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Weak magnetic field accelerates chloroacetamide removal by zero-valent iron in drinking water



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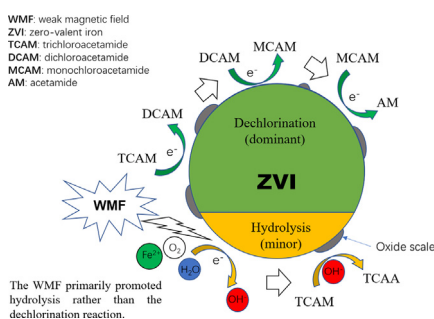
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HIGHLIGHTS

- Effects of WMF on the CAM removal by ZVI was studied.
- WMF strengthens TCAM removal by ZVI, especially at low ZVI doses and high pH.
- Dechlorination is dominant and hydrolysis is secondary for TCAM removal by WMF-ZVI.
- WMF primarily increased hydrolysis not the reduction of TCAM.

GRAPHICAL ABSTRACT



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ABSTRACT

Chloroacetamides (CAMs) as a class of highly toxic nitrogenous disinfection by-products (N-DBPs) have been widely detected in drinking water. It has been reported that weak magnetic field (WMF) could improve the removal ability of zero-valent iron (ZVI) to some pollutants, but CAMs removal by ZVI coupled with WMF has never been studied. This study through oxalic batch experiments was executed to investigate the effect of WMF on trichloroacetamide (TCAM) removal by different doses of ZVI under different pH levels and to explore how WMF works on TCAM removal for the first time. The results showed that the WMF improved TCAM removal by ZVI and the strengthening effect of WMF was more significant at lower ZVI dose or higher pH conditions. The formation of trichloroacetic acid indicated the occurrence of TCAM hydrolysis. Chlorine mass balance was observed in TCAM and its potential products, dichloroacetamide, monochloroacetamide, and chloride, indicating these were all the products and a dechlorination process occurred when TCAM contacted with ZVI. By calculating the yields of hydrolytic products and dechlorinated products, it was determined that dechlorination of TCAM was the dominant reaction for TCAM removal by ZVI with and without WMF, while hydrolysis reaction played a minor role. Mechanism analysis showed that the WMF promoted TCAM hydrolysis through impacting the electromigration within the oxide scale and improving the migration of paramagnetic oxygen to the surface of magnetized ZVI. Taken together, ZVI coupled with WMF is a potential effective technology for TCAM removal in effluent of chlorination.

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1. Introduction

Disinfectant application during drinking water treatment reduces the microbial risk but poses chemical risks through the formation of disinfection by-products (DBPs) [1]. The presence of DBPs in drinking water is a public health issue due to their potential adverse health effects in humans [2–4]. Among various classes of carbonaceous DBPs (C-DBPs) and nitrogenous DBPs (N-DBPs), haloacetamides (HAMs), especially chloroacetamides (CAMs), have attracted significant attention due to their high cyto- and genotoxicity [5–8]. Moreover, because of the reaction of indelible hydrophilic CAM precursors with chlor(am)ine [9,10], CAMs have been detected in the drinking water of many countries [1,2,11–15]. Although the pretreatments to remove CAM precursors [7,9,16,17] and the alternative disinfection methods [18,19] can mitigate their formation potential, CAMs remain ubiquitous in drinking water. Therefore, an effective method for improving CAM removal is urgently needed for safer drinking water.

Zero-valent iron (ZVI) is applied to remove pollutants widely and is readily available, economical, and nontoxic [20–22]. Its usefulness for DBPs removal has been investigated in several previous studies [23–25]. However, most studies have focused on C-DBPs instead of N-DBPs. For example, Xiao et al. [24] used activated carbon-supported nanoscale ZVI/activated carbon (NZVI/AC) to remove trihalomethanes (THMs) from drinking water, and found that NZVI/AC accelerated removal rate of THMs compared with NZVI alone. Tang et al. [26] established a detailed kinetic model to quantitatively evaluate the effect of iron corrosion films on the removal of BrO_3^- and chloroacetic acids. To date, few studies have investigated the removal of the more genotoxic, cytotoxic, and carcinogenic N-DBPs by ZVI. A single previous study focused on the dechlorination of CAMs by copper powder reinforced ZVI, resulting in a markedly improved CAMs removal efficiency in the presence of Cu [27].

To improve the efficiency of the reaction system, new ZVI technology is constantly emerging. For example, nano-sized ZVI and bi-metallic systems were proposed to improve the efficiency of ZVI, but their high cost and potential toxicity hinder their application [28–33]. Recently, weak magnetic field (WMF) reinforced ZVI was demonstrated to remarkably improve the removal of selenite [20] and Cu^{2+} from drinking water [34]. The WMF enhancement of contaminants removal by ZVI arises from the effect of the Lorentz and magnetic gradient forces [20,35]. The movement of charged particles under the Lorentz force in the magnetic field leads to strengthened convection in the solution and improved mass transport [34,36]. Under the influence of a magnetic gradient force, paramagnetic substances gravitate towards stronger magnetic fields [35]. Ferromagnetic ZVI is magnetized in WMF and produces a heterogeneous magnetic field around its surface. Therefore, the magnetic field near the ZVI surface is stronger than that of the bulk solution, which results in the uneven distribution of the product Fe^{2+} and accelerated the corrosion of ZVI [20,37].

