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Comparative study of ferrate and thermally activated persulfate treatments for removal of mono- and dichlorobenzenes from groundwater

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1.Introduction

Chlorobenzenes (CBs) are a family of aromatic organic compounds released into the aquatic environment from several different sources. Less chlorinated agents of CBs – monochlorobenzene (MCB) and isomers of dichlorobenzene such as 1,2-dichlorobenzene (1,2-DCB), 1,3-dichlorobenzene (1,3-DCB) and 1,4-dichlorobenzene (1,4-DCB) – are widely used e.g. in dry cleaning, in degreasing of metal surfaces or as industrial solvent in the synthesis of pesticides and dielectric fluids. Due to their widespread applications in various industrial fields, CBs are one of the major organic contaminants in surface- and groundwaters [1-2].

Several sample-preparation and analytical methods are used to determine MCB, 1,2-DCB, 1,3-DCB and 1,4-DCB in water matrices. For quantitative analysis of CBs, the gas chromatograph (GC) coupled with electron capture detector (ECD), flame ionization detector (FID) or mass spectrometer (MS) is the most frequently applied analytical system following liquid-liquid extraction (LLE) or solid phase microextraction (SPME) of these analytes. Depending on the applied analytical procedure, detection limits of the four chlorobenzene compounds change in the range of 0.007-3.0 μg/L [3-8].

For the removal of CBs from different water matrices, biological and chemical technologies have been developed. For example, by applying *Acidovorax avenae sp.* community for biodegradation of CBs in a polluted aquifer, 100% removal efficiency was achieved within two days for the above mentioned chlorobenzenes [9]. A similarly efficient way is offered by the *Acidovax* and *Pseudomonas sp.* communities for the removal MCB from contaminated groundwater, however it should be noted, that this way the interaction time amounts to nine days [10]. A microwave (MW) assisted zero valent iron (nZVI) technology was developed for the removal of MCB from model solutions by applying nZVI in concentration of 20 g/L and 5-minute MW treatment time (2.45 GHz, 750W) resulting in a 83% removal efficiency [11]. Supercritical water oxidation and TiO_2 photocatalysis were also successfully applied for the degradation of MCB by using 0.8 mM TiO_2 and near UV radiation [12].

Among the current commonly used advanced oxidative water treatment processes, ferrate and persulfate technology have gained great interest. Ferrate ion (FeO_4^{2-}) is a powerful oxidative reagent with 2.2 V redox potential under weak acidic condition. During the oxidation process, ferrate is reduced forming ferric hydroxide, which is able to adsorb oxidation by-products due to its high specific surface area [13-16]. FeO_4^{2-} treatment can be effectively applied to degrade several organic compounds e.g. fulvic acid [17], pharmaceuticals [18], personal care products

[19], bisphenol-A [20], carbohydrates [21], phenol and chlorophenols [22], trichloroethylene [23] in the water phase.

Persulfate anion ($S_2O_8^{2-}$) is a strong oxidizing agent having 2.0 V redox potential (E_0). $S_2O_8^{2-}$ can be transformed to more effective sulfate radical (E_0=2.6 V) using different activation methods (e.g. heat, Fe^{2+} addition, UV light) [24, 25]. In the literature, the application of thermally activated persulfate for the removal of organic compounds – such as perfluorooctanoic acid [26], polyvinyl alcohol [27], antipyrine [28], ibuprofen [29], sulfamethoxazole [30], diuron [31], carbamazepine [32], trichloroethylene [33], aniline [34] – is well demonstrated. Previous studies established, that in heat-activated persulfate systems sulfate and hydroxyl radicals are generated. The distribution of these is strongly pH dependent: at pH<7 $SO_4^{.-}$ is the important species, while at pH>9 OH^- is the dominant free-radical, and at pH:7–9 both two radicals participate in the oxidative process [25, 34]. Some papers emphasized that an inhibition effect can be observed in the presence of HCO_3^- (6100 mg/L), Cl^- (3550 mg/L) and humic acids (100 mg/L) on the degradation of organic compounds by thermally activated persulfate. These phenomena provide a key information to clarify the oxidative effect of persulfate in contaminated groundwater matrices [34, 35].

In spite of the wide application field of these oxidative agents in the literature there are only a few studies dealing with MCB and DCBs removal from water matrices applying ferrate or persulfate treatments. MCB and DCBs removal were investigated from organic hydrocarbon polluted groundwater (COD_{Cr} 1090 mg/L) by the combination of ferrate and hydrogen-peroxide oxidative agents. It was concluded that by applying 400 mg/L ferrate concentration followed by 45-minute treatment time, and with the addition of hydrogen peroxide solution in two steps (2x5 mL cc. H_2O_2 per liter) with a reaction time of 24 hours, the removal efficiencies of MCB, 1,2-DCB, 1,3-DCB and 1,4-DCB were 72%, 70%, 73%, 73%, respectively [36]. Simultaneous removal of 59 volatile organic compounds from model solutions was studied by using thermally activated persulfate in concentration of 1000 mg/L. It was established that having 0.09 mg/L MCB and DCBs initial concentrations with 72 hours treatment time, the removal of MCB, 1,2-DCB, 1,3-DCB and 1,4-DCB amounted to 90%, 60%, 63% and 86%, respectively [37]. 100% removal efficiency was achieved for MCB from contaminated groundwater (TOC 84.2 mg/L) by applying thermally activated persulfate in molar ratio of 1:200 and with 2-hour treatment time [38]. In another experiment Fe^{2+} activated persulfate in concentration of 80 mg/L was used to remove 1,4-DCB from groundwater having 0.004 mg/L initial concentration. Following a 20-hour treatment time the removal efficiency was 85% [39].

