) mode at 70 eV and helium (flow rate of 1 ml min^{-1}) was used as carrier gas. The injection port was maintained at 300 °C. The column temperature was held at 80 °C for 1 min, and then programmed at 12 °C/min to 200 °C (hold 1 min), 8 °C/min to 280 °C (hold 15 min), then at 2 °C/min to 300 °C. The total organic carbon (TOC), which is used to represent the total concentration of contaminants in CGW, was determined using a TOC analyzer (Shimadzu TOC-VCPH, Japan) after dilution of the samples. The concentration of H_2O_2 and persulfate were measured using the iodide-spectrophotometric method described by Zhong et al [30]. The concentration of permanganate ion (MnO_4^-) was measured with a UV-spectrophotometer (UV-2250, Shimadzu) at a wavelength of 525 nm [69, 70]. Sulfate, ferrous ion and total dissolve iron were measured using a Hach DR2800 spectrophotometer (Loveland, CO) based on the modulated Hach methods (No. 8051, 8146, 8008). The pH of samples was determined using PHS-3C pH meter (Leici Instrument Co., Shanghai).

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3. Results and discussion

3.1. Batch experiments

3.1.1. Comparison between oxidants for degradation of leachate TOC—The results of degradation of TOC in CGW by the three oxidants (persulfate, H_2O_2, and permanganate) are shown in Fig. 1. TOC decreases significantly in the first 10 d (total removal percentage ~80%) for persulfate, and complete removal is observed in 26 d (Fig. 1(a)). Biodegradation is unlikely to have contributed significantly to the TOC removal, due to suppression of microbial activity by the high oxidation-reduction potential (2.01 V) and low pH (2~3) in the solution. In contrast to persulfate, TOC degradation by H_2O_2 and permanganate was not significant over the entire period of the experiment (50 d). These results show that persulfate is the strongest among the three oxidants for leachate TOC degradation.

The results of oxidant consumption during the experiment are presented in Fig. 1(b). Permanganate concentration is stable for the entire testing period, indicating no consumption. This result, together with the observed absence of TOC removal, shows that permanganate is ineffective for degradation of leachate TOC. The concentration of H_2O_2 is observed to decrease significantly. However, there was minimal removal of TOC by H_2O_2. This indicates that H_2O_2 experienced significant non-oxidative decomposition, consistent with its lower stability. Persulfate exhibited a 20% reduction by the end of the experiment. The relative oxidative effectiveness of H_2O_2 and persulfate observed herein are similar to the results in our prior study for 1,4-dioxane oxidation [30]. A possible reason could be a lower concentration of radicals in H_2O_2 solution than in persulfate solution, which was indicated by the much lower intensity of EPR signal of HO• in H_2O_2 solution [30]. Results of this comparison show that persulfate is superior to the other two commonly used ISCO oxidants, H_2O_2 and permanganate, for degradation of TOC in CGW.

3.1.2. Oxidation of TOC in CGW by persulfate—Biodegradation, persulfate-based degradation, and Fe_3O_4-activated persulfate degradation of TOC in CGW were compared and the results are presented in Fig. 2. In the biodegradation experiment in which persulfate is absent (CGW+biodegradation in Fig. 2(a)), TOC in CGW decreases rapidly in the first 5 d, showing a degradation rate even higher than for persulfate-based oxidative degradation (CGW+PS in Fig. 2(a)). The relative TOC concentration (C/C_0), however, stabilizes after 10 days at a level of ~30%. In the control experiment with NaN_3 as the bacterial metabolism inhibitor (CGW+NaN_3 in Fig. 2(a)), no significant decrease of TOC is observed during the entire phase of the experiment. The result confirms that TOC loss in the experiment is not due to adsorption to vials, photochemical decomposition, volatilization, or other physicochemical processes. Incompleteness of the degradation indicates that biodegradation is not effective for removal of the refractory species in the CGW. This is in contrast to persulfate-based chemical oxidation, which causes complete degradation.

The presence of Fe_3O_4 does not cause decrease of TOC in CGW if the biological activity is suppressed by NaN_3 (CGW+NaN_3+Fe_3O_4 in Fig. 2(a)), and no production of soluble Fe was observed (CGW+NaN_3+Fe_3O_4 in Fig. 2(b)), showing that Fe_3O_4 by itself does not cause degradation. In addition, the relative concentration of TOC (C/C_0) remained stable at 1 for 2

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h in the presence of Fe_3O_4 in the CGW (no persulfate and no sodium azide) (Fig. S8, SI), indicating no adsorption of TOC to Fe_3O_4. The Fe_3O_4, however, significantly enhances degradation of TOC by persulfate, causing a reduction in the time for complete degradation compared to persulfate alone (Fig. 2(a)). Persulfate-based reaction generally causes pH in the system to decrease [40]. As shown in Fig. S3, SI, the presence of Fe_3O_4 caused earlier stabilization of pH than in the absence of Fe_3O_4, which also indicates faster reaction. This result shows that the reaction between persulfate and the contaminants can be enhanced in the presence Fe_3O_4, likely due to heterogeneous activation of persulfate by Fe_3O_4. Hou et al also have reported that persulfate can be activated by Fe_3O_4, which increased the degradation efficiency of tetracycline by 50.5% [66].

Production of soluble Fe started at 2 d and the Fe concentration increased linearly with time of contact (CGW+PS+Fe_3O_4 in Fig. 2(b)). This is in contrast to the minimal soluble Fe production in the entire phase of experiment in the absence of persulfate (CGW +NaN_3+Fe_3O_4 in Fig. 2(b)). The result shows that persulfate reacts with the Fe_3O_4 particles during the degradation process, which follows a zero-order kinetics shown by the linearity observed (the zero-order rate constant is 2.6 mg/(L·d)). Such zero-order kinetics implies a surface reaction mechanism for persulfate activation.

