

Chemical Degradation of Drinking Water Disinfection Byproducts by Millimeter-Sized Particles of Iron–Silicon and Magnesium–Aluminum Alloys

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Trihalomethanes (THMs) and haloacetic acids are ubiquitous in chlorinated drinking water as disinfection byproducts (DBPs), and long-term consumption of water containing chloroform and trichloroacetic acid (TCAA) has resulted in the development of cancers, liver damage, and other serious conditions.^{1,2} Removal and/or degradation of DBPs in drinking water systems is critical for maintaining safe drinking water supplies.³ Microbial biodegradation^{4–8} and chemical degradation^{9–18} with zero-valent iron (ZVI) and bimetallic nanoparticles (Ni/Fe, Pd/Mg, Pd/Sn, etc.) have been investigated for the breakdown of haloacetic acids and other chlorinated organic pollutants. However, both are problematic for drinking water systems. THMs are biodegradable via cometabolism by ammonia-oxidizing bacteria under aerobic conditions but lack sufficient rates of biodegradation in drinking water systems,^{4–8} partly because of their oligotrophic nature and the presence of chlorine, whereas TCAA is relatively resistant to biodegradation.^{7,8} The major problem with the use of ZVI and bimetallic systems is the release of metals, which deteriorates water quality. In this context, common elements such as Si, Al, and Mg are suitable candidates because of their natural occurrence, high abundance in the environment, and environmentally benign nature. However, the overwhelming oxidation of Mg by water¹⁹ and rapid oxidation of Si and Al under ambient conditions limit their use for water treatment.²⁰ To improve the corrosion performance of zero-valent metals while maintaining sustainable reactivity has been a significant challenge in exploring such systems for drinking water treatment. It has been reported that the corrosion resistance of Fe and Mg can be enhanced by alloying them with Si and Al, respectively.^{21,22} Thus, Fe–Si and Mg–Al alloy particles were explored in this study.

Bimetallic particles have been prepared by the reductive deposition approach, as described in the literature.^{12–15} Drawbacks of this approach are weak metal adhesion, difficulties in controlling the uniformity, and the intensive use of chemicals. Here the Fe–Si and Mg–Al alloy particles were prepared by mechanical milling. The degradation efficiencies of DBPs using particles of Fe, Fe–Si alloy, Mg–Al alloy, and their mixtures as filtration materials are compared in Table 1. In comparison with Fe, Fe–Si alloy particles significantly reduce the release of Fe while maintaining the same degradation efficiency, and Mg–Al provides better degradation efficiency. Interestingly, mixtures of Fe and Mg–Al alloy particles show much higher degradation efficiency than Fe or Mg–Al alone, particularly for chloroform, carbon tetrachloride, and TCAA, and release much less Fe ion. More importantly, mixtures of Fe–Si and Mg–Al alloy particles present the best performance in terms of degradation efficiency and release of metals. The mechanism for the degradation of chlorinated

organic compounds by ZVI (including bimetallic particles) is essentially the oxidation of metals by the compounds, which involves adsorption of the compound onto the surface of the metal, direct electron transfer from the metal to the compound, and catalytic hydrogenolysis.^{10,16–18} Hozalski et al.¹¹ demonstrated that TCAA was degraded via sequential hydrogenolysis by ZVI much faster than dichloroacetic acid (DCAA) and monochloroacetic acid (MCAA). Our observations, in batch experiments for degradation of TCAA (Figure S1 in the Supporting Information), are in agreement with Hozalski et al.'s results. The interesting results here are the enhanced degradation and reduced release of metals by the mixed phase of particles (Table 1), and this was mechanistically investigated using electrochemical methods.