Considering the above mentioned results and further literature data, it is clear that the removal efficiency of given organic contaminants depends on the chemical properties and the concentration of oxidative agent applied, the molar ratio (oxidative agent/contaminant) as well as the chemical composition of water to be treated (TOC, COD, salt content, etc.). In addition to these facts, it was also established that the removal efficiency values of MCB and DCBs are practically the same at high dose of ferrate (400 mg/L) and hydrogen-peroxide (5 mg/L), however, in case of persulfate treatment MCB and 1,4-DCB achieved about 20-30% higher degradation than the 1,2 and 1,3-DCB isomers.

In this paper the removal of MCB, 1,2-DCB, 1,3-DCB and 1,4-DCB from model and groundwater solutions were studied using ferrate and thermally activated persulfate treatments. In order to compare the oxidative effect of these agents, during the entire experimental work, the same ferrate and persulfate dosages were applied. Removal efficiencies were calculated on basis of the concentration values of target molecules determined by SPME/GC-MS method before and after the treatment of model and groundwater solutions having the same initial CBs concentration, containing the chlorobenzenes separately and all four together as well.

2. Materials and methods

2.1. Chemicals

All chemicals applied in the experiment were of analytical grade and purchased from Sigma Aldrich-Ltd., Hungary. For preparation of standard and model solutions of MCB, 1,2-DCB, 1,3-DCB and 1,4-DCB, methanol and ultrapure water (produced by Milli Q Plus equipment) were used. Potassium ferrate solution in concentration of 1 g/L was synthesized by an electrochemical process applying the method as mentioned in the previous article [40]. Sodium persulfate stock solution was prepared by dissolving sodium persulfate (Sigma Aldrich-Ltd., Hungary) in ultrapure water. For pH adjustment sulfuric acid and for regulation of buffer capacity of model solutions sodium-hydrogen-carbonate were applied.

2.2. Solution preparation

Model solutions containing the four chlorobenzene compounds (MCB, 1,2-DCB, 1,3-DCB, 1,4-DCB) separately and mixed in concentration of 100 μg/L were prepared by using methanol and ultrapure water. In order to harmonize the buffer capacity of model solutions

and the chlorobenzene free groundwater, sodium carbonate solution was added to the model solutions resulting in HCO_3^- concentration of 565 mg/L. Groundwater was filtered through a glass membrane (Millipore, 0.45 μm), and analyzed by methods listed in *subchapter 2.4*. The groundwater was spiked with the four chlorobenzene target compounds in concentration of 100 μg/L. After this procedure 10 cm^3 model and groundwater solutions were transferred into septum sealed vials. For getting a measuring curve a row of solutions was prepared in 1−100 μg/L concentration range from certificated material applying also matrix-matching.

2.3. Instrumentation and operating conditions

The measurement of chlorobenzene compounds was carried out by a Bruker SCION 436 GC-MS equipment. Separation of the compounds was obtained on a BR-5 column (30 m × 0.25 mm, df=1 μm) using helium (purity: 6N) as carrier gas (flow rate 2 ml/min). The temperature of manifold, filament and transfer line was 40°C, 200°C, 220°C, respectively. For analytical measurements the scan mode was selected.

For the enrichment of chlorobenzene compounds from the liquid sample SPME fibers were applied (Supelco, PDMS, 100 μm). Before the first application, SPME fiber was conditioned in the GC-MS injector port at 250°C for 30 min. After this procedure the SPME fiber was introduced into the septum sealed vial containing 10 cm^3 water sample and immersed directly into the solution for 5 minutes, then injected to the GC-MS port. GC-MS temperature program started at 60°C maintained for 1 minute, then ramped at 10°C/min up to 160°C (total elution time was 11 min). Injector temperature was 250°C and used in splitless mode.

2.4. Chemical analysis of groundwater

Groundwater was obtained from a hydrocarbon contaminated area in Hungary and its physico-chemical parameters were measured according to standard methods. Total inorganic carbon (TIC), total organic carbon (TOC), total nitrogen (TN) concentrations were determined by applying a Multi N/C 2100S TC-TN analyzer (Analytik Jena, Germany) according to the valid international standards (EN ISO 5667-3:1995 and MSZ EN 12260:2004). Specific electric conductivity and pH were measured according to standard methods [41]. The absence of the four target compounds was checked by SPME/GC-MS method.

2.5. Ferrate and persulfate treatments

10 cm³ model and spiked groundwater solutions having 100 μg/L initial CB concentrations were transferred into septum sealed vials and calculated amounts of ferrate solution were added by using an injection syringe, resulting in 10, 20, 30 and 50 mg/L ferrate concentration (molar ratios of MCB:ferrate changed between 1:94−1:473 and of DCBs:ferrate between 1:122−1:612). According to our preliminary investigations the pH was adjusted by addition of sulfuric acid in the pH range of 5-11. The solutions were continuously stirred at room temperature for 30 minutes.

In case of persulfate treatment sodium persulfate solution was added to the solutions to be treated in concentration of 10, 20, 30 and 50 mg/L (molar ratios of MCB:persulfate changed between 1:59–1:295 and of DCBs:persulfate between 1:76–1:382) in a similar way as mentioned above. It should be noted that the pH of single model solutions containing sodium persulfate in concentration of 10, 20, 30 and 50 mg/L decreased from 6.0 to 4.3; however, in the presence of groundwater matrix the pH remained at 8.5 due to the high buffer-capacity of groundwater. The thermal activation of persulfate was carried out at 40°C, 50°C, 60°C for 1 hour in the headspace autosampler unit of the GC-MS system.