The results of persulfate consumption and sulfate production are presented in Fig. 3(c). For the entire phase of experiment, the total sulfur concentration, which is the sum of concentration of persulfate and sulfate, remains stable at the initial concentration (C/C_0=1). The result indicates that sulfate is the only product for persulfate decomposition and no precipitation of persulfate or sulfate occurs. Two stages of sulfate production are observed and they are separated at 6 d and 12 d in the presence and absence of Fe_3O_4, respectively, corresponding to the phases of ongoing and post contaminant degradation. By the end of 12 days when ~95% of the TOC was removed by persulfate in the presence or absence of Fe_3O_4, the relative concentrations of persulfate remaining in the system were similar at 81% and 85%. This result shows that consumption of persulfate by Fe_3O_4 for leachate compound degradation is limited. The results of persulfate consumption and sulfate production are in contrast to the results of our previous study on activation of persulfate by iron filings for 1,4-dioxane degradation, for which very significant decrease and increase of persulfate and sulfate concentrations, respectively, were observed in the first 15 minutes [30].

Based on the pattern of TOC degradation, soluble Fe production, and sulfate production, a surface activation mechanism is speculated for Fe_3O_4 to activate persulfate to degrade the leachate compounds in CGW. Persulfate was activated at the surface of Fe_3O_4 solids to generate sulfate radicals via surface reaction. The radicals attack the leachate compounds in the neighboring solution and cause TOC degradation, or they may react with surface structures of Fe_3O_4 to produce soluble Fe. Degradation of leachate compounds seems to be preferential to reaction with surface structures of Fe_3O_4, as indicated by the delayed production of soluble Fe (Fig.2(b)) and a significantly lower sulfate production rate in the second stage when the leachate compounds were depleted (Fig.2(c)).

3.1.3. Degradation of TOC in aged CGW—Results of TOC removal by persulfate in aged CGW are presented in Fig. 3(a). TOC removal is complete in either presence or

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absence of Fe_3O_4. However, the degradation is faster in the presence of Fe_3O_4 in the first 3 days, yielding 21% more removal of TOC than in the absence of Fe_3O_4. Production of soluble Fe starts at 1 d, and the Fe concentration again increases linearly with time under acidic condition (Fig. S9, SI). The zero-order rate constant for Fe production is 1.8 mg/(L•d) (Fig. 3(b)), which is smaller than for TOC removal for CGW (2.6 mg/(L·d)). Production of sulfate over time shows a two-stage pattern, compromising a fast stage and a slow stage, which are separated at 3 d and 6 d in the presence and absence of Fe_3O_4, respectively (Fig. 3(c)).

3.1.4. The pseudo-first-order rate constants of TOC degradation—Due to the stoichiometrically great excess of oxidant to contaminants as indicated by the large initial molar ratio between oxidant and TOC (10:1), The reactions are assumed to follow pseudo-first order kinetics and the reaction rate constants are presented in Fig. S2, SI and Table 3. The pseudo-first-order rate constant for TOC biodegradation in CGW (leachate only) is 0.14 d^{-1}. The rate constant for TOC degradation by persulfate alone is 0.16 d^{-1}, which is similar to that for biodegradation. The rate constant in the presence of both persulfate and Fe_3O_4 is 0.27 d^{-1}, which is significantly higher than that for persulfate alone. This result demonstrates that the reaction between persulfate and the contaminants can be enhanced by Fe_3O_4. The rate constant for TOC removal by persulfate in aged CGW is 0.34 d^{-1}, which is larger than for CGW, indicating that persulfate can degrade compounds refractory to biodegradation even faster than the biodegradable compounds. The comparison of the reaction rate not only shows that persulfate-based chemical oxidation is superior to biodegradation, but also indicates that Fe_3O_4 can effectively activate persulfate to provide stronger oxidation condition for TOC degradation in CGW.

3.2 Degradation of leachate TOC under dynamic flow conditions

The results of degradation of TOC in porous media under dynamic flow condition are presented in Fig. 4. For the sand-packed column, breakthrough curves (BTCs) of pentafluorobenzoic acid (PFBA), a nonreactive tracer, are symmetrical for arrival and elution waves, and C/C_0 is approximately 0.5 at PV of 1, indicating ideal transport and uniform packing of the column (Fig. S4, SI). In the absence of persulfate (leachate only), C/C_0 of TOC increases and forms plateau with C/C_0 of 1, and then decreases and forms a secondary plateau with C/C_0 of 0.6 at PV of 5 (Fig. 4(a)). Such a decrease of C/C_0 and formation of the secondary plateau can be a result of accumulative growth of the microbes in the column (i.e., formation of biofilm), which can enhance efficiency of biodegradation. The plateau C/C_0 of the BTC in the presence of persulfate, however, is close to 1, indicating insignificant degradation. The hydraulic residence time (t_r) in the column was ~9 h. Such a short residence time is the likely reason for the minimal degradation (no significant degradation is observed within 9 h in batch experiment).

