Effect of cations and ferric-oxide/hydroxide precipitation on the removal of chlorobenzene compounds from model solutions applying ferrate treatment

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ABSTRACT

The effect of cations (Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}) as common compounds of groundwater and ferric-oxide/hydroxide precipitation formed during the ferrate treatment on the removal of monochlorobenzene (MCB) and dichlorobenzene (1,2-DCB and 1,3-DCB) from model solutions were studied. The model solutions contained the three CB-compounds and sodium–hydrogen–carbonate in the concentration of 10 and 150 mg/L, respectively. To investigate the cation effect only one or simultaneously all the four cations were added to the model solutions in a molar ratio (CB-s:cations) of 1:1 or 1:4, respectively. The ferrate treatment was carried out by the addition of highly alkaline sodium ferrate solution (6 g/L) to the model solutions resulting in a CB-s:Fe(VI) molar ratio of 1:5. To adjust the pH from 12 to the optimal 7, high purity 5 M sulphuric acid was used and the freshly formed suspension was stirred for 30 min at room temperature. In the liquid phase, the concentration of CB-s, the purgeable carbon content, the cations and the chlorine as oxidation by-product were measured by headspace gas chromatography–mass spectrometry, total organic carbon analyzer, flame atomic absorption spectroscopy, and ion chromatography, respectively. Comparing the removal efficiency values of CB-s obtained by ferrate treatment in absence or presence of cation(s), it can be established that the degradation of these target pollutants increased in presence of cations in the following order: Zn^{2+} (3%) < Mg^{2+} (30%) < Ni^{2+} (50%) < Ca^{2+} (72%). However, the ferric-oxide/hydroxide precipitate did not affect the CB-s removal, but a considerable part of cations was removed from the liquid phase due to co-precipitation and adsorption processes. It should be emphasized that the cation removal was nearly twice higher in the case of ferrate treatment than those of ferric hydrolysis due to the smaller grain size and higher specific surface area of ferric-oxide/hydroxide particles.

Keywords: Ferrate treatment; Chlorobenzene compounds; Cation effect; Ferric hydrolysis

1. Introduction

Due to the ability of ferrate(VI) to act as oxidant, coagulant and disinfectant in water treatment, its application has been widely studied during the last two decades. Recently Rai et al. [1] published an excellent critical review on the ferrate-based remediation of soil and groundwater, summarizing the eco-sustainable performance of ferrate(VI) in the water treatment technologies. Sharma et al. [2] and

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Jiang et al. [3] were focused on the application of ferrate technology in the wastewater treatments for removal of pharmaceutical residues and emerging micropollutants including pharmaceutical and personal care products, as well as endocrine-disrupting chemicals, respectively. In spite of a huge number of papers reported on the degradation of different organic pollutants by ferrate at different experimental conditions characterizing the kinetics and mechanism of oxidation processes, there are some fundamental issues which have not yet been investigated thoroughly and are critical to apply ferrate in full-scale water treatment or environmental remediation [4]. Among others, the impact of water quality characteristics on the ferrate efficiency should be highlighted. For example, in case of groundwater remediation before the ferrate treatment, it is necessary to determine some chemical properties of water to be treated which can influence the oxidation, coagulation and adsorption processes. Among others, the concentration and the chemical character of cations and anions present in water to be treated can inhibit or even assist the oxidation processes by ferrate.

Recently, Feng et al. [5] investigated the effect of these constituents on the degradation of fluoroquinolone (FLU) antibiotic drug by ferrate at a molar ratio of 20:1 (Fe(VI):FLU) at pH 7.0. The presence of anions (Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-) had not any influence on the removal of FLU, just the monovalent cations (Na^+, K^+). However, the divalent alkaline earth metal cations (Mg^{2+}, Ca^{2+}) decreased the removal efficiency of FLU. This phenomenon was explained by the increased autodecomposition of Fe(VI) in the presence of these divalent cations. The same research group studied the ammonia-related activation of Fe(VI) for the degradation of flumequine (FLUM) which is also an antibiotic drug [6]. The oxidation efficiency was at least five times higher when ammonia was applied at pH = 8 and the molar ratio of 20:1 [Fe(VI):FLUM]. This phenomenon was observed not only in model solutions but also in river and wastewater matrices containing different amounts of natural organic matter. The effect of dissolved organic matter was also demonstrated by the addition of humic acid (HA). It has been found that HA hampers the removal of FLUM because both compounds consume the ferrate. Similar observations were made by Horst et al. [7] and Yang et al. [8].