After the ferrate and heat-activated persulfate treatments, the concentration of the four chlorobenzene compounds were measured by applying SPME/GC-MS method as mentioned in *subchapter 2.3*.

3. Results and discussion

3.1 Ferrate treatment

In the oxidation processes of ferrate pH plays a dominant role, since the stability (self-decomposition) and the reactivity of ferrate(VI) strongly depend on pH. On the other hand, the protonation or deprotonation of target molecules at the given pH also influence the oxidation pathway. Therefore, the effect of pH on the removal efficiency of the four target molecules was studied in the pH range of 5-11 (Fig. 1). It can be established, that the highest removal efficiency for the four investigated compounds was achieved at pH=7; however, it should be noted that the attack of ferrate was most efficient in case of 1,2-DCB, where due to the ortho position of chlorine substituent the nucleophilic character of the target molecules was greater, than in case of the meta or para positions.

Fig. 2-4 demonstrate the removal efficiency of MCB and DCB-s at four different ferrate dosages from model solutions containing only one target compound (Fig. 2), or all four compounds simultaneously (Fig. 3) or these target compounds in the presence of groundwater matrix (Fig. 4). The physicochemical parameters of groundwater are listed in Table 1. As it was expected, increasing ferrate concentrations resulted in higher degradation of target molecules. The highest removal was achieved for 1,2-DCB in all cases; however, the removal efficiency values decreased in the following order: single model solution > four compounds model solution > groundwater containing the four CBs. The decreasing tendency can be attributed to the increasing ratio of organic matter/oxidative agents.

3.2. Thermally activated persulfate treatment

At first the effect of activation temperature on the removal of the four target compounds was studied. As Fig. 5 demonstrates, with increasing temperature from 40°C to 60°C, the removal efficiency increased for all CB-s investigated, applying 1-hour treatment time. Therefore, 60°C activation temperature was used during the remaining experimental work. The influence of persulfate dosage on the degradation of the four target compounds was investigated in concentration range of 10-50 mg/L treating three different water samples containing the MCB and DCB compounds separately (Fig. 6), and mixed (Fig. 7), as well as mixed in the presence of groundwater matrix (Fig. 8). On basis of results presented on these figures it can be established that the degradation of all target molecules increased with an increasing concentration of persulfate, and the highest degradation rate was observed in case of MCB and 1,4-DCB. At increasing concentration of organic compounds in the solutions the removal efficiency values decreased, although this "matrix-effect" caused only by the target molecules (Fig. 7) was relatively small (about 6-8%). However, the presence of groundwater matrix (TOC 84.7 mg/L, Cl^- 78.1 mg/L, HCO_3^- 565 mg/L) strongly hampered the removal of CB compounds (Fig. 8). These observations harmonize with the literature data summarized in review of Matzek and Carter [25]. This means that the effect of bicarbonate and chloride ions, as well as humic substances are responsible for this phenomenon which could result in scavenging of the sulfate free radicals and could limit its oxidation efficiency.

3.3 Comparison of ferrate and thermally activated persulfate treatment

Since the application of 30 mg/L ferrate and 50 mg/L thermally activated persulfate resulted in target compound/oxidative agent similar molar ratios, the degradation rates of the four chlorobenzene compounds were compared at these concentrations of the oxidative agents at Table 2. On basis of these data the following conclusion can be drawn:

- The persulfate has higher average removal efficiency than the ferrate for all target molecules in solutions containing the target molecules separately or their mixture.
- In presence of groundwater matrix with considerable bicarbonate and chlorine ion concentrations, the mean degradation rate of chlorobenzene compounds achieved a similar level (14%) for both treatments due to the considerable reduction of persulfate efficiency.
- Ferrate and persulfate, as electrophilic compounds, attack different points of aromatic compounds. Ferrate removes better 1,2-DCB, while persulfate is more efficient for the removal of MCB and 1,4-DCB.
- An important advantage of ferrate treatment is the removal of oxidation by-products by adsorption on the ferric hydroxide forming continuously during the oxidation process [13-16]. In case of persulfate treatment these reaction products remain in the treated solutions.
- On the other hand, the application of persulfate treatment is a relatively simple technological step, since this oxidation agent is a stable chemical compound, and its thermal activation can be easy realized. The ferrate technology needs continuous on-site production of sodium ferrate solution in order to eliminate the limitations caused by self-decomposition and storage.

Conclusion

Considering the results and observations of these experiments, it can be stated that for remediation of groundwater containing chlorobenzene compounds both treatment can be applied; however, the thermally activated persulfate treatment is a cheaper and simpler process compared to the ferrate treatment. Nonetheless, in case of high HCO_3^- and Cl^- ion contents of groundwater, the scavenging of persulfate radicals is a critical step. In order to select the most efficient oxidative treatment procedure at first the TOC, TIC and Cl^- concentrations of groundwater have to be determined in a laboratory scale experiment. Ferrate

may be preferred first of all at high concentration of interfering compounds mentioned above or in case of formation of toxic by-products.

Acknowledgement

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Figure captions:

Fig. 1: CB removal efficiency applying 50 mg/L ferrate dosage at various pH values from model solutions having 0.1 mg/L initial CB concentrations and containing the four chlorobenzene compounds in mixed

Fig. 2: CB removal efficiency applying various ferrate dosages at pH=7 from model solutions having 0.1 mg/L initial CB concentrations and containing the four chlorobenzene compounds separately.