The presence of Fe_3O_4 in the sand enhanced both biodegradation and persulfate degradation of the leachate compounds. In the absence of persulfate, C/C_0 increases to 1 at ~1.5 PV with injection of CGW, and then decreases rapidly to the secondary plateau of ~0.3. This C/C_0 is significantly lower than that formed in the sand containing no Fe_3O_4, and is identical to the stabilized C/C_0 for biodegradation in the batch experiment. The persulfate-based oxidation

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caused a significantly lower plateau of C/C_0 (~0.3) for CGW, despite the limited residence time (9 h). This is in contrast to the minimal degradation of TOC in the column containing no Fe_3O_4. Significant removal of TOC was also observed for aged CGW in the presence of Fe_3O_4, shown by a plateau C/C_0 significantly less than 1 (~0.6). These results indicate that Fe_3O_4 can significantly enhance degradation of leachate TOC by persulfate.

The BTCs of persulfate and sulfate with persulfate injection are presented in Fig. 4(b). No decrease of persulfate concentration is observed either with the presence or absence of Fe_3O_4, for CGW or aged CGW. Limited production of sulfate is observed and the C/C_0 values of sulfate at the plateaus are similar. The results show that Fe_3O_4 alone does not cause significant decomposition of persulfate. Persulfate-based reaction caused pH in the system to decrease, however, no significant production of soluble Fe was observed (Fig. 4(c)). This observation shows that the reaction between persulfate and Fe_3O_4 is not significant in the presence of leachate compounds with maintained concentrations due to continuous injection. The results indicate the Fe_3O_4 can activate persulfate to preferentially react with leachate compounds, causing high efficiency of leachate compound degradation.

4. Conclusions

Persulfate is superior to hydrogen peroxide and permanganate for oxidative removal of landfill leachate compounds from contaminated groundwater. Persulfate-enhanced oxidation also has advantages over biodegradation for the leachate removal in that it shows non-selectivity to the compounds and causes complete degradation of the species that are refractory to biodegradation. Magnetite can enhance performance of persulfate for leachate compound degradation without significant consumption of the persulfate. Results of the column experiments demonstrate that significant degradation of the leachate compounds by persulfate can be achieved in porous medium containing magnetite under dynamic flow conditions.

Results of this study show that persulfate-based in-situ chemical oxidation (ISCO) method has good potential for treating groundwater contaminated by mature landfill leachate. A conceptual application of this method is the construction of persulfate-enhanced oxidation reactive zone, e.g., Fe_3O_4-based permeable reactive barrier or curtain wall, downgradient of the source of landfill leachate contamination. The distance between the location of contamination occurrence and the reactive zone will allow a hydraulic residence time sufficiently long for natural attenuation to remove the portion of biodegradable compounds. Persulfate is injected upgradient of the reactive zone. Perfusion and activation of persulfate in the zone is anticipated to cause complete degradation of the refractory leachate compounds.

Supplementary Material

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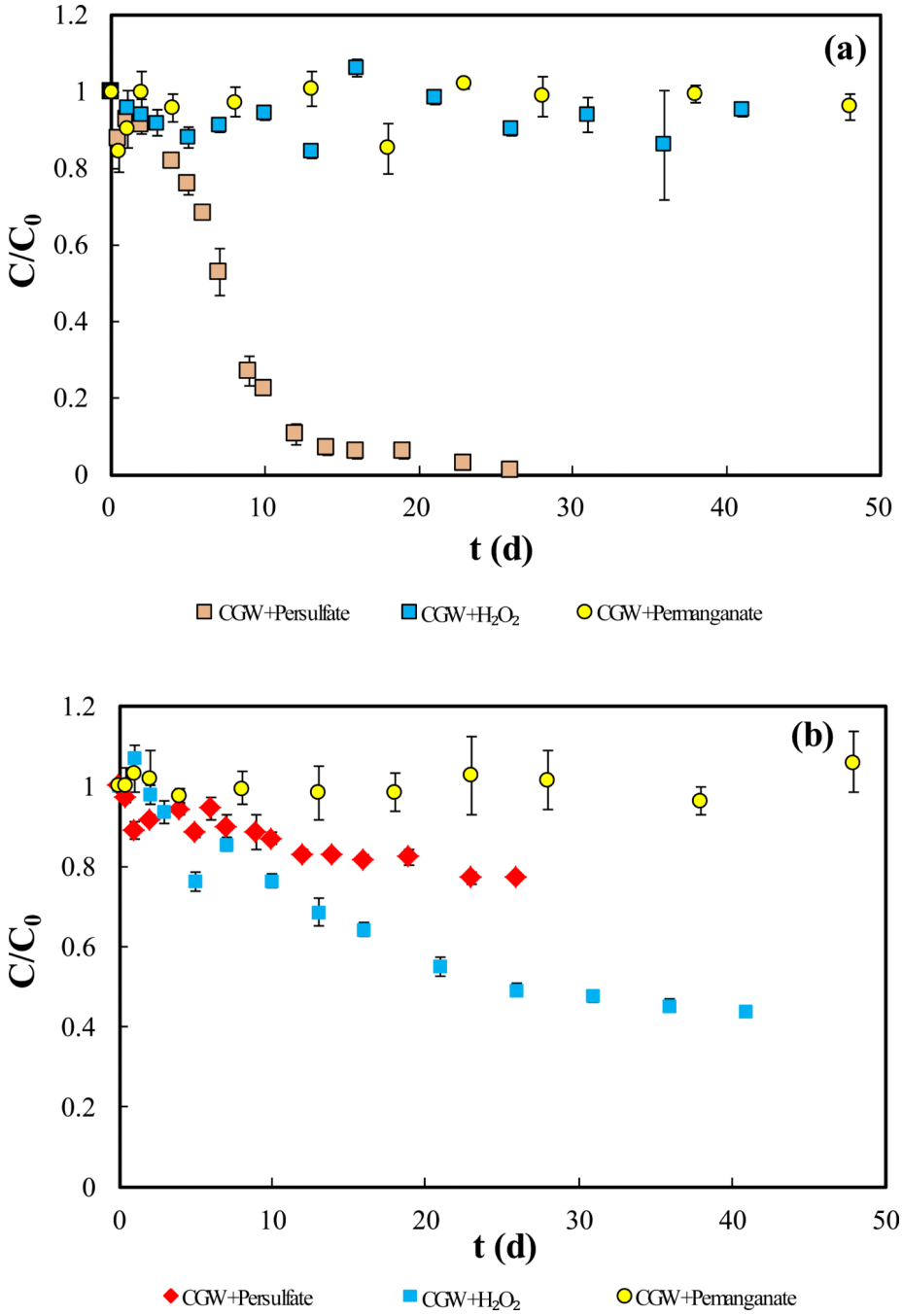