The effect of co-existing ions on the removal of oxytetracycline (OTC) was studied by Zheng et al. [9] applying ferrate treatment at a molar ratio of 20:1 (Fe(VI):OTC) and pH 7. They established that Ca^{2+}, Mg^{2+}, CO_3^{2-}, PO_4^{3-} and HCO_3^- could inhibit the OTC degradation, while Na^+, Cl^-, NO_3^-, SO_4^{2-} had not any influence on the removal efficiency of OTC at ion concentrations of 5 and 20 mM/L. The effect of Ca^{2+} and Mg^{2+} ions was explained by their complex formation with OTC hindering the oxidation reaction of OTC with ferrate [10,11]. Since CO_3^{2-} and HCO_3^- anions are known as a free radical scavenger, they can reduce the OTC removal rate. It has been also reported that HCO_3^- can form inner-sphere monodentate complexes with the surface functional groups of $Fe(OH)_3$ [12], therefore bicarbonate ions and OTC will competitively react with $Fe(OH)_3$ resulting in lower adsorption rate for OTC. Ma et al. [13] drew the attention to another way of alkaline earth metal effect, namely, ferrate can be activated by Ca^{2+} ion at pH 9–10 to generate O_2. The function of Ca^{2+} is to facilitate O–O

coupling between two FeO_4^{2-} ions by bridging them together. Similar activating effects were also observed with Mg^{2+} and Sr^{2+}. It should be noted that calcium effect was described not only for ferrate treatment. The abundantly present Ca^{2+} ion showed also a great influence on the removal of different pollutants applying photocatalytic oxidation [14] or ultrafiltration [15].

Luo et al. [16] investigated the effect of chloride, ammonium, and bicarbonate on the degradation of pharmaceuticals (carbamazepine, naproxen, trimethoprim, sulphonamide) in hydrolyzed urine matrix applying ferrate treatment. This oxidation agent showed promising results by displaying mild inhibitory effect from chloride and enhancement from ammonium (when the Fe(VI)/ammonium ratio was ≥0.0012) and bicarbonate. An important observation was made by Feng et al. [17] related to the accelerated oxidation of organic contaminants by ferrate applying reducing additives (arsenite, selenite, phosphate, nitrate, iodine, thiosulfate, hydroxylamine). The acceleration was attributed to the rapid formation of Fe(V) and Fe(IV) species in the presence of these one or two-electron transfer reductants. Comparing the effect of these six anions the sulfite was the most effective to enhance the oxidation processes degrading the target organic molecules at pH 8.

The effect of Cl^-, Na^+, Ca^{2+}, Mg^{2+} on the degradation of acesulfame potassium (ACE) by acid-activated ferrate was studied by Ghosh et. al. [18]. The oxidative transformation of ACE by ferrate treatment was not affected by the presence of these inorganic ions. However, the presence of natural organic materials resulted in a considerable reduction in removal efficiency.

Evaluating the published observations on the cation effect it can be concluded that Ca^{2+} and Mg^{2+} ions reduced the removal of FLUM and OTC, however, in the case of ACE, these ions had no significant influence on the degradation of this pharmaceutical. It means the chemical structure and the complex forming properties of target molecules and of course, the experimental conditions (e.g. molar ratios of Fe(VI):target molecule:cation) play a dominant role in the formation of the potential cation effect. Therefore, any generalization is extremely difficult.

