



Reductive dechlorination of haloacetamides in drinking water by Cu/Fe bimetal



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ABSTRACT

Haloacetamides (HAcAms), a class of highly toxic nitrogenous disinfection by-products (N-DBPs), have been widely detected in drinking water. The control of DBPs is an important measure to ensure the safety of drinking water. Due to the presence of residual chlorine and organic compounds that failed to be effectively removed, HAcAms could be formed in the finished drinking water distribution systems. In the study, Cu/Fe bimetal with different molar ratios of Cu to Fe was synthesized. This study reported that Cu/Fe bimetal reduced trichloroacetamide (TCACAm) to dichloroacetamide (DCACAm) and monoacetamide (MCACAm), and the reduction ability of Fe was greatly improved due to the incorporation of Cu. The optimal HAcAm removal was achieved when the molar ratio of Cu to Fe was 2.0%, Cu/Fe bimetal could reach complete degradation of TCACAm within 1 h. With the increase of Cu/Fe bimetal dose or the decrease of solution pH, the reduction ability of Cu/Fe bimetal for HAcAm removal also increased. The calculated integrated toxicity values from HAcAms, which was used to reflect the comprehensive control effect of Cu/Fe bimetal for HAcAms, were also reduced with the decrease of solution pH and the increase of bimetal dose. The release of Cu²⁺ was not detected during the whole treatment process, Cu/Fe bimetal may be an excellent material for controlling DBPs as the end – control methods in tap water.

1. Introduction

To guarantee the safety of drinking water, disinfection process (e.g., chlorination and chloramination) was adopted in utilities for deactivating harmful waterborne pathogens [1]. However, the disinfection by-products (DBPs) formed due to the reaction between disinfectants (e.g., chlorine and chloramines) and natural organic matter, anthropogenic chemicals or halides [2,3]. DBPs have received much attention because its healthy risk [4], especially N-DBPs (e.g., haloacetamides [HAcAms] and haloacetonitriles), which showed higher cytotoxicity and genotoxicity in mammalian cell assays compared to regulated trihalomethanes and haloacetic acids [5–7]. Among the N-DBPs, Plewa et al. found that HAcAms were the most cytotoxic class and the second-most genotoxic class DBPs, by comparing the cytotoxicity and genotoxicity of more than 80 regulated and unregulated DBPs [6,8]. HAcAms had been also detected in chlorinated and chloraminated drinking water in many countries, and the chlorinated HAcAms presented higher concentration than their brominated and iodinated analogues

[2,5,9–11]. Moreover, the elevated toxicity of monochloroacetamide (MCACAm), dichloroacetamide (DCACAm), and trichloroacetamide (TCACAm) was also observed based on metabonomics in recent studies [12–15]. Therefore, it is necessary to control the HAcAms, a class of representative N-DBPs in the drinking water.

Generally, the removal of DBP precursors by pre-treatment methods (e.g., UV/H₂O₂ pre-treatment) before disinfection was a sound strategy to control DBP formation, and have shown promising results [16–21]. Researchers also made efforts to investigate HAcAm formation mechanisms for reducing their formation effectively [22–25]. Actually, with the presence of residual chlorine, more or less DBPs will form in finished drinking water distribution systems [26]. Especially, the conventional water treatment processes cannot effectively remove hydrophilic and/or low-molecular weight precursors [16,27–29]. This has caused increased formation of DBPs such as HAcAms [16,19]. There is relatively little information available on removing HAcAms themselves (also known as end-control), not HAcAm precursors.

Reductive dehalogenation technologies are good control strategies

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which can transform the highly toxic halogenated organic compounds (HOCs) to low toxic organic compounds and halide ions [30,31]. HOCs can be reductively dehalogenated via multiple processes, e.g. the zero-valent iron (ZVI) technologies which including nano-ZVI and bimetal technologies [32–34], Sulfite/UV process [30]. As known, most DBPs are HOCs, the reductive dehalogenation technologies such as bimetal technologies might be ideal control methods for DBPs.

The unlined cast iron pipes, and sometimes copper pipes were used to distribute the finished drinking water from DWTPs to consumers [35,36]. Previous studies have found that the existence of ZVI in distribution systems could transform antibiotics to form HACams, and HACams were further reduced by the electron releases from ZVI [3]. Our previous study reported that the addition of Cu could significantly improve the reductive dehalogen effect of ZVI on HACams [37], the potential difference in the primary battery system of Cu and Fe was 0.78 V, which accelerated the corrosion of Fe and the transmission of electrons to pollutants. However, Cu and Fe were simply mixed in above-mentioned system, which resulted in the lower degradation efficiency of the Cu and Fe mixed system. Many studies have found that the bimetallic system (e.g. Cu/Fe bimetal) had a good effect on the degradation of HOCs [34,38,39]. Nevertheless, the removal of N-DBPs by bimetallic system were rarely reported. Therefore, the objective of this study was to explore the dehalogenation effect of Cu/Fe bimetal to HACams, the representative N-DBPs in drinking water. The effects of the key parameters, including reaction time, molar ratios of Cu to Fe, bimetal dose, pH, and, the changes of HACams concentrations and integrated toxic risk caused by HACams, were examined.

