

Dehalogenation of trihalomethanes by a micro-alloyed aluminium composite under flow conditions

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Abstract

A new method for dehalogenation of trihalomethanes (THMs) by a low-cost and highly effective micro-alloyed aluminium composite (MAIC) in a semi-flow system (SFS) was studied. Addition of micro-alloyed elements significantly accelerated the rate of Al corrosion and enhanced reduction activity by destabilising the oxide film. THM dehalogenation by the MAIC followed pseudo first-order kinetics with respect to degradation of substrate. Batch experiments showed that complete dehalogenation of CHCl_3 , CHBrCl_2 and CHBr_3 could be achieved within 120, 75 and 30 min, respectively, which periods are 5 to 10 times shorter than those of the bimetallic complexes and zero-valent iron. Additional advantages of the MAIC, related to other zero-valent metals, are capability of CH_2Cl_2 degradation and working under high pH conditions. Dehalogenation kinetics is mass-transport limited since it could be accelerated by using the SFS and by increasing the composite surface area. Presence of NaCl in solution increased the dehalogenation rate up to the concentration corresponding to seawater. The MAIC could be a promising reactive reagent for the remediation of the THM-contaminated ground- and seawater.

Keywords: micro-alloyed aluminium composite, chloroform, bromodichloromethane, bromoform, dehalogenation, reduction, semi-flow system, groundwater, seawater

Introduction

Disinfection is the essential stage in a water treatment plant during the production of potable water. This process is carried out most frequently by chemical methods such as chlorination and ozonation or by ultraviolet irradiation (EPA, 1981; Wagenet, 1988; Camel and Bermond, 1998; Craik et al., 2001; Otaki et al., 2003; Jyoti and Pandit, 2004). Chlorination by free chlorine, as a major method of water disinfection used worldwide, possesses many advantages, but also a significant disadvantage. During this process, chlorination by-products (CBPs), mainly the trihalomethanes (THMs), are formed from naturally occurring and anthropogenic organic compounds present in water (humic and fulvic acids, polyhydroxyaromatics, tannins, proteins, amino acids, etc.) (Li et al., 1996; Hekap, 2002; Egorov et al., 2003; Nikolaou et al., 2004). The factors which enhance the amount of the THMs formed include $\text{pH} > 7$, higher water temperature, and an excess of chlorine. Especially problematical is the chlorination treatment of seawater, before distillation for obtaining potable water, due to the presence of other halogens, particularly bromide (Shams et al., 1991). Chlorine reacts with the bromide ion present in the water and liberates elemental bromine: $\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$ (EPA, 1981; Saeed, 1999). Both chlorine and bromine react with organics in water to produce a series of trihalomethanes. Additionally, the THMs are widely used as refrigerants, propellants, solvents in degreasing, cleaning and extracting, or as synthetic intermediates for plastics and pesticides. Due to their accidental spills, leakages and improper disposal, these compounds have been continuously released into soil and natural water bodies. Because of their potential harm

to human health, THMs are of great concern regarding public health.

Chloroform, bromodichloromethane and bromoform were chosen for this study, because they constitute over 98% of the total formed THMs in water and have been classified by the EPA as probable human carcinogens (cancer group L) (EPA, 2006). In addition, they may cause birth defects and may damage the nervous system (Magnus et al., 1999; Boorman, 1999). Due to health hazards, regulatory limits for the concentrations for a number of the THMs in drinking waters have already been set by the EPA with a maximum contaminant level (MCL) of $80 \mu\text{g}\cdot\text{L}^{-1}$ for total THMs, as a yearly average (EPA, 2006). Considering the fact that the THMs are known as non-biodegradable and that currently applied physico-chemical treatments do not destroy them, but remove them from the aqueous medium by a mass transfer mechanism, destructive methods are necessary for their total degradation in drinking water supplies (Tang and Tassos, 1997).

There has been increasing interest in developing an abiotic reductive transformation method to degrade the THMs to non-toxic or biodegradable compounds over the past few years. Several different types of reducing media have been examined including zero-valent metals (Fe, Zn) (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Boronina et al., 1995), bimetallic complexes (Pd/Fe, Pd/Zn) (Grittini et al., 1995; Muflikian et al., 1995; Fennelly and Roberts, 1998; Cheng and Wu, 2000), colloidal-size iron (Cantrell and Kaplan, 1997) and nano-scale iron materials (Lien and Zhang, 1999, 2001). The reactive reagent most successfully deployed to date has been zero-valent iron (Fe(0)). Fe(0) shows great capability in treating many halogenated organic contaminants (Gillham and O'Hannesin, 1994), but it fails to degrade dichloromethane. A similar problem exists in using bimetallic catalysts (Lien and Zhang, 1999) and supported Pd catalysts (Lowry and Reinhard, 1999). Because complete degradation is not achieved, the accumulation of dichloromethane requires further treatments, considering that its MCL

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is only $5 \mu\text{g}\cdot\text{l}^{-1}$ (WHO, 1984). Additionally, Fe(0) activity is strongly affected by pH (Chen et al., 2001). In aqueous systems, corrosion of iron by water leads to increased pH and the formation of insoluble iron hydroxide, which may form a surface layer on the metal that inhibits its further dissolution (Matheson and Tratnyek, 1994).