Another important question is the participation of ferric-oxide/hydroxide precipitation formed during the ferrate treatment in the removal of organic pollutants and their oxidation by-products, as well as different inorganic compounds during the ferrate treatment processes. To characterize this step Graham et al. [19] studied the oxidation and coagulation of humic substances by potassium ferrate and comparing the observations with the use of ferric chloride. They concluded that ferrate could degrade the organics first and the degraded organic matter could be removed easily by coagulation. However, the coagulation strongly depends on the properties of natural organic materials, the pH, and the added amount of coagulant metal ions. Applying ferrate the coagulation behavior can be affected by the kinetics and the extent of oxidation and charge interaction between cationic Fe hydrolysis species and $Fe(OH)_3$ precipitation. The relative importance of charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in amorphous hydroxide precipitate was discussed by Duan and Gregory [20]. They established

that in many practical cases is not easy to distinguish between the precipitation and adsorption mechanism.

It was a considerable step forward when Goodwill et al. [21] characterized the particles formed during the ferrate treatment and ferric hydrolysis. They established that the ferrate resultant particles had a negative surface charge resulting in a stable colloidal suspension; however, the size distributions of particles for the two iron sources were significantly different. Ferrate ion addition produced a considerable amount of nanoparticles with diameters less than 100 nm, while the ferric hydrolysis resulted in a significant amount of larger particles with diameters greater than 200 nm. The X-ray photoelectron spectroscopy analysis indicated that ferrate reduction yield particles comprising Fe_2O_3 (hematite), which was not detected in the ferric resultant particles. It means the physical and chemical properties of precipitations resulting from ferrate reduction and ferric hydrolysis are different therefore their adsorption capacities deviate from each other.

Filip et al. [22] studied the reaction of potassium-ferrate with week-acid dissociable cyanides, namely $K_2[Zn(CN)_4]$ and $K_3[Cu(CN)_4]$. They established that during the ferrate treatment Zn^{2+} and Cu^{2+} ions can be completely removed from the solution due to their co-precipitation with iron(III) oxy-hydroxides and their incorporation into the structures of two-line and seven-line ferrihydrates. However, in the case of Cd^{2+} and Ni^{2+} ions, the metal carbonates play a dominant role resulting in the formation of solid $CdCO_3$ in the precipitate, while $NiCO_3$ remains predominantly in solution due to its high solubility.

Considering the literature data focused on the development of ferrate treatment technologies for the removal of organic or inorganic pollutants from different water matrices, it is evident that several chemical compounds of water to be treated can influence the efficiency of pollutant removal. To develop a ferrate-based remediation technology for CB-s polluted groundwater an experimental series was carried out to study the single and joint effects of divalent alkaline earth metal cations (Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}) on the removal of CB-compounds at constant CB-s and $NaHCO_3$ concentrations as well as at the same (CB-s: ferrate) molar ratio. In addition to these experiments, the effect of ferric-oxide/hydroxide precipitation formed during the ferrate treatment or ferric hydrolysis was also investigated to clarify its role in the removal of CB-s and other dissolved compounds by co-precipitation or adsorption processes.

2. Materials and methods

2.1. Chemicals

All chemicals used during the experiments were analytical grade. CB-compounds were purchased from Sigma-Aldrich Ltd., (Budapest, Hungary). Ultrapure water (resistivity 18 MΩ cm) used for the preparation of model solutions was produced by Humancorp P.NIX EDI 180 equipment (Seoul, Republic of Korea). Sodium ferrate solution with a concentration of 6 g/L was prepared by electrochemical method applying cast iron anode and 15 M NaOH solution. Ferric chloride heptahydrate, sodium hydrogen carbonate, and sulfuric acid $Ca(NO_3)_2$, $MgSO_4 \cdot 7H_2O$, $ZnSO_4$, and $NiSO_4$

were purchased from VWR Chemicals Ltd., (Debrecen, Hungary).