Fig. 3: CB removal efficiency applying various ferrate dosages at pH=7 from model solutions having 0.1 mg/L initial CB concentrations and containing the four chlorobenzene compounds in mixed.

Fig. 4: CB removal efficiency applying various ferrate dosages at pH=7 from spiked groundwater having 0.1 mg/L initial CB concentrations and containing the four chlorobenzene compounds in mixed.

Fig. 5: CB removal efficiency applying 50 mg/L thermally activated persulfate dosages at various temperature from model solutions having 0.1 mg/L initial CB concentrations and containing the four chlorobenzene compounds in mixed.

Fig. 6: CB removal efficiency applying various thermally activated persulfate dosages from model solutions having 0.1 mg/L initial CB concentrations and containing the four chlorobenzene compounds separately.

Fig. 7: CB removal efficiency applying various thermally activated persulfate dosages from model solutions having 0.1 mg/L initial CB concentrations and containing the four chlorobenzene compounds in mixed.

Fig. 8: CB removal efficiency applying various thermally activated persulfate dosages from spiked groundwater having 0.1 mg/L initial CB concentrations and containing the four chlorobenzene compounds in mixed.
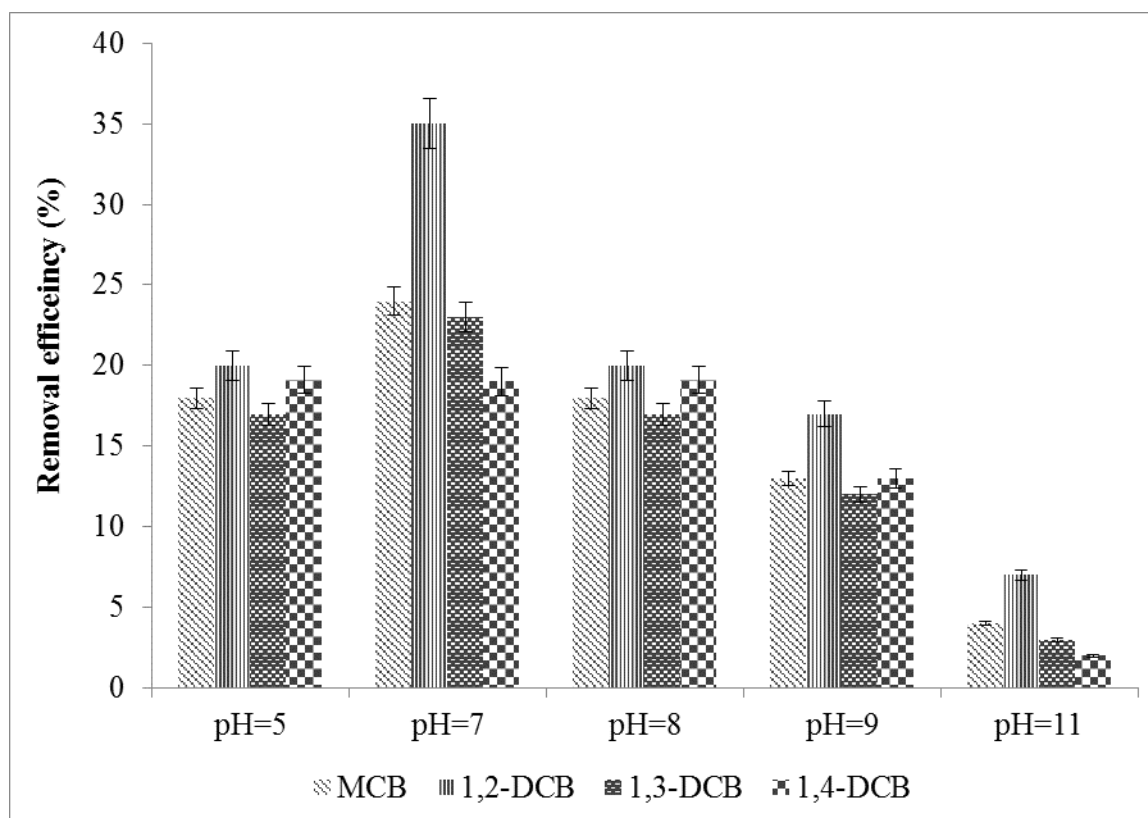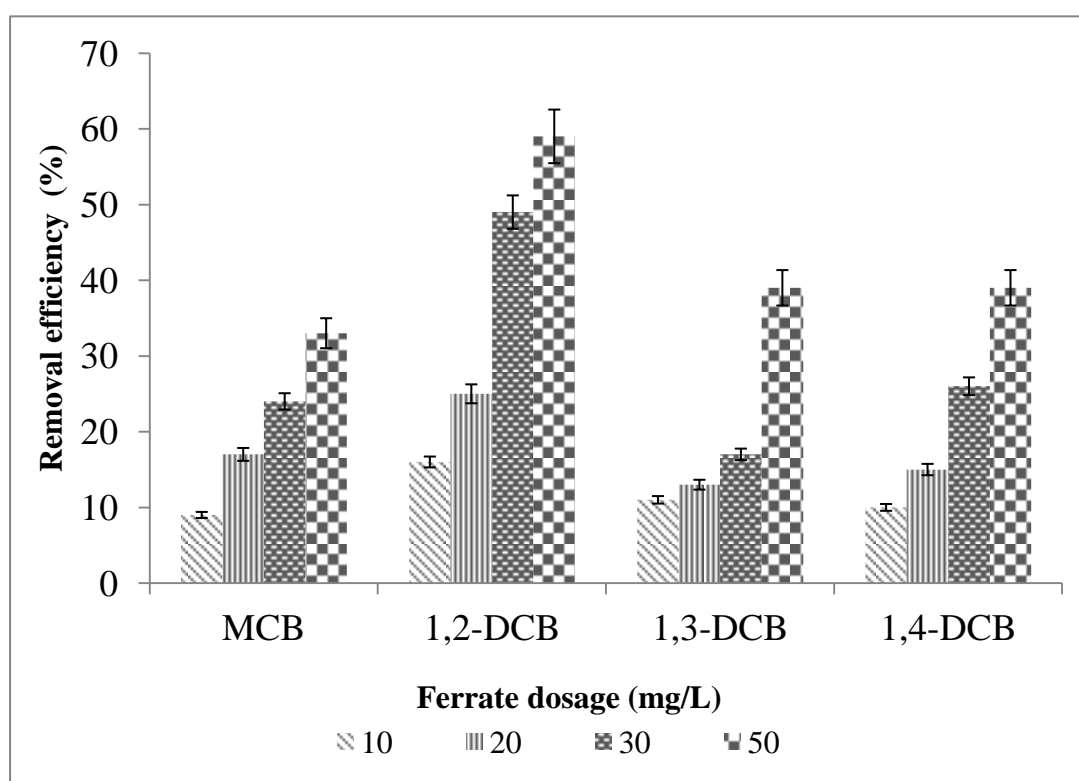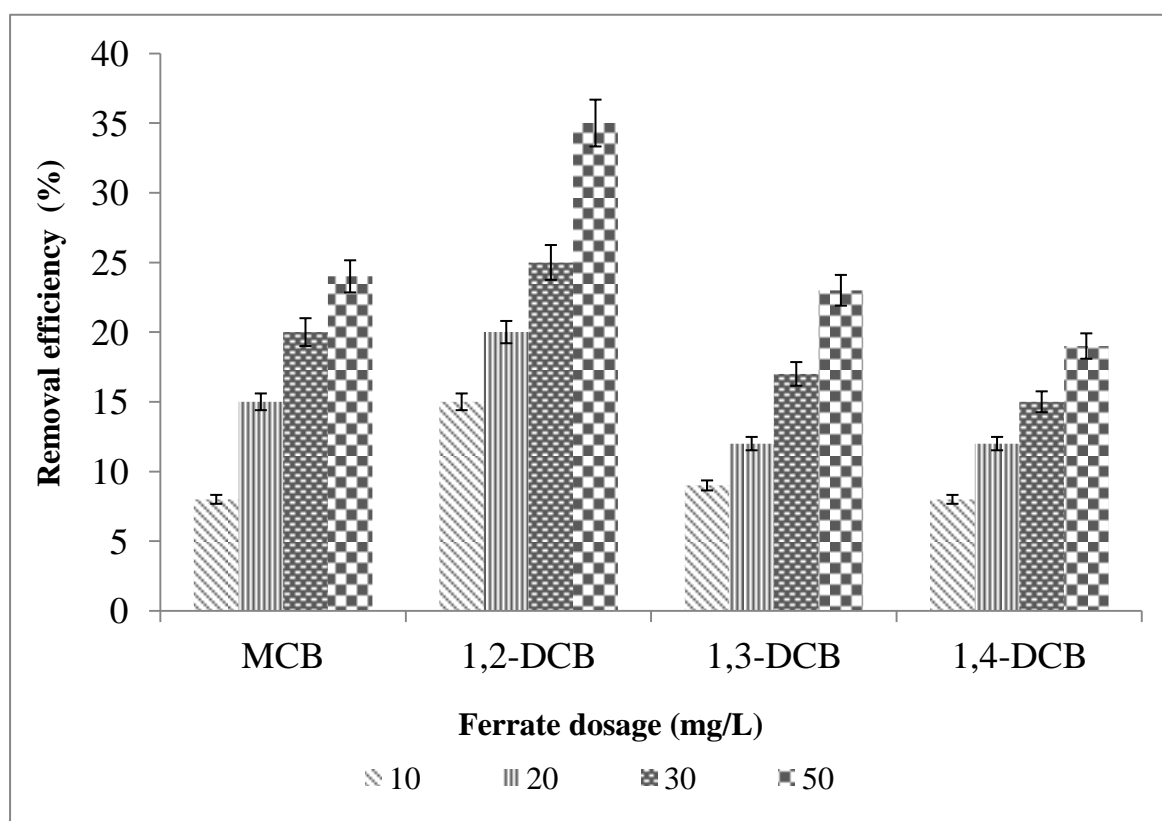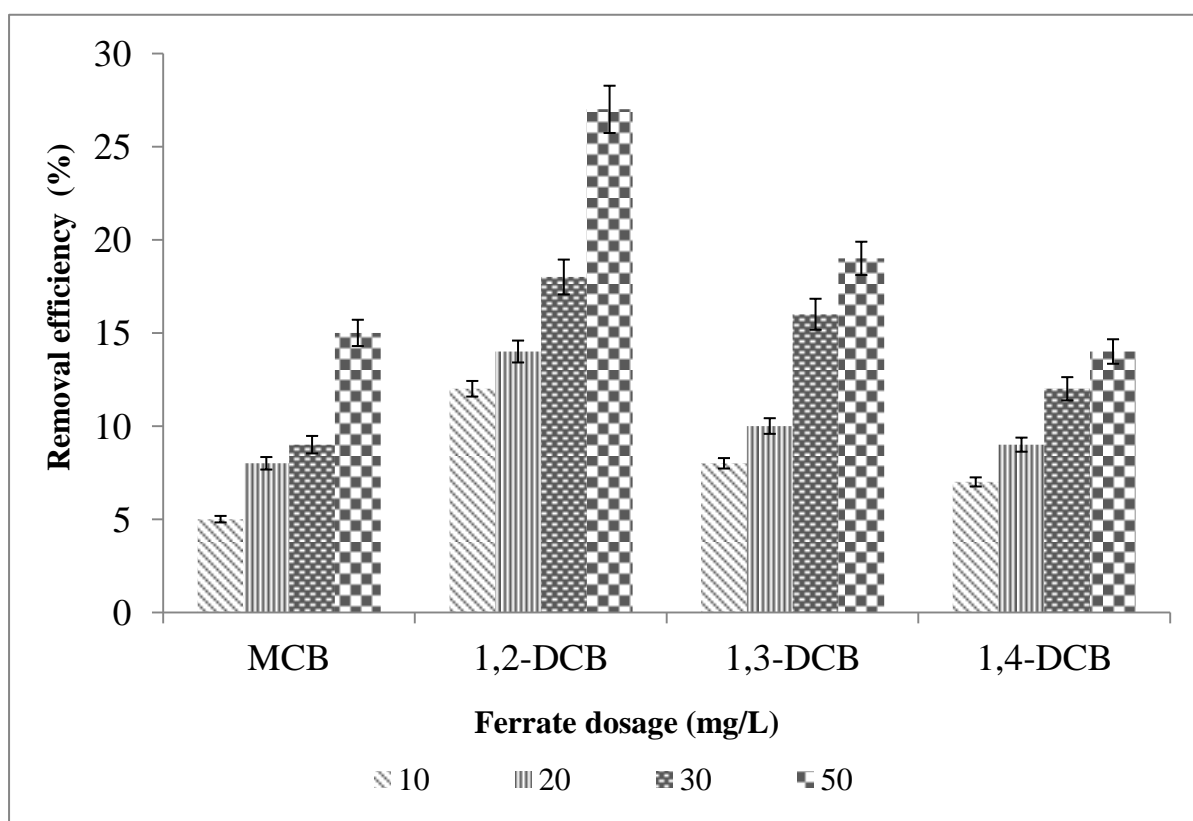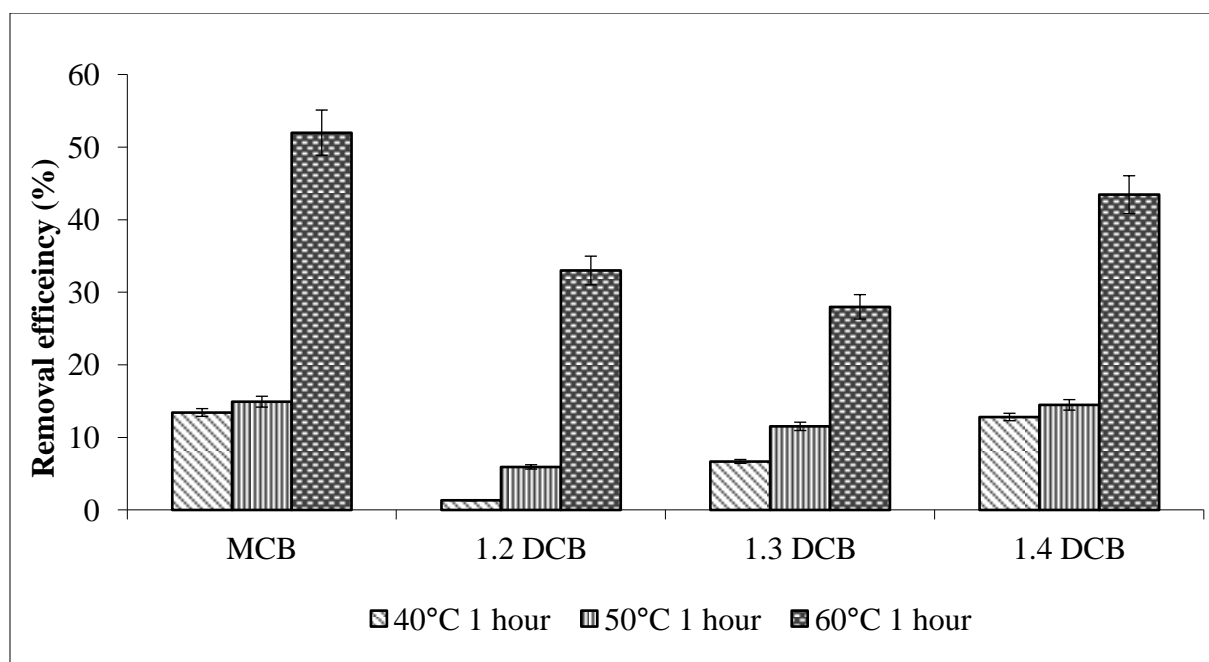
Fig. 1