This paper presents the results of a new method developed for dehalogenation of the THMs, by using the micro-alloyed aluminium composite (MAIC) in the semi-flow system. The MAIC is a very strong reductant, with reduction potential of about -1.5 V/SCE (saturated calomel electrode), and therefore a better medium than Fe(0) for reduction dehalogenation. On the contrary, compared to zero-valent iron, it may serve as a better reactive reagent under high pH conditions, because the presence of OH^- ions does not cause the formation of oxide precipitates, but facilitates the removal of aluminium oxide (Birnbaum et al., 1997; Bojic et al., 2004). In addition, a large amount of OH^- ions generated in reaction to the MAIC with water may perform base-catalyzed hydrolysis of the C–X bond, a parallel process of dehalogenation with less significance than reduction (Brewster, 1954). The additional effect of OH^- ion production is not only chemical degradation of water pollutants, but their co-precipitation on insoluble $\text{Al}(\text{OH})_3$ formed between Al^{3+} and OH^- ions, which intensifies treatment efficiency (Bojic et al., 2001; Bojic et al., 2003; Bojic et al., 2004; Purenovic et al., 2004). Since the dehalogenation of the THMs occurs at the surface of the composite, mass transport becomes a very important kinetic factor. In order to improve mass transport in this study, the treatment of the THMs in aqueous solutions was performed using the SFS, where molecular diffusion was substituted by convective transport, whereby more efficient degradation was accomplished than in stationary conditions (Bojic et al., 2001; Bojic et al., 2003; Bojic et al., 2004).

Experimental

Chemicals

All chemicals were of AR grade, unless otherwise indicated. HPLC grade chloroform, pentane and methanol were purchased from Aldrich; $\text{Hg}(\text{CNS})_2$, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, NaCl and HNO_3 from Merck (Germany); Na_2SO_4 , NaOH and H_2SO_4 from Zorka (Serbia), reagent-grade bromoform and bromodichloromethane from Fluka (Germany). All the reagents were used without further purification. Ultra-pure water ($18 \text{ M}\Omega\cdot\text{cm}$) was used to prepare all aqueous solutions.

Composite and experimental system

The micro-alloyed aluminium composite was formed of iron wire (mesh 1.2×1.2 , $\text{Ø}0.6$) metallised with the micro-alloyed aluminium (MAI) by means of a special gas burner (Metco, USA). The MAI was prepared by alloying 99.8% aluminium with: Sn, Ga and Bi (0.105%, 0.098% and 0.040%, respectively). Because of numerous micro-galvanic cells in the MAI based on Al/(Sn, Ga and Bi) redox couples and a macro-galvanic cell $\text{Fe}/\text{Al}_{\text{Micalloy}}$ in aqueous environment, the composite behaves as a very strong reductant. Its reduction efficacy is enlarged by means of a shapeless surface in the form of fish scales, with many micro-pores. The composite readily reacts with water reducing it to H_2 , with generation of OH^- ions. Substances dissolved in water which are exposed to the MAIC surface by diffusion, also become participants in different reactions initiated by the MAIC, such as the reduction, hydrolysis, addition, etc. Detailed physico-chemical

characteristics of the composite have been presented previously (Bojic et al., 2001; Bojic et al., 2003; Bojic et al., 2004; Purenovic et al., 2004).

Batch experiments were carried out in the original semi-flow system. This system comprised several parts, preferably made of high-density polyethylene: a composite chamber of 1.0 l volume, with the MAIC wires placed perpendicular to the direction of the water flow; a main bath of 10 l volume for storing the water solution; a peristaltic pump and a thermostat connected to water jackets of the main bath and the composite chamber. The composite chamber was located above the main bath and aqueous solutions were transported to it by a peristaltic pump. After passing through the composite chamber, where pollutants were exposed to the MAIC, the solution was returned to the main bath by free fall. This formed a closed loop to enable the system to operate in a flow mode. Entering and returning tubes of the composite chamber were placed in the main bath, in order to prevent plugging of $\text{Al}(\text{OH})_3$ precipitate, accumulated on the bottom. A detailed schematic description of the SFS has been presented previously (Bojic et al., 2001; Bojic et al., 2003; Bojic et al., 2004).

Experimental procedure

Aqueous solutions of CHCl_3 , CHBrCl_2 and CHBr_3 were prepared in ultra-pure water, with the initial weight concentrations $10.0 \text{ mg}\cdot\text{l}^{-1}$. For studying of Cl^- ion effects on dehalogenation of CHCl_3 , a series of CHCl_3 solutions were prepared by adding 0.5, 1.0, 2.0, 3.0 and $5.0 \text{ g}\cdot\text{l}^{-1}$ NaCl. Where necessary, the initial pH of the solutions was adjusted pH-metrically to 7.0, by adding a few drops of NaOH ($0.1 \text{ mol}\cdot\text{l}^{-1}$) or H_2SO_4 ($0.1 \text{ mol}\cdot\text{l}^{-1}$), without buffering.