Table 1. Degradation of DBPs in Deionized Water in Columns Packed with Different Filtration Materials^a

DBPs	conc. (mg L ⁻¹)	degradation (%) ^b				
		Fe	Fe–Si (72:28)	Mg–Al (50:50)	Fe/Mg–Al ^c	Fe–Si/Mg–Al ^c
CHCl ₃	0.12	21.6	19.4	39.1	67.4	72.5
CCl ₄	0.06	26.5	22.5	56.8	78.4	87.6
TCAA	1.0	14.2	13.3	21.5	58.1	54.5
BrO ₃ ⁻	0.1	26.7	23.5	54.2	66.3	74.4
ClO ₂ ⁻	1.0	37.4	38.5	63.1	68.0	87.2

metal	conc. (mg L ⁻¹)	effluent concentration of metal ions (mg L ⁻¹) ^b				
		Fe	Fe–Si (72:28)	Mg–Al (50:50)	Fe/Mg–Al ^c	Fe–Si/Mg–Al ^c
Fe	<0.01	2.38	0.09	0.013	0.36	0.02
Al	0.026	0.027	0.029	0.143	0.094	0.091
Mg	<0.1	0.13	0.14	4.06	2.41	2.68
effluent water pH		5.8	5.8	8.8	7.5	7.8

^a Column: 15 cm i.d., 30 cm bed height. Particle size: Fe, 1–2 mm; Fe–Si alloy, 0.5–1 mm; Mg–Al alloy, 2–3 mm. Water passed through the column at a flow rate of 176 L h⁻¹, contact time <2 min. ^b Average results of three replicate column tests with relative standard deviations of <15%. ^c The mass ratio of the two phases of particles was 1:1.

Fe–Si alloy was employed as a cathode and tested for the dechlorination of TCAA by potentiostatic electrolysis. For comparison, Fe and other metals (Pt, Ni, and Zn) were also tested, and the results are shown in Figure 1a. Clearly, the dechlorination rate increased with decreasing potential. Since the electrons are supplied from an external source in the potentiostatic electrolysis, dechlorination rates on different electrode materials at the same potential, as shown in Figure 1a, reflect the surface adsorption and catalytic capabilities of the materials. The Fe–Si alloy electrode provided a significantly higher dechlorination rate than the Fe and Ni electrodes at potentials below -0.8 V and showed comparable performance with Pt between -1.35 and -1.1 V. This more than likely indicates the presence of a catalytic effect by the Fe–Si material. At negative potentials (-0.95 V and lower), the formation of hydrogen gas was observed, and the volume of the

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gas generated increased as the potential became more negative. This side effect decreases the utilization efficiency of electrons for the reductive dechlorination. A potential range from -0.75 to -1.0 V was found to be the optimum for dechlorination of TCAA in water using the Fe–Si alloy.

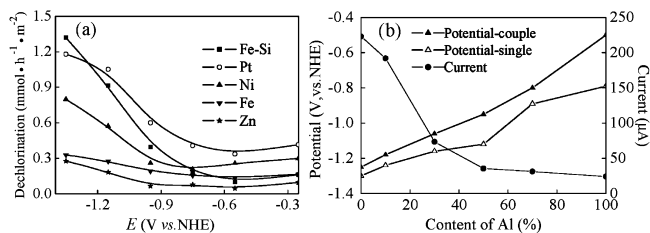


Figure 1. (a) Dechlorination rate of TCAA as a function of applied potential in potentiostatic electrolysis using different materials as the electrode. The Fe–Si alloy consisted of 72% Fe and 28% Si. (b) Effect of Al content in the Mg–Al alloy on corrosion potential and current. For details of the experiments, see the Supporting Information.

Figure 1b shows that the corrosion potential of the Mg–Al alloy increases with rising Al content, indicating that its reactivity decreases with increasing Al levels. Relative to the 70:30 Mg–Al alloy, the potential of the 50:50 Mg–Al alloy is slightly increased (from -1.06 to -0.95 V) while the corrosion current is significantly decreased by 50%. This indicates that the 50:50 Mg–Al alloy provides sufficient reactivity for rapid dechlorination while having minimal corrosion. The coupled Fe–Si/Mg–Al system can be adjusted for the required reactivity for targeted compounds by varying the content of Al in the Mg–Al alloy. The above results suggest that the mechanism of the system for degradation of chlorinated organic pollutants is that Mg–Al supplies electrons for the reductive reaction and Fe–Si acts as a catalyst and provides the sites for the reaction (Figure S2).