2.2. Preparation of model solutions

Three CB-compounds, monochlorobenzene (MCB), 1,2-dichlorobenzene (1,2-DCB), and 1,3-dichlorobenzene (1,3-DCB) as frequently detected organic pollutants were selected for the experiments. Considering the CB concentrations of the polluted groundwater to be treated, 10 mg/L initial concentration was selected for all of these organic compounds. Three different model solutions were prepared. The first one contained only the CB-compounds, the second one the CB-compounds and one cation (Ca, Mg, Zn or Ni in a molar ratio of 1:1), and the third one the CB-compounds and all four cations (molar ratio 1:4). Each solution contained sodium hydrogen carbonate in a concentration of 150 mg/L in order to simulate the buffer capacity of groundwater. 100 cm^3 of these solutions were treated in a closed system to eliminate the loss of chlorobenzene compounds by evaporation.

2.3. Analytical methods

To determine the degradation of chlorobenzene compounds, head-space gas chromatography coupled with a mass spectrometer (Bruker SCION 436 GC, Billerica, MS, US) was used. The operating conditions are listed in Table S1. The measurements were performed in scanning mode (m/z = 30–300). A total organic carbon (TOC) analyzer (A Multi N/C 3000 total organic carbon (TOC) analyzer (Analytik Jena, Germany)) was used to determine the purgeable organic carbon content (POC) of the treated model solutions. To follow the formation of chloride as an oxidation by-product, a Dionex ICS-1100 ion chromatography (Sunnyvale, CA, US) was applied. The concentration of cations in the liquid phase was determined by flame atomic absorption spectrometer (Thermo Scientific iCE3300, Waltham, MS, US). The ferrate concentration was measured by spectrophotometer (Analytik Jena, Specord 210 Plus) at a wavelength of 507 nm. The pH was checked by Jenway 3510 pH-meter (Staffordshire, UK).

2.4. Treatments applying ferrate or ferric chloride

To 100 cm^3 model solutions, the same amount of iron was added in the chemical form of Fe(VI) or Fe(III). The molar ratio between the CB-s and Fe(VI) or Fe(III) was 1:5. After the addition of the strongly alkaline ferrate solution to the model solutions, the pH increased to 12. In order to activate the ferrate, the pH was adjusted to the optimal 7 by the addition of 5 M sulfuric acid. Our former results [23] with acid-activated ferrate harmonize very well with the observations of Manoli et al. [24,25], that acid activation results in enhanced oxidation at a shorter time Fe(VI) without acid activation. The pH-adjusting was taken about 30 s and it was controlled by the glass electrode (Jenway 924 080, 924 005) connected to pH-meter (Jenway 3510). The solutions containing freshly formed ferric-oxide/hydroxide were stirred for 30 min by means of a polypropylene-coated magnetic stirrer. The liquid phase was investigated by head-space gas chromatography–mass spectrometry (HS/

GC-MS), TOC, flame atomic absorption spectroscopy, and ion chromatography (IC) methods following a decantation step. To simulate the iron oxide/hydroxide formation in the case of Fe(III) containing model solutions a calculated amount of NaOH was added to the model solutions to achieve the same pH-change as for the ferrate treatment. All other steps were carried out in the same way as mentioned above.

3. Results and discussion

3.1. Ferrate treatment of CB-s model solutions

The removal efficiencies of three CB-compounds obtained by ferrate treatment in the absence and presence of one or four cations at molar ratios of 1:1:5 and 1:4:5 [CB-s:cations:Fe(VI)] are demonstrated in Fig. 1. It can be seen, that the removal efficiency for the CB-s at the same experimental conditions increased in the following order 1,2-DCB < 1,3-DCB < MCB. These results deviate from our former published data, where even the 1,2-DCB was the best removable compound [23]. However, in this case, the CB-s:Fe(VI) molar ratio amounted to 1:500 because the groundwater to be treated had relatively high TOC content (85 mg/L). It means both the concentration of ferrate as an oxidizing agent and the mass of ferric-oxide/hydroxide precipitation as adsorbent, were considerably higher than in the present experiment.