Batch experiments were carried out in the SFS. A volume of 8.0 l THM aqueous solution was equilibrated at 25°C , transferred to the main bath and the peristaltic pump and thermostat were run. The flow rate of the peristaltic pump was maintained at $90 \text{ l}\cdot\text{h}^{-1}$. During the MAIC treatment, the temperature was kept at $25 \pm 0.5^\circ\text{C}$. Samples were withdrawn every 15 min from the surface layer of the water phase in the main bath, where flow was laminar, using a glass syringe and 50 ml volume sampling Teflon tube. Samples were left to stand for the precipitate $\text{Al}(\text{OH})_3$ settle down. During treatment the pH was monitored by a digital pH-meter HACH SensIon 3 (HACH, USA), with a HACH gel-filled combination glass electrode. The effects of the composite wires area per solution volume (CWASV) on the THM dehalogenation efficiency was studied by varying the number of the composite wires. These experiments were done with 4, 8, 16, 24 and 32 composite wires, equivalent to CWASVs of 50, 100, 200, 300 and $400 \text{ cm}^2\cdot\text{l}^{-1}$, respectively. A parallel experiment with CHCl_3 was conducted in the SFS to determine the efficacy of the reductive dehalogenation by native Al. Instead of the MAIC, aluminium wires of the same dimensions (mesh 1.2×1.2 , $\text{Ø}0.6$) were applied. A study of the MAIC dissolution rate as a function of Cl^- ion concentration was carried out in a series of NaCl aqueous solution concentrations: 0, 0.5, 1.0, 2.0, 3.0 and $5.0 \text{ g}\cdot\text{l}^{-1}$. To enable homogenisation of $\text{Al}(\text{OH})_3$ suspensions that appear during the MAIC treatment, the SFS was modified by replacing the rectangular main bath with a cylindrical vessel placed on a magnetic stirrer. During the treatment, solutions were stirred vigorously, and the samples were removed from the bottom of the main bath, where there was greater turbulence. The other conditions in the experiments were the same as in the batch experiments. All experiments were carried out non-stop for 120 min.

Control experiments, performed in the SFS without the composite, showed insignificant losses of the THM compounds via volatilisation to the headspace of the baths, over a period of much longer than 120 min. Furthermore, CHCl_3 , CHBrCl_2 and CHBr_3 were found to be stable in aqueous solutions at pH 9, and 25°C. No Cl^- and Br^- ions were detected in solutions after more than 24 h. Also, the presence of Cl^- ion in the solutions, in a range from 0.5 to 5 g·l⁻¹, did not influence the THM stability. All experiments were done at least in triplicate.

Analytical methods

The THM concentrations in aqueous solutions were determined by using a Varian 3400 gas chromatograph with a capillary column 25 m in length, film thickness 0.25 µm, ID 0.32 mm. Hydrogen was used as a carrier gas, with a flow rate of 2 ml·min⁻¹. The initial oven temperature was 40°C. The column temperature was increased by 10°C·min⁻¹ up to 90°C, and by 15°C·min⁻¹ up to 190°C. The aqueous samples were filtered through a 0.45 µm pore size acid-washed nitrocellulose membrane filter (Millipore Corporation, Bedford, Mass., USA), to remove un-dissolved particles and extracted by using pentane (Standard Methods, 1998; Munch and Hautman, 1995). Pentane extracts were desiccated by sodium sulphate salt, previously heated and dried for 2 h at 105°C in an oven.

The total aluminium concentration in samples of $\text{Al}(\text{OH})_3$ aqueous suspensions was determined by flame atomic absorption spectroscopy using a VARIAN SpectrAA-20, in a nitrous oxide-acetylene flame (Standard Methods, 1998). Before analysis, the $\text{Al}(\text{OH})_3$ precipitate was dissolved by 1 mol·l⁻¹ HNO_3 , and samples were diluted to suitable concentrations.

The chloride anions were determined in the filtered aqueous samples by the ferric thiocyanate method, using a Varian Cary 50 spectrophotometer (Standard Methods, 1998).

Results and discussion

During the treatments of the THM aqueous solutions by the MAIC, the pH value of solutions measured in the main bath increased. Figure 1 shows that pH change occurs mainly in the first 30 min of the treatments, reaching a pH value of 9. During subsequent periods of treatment, it was almost constant.

The composite is highly reactive, due to its electrochemical and mechanical characteristics, and contact with water causes its reduction to H_2 and OH^- ions. Many factors affect the stability of the MAI, thereby accelerating corrosion of the metal. Corrosion of metals is essentially a micro-galvanic process comprising a partial anodic reaction and a partial cathodic reaction that occurs simultaneously on the metal surface. In the case of the MAIC, these processes are intensified by local cells, formed between couples of Al and micro-alloyed elements. In addition, there is a macro-galvanic cell MAI/Fe in the composite, where the MAI behaves as a sacrificial anode. Both phenomena significantly decrease the open circuit potential of the MAI, related to native Al. The oxide film is destabilised by the presence of different defects (lattice defects: vacancies and interstitials, as well as macro-defects: inclusions, second-phase particles of the same size and shape, crystal structure and the degree of non-crystallinity) which arise by incorporation of micro-alloyed elements.