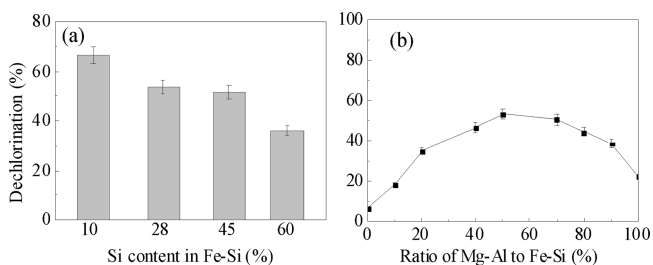


Figure 2. Influence of (a) Si content in the Fe–Si alloy and (b) the ratio of 50:50 Mg–Al to 72:28 Fe–Si alloy particles on the dechlorination efficiency of TCAA. Error bars represent 95% confidence intervals.

The corrosion resistance and brittleness of the Fe–Si alloy increase with increasing Si content, and the corrosion resistance is significantly improved when Si is $>14\%$.²³ The high brittleness is favored for mechanical milling, while the increase in Si content reduces the magnetic intensity of the Fe–Si alloy²¹ and decreases the dechlorination efficiency (Figure 2a). The magnetic separation of Fe–Si particles with 28% Si from Mg–Al particles is readily performed, and this is important for reuse of the Fe–Si particles and repacking of the column. Therefore, a Si content of 14–28% is optimal with respect to degradation efficiency, corrosion resistance, mechanical milling, and magnetic intensity. The influence of the Mg–Al to Fe–Si mass ratio on dechlorination efficiency is shown in Figure 2b. Relatively constant dechlorination efficiencies (40–55%) were obtained over a wide range of the ratio (30–90%). This feature is important in routine applications to maintain a constant degradation performance during gradual consumption of

the Mg–Al particles. A pilot-plant system with six columns (40 cm i.d.) in parallel was tested at a drinking water plant (Figure S3). Each column was loaded with 27 kg of Fe–Si and 27 kg of Mg–Al (bed height 30 cm), and the flow rate was $1.26 \text{ m}^3 \text{ h}^{-1}$. The degradation efficiency for $72\text{--}175 \text{ }\mu\text{g}$ of chloroform/L ranged between 55–79%, and no significant amounts of metals were leached into the treated water during a period of 10 months. This demonstrates the long durability of Fe–Si and Mg–Al particles.

In conclusion, the candidature of Fe–Si and Mg–Al alloys for drinking water treatment has been substantiated by their enhanced corrosion resistance and catalytic effect on DBP degradation. The millimeter-sized particles of Fe–Si and Mg–Al alloys are obtained by mechanical milling and are stable under ambient conditions. In contrast, ZVI and bimetallic nanoparticles undergo rapid oxidation under ambient conditions and must be kept under anaerobic conditions, leading to difficulties in storage and maintenance.^{12–15,19} The mechanical milling provides uniformity, is free of chemicals, does not generate secondary wastes, and overall shows superiority to the reductive deposition approach for preparation of bimetallic particles. The release of metals (Fe, Al, Mg) into treated water from the coupled Fe–Si/Mg–Al system is negligible in comparison with their background concentrations in unprocessed water. The proposed method possesses advantages of relatively constant degradation performance, long-term durability, no secondary contamination, and ease of handling, storage, and maintenance relative to nanoparticle systems. Additionally, millimeter-sized particles do not present the safety issues or potential hazards to human and environmental health that nanoparticles do. The proliferation of the use of nanoparticles is leading to increasing health and environmental concerns and consideration of the need to regulate their use.^{24,25}

Supporting Information Available: Figures S1–S3 and a description of the experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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