Based on our present results, it can be stated, that the divalent of cations had a clear influence on the CB-s removal. At molar ratios of 1:1:5 their effect increased in the order of $Zn^{2+} < Mg^{2+} < Ni^{2+} < Ca^{2+}$. Comparing the removal efficiencies of CB-s obtained for model solutions with or without Ca content, the presence of Ca resulted in about 72% increment in the CB-s removal. However, if the four cations were simultaneously present in the model solutions at molar ratios of 1:4:5, the average increment became lower (30%) due to the changes in molar ratios. It should be noted that the effect of Zn ions in the case of DCB-s is not significant.

The cation effect was also well observable measuring the purgeable organic carbon content of the treated model solutions containing only the CB-s or the CB-s and the four cations (Table 1). Although this analytical technique does not give molecular specific information, the trend is clear. In the presence of four cations, the removal efficiency of volatile organic compounds increased nearly by 50%.

Since the oxidation of CB-s with ferrate results in the cleavage of chlorine from the benzene ring, the measurement of chloride concentration of the treated model solutions by IC offers a simple way to follow the degradation processes of target molecules. The chlorine recovery calculated on basis of the chlorine content of CB-compounds
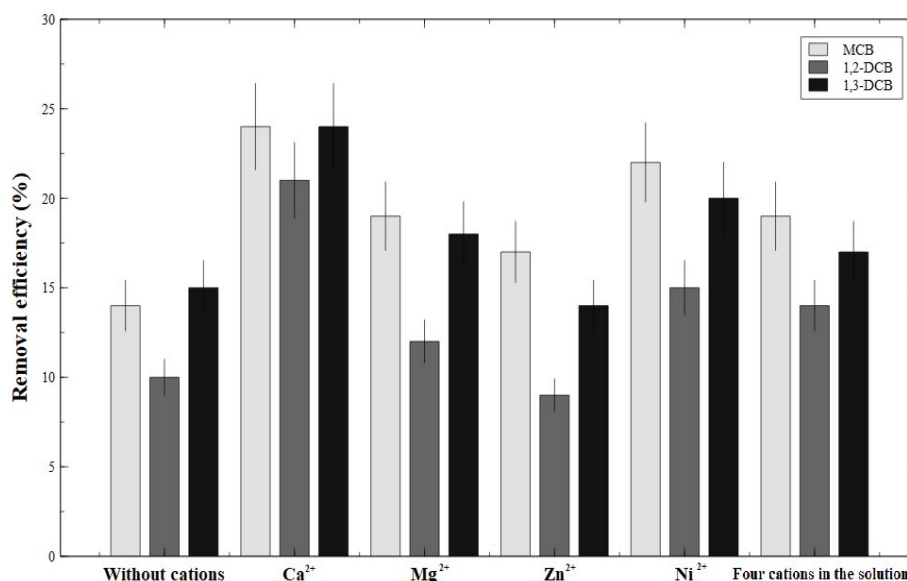

Fig. 1. Removal efficiency of CB-compounds applying ferrate treatment at molar ratios of 1:1:5 and 1:4:5 [CB-s:cations:Fe(VI)].

Table 1
The removal efficiency of purgeable organic carbon content and chlorine recovery calculated on basis of the chlorine content of CB-compounds in the solution before the ferrate treatment and the chloride concentration in the treated solution measured by ion chromatography

Removal efficiency (%) of purgeable organic carbon content		Chlorine recovery (%)	
in absence of cations	in presence of four cations	in absence of cations	in presence of four cations
16	24	17	21

in the solutions before the ferrate treatment and the measured chloride concentration in the treated solutions had about 23% increment in the presence of cations (Table 1). To clarify the mechanism of oxidation and the formation of oxidation by-products it would be necessary to identify their chemical structure in the absence and presence of cations investigated. In the next step, these compounds will be investigated by the UHPLC-Q-TOF system, and a clear picture can be formed on the reaction mechanism.