The MAI dissolves according to the anodic half-reaction:



while hydrogen evolution is the essential reduction processes at

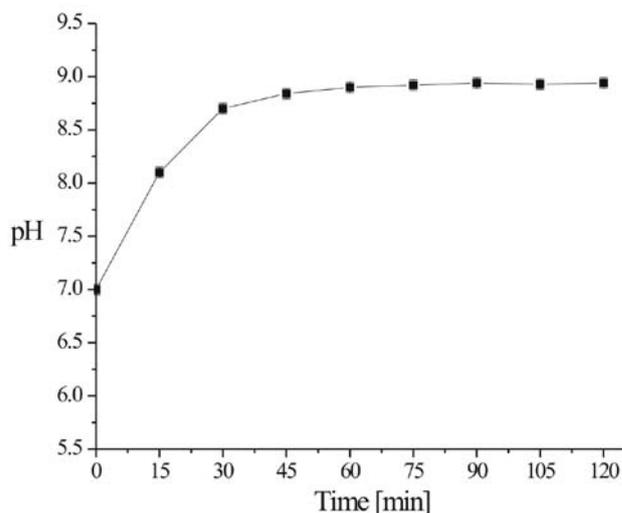


Figure 1

Monitoring of pH in the THMs aqueous solutions, during the MAIC treatment in the SFS. Initial pH was 7.0, temperature was kept at 25±0.5°C, flow rate was 90 l·h⁻¹ and the CWASV was 200 cm²·l⁻¹. Error bars represent the standard deviation of triplicate sample means.

the inter-metallic cathodes:



This reaction generates hydroxide ions, which increase the pH of the solution (Fig. 1). The reduction reaction will cause local alkalisation around cathodic particles, which is usually higher than the pH of the bulk solution (Davis, 1998). Aluminium oxide is not stable in such an environment, and aluminium around the particles will rapidly dissolve (alkaline pits) (Nisancioglu, 1992; Davis, 1998).

Figure 1 also shows that the pH of solutions did not increase significantly, suggesting that other processes, mainly formation of insoluble aluminium hydroxides, balanced the hydroxide produced by water reduction:



The equilibrium which arises between the process of OH^- ion generation by reduction of water (Eq. (1)) and its dissipation by production of $\text{Al}(\text{OH})_3$, forms a specific buffer system capable of keeping the pH of the solution constant. Because of that, in many of our previous studies of the MAIC treatments, the pH of the treated samples reached a value of about 9 after 30 to 60 min, irrespective of the initial conditions (Bojic et al., 2003; Bojic et al., 2004; Purenovic et al., 2004).

Addition of Cl^- ions to the solution significantly increased the dissolution rate of the MAI. Curves in Fig. 2 show an almost linear increase of total aluminium concentration in a bulk solution vs. time, in all investigated NaCl concentration ranges.

Aggressive chloride ions attack weak sites in the oxide, producing a highly localised type of corrosion-pitting (Scamans et al., 1987; Nisancioglu, 1992). They are incorporated in the passive film by occupying anion vacancies. This results in a decrease of anion vacancies and increase of the cation vacancies. When the cation vacancies accumulate at the metal interface, a breakdown of the films occurs. In addition, the solvation of Al^{3+} ions is made easier by chloride ions due to complexation (Cotton and Wilkinson, 1972; Lurie, 1978). These phenomena

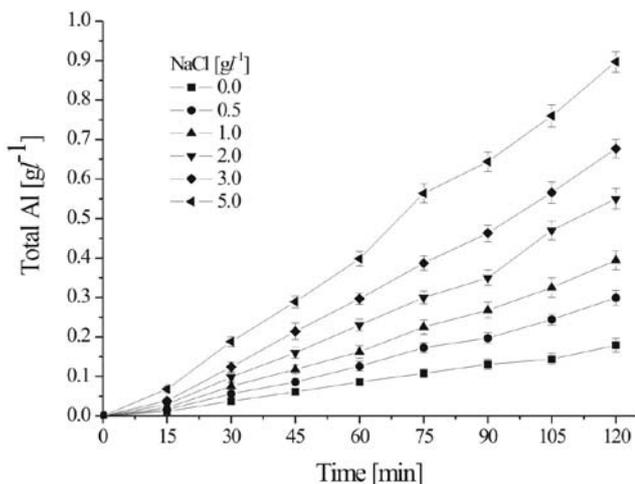


Figure 2

Change of the total aluminium concentration in the water phase during dissolution of the MAIC in NaCl solutions with initial concentrations: 0, 0.5, 1.0, 2.0, 3.0 and 5.0 g·l⁻¹, in the SFS. Initial pH was 7.0, temperature was kept at 25±0.5°C, flow rate was 90 l·h⁻¹ and the CWASV was 200 cm²·l⁻¹. Error bars represent the standard deviation of triplicate sample means.

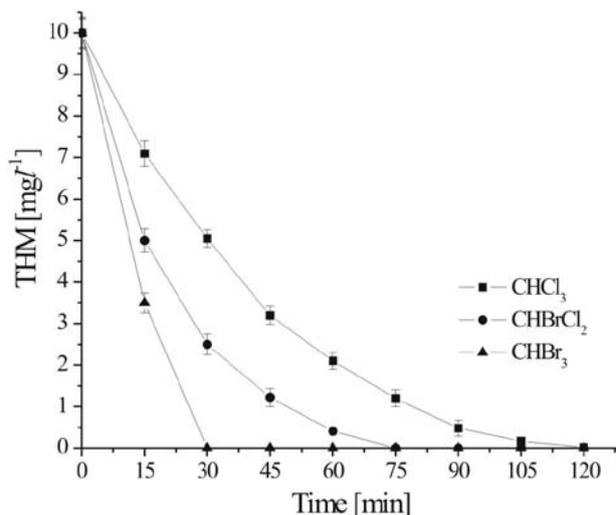


Figure 4

Change of the THMs concentrations during the MAIC treatment, in the SFS. Initial concentrations of the THMs were 10 mg·l⁻¹, initial pH was 7.0, temperature was kept at 25±0.5°C, flow rate was 90 l·h⁻¹ and the CWASV was 200 cm²·l⁻¹. Error bars represent the standard deviation of triplicate sample means.