WMF reinforced ZVI is a chemical and energy-free method and has been reported to accelerate the removal of various metal ions (e.g., Se(IV)/Se(VI), As(III)/As(V) and Sb(III)/Sb(V)) [20,35]. However, research on WMF-ZVI for enhancing the removal of organic contaminants such as CAMs or N-DBPs is lacking. To provide more effective technology for CAMs removal during drinking water production, ZVI with WMF as an effective, economical, and low energy method was studied herein. In the actual process of drinking water treatment, dissolved oxygen (O_2) often exists in the water. It has also been reported that O_2 plays an important role in the ZVI system. More importantly, oxygen is a paramagnetic substance [38,39] which would be affected by the magnetic field gradient force. The authors hypothesize that the presence of WMF could accelerate the transport of O_2 to the surface of the ZVI and, therefore, the reaction between O_2 and ZVI may affect CAMs removal efficiency.

The objective of this study was to evaluate 1) the effect of an external WMF on the removal of CAMs by ZVI under various ZVI dosages

and pH conditions, 2) the mechanism of CAM removal by ZVI, and 3) the mechanism underlying the improved CAM removal by ZVI under a WMF.

2. Materials and methods

2.1. Materials

In this study, a series of 1000 mL glass batch reactors were used and the ZVI powders were supplied by Sigma-Aldrich (St Louis, Missouri, USA). The water used in the batch reactors was prepared with ultrapure water and TCAM. Sodium acetate (0.1 M), 2-(N-morpholino) ethanesulfonic acid (MES, 0.03 M) and Tris (hydroxymethyl) aminomethane (Tris, 0.05 M) were used as buffers to maintain a pH of 7.0 ± 0.2 [40] unless otherwise stated.

All chemicals were of analytical grade. Standards chemicals of 3 CAMs, MCAM, DCAM, and TCAM, were purchased from Alfa Aesar (Karlruhe, Germany). Trichloroacetic acid (TCAA), dichloroacetic acid (DCAA) and monochloroacetic acid (MCAA) standards were supplied by Sigma-Aldrich (St Louis, Missouri, USA). Tris (99.9%) and MES (99%) were obtained from Aladdin Industrial Inc (Shanghai, China). Ultrapure water for preparing solutions was produced using a Millipore Milli-Q Gradient water purification system (Billerica, MA, USA).

2.2. Batch experiments

Batch experiments using glass reactors were performed to investigate the effect of a WMF on CAM removal by ZVI under different ZVI dosages and pH conditions as well as the behind mechanism. The batch reactors were first filled with 1000 mL of $5.2 \mu\text{M}$ ($850 \mu\text{g/L}$) TCAM solution and then buffer was added to reach the required pH levels. Afterwards, pre-weighed ZVI powder was added to the solution to achieve the desired concentrations.

In experiment 1, different concentrations of ZVI (0.5, 1.0, and 5.0 g/L) were used in different batch reactors, with and without application of WMF. The ZVI dosage decided in this study was in the range of commonly used concentration in previous studies [41,42]. As shown in Fig. SM1 (Supplementary materials), a piece of circular neodymium-iron-boron permanent magnet (5 mm \times 25 mm ID) was placed under the reactor to provide magnetic field. The axis lines of the beakers were aligned with the center of the magnetic field. A plastic board was placed between the beakers and magnets to prevent the iron powder from agglomerating due to the magnetic force. The WMF was non-uniform, and the strongest magnetic field intensity was approximately 20 mT, and the distribution of magnetic field is shown in Fig. SM1b. In experiment 2, three pH conditions, 6.0, 7.0, and 8.0, were selected to further investigate the effect of WMF on CAMs removal by 5.0 g/L ZVI under acidic, neutral, and alkaline conditions. As shown in Fig. SM1a, the batch reactors were placed on an agitator and the solution was continuously stirred.

TCAM is hydrolyzed quite slowly under neutral conditions (hydrolysis rate constant = 0.003 h^{-1}) and mainly produces TCAA in aqueous environments [43]. Recently, the stepwise dechlorination of TCAM was elucidated in the presence of ZVI [27]. However, the effect of WMF on the degradation mechanism of TCAM by ZVI is unknown. To investigate this mechanism, the concentrations of TCAM, its potential intermediate products (DCAM, MCAM) and its potential end dechlorination and hydrolysis products (Cl^- and TCAA, respectively) in 1.0 g/L ZVI group were monitored since 1.0 g/L ZVI can guarantee the reaction neither too fast nor too slow.

Water samples were collected 8 times within 24 h using a 20-mL glass syringe at selected time intervals and immediately filtered through 0.22- μm syringe filters. To obtain a real oxic situation during water treatment, all glass reactors were open to the atmosphere at room temperature ($25 \pm 2^\circ\text{C}$).