Fig.1.

Comparison between oxidants for degradation of TOC in CGW. (a) Relative concentration of TOC versus time; (b) Relative concentrations of oxidants versus time. CGW in legend represents leachate contaminated groundwater.

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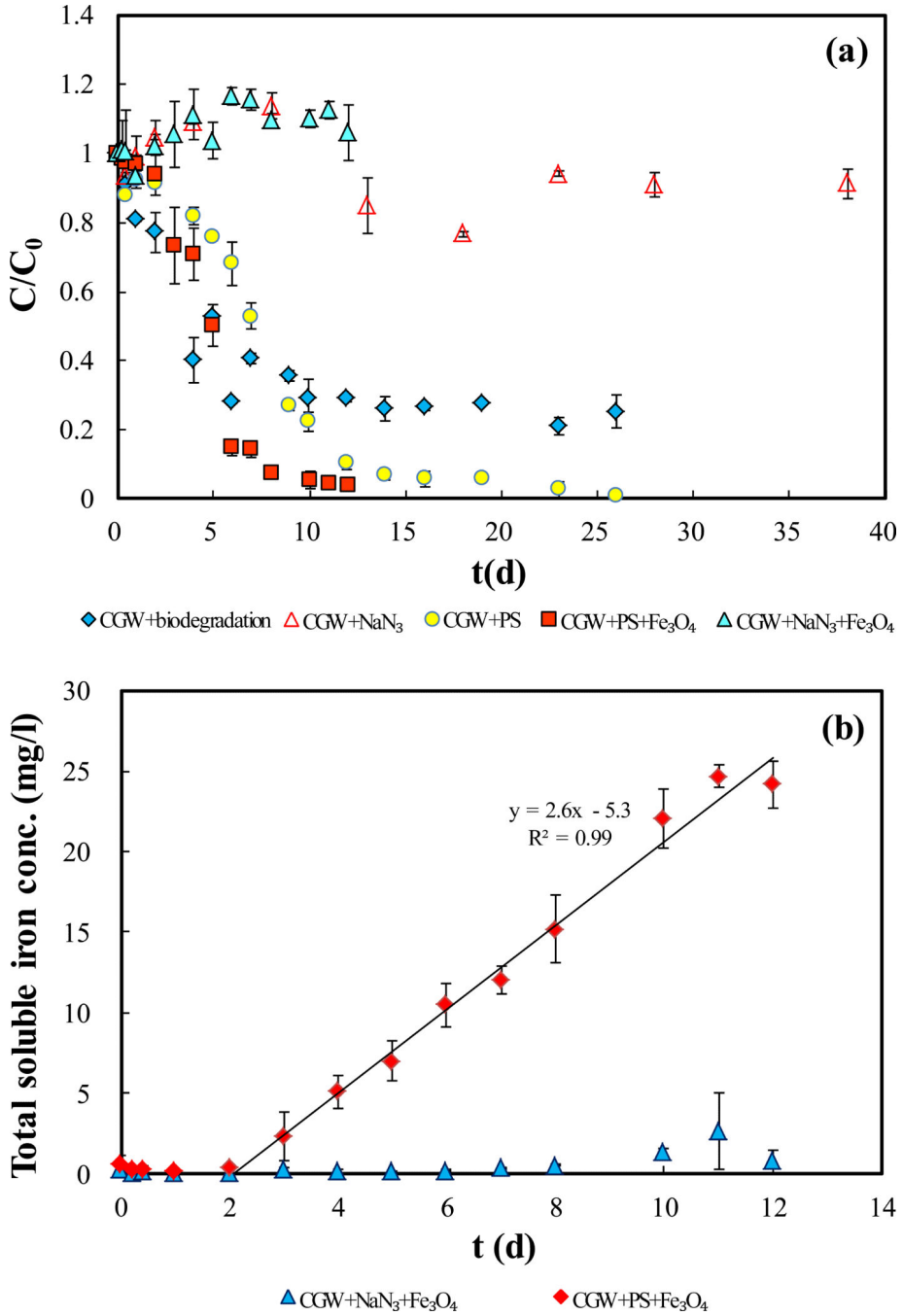