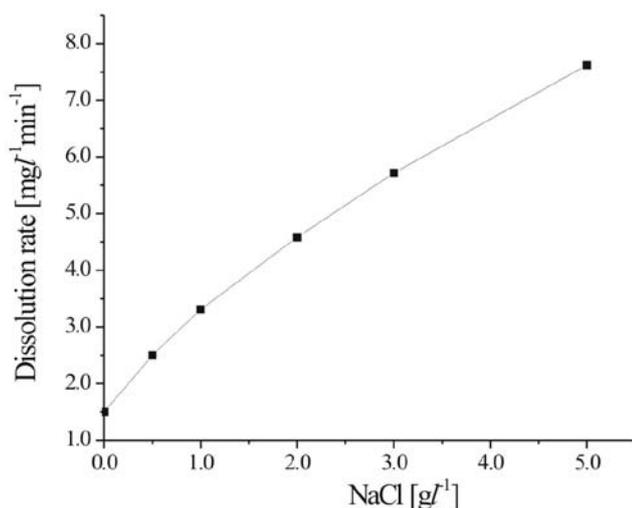


Figure 3

Dissolution rate of the MAIC vs. NaCl concentration

lower the open circuit potential and polarisation resistance and intensify dissolution of the composite (Purenovic et al., 2000).

An increase in Cl⁻ ion concentration increases its aggressive influence on the oxide, resulting in acceleration of the MAI dissolution (Fig. 3). Chloride adsorption was primarily localised to the corroding pit sites. To balance the positive charge produced by aluminium dissolution (Eq. (1)), chloride ions will migrate into the pit. Berzins et al. (1977) found that the amount of chloride adsorbed, w_{Cl} , was a linear function of chloride concentration and time according to the equation:

$$\log w_{Cl} = 0.64(\log[Cl] + \log t) - 7.8 \quad (4)$$

The authors suggest that there is no threshold for the chloride concentration below which pitting will not occur. Our results are in accordance with the findings of Berzins et al. (1977), because the dissolution rate is significantly increased even at

0.5 g·l⁻¹ NaCl and shows linear growth in the 0 to 5 g·l⁻¹ concentration range. However, in the MAI case, the corrosion process is about two orders of magnitude faster compared to native Al, considering the fact that it is an activated micro-alloy. The dehalogenation of CHCl₃, CHBrCl₂ and CHBr₃ by the micro-alloyed aluminium composite treatment was carried out in the SFS. The experiments were done with the aqueous solutions of each compound as a sole component, at an initial concentration of 10 mg·l⁻¹. Figure 4 shows an exponential decrease in the THM concentrations during treatment, which indicates great dehalogenation capability of the composite. A rapid decrease of the THM concentrations was observed at the very beginning of the treatment. After 30 min, more than 50% of every THM was degraded. A much slower concentration drop was observed during the subsequent period of the MAIC treatment. Figure 4 also shows that the degradation curves of all compounds have similar profiles. A linear regression analysis of the obtained results ($R^2 > 0.98$) indicates the same dehalogenation kinetics and mechanism, which could be adequately described as pseudo-first order kinetics (Matheson and Tratnyek, 1994; Plagentz et al., 2006).

Through contact with the MAIC, the concentration of CHCl₃ was reduced to below maximum contaminant level (MCL) 30 µg·l⁻¹ (Standard Methods, 1998) after 120 min, or equivalent to a half-life of about 30 min. The obtained result shows that the MAIC dehalogenation activity is many times greater compared to Fe(0), considering the fact that in studies of Plagentz et al. (2006) and Feng and Lim (2005), CHCl₃ is completely degraded after more than 10 h. An increasing chloride concentration was also detected in the aqueous phase as the dehalogenation process proceeded. The total chloride mass in the aqueous phase at the end of the experiment was over 95% of its initial mass. The reasonably good mass balance achieved in the aqueous phase indicated complete dehalogenation of CHCl₃, with insignificant appearance of the main intermediate by-product CH₂Cl₂. Contrary to the MAIC, in the case of similar reductive dehalogenation treatment by zero-valent iron and bimetallic complexes, dichloromethane accumulates in the aqueous system due to its low reduction rate (Matheson and Tratnyek, 1994; Feng and Lim, 2005). Capability of CH₂Cl₂ degradation is attributed to