2.3. Analytical methods

A pH meter (FE20-FiveEasy, Mettler Toledo, Switzerland) was used to measure the solution pH. The magnetic field intensity was measured using a Tesla meter (HT201, Shanghai Hengtong Magnetic & Electric Technology Co., Ltd). To extract the CAMs, 2 mL of methyl *tert*-butyl ether and 2 g of anhydrous sodium sulfate were dosed into 10 mL of the filtered aqueous sample and shaken using an IKA oscillator (Staufen, German) at 2800 rpm. After a certain contact time, the CAMs were quantified using gas chromatograph (GC), coupled with an electron capture detector (ECD, QP 2010 plus, Shimadzu, Japan), according to a previously reported analytical method described elsewhere [2,10]. The detection limits for TCAM, DCAM, and MCAM were 0.01, 0.01 and 0.05 μM respectively. Three HAAs (MCAA, DCAA and TCAA) were also analyzed by GC/ECD (QP 2010 plus, Shimadzu, Japan) according to the US EPA method 552.2 [44]. Chloride ions were quantified using an ion chromatograph (Dionex ICS-5000, USA).

3. Results and discussion

3.1. Effect of the WMF at different ZVI dosages

The effect of WMF on TCAM removal by ZVI was investigated under various ZVI dosages over a 24 h contact time and the results are shown in Fig. 1. With increasing ZVI dosage, the removal of TCAM by ZVI was improved both in presence and absence of the WMF. The ZVI reaction is a surface reaction, as has been demonstrated in previous studies [45,46], and the increased ZVI dosage increased the number of surface reaction sites, enhancing the reaction between ZVI and TCAM, which agrees with previous studies [47–49]. Among the three dosages tested, only the highest dosage of 5.0 g/L ZVI degraded TCAM to reach a level below detection limit after 6 h of contact time.

Remarkably, the presence of WMF increased the removal rate of TCAM by ZVI. As shown in Fig. SM2, the degradation of TCAM in the first 3 h was fitted well using pseudo-first-order kinetics. The kinetic constants, k_{obs} , for TCAM degradation by 0.5, 1.0, and 5.0 g/L ZVI were 0.121, 0.355, and 0.690 h^{-1} without the WMF and 0.167, 0.426, and 0.843 h^{-1} with the WMF, respectively. The WMF improved the degradation of TCAM by 38, 20, and 22% at ZVI concentration of 0.5, 1.0 and 5.0 g/L, respectively (Table SM1). However, the degradation of TCAM after 3 h did not fit first-order kinetics, and TCAM concentrations dropped rapidly in the first 6 h and then slightly decreased thereafter

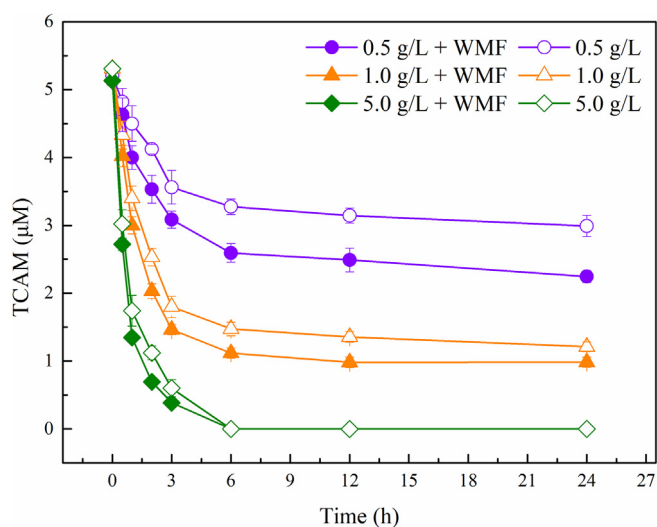


Fig. 1. Effects of the WMF on TCAM removal by ZVI at different ZVI dosages. Initial TCAM molar concentration = $5.22 \pm 0.09 \mu\text{M}$, pH = 7.0, T = $25 \pm 2^\circ\text{C}$.

for all dosages. This is because the reactive sites on the surface of ZVI were covered by the produced iron oxide or iron hydroxides with increasing reaction time and the reactivity of ZVI decreased, as observed in previous studies [28].

The total removal efficiency within 24 h increased by 23, 5, and 0% for the 0.5, 1.0, and 5.0 g/L ZVI groups in the presence of the WMF. In conclusion, the WMF enhanced the removal of TCAM by ZVI and played a greater role in TCAM degradation when there is little resistance to O_2 or Fe^{2+} migration at the low ZVI dosages. However, as shown in Fig. 1, the increase of ZVI dose improved TCAM removal. Therefore, to reach a high TCAM removal by ZVI coupled with WMF in practice, a further study should be done to investigate the optimal ZVI dose. Because the enhanced TCAM removal could be explained by that the WMF enhanced mass transfer in the aqueous solution, leading to uneven distribution of paramagnetic Fe^{2+} , which accelerated the corrosion of ZVI [20,35] and enhanced its activity. In practical application consideration, this observation can be used to optimize the dose of ZVI for DBP removal. In the presence of a WMF, the use of a minimum amount of ZVI can achieve a reasonable removal of DBPs by maximizing the WMF effect. In view of the best effect of 5.0 g/L on the removal of TCAM, 5.0 g/L was decided in the following pH experiment to clearly see the differences caused by pH.