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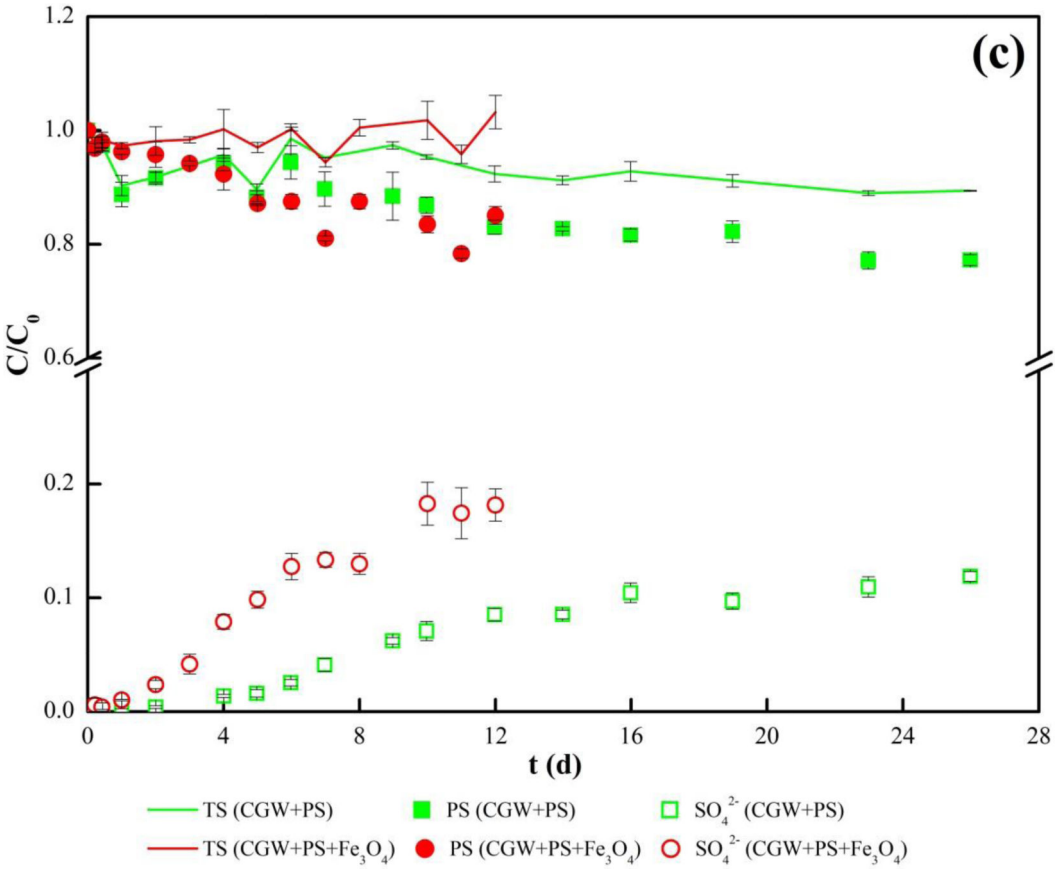

Fig.2.

Degradation of TOC in CGW in batch reactor system. Controls of CGW + NaN_3, CGW + NaN_3 + Fe_3O_4 are also included to examine physicochemical degradation of leachate compounds in the absence of persulfate. (a) Relative concentration of TOC; (b) Concentrations of total soluble iron; (c) Relative concentrations of sulfur species. PS ,TS and CGW in legend represent persulfate, total sulfur and leachate contaminated groundwater, respectively.

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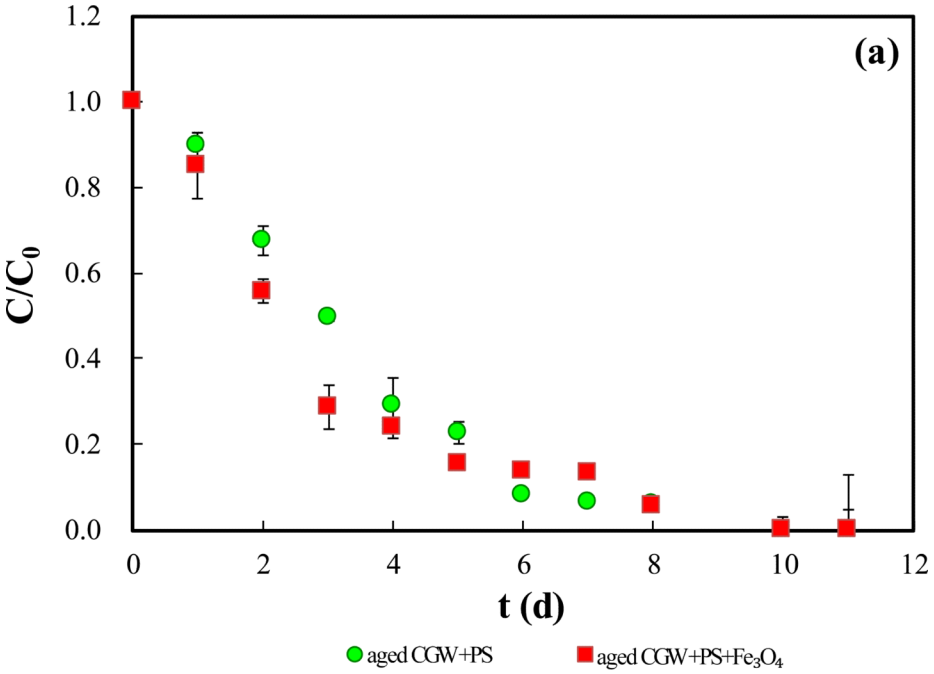