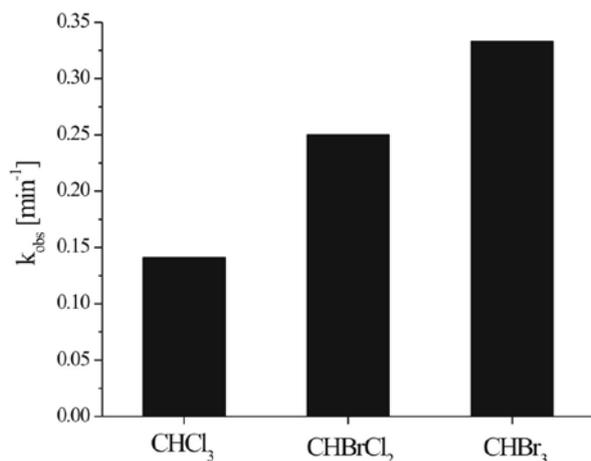


Figure 5

Dehalogenation rate constants of CHCl_3 , CHBrCl_2 and CHBr_3

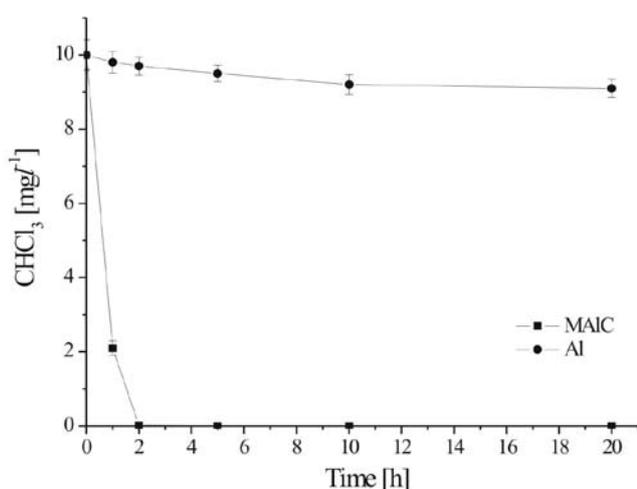


Figure 6

Dehalogenation of CHCl_3 by the MAIC and by native Al, in the SFS. Initial concentration of the CHCl_3 was 10 mg l^{-1} , initial pH was 7.0, temperature was kept at $25 \pm 0.5^\circ\text{C}$, flow rate was 90 l h^{-1} and the CWASV was $200 \text{ cm}^2 \text{ l}^{-1}$. Error bars represent the standard deviation of triplicate sample means.

high reducibility of the MAIC and generation of a large amount of OH^- ions at the composite surface, which initiate the base hydrolysis reaction typical for halogenated alkanes (Brewster, 1954; Hine et al., 1954; Shams El Din et al., 1998). In addition, the chloride mass balance indicated insignificant losses of the THM compounds via volatilisation to the headspace of the baths and negligible adsorption of CHCl_3 to the polyethylene wall and the composite surface during the experiment. Here, it is important to point out that adsorption on the composite surface is practically impossible, due to continual dissolution of the MAIC during the treatment. The results also show significant differences in dehalogenation rates between CHCl_3 , CHBrCl_2 and CHBr_3 . These differences are observed by comparing the rate constants (k_{obs}), shown in Fig. 5.

Compared to CHCl_3 , the brominated methanes CHBrCl_2 and CHBr_3 showed considerably faster degradation. Due to these fast dehalogenation kinetics their half-lives are significantly shorter, 14 min for CHBrCl_2 and 9 min for CHBr_3 . Figure 5 shows that CHBrCl_2 was completely degraded within 75 min (concentration below $\text{MCL} = 25 \text{ } \mu\text{g l}^{-1}$) (Standard Methods, 1998) and

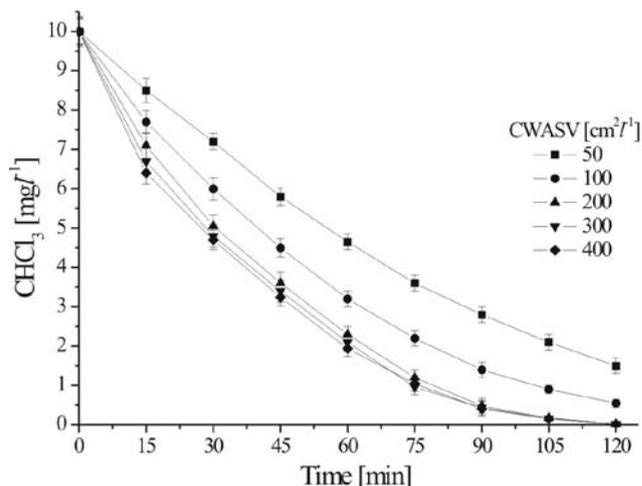


Figure 7

The effects of the composite surface area on the dehalogenation of CHCl_3 by the MAIC, in the SFS. The CWASV were 50, 100, 200, 300 and $400 \text{ cm}^2 \text{ l}^{-1}$, initial concentration of CHCl_3 was 10 mg l^{-1} , initial pH was 7.0, temperature was kept at $25 \pm 0.5^\circ\text{C}$ and flow rate was 90 l h^{-1} . Error bars represent the standard deviation of triplicate sample means.

concentration of CHBr_3 was below MCL ($5 \text{ } \mu\text{g l}^{-1}$) after less than 30 min. The facile decomposition of brominated THMs is attributed to the large size of the bromine atoms, causing greater polarisation of the C–Br bonds and making their cleavage easier (Hine and Ehrensox, 1958). For the same reason, the hydration energy of Br^- ion is greater than that of the Cl^- ion, which also accelerates the dehalogenation reaction in aqueous solutions.

Results of comparison of CHCl_3 dehalogenation by the MAIC and by native Al are shown in Fig. 6. The MAIC rapidly degraded CHCl_3 , while a slow degradation was observed using native Al (Fig. 6).

Observed rate constants of the MAIC and native Al were 4.99 and 0.042 h^{-1} , respectively. This indicated that the MAIC increased the degradation rate by a factor of about 120 compared to native Al. The poor performance of native Al is a consequence of the formation of a protective oxide layer on the Al surface that inhibits its reduction activity at near neutral pH. The effect of the composite surface area on the treatment efficiency is shown in Fig. 7. In the interests of simplicity, a geometric area that is proportional to specific one is set, bearing in mind high reproducibility of the composite surface structure (Bojic, 1997; Bojic et al., 2004).