3.2. Effect of the WMF under different pH conditions

The effect of the WMF on TCAM removal by ZVI at pH 6.0–8.0 is shown in Fig. 2. The removal rate of TCAM by ZVI decreased with increasing pH from 6.0 to 8.0, regardless of the WMF. TCAM rapidly degraded to below the detection limit ($0.01 \mu\text{M}$) after 2 h under acidic conditions (pH 6.0) and after 6 h under neutral conditions (pH 7.0), while under alkaline conditions (pH 8.0) the TCAM concentration decreased slowly and was much higher than the detection limit after 24 h. These results indicate that at higher pH, the TCAM removal efficiency decreased, which is consistent with previous studies regarding the removal of halogenated aliphatics and the antibiotic metronidazole by ZVI [46,50]. This phenomenon occurs because it is difficult to form an oxide film on the surface of ZVI under acidic conditions, leading to more available active sites on the ZVI surface [27]. At pH 7.0 and 8.0, degradation in the first 3 h fits pseudo-first-order kinetics well. The ratio of the kinetic constant (k_{obs}) in the samples with the WMF to those without WMF was 1.22 at pH 7.0 and 1.77 at pH 8.0 (Fig. SM3). This indicates that the WMF plays a greater role when the pH condition is

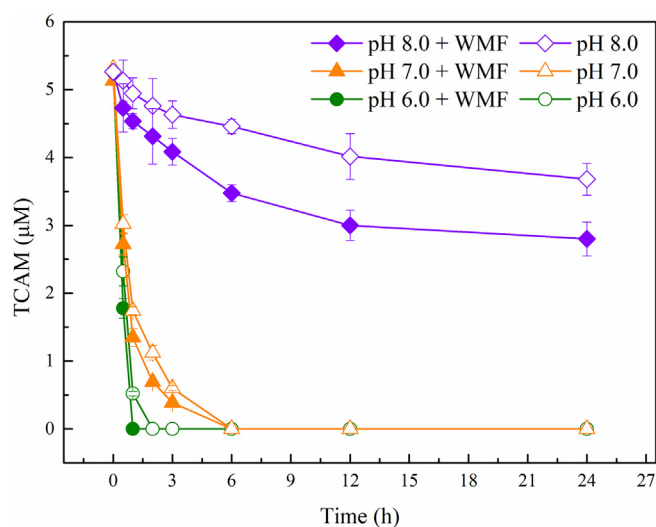


Fig. 2. Effects of the WMF on TCAM removal by ZVI under various pH conditions. Initial TCAM molar concentration = $5.22 \pm 0.09 \mu\text{M}$, T = $25 \pm 2^\circ\text{C}$, ZVI dosage = 5.0 g/L.