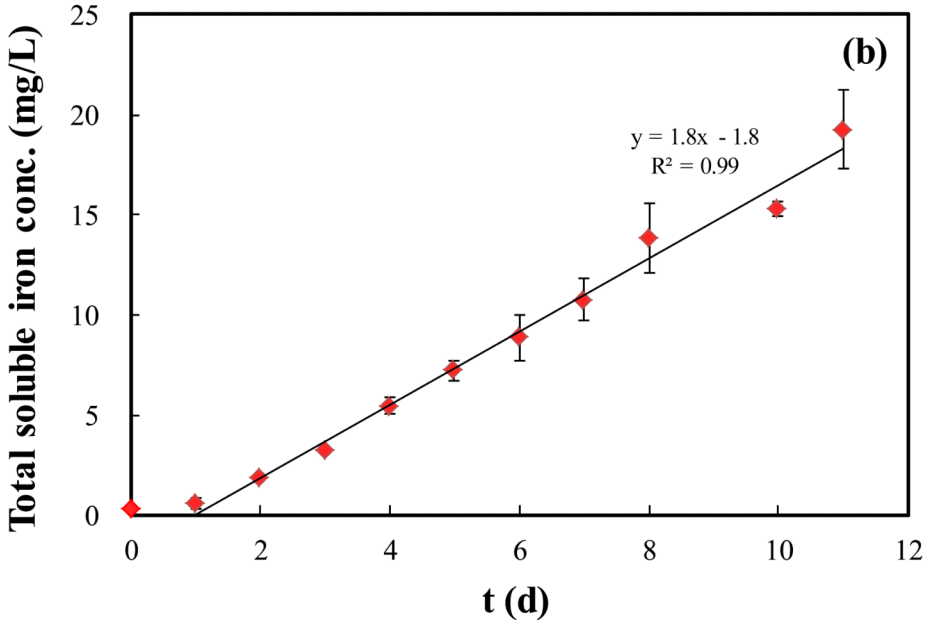

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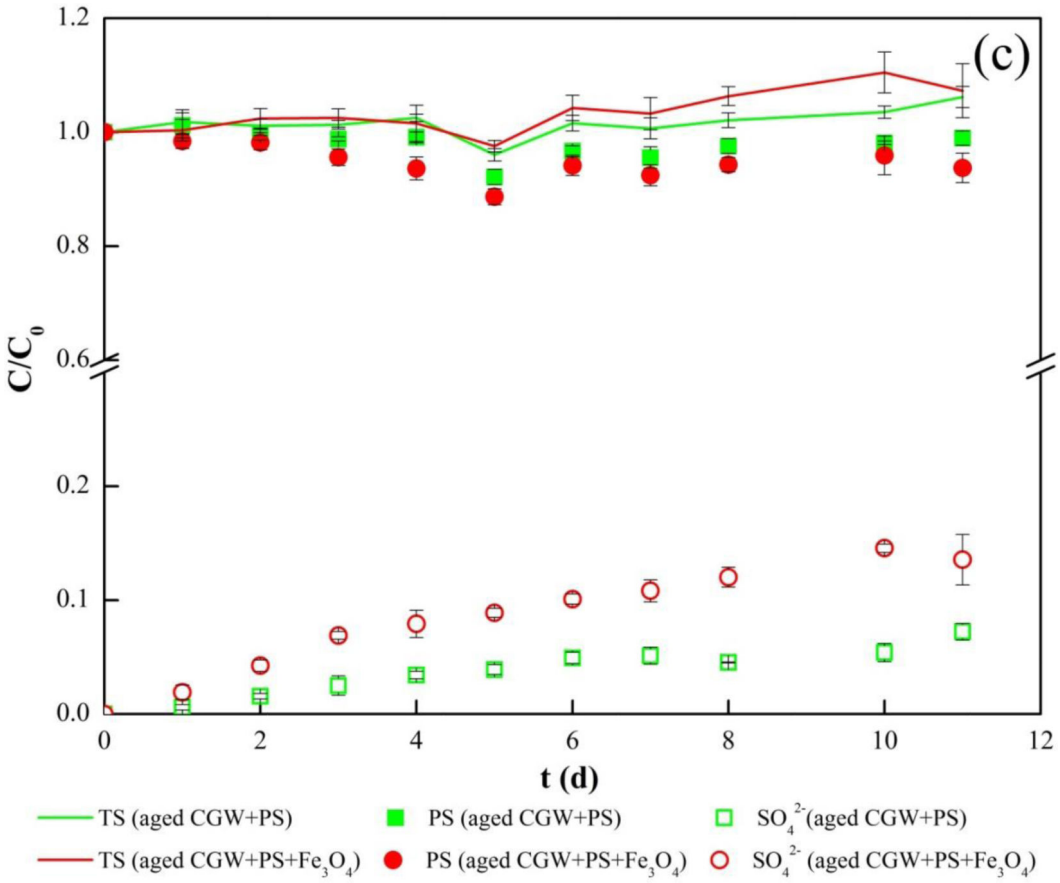

Fig.3.

Degradation of TOC in aged CGW by persulfate in batch reactor system (a) Relative concentration of TOC; (b) Concentration of total iron; (c) Relative concentrations of sulfur species. PS, TS and aged CGW in legend represent persulfate, total sulfur and aged leachate contaminated groundwater, respectively.