The study was carried out on CHCl_3 as example. Obtained data show that by increases of the composite area in the range of 50 to $400 \text{ cm}^2 \text{ l}^{-1}$ CWASV, efficiency of CHCl_3 degradation increases. However, the CHCl_3 dehalogenation rate does not increase linearly with area, which is obvious through the comparison of dehalogenation constant rates vs. CWASV (Fig. 8).

Figure 8 shows that the CHCl_3 degradation rate increase is almost linear with an increase in CWASV from 50 to $200 \text{ cm}^2 \text{ l}^{-1}$ ($\text{tg}\alpha = 3.34 \cdot 10^{-4}$, $R^2 = 0.97$). A further increase in CWASV from 200 to $400 \text{ cm}^2 \text{ l}^{-1}$ leads to a loss of linearity and the slope of the function k_{obs} vs. CWASV decreases ($\text{tg}\alpha = 1.51 \cdot 10^{-4}$, $R^2 = 0.79$). In a heterogeneous system: the MAIC is immersed in a water solution, and reaction of CHCl_3 dehalogenation occurs at the MAIC/ H_2O interface. A general model for surface reactions comprises a few steps: mass transport, adsorption, desorption and chemical reaction at the surface (Spiro, 1989). Any one, or a combination of these steps may be rate limiting. An increase in

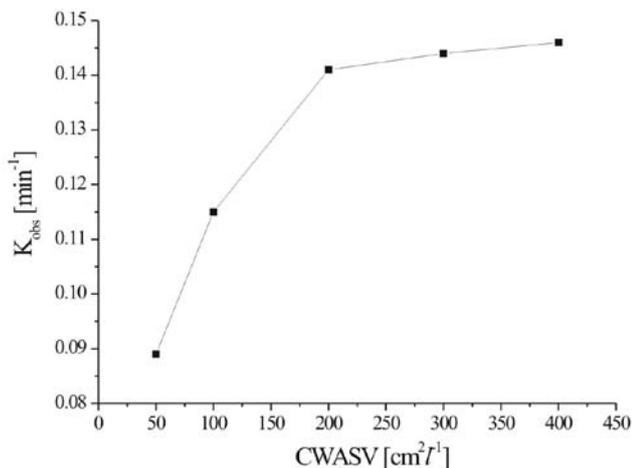


Figure 8

Effect of the composite wires area per solution volume on CHCl_3 dehalogenation rate constants by the MAIC

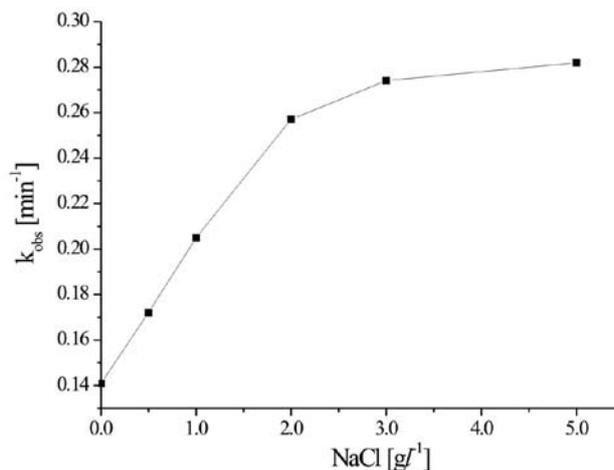


Figure 10

Rate of CHCl_3 dehalogenation by the MAIC vs. NaCl concentration

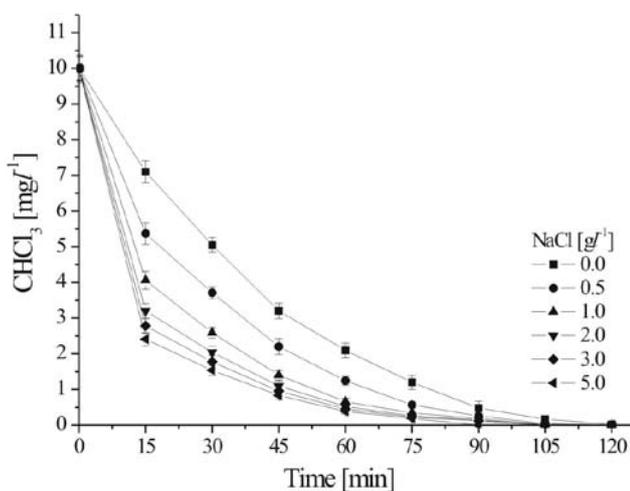


Figure 9

The effects of Cl^- ion on the dehalogenation of CHCl_3 by the MAIC, in the SFS. Initial concentrations of NaCl were 0, 0.5, 1.0, 2.0, 3.0 and 5.0 $\text{g}\cdot\text{l}^{-1}$, initial concentration of CHCl_3 was 10 $\text{mg}\cdot\text{l}^{-1}$, initial pH was 7.0, temperature was kept at $25\pm 0.5^\circ\text{C}$, flow rate was $90\text{ l}\cdot\text{h}^{-1}$ and the CWASV was $200\text{ cm}^2\cdot\text{l}^{-1}$. Error bars represent the standard deviation of triplicate sample means.