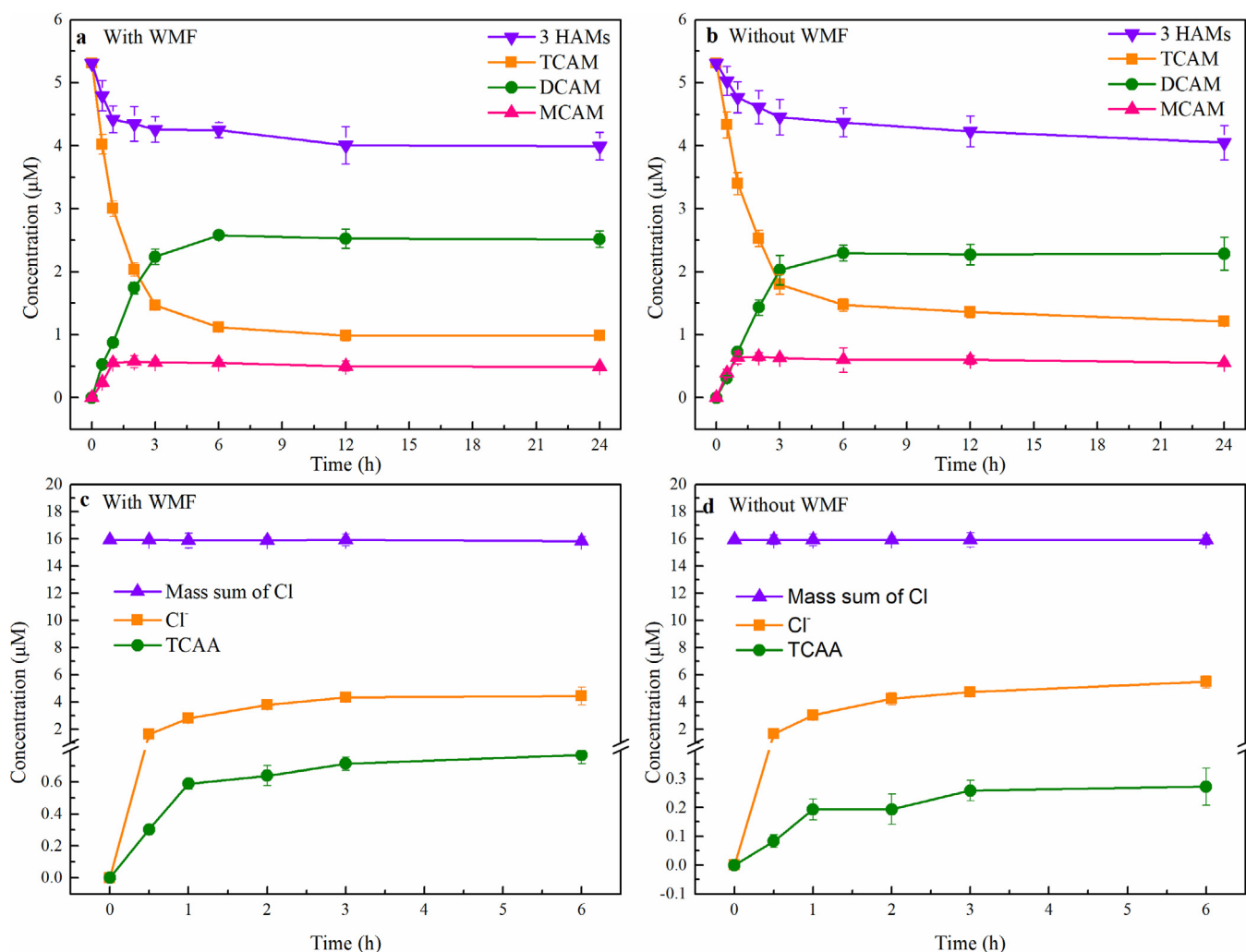


Fig. 3. Degradation of the 3 CAMs by ZVI with and without the WMF. (a) The 3 CAMs in the system with the WMF; (b) the 3 CAMs in the system without the WMF; (c) chlorinated products in the system with the WMF; (d) chlorinated products in the system without the WMF. Initial TCAM concentration = $5.22 \pm 0.09 \mu\text{M}$, pH = 7.0, T = $25 \pm 2 \text{ }^\circ\text{C}$, ZVI dosage = 1.0 g/L.

unfavorable for the reaction of ZVI. And the similar phenomenon was also observed at the ZVI dose of 0.5 g/L (Fig. SM4).

A previous study found a 10.8–383.7-fold increase in Cu^{2+} removal by ZVI as a result of application of a WMF [25]. The enhanced efficacy of ZVI observed in this study was not as dramatic as that found in the previous study, but the above results clearly indicate that the WMF promoted TCAM removal at all ZVI dosages and pH conditions. A more significant enhancement may be achieved through adjusting the dosage of ZVI, pH, contact time, and magnetic field intensity. Regardless, it can be seen that ZVI with WMF is a promising technology for TCAM removal from water.

3.3. Reactions occurred to CAMs during removal

3.3.1. Dechlorination

The mechanism underlying CAM degradation by ZVI was examined and Fig. 3 presents the concentrations of 3 CAMs and their related end products after TCAM dechlorination in the absence and presence of the WMF. The ZVI dose of 1.0 g/L was chosen to avoid the reactions being too fast or too slow, so that the products could be quantified. As shown in Fig. 3a and b, the concentrations of DCAM and MCAM increased with decreasing TCAM concentration over 24 h, which was similar as observed previously [27]. The formation of Cl^- was also observed in Fig. 3c and 3d, which is additional evidence of the dechlorination

process. It should be noted that the molar sum of the 3 CAMs decreased as a function of time, likely due to the formation of the acetamide (AM, Fig. SM5) which is usually the final product formed after losing 3 Cl^- or the formation of the corresponding TCAA via hydrolysis. The concentration of TCAA is shown in Fig. 3c and 3d, while AM was not detected, which is similar to previous results where only TCAA was detected in the first few hours of the copper catalyzed dechlorination of CAMs by ZVI [27]. The generation of TCAA proved that hydrolysis process was occurring. The Cl^- mass sum calculated using Eq. (1) is shown in Fig. 3c and d. Both with and without WMF, the Cl^- mass sum was constant over 6 h, indicating no Cl^- mass loss and that AM was not generated. This is likely because 1.0 g/L ZVI could transform TCAM to DCAM and MCAM in the first 6 h, but its reactivity was insufficient to continue the dechlorination to form the final product.

$$\text{Molar mass sum of Cl} = 3[\text{TCAM}]_t + 2[\text{DCAM}]_t + [\text{MCAM}]_t + 3[\text{TCAA}]_t + [\text{Cl}^-]_t \quad (1)$$

where $[\text{TCAM}]_t$, $[\text{DCAM}]_t$, $[\text{MCAM}]_t$, $[\text{TCAA}]_t$ and $[\text{Cl}^-]_t$ represent the concentration of TCAM, DCAM, MCAM, TCAA, and Cl^- in the system at time t (h), respectively.

3.3.2. Hydrolysis

TCAA has been observed as a hydrolysis product of TCAM in previous studies [13,27]. To investigate TCAM hydrolysis in the presence

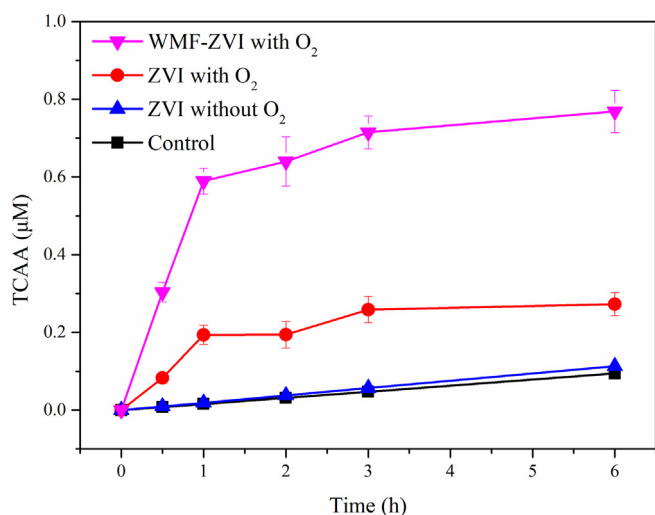
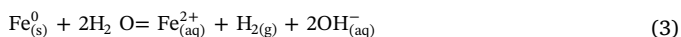
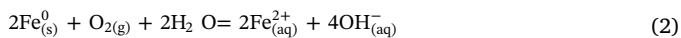