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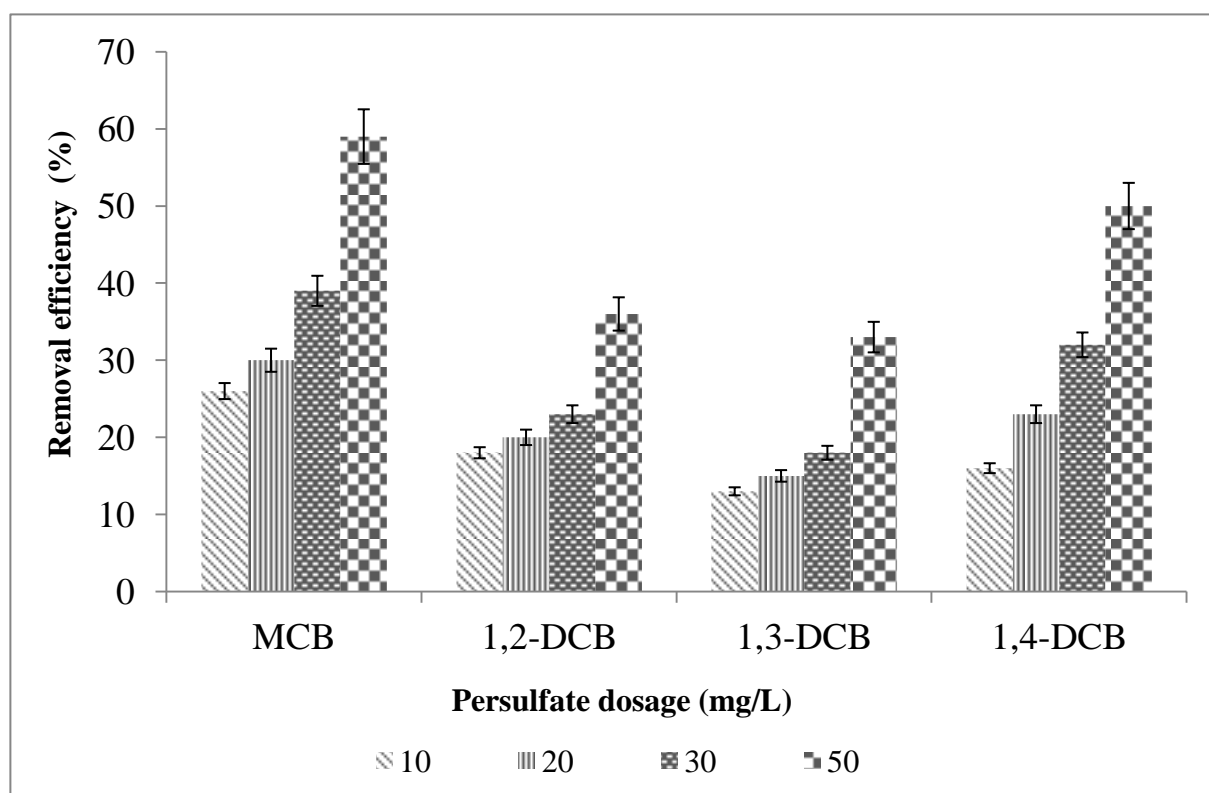
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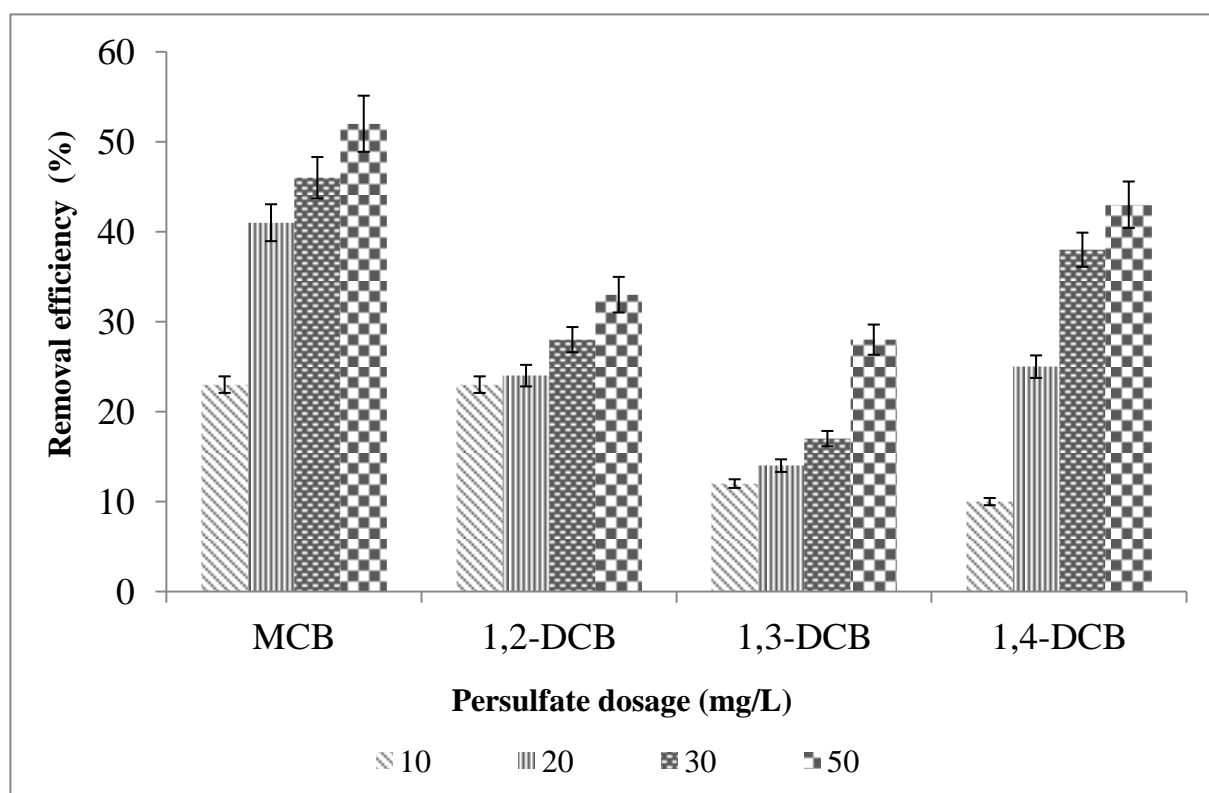
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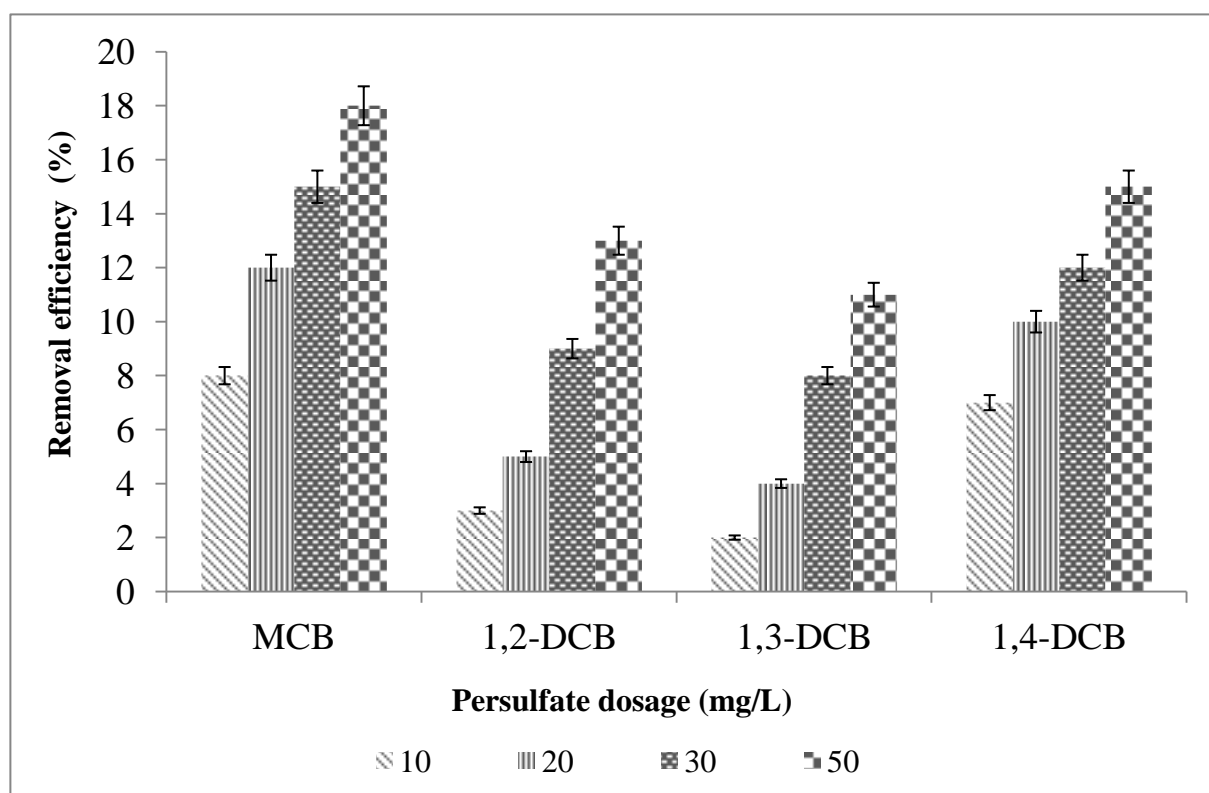
Table 1. Physicochemical parameters of groundwater