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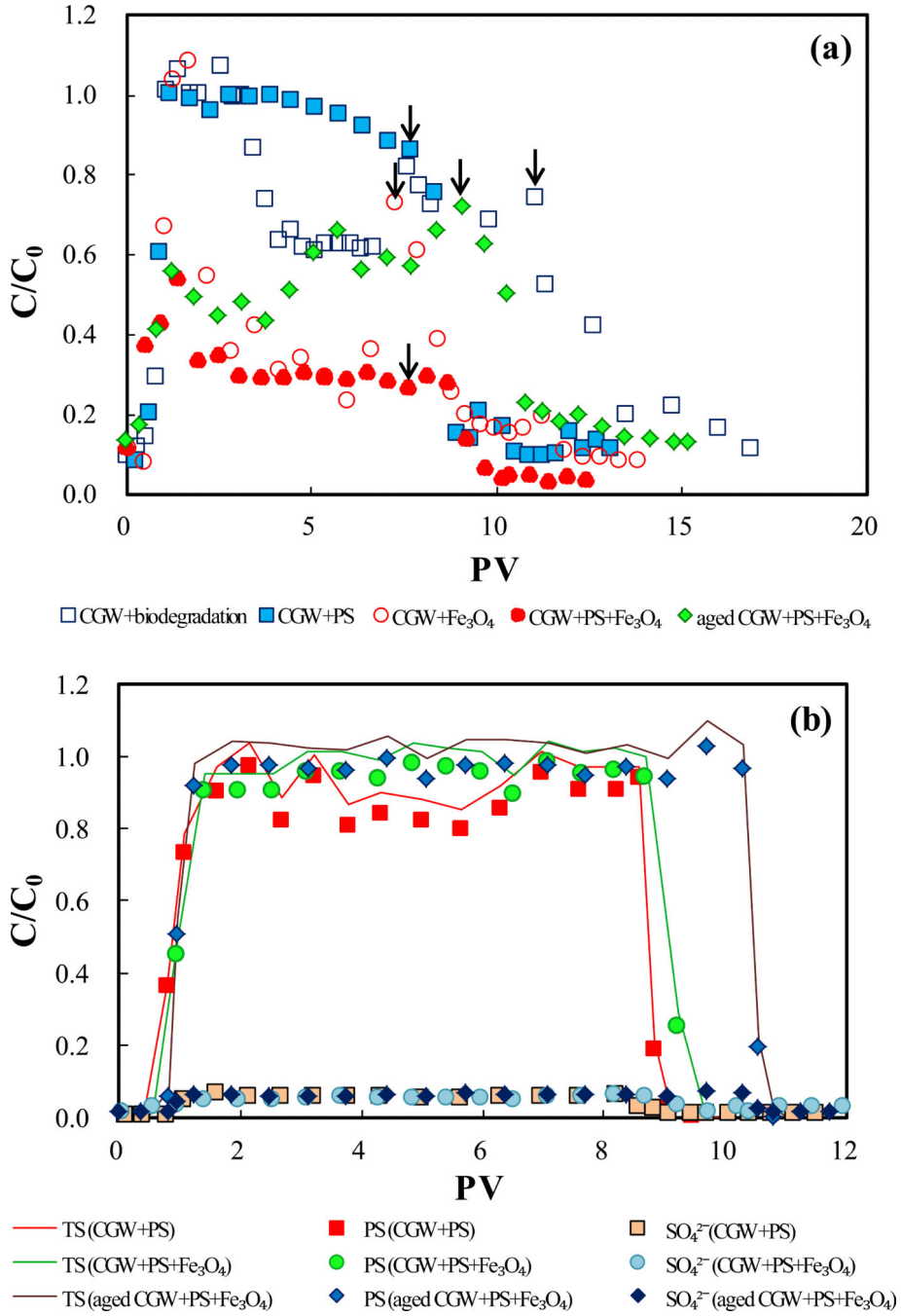

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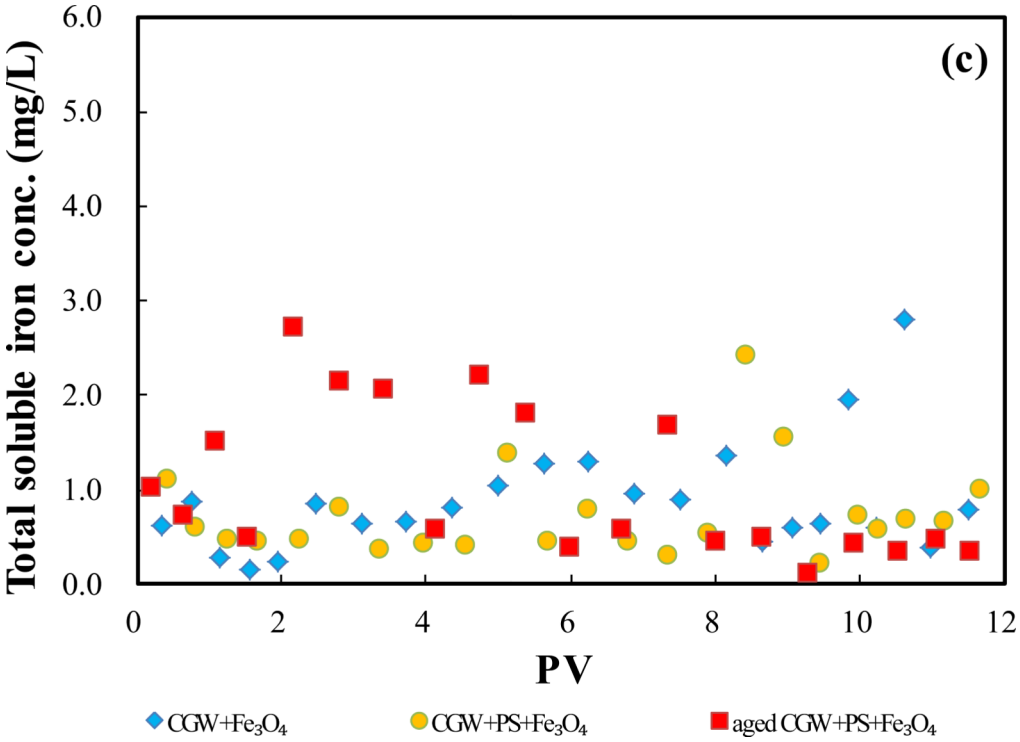

Fig.4.