Summarizing these results obtained by three different methods, it can be stated that the efficiency of CB-removal by ferrate treatment is significantly influenced by cations present in the water to be treated. Since the oxidation changed the character of CB-compounds by the loss of chlorine, their new fragments with positive charge can be neutralized on the negatively charged ferric-oxide/hydroxide nanoparticles characterized by Goodwill et al. [21]. In this way, the role of ferric-oxide/hydroxide precipitation as an adsorbent for the degraded organic compounds can be interpretable. However, there is another important question, what is the fate of cations in the treated water?

Due to the possible co-precipitation of metal-hydroxides and the adsorption of cations on the surface of ferric-oxide/hydroxide precipitation formed during the ferrate reduction, it is expected, that the concentration of cations in the liquid phase will be decreased. As Fig. 2, demonstrates the removal of cations with two positive charges was different and showed an increasing tendency in the following order of $Ca^{2+} < Zn^{2+} < Mg^{2+} < Ni^{2+}$ when only one cation was added to the CB-model solutions. This phenomenon harmonizes with the solubility of these metal-hydroxides (Ca > Mg > Ni > Zn) with the exception of Zn which forms a hydroxide complex in excess of strong alkaline compounds [26]. This complex formation results in higher solubility. However, in the presence of four cations, the excess of strong alkaline compounds (NaOH) decreased due to the higher amount of metal-hydroxides formed during the ferrate treatment. Therefore, only a lower part of Zn remained in hydroxide complex form and the order of removal partly changed in the following manner: Ca < Mg < Zn < Ni.

3.2. Treatment of CB-s model solutions with ferric chloride

In order to clarify the effect of ferric-oxide/hydroxide precipitate formed during the ferrate treatment on the chemical composition of the treated CB-solutions, the same amount of ferric-hydroxide was formed in the model solutions by addition of $FeCl_3$ and NaOH as described in subchapter 2.4.

According to the results obtained by HS/GC-MS and POC measurements of treated solutions, it can be stated that the original CB-compounds with polarity index of 2.7 were not adsorbed on the ferric-oxide/hydroxide precipitation formed at a molar ratio of 1:5 [CB-s:Fe(III)]. The presence of cations investigated had not any influence on the CB-removal. In spite of our observation, the adsorption of different organic matter on amorphous hydroxides could also be effective, although this generally requires higher coagulant dosages [20]. Comparing the removal efficiency values of cations demonstrated in Figs. 2 and 3, it can be established that in the case of ferrate treatment the removal percentages are significantly higher than that of ferric hydrolysis. This can also be explained by the nanoparticle formation of ferric-oxide/hydroxide resulting in negatively charged particles with higher specific surface area and higher adsorption capacity for cations with positive charges [21]. The cation removal followed the order of $Zn^{2+} < Ca^{2+} < Mg^{2+} < Ni^{2+}$. It seems so that the hydroxide complex formation of Zn at these experimental conditions (molar ratio 1:1:5) achieved a higher rate than in presence of four cations (higher ionic strength), where this order changed to $Ca^{2+} < Zn^{2+} < Mg^{2+} < Ni^{2+}$ (Fig. 3).