pH	8,53
Specific electric conductivity (µS/cm, 20°C)	1470
NO_3^- (mg/L)	11,3
NO_2^- (mg/L)	<0,01
NH_4^+ (mg/L)	<0,01
SO_4^{2-} (mg/L)	271
Cl^- (mg/L)	78,1
HCO_3^- (mg/L)	565
Total hardness (nK°)	36,4
Total organic carbon (mg/L)	84,7
Total inorganic carbon (mg/L)	113
Total nitrogen (mg/L)	2,50
Chlorobenzene compounds (µg/L)	n.d.[*]

[*] not detectable

Table 2. Removal efficiency values for the four chlorobenzene compounds applying ferrate and thermally activated persulfate treatments at nearly the same molar ratios of target molecules/oxidative agent

Chlorobenzene compounds	30 mg/L ferrate			50 mg/L persulfate		
	single	mixed	mixed + groundwater	single	mixed	mixed + groundwater
MCB	24	20	9	59	52	18
1,2-DCB	49	25	18	36	33	13
1,3-DCB	17	17	16	33	28	11
1,4-DCB	26	15	13	50	43	15
Average removal efficiency	29	19	14	44	39	14

*chlorobenzene:oxidative agent

Highlights:

- Comparison of ferrate and thermally activated persulfate treatments for removal of chlorobenzene compounds from model solutions and groundwater

- Ferrate and persulfate remove with highest efficiency 1,2-dichlorobenzene and monochlorobenzene, respectively.

- The influence of water matrix on the removal efficiencies is higher in case of persulfate treatment than those of ferrate.