CHCl_3 degradation rate with increasing CWASV (Figs. 7 and 8), indicates that the dehalogenation process is mass-transport controlled. Additional support for the importance of mass transport to the kinetics of dehalogenation comes from the effect of the convection: conditions employed in this study (using of SFS), increased the degradation rate by a factor of about 2.5 times, compared to stationary conditions (results not shown). Results in Fig. 8 show that as the composite area increases above $200\text{ cm}^2\cdot\text{l}^{-1}$ CWASV, the process rate is not changed significantly. This shows that the transport- and reaction-limited process kinetics are of equal importance and thus mixed kinetics occurs, leading to setting the value of $200\text{ cm}^2\cdot\text{l}^{-1}$ CWASV as optimal.

Since a good part of the formed THMs remains in the brine, it was of interest to establish the effect, if any, of major seawater components on the THM dehalogenation by the MAIC. The study was carried out on CHCl_3 , in synthetic waters based on a series of NaCl solutions concentrations: 0.0, 0.5, 1.0, 2.0, 3.0 and $5.0\text{ g}\cdot\text{l}^{-1}$, where a concentration of $3.0\text{ g}\cdot\text{l}^{-1}$ corresponds to that of ordinary seawater. Results in Fig. 9 show that CHCl_3 dehalogenation

efficiency increased with increasing NaCl concentrations.

The presence of Cl^- ions in solution intensifies dissolution of the MAIC (Figs. 2 and 3) and enhances reduction ability of the composite, causing an increase of the CHCl_3 degradation rate. However, the CHCl_3 dehalogenation rate does not grow linearly with NaCl concentration (Fig. 10).

Figure 10 shows that an abrupt jump of dehalogenation rate happens with an increase in NaCl concentration from 0 to $2.0\text{ g}\cdot\text{l}^{-1}$. By further increasing the concentration to $3.0\text{ g}\cdot\text{l}^{-1}$ and $5.0\text{ g}\cdot\text{l}^{-1}$, the CHCl_3 degradation rate decreased, in contrast to the MAIC dissolution rate which linearly increased under the same conditions (Figs. 2 and 3). The stabilising effect of neutral salts to THMs was noted also by Shams El Din et al. (1998), Hine (1950) and Hine and Dowell (1954) and was attributed in the case of NaCl to common ion effect. The presence of a neutral salt lowers the solubility of CHCl_3 in water, thus decreasing the probability of contact with the composite surface. In addition, the common ion effect of Cl^- ion suppresses the breaking of the C-Cl bond by shifting the dissociation equilibrium in the opposite direction. In both cases, the intensity of effects increases with NaCl concentration. Figure 10 shows that with increasing NaCl concentration up to $2.0\text{ g}\cdot\text{l}^{-1}$ enlargement of the MAIC reduction activity is more significant than the negative salt effect and the common ion effect. With further increases in salt concentration, the dissolution degree of the MAIC is increased linearly, but CHCl_3 is more stable, which retards the increase in dehalogenation rate. An optimal NaCl concentration at which the CHCl_3 degradation rate has a comparatively high value is about $2.0\text{ g}\cdot\text{l}^{-1}$, whereby the dehalogenation rate is two times higher than in water solution (Fig. 10).

Conclusions

In the presented study, the dehalogenation of the THMs by the micro-alloyed aluminium composite in the semi-flow system was investigated in order to control the concentration of the THMs in ground- and seawater. The strong reducing capability of the MAIC is based on addition of micro-alloyed elements, which significantly increases the number of micro-galvanic cells and enhances corrosion of the metal. Reduction activity of the MAIC is also enhanced by irregular and shapeless surface appearance of the composite, which increases the surface contact area for the THMs. Because of that, the k_{obs} value for CHCl_3 dehalogenation by the MAIC was about 120 times higher than by

native Al and nearly an order of magnitude higher than by Fe(0). Reduction dehalogenation of the THMs by the MAIC followed pseudo-first-order kinetics. The reduction rates of brominated methanes were higher than those of their chlorinated counterparts following the order: $\text{CHBr}_3 > \text{CHBrCl}_2 > \text{CHCl}_3$. Under the set conditions in this study, mass transport of the THMs to the MAIC surface appeared to be an important determinant of the dehalogenation rate. Presence of NaCl in the solution has a double role in dehalogenation kinetics. It increases the dissolution rate of the MAIC increasing in this way the rate of dehalogenation. On the other hand, it stabilises the C–Cl bond by the common ion effect. Therefore, at the higher concentrations of NaCl the dehalogenation rate did not increase with salt concentration. However, in the solution that corresponds to seawater, the dehalogenation rate is more than two times higher than in the groundwater-like solution.

The MAIC demonstrated several advantages in enhancement of the THM dehalogenation treatments when comparing these to the treatments with the Fe(0) and bimetallic complexes. It effectively degraded halogenated methanes under high pH conditions where conventional reagents such as zero-valent metals are deteriorated. Good mass balance of Cl^- ion indicated complete degradation of CHCl_3 and possible capability of degrading dichloromethane, a recalcitrant contaminant that cannot be degraded by zero-valent metals. However, before this technology can be fully optimised for environmental applications, further study is needed comprising detailed investigation of the dehalogenation mechanism, determination of by-products and the potential production of dissolved Al^{3+} and micro-alloyed metals.

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