Fig. 4. The generation of TCAA under different conditions. TCAA concentrations in the control and ZVI without O₂ groups were calculated based on our previous study [23]. The other data was from this study. Temperature = 25 ± 0.2 °C, pH = 7.0 ± 0.2, initial TCAM concentration = 5.3 µM, ZVI dosage = 5.0 g/L.

of ZVI and WMF, the concentrations of TCAA as a TCAM hydrolysis product in different treatment groups (control with only TCAM, ZVI without O₂, ZVI with O₂ and WMF-ZVI with O₂) are shown in Fig. 4. No significant difference between the control and ZVI without O₂ groups was observed, indicating the effect of ZVI on TCAM hydrolysis under anoxic conditions was negligible, which agrees with a previous study [27]. However, the concentration of TCAA formed in the ZVI with O₂ group was much larger than that in the ZVI without O₂ and reference groups, indicating that O₂ is a precondition for enhanced TCAM hydrolysis and TCAA formation by ZVI.

Previous studies showed that the ZVI reacted with pollutants, dissolved O₂ (Eq. (2)), and water (Eq. (3)) [20,51]. The produced Fe²⁺ was unstable and further reacted with O₂ and water to generate Fe³⁺ and OH⁻ (Eq. (4)).



It is observed in Fig. 4 that the rate of TCAA formation slowed down with time under the aerobic condition, which could be explained by that the oxide film was being formed increasingly on the surface of ZVI and inhibited the reaction. The yellowish was observed in the batch reactor in 5–6 h, which is another evidence of oxide film formation. With the oxide film, the improved TCAM removal could be explained by accelerated migration of Fe²⁺ in the oxide film. Stratmann and Müller (1994) [52] pointed out that in the ZVI/H₂O system, the reduction of oxygen is mainly in the oxide layer. However, in this study, the oxygen reduction was observed at the early stage of the reaction when little oxide film was formed, concluded by the enhanced TCAM hydrolysis in 0.5–1 h in Fig. 4. It is a good evidence for the reduction of oxygen at the metal/solution phase boundary.

CAMs are easily hydrolyzed under alkaline conditions [14,41]. Therefore, the enhanced hydrolysis by the co-presence of ZVI and O₂ is likely due to OH⁻ production *in situ* in the local area near the ZVI surface where the reaction of ZVI and O₂ occurred (Eq. (2)), leading to the enhanced the hydrolysis of the CAMs. Evidently, the WMF enhanced TCAM hydrolysis and TCAA formation (Fig. 4), indicating that OH⁻ formation from the reaction of ZVI and O₂ was enhanced, which was likely due to the acceleration of the paramagnetic O₂ [38,39]

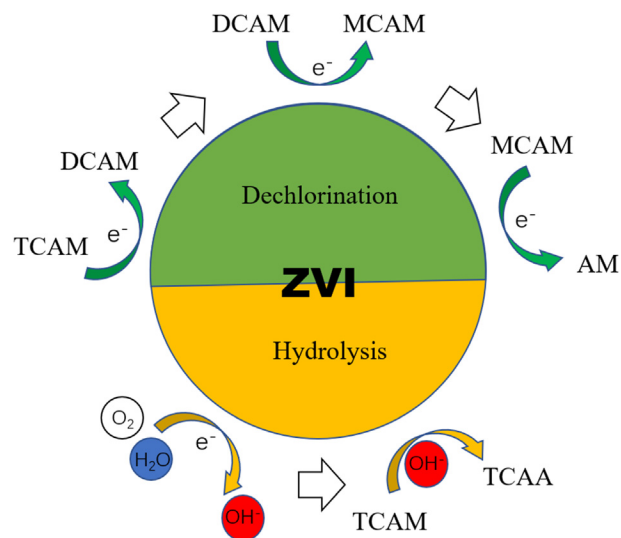


Fig. 5. Reaction pathways of dechlorination and hydrolysis for CAMs.

transportation toward the ZVI surface. To sum up, in the early phase before oxide film formation, oxygen reacted with ZVI by direct contact and the migration of oxygen was enhanced by WMF. Afterwards, the WMF accelerated the transform of Fe²⁺ in the oxide film and therefore improved the TCAM removal.

Based on the discussion above, the complete reaction mechanism is summarized in Fig. 5.

3.4. Effect of the WMF on hydrolysis and dechlorination

3.4.1. Proportion of hydrolysis and dechlorination

The amount of hydrolysis ([Hydrolysis]) and dechlorination ([dechlorination]) in the system and their proportions were calculated using Eqs. (5)–(8) and shown in Fig. 6.

$$[\text{Hydrolysis}] = [\text{TCAA}]_t \quad (5)$$

$$[\text{Dechlorination}] = [\text{TCAM}]_{\text{ini}} - [\text{TCAM}]_t - [\text{TCAA}]_t \quad (6)$$

$$\text{Proportions of Dechlorination} = \frac{[\text{Dechlorination}]}{[\text{TCAM}]_{\text{ini}} - [\text{TCAM}]_t} \quad (7)$$

$$\text{Proportions of Hydrolysis} = \frac{[\text{Hydrolysis}]}{[\text{TCAM}]_{\text{ini}} - [\text{TCAM}]_t} \quad (8)$$

where [TCAM]_{ini} is the initial TCAM concentration.