4. Conclusion

It was demonstrated that cations (Ca^{2+}, Mg^{2+}, Ni^{2+}; Zn^{2+}) which are present in common groundwater can influence, mostly increase the efficiency of ferrate treatment at pH 7 applied for removal of CB-compounds. But due to the co-precipitation of their hydroxides and/or adsorption of these cations on the ferric-oxide/hydroxide nanoparticles, they will be partly removed from the water phase. Therefore
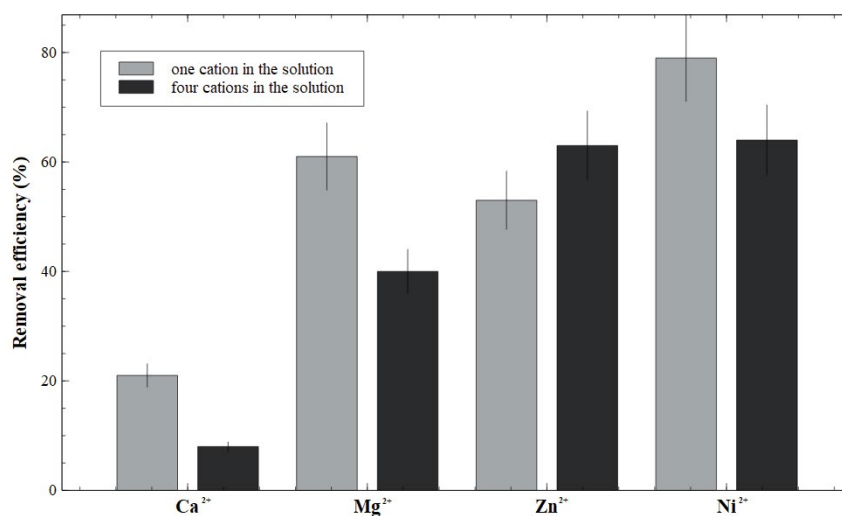

Fig. 2. Removal efficiency of cations applying ferrate treatment at molar ratios of 1:1:5 and 1:4:5 [CB-s:cations:Fe(VI)].
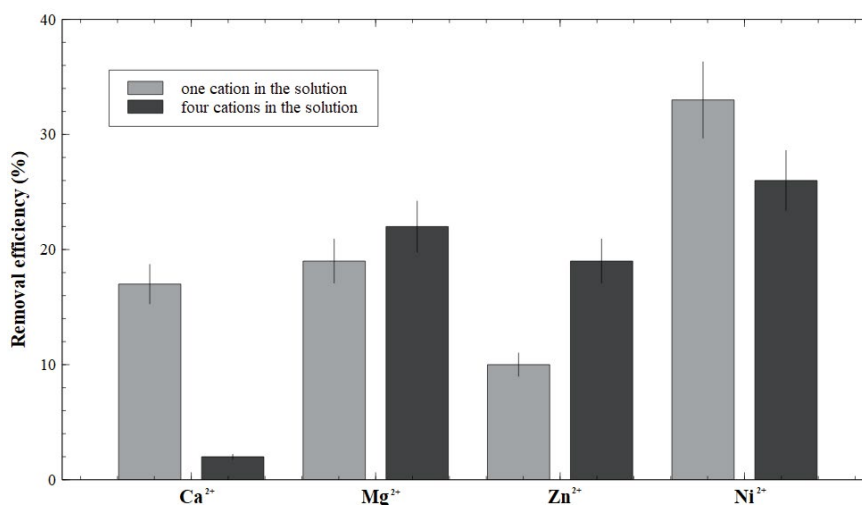
Fig. 3. Removal efficiency of cations applying $FeCl_3$ for formation of ferric-oxide/hydroxide precipitation at molar ratios of 1:1:5 and 1:4:5 [CB-s:cations:Fe(III)].

it would be necessary for the development of groundwater remediation technologies to know exactly what is the expected effects of cations on the degradation of organic pollutants at different CB-s:Fe(VI) molar ratios. After determining the chemical composition (concentration of organic pollutants, cations, anions, and dissolved oxygen) of polluted groundwater it would be possible to select the appropriate concentration of ferrate which is optimal from both environmental and economic points of view. On basis of our former laboratory-scale study [27] and our current results, as well as the recently published observations of Cataldo-Hernandez et al. [28], a pilot study will be prepared for remediation of groundwater polluted with CB contaminants.

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Supplementary information

Table S1
Operating conditions of HS/GC-MS

Analytical column	Agilent (Santa Clara, CA, US) DB-624 (30 m × 0.25 mm × 1.4 μm)
Sample preparation/time of thermostat	10 min
Sample preparation/temperature of the thermostat	80°C
Injector temperature	230°C
Split ratio	1:10
Temperature program of the capillary column oven	40°C hold 2 min 8°C/min to 180°C 15°C/min to 230°C
Transfer line temperature	250°C
Ion source temperature	230°C