Degradation of TOC in CGW and aged CGW in sand column under dynamic flow conditions. (a) Breakthrough curves of TOC; (b) Breakthrough curves of persulfate, total sulfur and sulfate; (c) Elution curves of total soluble iron. PS, TS, and CGW and aged CGW in legend represent persulfate, total sulfur, and leachate contaminated groundwater and aged leachate contaminated groundwater, respectively. Arrow indicates the start of water elution.

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Table 1

Water quality of the stock landfill leachate

Parameter	Concentration (mg/L)
TOC	3415 ± 102
COD	6912 ± 297
BOD5	565 ± 19
BOD5/COD	<0.1
NH_4^+–N	1845 ± 18
NO_3^-–N	18.1 ± 6.6%
NO_2^-–N	0.71 ± 0.56%
Lithium (Li)	8.4
Sodium (Na)	2139
Potassium (K)	1399
Magnesium (Mg)	236
Calcium (Ca)	184
Iron (Fe)	1.7
Manganese (Mn)	0.3
Nickel (Ni)	0.2
Cobalt (Co)	0.07
Strontium (Sr)	0.75
Copper (Cu)	< 0.005 (D.L)
Selenium (Se)	< 0.075 (D.L)
Plumbum (Pb)	< 0.042 (D.L)
pH	7.82

D.L: Detection Limit

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Table 2

Organic compounds in the landfill leachate contaminated groundwater identified by GC-MS

Formula	Organic compounds
C_6H_{14}	Pentane, 3-methyl-
C_6H_{14}	n-Hexane
C_6H_{12}	Cyclopentane, methyl-
$C_9H_{18}O_2$	Nonanoic acid
$C_{10}H_{20}O_2$	n-Decanoic acid
$C_7H_{12}O_4$	Propanedioic acid, diethyl-
$C_{13}H_{22}O$	5,9-Undecadien-2-one, 6,10-dimethyl-
$C_{12}H_{26}O$	1-Dodecanol
$C_{16}H_{34}$	Hexadecane
$C_{12}H_{26}O$	1-Dodecanol
$C_8H_{16}O$	Cyclohexanol, 2,4-dimethyl-
$C_{12}H_{24}O_2$	Dodecanoic acid
$C_{12}H_{26}O$	1-Dodecanol
$C_{16}H_{34}$	Hexadecane
$C_{12}H_{14}O_4$	Diethyl Phthalate
$C_{14}H_{26}O_3$	Undecanoic acid, 4,8-dimethyl-10-oxo-
$C_{19}H_{40}$	Pentadecane, 2,6,10,14-tetramethyl-
$C_{13}H_{28}O$	n-Tridecan-1-ol
$C_{17}H_{36}$	Heptadecane
$C_{19}H_{40}$	Pentadecane, 2,6,10,14-tetramethyl-
$C_{11}H_{24}$	Nonane, 3,7-dimethyl-
$C_{14}H_{30}O_2$	Ethanol, 2-(dodecyloxy)-
$C_{14}H_{28}O_2$	Tetradecanoic acid
$C_{14}H_{30}O$	1-Tetradecanol
$C_{14}H_{23}F_3O_2$	trans-2-Dodecen- 1-ol, trifluoroacetate
$C_6H_{10}N_6O_3$	Furazan-3-carboxamide
$C_{14}H_{28}O_2$	Tetradecanoic acid
$C_{15}H_{30}$	1-Pentadecene
$C_{17}H_{36}O$	n-Heptadecanol-1
$C_{17}H_{36}$	Heptadecane
$C_{14}H_{30}O_2$	Ethanol, 2-(dodecyloxy)-
$C_{16}H_{34}$	Hexadecane
$C_{15}H_{30}O_3$	Methoxyacetic acid, dodecyl ester
$C_{14}H_{28}O_2$	Tetradecanoic acid
$C_7H_{12}N_2O_4$	5-Cyano-desoxinojirimycin
$C_{12}H_{19}NO_7$	1,3-Dioxolane-4-acetic acid

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Formula	Organic compounds
$C_{15}H_{28}O_2$	Cyclopentadecanone, 2-hydroxy-
$C_{15}H_{30}O_2$	Pentadecanoic acid
$C_{16}H_{22}O_4$	1,2-Benzenedicarboxylic acid
$C_{15}H_{32}O$	n-Pentadecanol
$C_{25}H_{36}O_7$	4,13,20-Tri-O-methylphorbol 12-acetate
$C_{17}H_{34}O_2$	Hexadecanoic acid, methyl ester
$C_{18}H_{34}O_2$	Oleic Acid
$C_{17}H_{16}OS$	3,3-Di-p-tolyl-thietan-2-one
$C_{16}H_{32}O_2$	n-Hexadecanoic acid
$C_{19}H_{40}O$	n-Nonadecanol-1
$C_{16}H_{33}I$	Hexadecane, 1-iodo-

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Table 3

Pseudo-first-order reaction rate constant k and half-life $t_{1/2}$ of TOC in batch experiments

Reactants	Rate constant *k* (day^{-1})	Half-life $t_{1/2}$ (day)
CGW + biodegradation	0.14	5.0
CGW + NaN_3	0.009	77
CGW + persulfate	0.16	4.3
CGW + hydrogen peroxide	0.002	347
CGW + permanganate	0.001	693
CGW + NaN_3 + Fe_3O_4	−0.011	n.a
CGW + persulfate + Fe_3O_4	0.27	2.6
Aged CGW + persulfate	0.35	2.0
Aged CGW + persulfate + Fe_3O_4	0.34	2.0

n.a: not available