As can be seen in Fig. 6, dechlorination was the dominant reaction and hydrolysis was secondary for TCAM degradation at all ZVI dosages, with and without the WMF. The hydrolysis proportion at each ZVI dosage was relatively stable over the course of 6 h. Both the increased ZVI dosage and presence of WMF increased the hydrolysis proportion. As shown in Fig. SM6, a good linear relationship was observed between the average proportion of hydrolysis and ZVI dosage in the both cases with and without the WMF. The results presented here agree with previous studies which examined chlorinated methane and nitro aromatic compound removal by ZVI [24,45,46]. The good linear relationship suggests that the hydrolysis reaction occurs on the surface of the ZVI, which is significantly influenced by its surface area. The WMF substantially improved the proportion of hydrolysis likely because it had a positive effect on the O₂ reduction step (Eq. (2)).

Direct dechlorination occurred via electron transfer between the ZVI and CAMs [27], while hydrolysis was an indirect reaction in the system which was catalyzed by OH⁻ produced from the reaction of ZVI and dissolved O₂. The dechlorination reaction is likely faster than the indirect hydrolysis reaction and can potentially explain why dechlorination was the dominant mechanism. Undoubtedly, the increase in ZVI

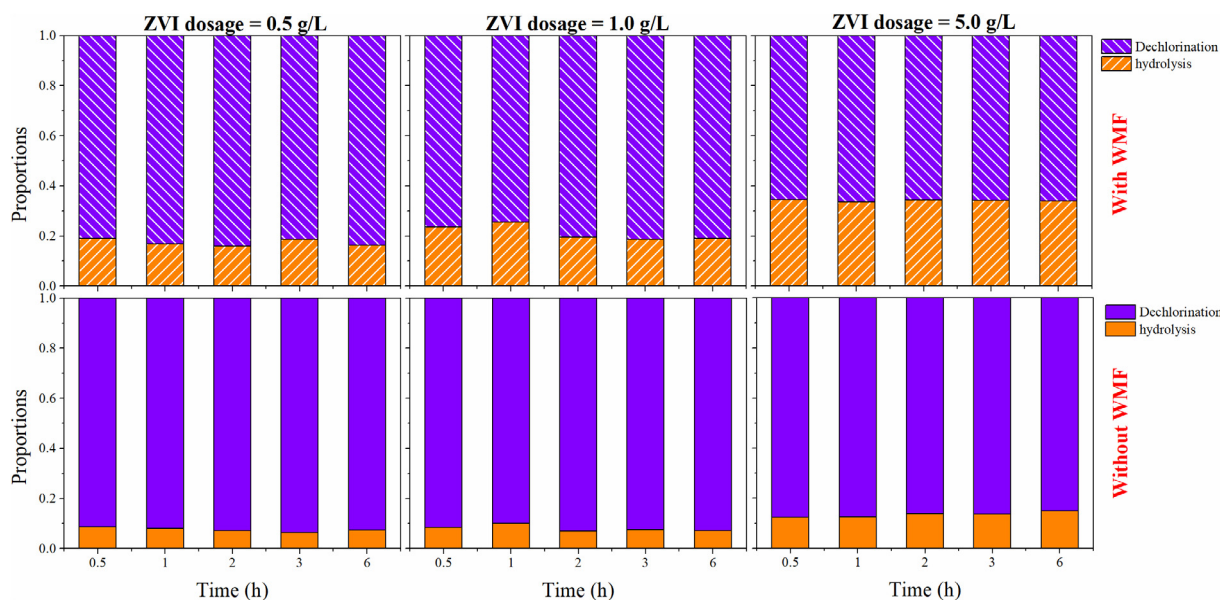


Fig. 6. The proportion of hydrolysis and dechlorination in the reaction system with and without the WMF. Initial TCAM concentration = $5.22 \pm 0.09 \mu\text{M}$, pH = 7.0, T = $25 \pm 2^\circ\text{C}$.

dosage and application of the WMF enhanced TCAM hydrolysis. However, it is still unclear whether the dechlorination was enhanced by the WMF.

3.4.2. Effect on dechlorination and hydrolysis

To demonstrate the effect of the WMF on the two mechanisms, under the same ZVI dosage, the ratios of [Hydrolysis] (or [dechlorination]) with the WMF to [Hydrolysis] (or [dechlorination]) without WMF are shown in Fig. 7. The ratio of the dechlorination reaction was almost 100%, indicating that the WMF did not impact the dechlorination reaction. The ratio for hydrolysis mechanism ranged from 200 to 400%, indicating that the WMF enhanced the hydrolysis.

As shown in Fig. 5, the dechlorination reaction is driven by the halogen in TCAM obtaining electrons from ZVI, while the hydrolysis reaction is driven by OH^- formation from the reaction of ZVI and dissolved O_2 . The WMF enhanced ZVI corrosion, which provided more electrons [34,35]. Therefore, hydrolysis instead of dechlorination was promoted by the application of the WMF. This indicates that O_2 received more electrons than TCAM when the WMF was applied. This is

because O_2 is paramagnetic and more likely to migrate to the region with larger magnetic field intensity (e.g. the surface of ZVI after magnetization by the WMF) driven by magnetic field gradient force. Thus, the WMF enhanced the contact of O_2 and ZVI, resulting in increased OH^- generation and enhanced TCAM hydrolysis.

Previous studies reported that the WMF had significant effects on the removal of non-paramagnetic substances by ZVI, such as As(III), As(V) and Se(IV) [20,35,53]. Although these species were not paramagnetic, they existed in the form of charged ions (e.g., AsO_4^{3-} and AsO_2^-) in water. The charged ions were likely affected by the Lorentz force in the magnetic field, and which has been proven to enhance mass transfer [54]. Thus, the removal of charged ions by ZVI was easily enhanced by application of the WMF. However, the uncharged and non-paramagnetic CAMs were largely unaffected by the WMF in this study. In summary, the WMF does not largely impact the uncharged and non-paramagnetic DBPs.

As stated before, the results showed that hydrolysis instead of dechlorination was promoted by the application of the WMF, which is positive information for WMF application in practice. In practice, ZVI

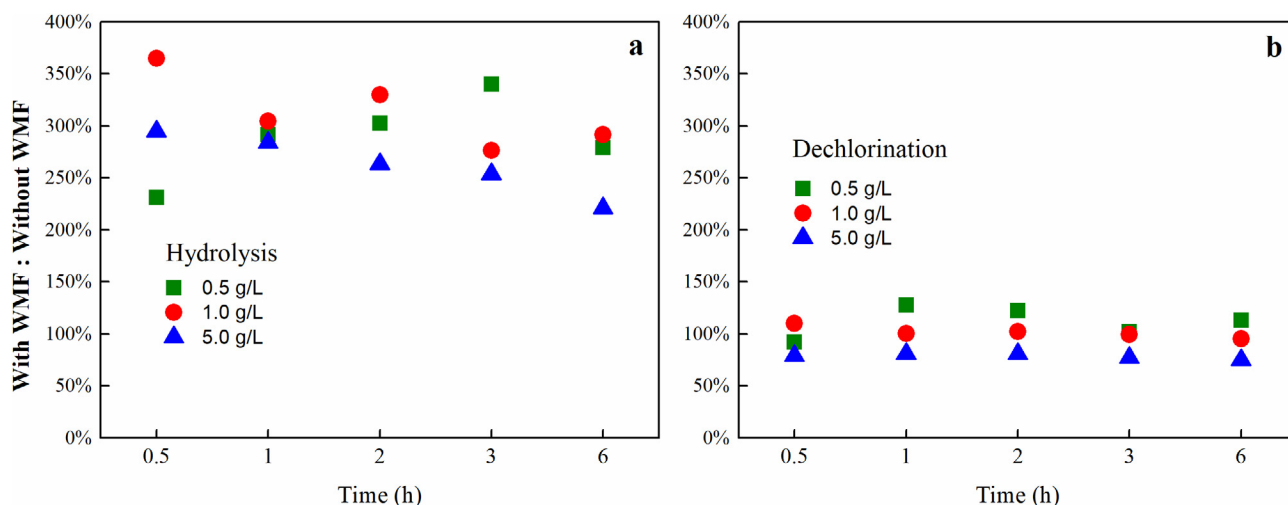


Fig. 7. Effect of WMF on the hydrolysis and dechlorination of TCAM by ZVI. Initial TCAM molar concentration = $5.22 \pm 0.09 \mu\text{M}$, pH = 7.0, T = $25 \pm 2^\circ\text{C}$; (a) the ratios of [Hydrolysis] with WMF to [Hydrolysis] without WMF; (b) the ratios of [dechlorination] with WMF to [dechlorination] without WMF.

should be used in reactors for a longer time, and oxide film can be formed inevitably on its surface. The formation of oxide film may lead to a lower dechlorination rate with time [27] while the hydrolysis reaction may still be enhanced by WMF due to the enhancement of the migration of dissolved oxygen to ZVI surface caused by the magnetic gradient force. Furthermore, the hydrolysis reaction of TCAM is beneficial to decrease the toxic risk of water because the combined toxicity (cytotoxicity plus genotoxicity, investigated by Plewa et al., 2008) of the dechlorination product MCAM (1309 M^{-1}) is much higher than TCAM (232 M^{-1}), while the concentration of hydrolysis product TCAA (161 M^{-1}) is much lower than that of MCAM or TCAM [5].

4. Conclusion

The WMF enhanced the removal of CAMs by ZVI and this effect was more significant at lower ZVI dosages and higher pH. The potential dechlorination products, DCAM, MCAM and Cl^- , were quantified and increased in concentration with decreasing TCAM. Another potential dechlorination product, AM, was not detected and the molar mass sum of Cl^- from TCAM, DCAM, MCAM and Cl^- was constant, indicating that AM was not generated.

ZVI promoted the hydrolysis of TCAM in O_2 -free conditions, while it greatly promoted the hydrolysis of TCAM under oxic conditions. The application of the WMF further promoted the hydrolysis of TCAM.

Dechlorination is a dominant reaction for TCAM removal by ZVI with and without the WMF, while the hydrolysis is secondary. The application of the WMF primarily promoted the hydrolysis reaction rather than the dechlorination reaction of TCAM with ZVI because the surface of ZVI was magnetized by the WMF and paramagnetic O_2 instead of the uncharged and non-paramagnetic TCAM is more likely to migrate via the magnetic field gradient force.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2018.09.212>.

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