2. Materials and methods

2.1. Materials

ZVI and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were obtained from Sinopharm Chemical Reagent Co., Ltd., China. TCACam (99%), DCACam (98.5%), and MCACam (98.5%) standard chemicals were purchased from Alfa Aesar (Karlsruhe, Germany). The buffer solution, including tris (hydroxymethyl) aminomethane (TRIS, 99.9%) and 2-(N-morpholino) ethanesulfonic acid (MES, 99%), were obtained from Aladdin Industrial Inc (Shanghai, China). All the other chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), and were at least analytical grade, unless otherwise noted. Ultrapure water was produced using a Millipore Milli-Q Gradient water purification system (Billerica, MA, USA).

2.2. Experimental procedures

(1) Cu/Fe bimetal were produced by adding Micron-ZVI into CuSO_4 solution, and then placed on the mechanical shaker under the sealing conditions, mixed reaction for 1 h. More details are described elsewhere [40]. The reaction between ZVI and CuSO_4 was shown in Eq. (1). The ZVI reduces the Cu^{2+} in the solution into Cu. Because the large size of the ZVI particles compared to produced Cu, Cu were attached to the surface of the ZVI particles, forming Cu/Fe bimetal. The particles were then filtered from solution and dried at 60 °C for 24 h under vacuum. As shown in Table SM1, the different dosages of Fe and CuSO_4 were designed to produce bimetals with different molar ratios of Cu to Fe. Five different particles (0.5%, 1.0%, 2.0%, 5.0%, 10%) were obtained in this study, and named by the molar ratios.



(2) Batch experiments were conducted on an agitator with six independent paddles and beakers (Fig. SM1). A certain amount of HACam (TCACam) and Cu/Fe bimetal (0.0–10.0 g) were added into each beaker (1500 mL) with 1000 mL buffer solution. The mixed

solutions were stirred simultaneously by the paddles at 550 r/min, and left to react for 24 h. Sodium acetate (0.1 M), Tris (0.05 M) and MES (0.03 M) were used as a pH 7.0 ± 0.2 buffer [41] unless otherwise noted, and the temperature constant were kept at 25 ± 0.2 °C.

2.3. Analytical methods

At selected time intervals, 15 mL of the solutions were withdrawn with a 20-mL gas-tight syringe and filtered immediately through a 0.22 μm membrane filter for analysis. 4 g of anhydrous sodium sulfate was added into 10 mL of the filtered solutions. During the HACams extraction process, the solution was mixed with 2 mL of methyl tert-butyl ether and shaken by an IKA oscillator (Staufen, German) at 2800 r/min for 1 min. The analysis of chlorinated HACams using a gas chromatograph (GC), coupled with an electron capture detector (ECD) (QP 2010 plus, Shimadzu, Japan). The detection limits for TCACam, DCACam and MCACam were 0.01, 0.01 and 0.05 μM , respectively. More details of this method have been presented in the previous studies [5,42]. The relative standard deviations ($n = 3$) of all of the samples were below 7%.

3. Results and discussion

3.1. Effect of the different molar ratios of Cu/Fe bimetal on HACam removal

Fig. 1 shows the effect of the bimetal with different molar ratios of Cu to Fe on HACams removal. As seen, both the ZVI alone (0.0%) and Cu/Fe bimetals (0.5–10%) had a degradation effect on TCACam, and the products were DCACam and MCACam. This was in agreement with the previous study [37], which found that ZVI could remove TCACam by stepwise dechlorination, as shown in Fig. 2. Because of the electronegativity of the halogen, the TCACam acted as an electron acceptor, and the ZVI acted as an electron donor in the reaction, resulting in a three-step reduction of TCACam. In this study, the results showed that the effect of Cu/Fe on the degradation of TCACam is much better than the effect of ZVI alone.

As shown in Fig. 1a, Cu/Fe bimetals could achieve the complete degradation of TCACam in 6 h, but ZVI alone need 12 h for that. Especially when the proportion (Cu/Fe molar ratio) is 2.0%, Cu/Fe could reach complete degradation of TCACam within 1 h. With the increase proportion of Cu in the Cu/Fe bimetal, degradation efficiency of TCACam first increased and then decreased, the optimal degradation appeared at the molar ratio of 2.0%. The introduction of Cu greatly promoted the reaction between Fe and TCACam. The potential difference between Fe and Cu was 0.78 V, higher than that between Fe and Fe^{2+} , which was 0.45 V. Therefore, the addition of copper formed an electrochemical system, which could accelerate the surface corrosion of ZVI, thus increasing the reactivity of ZVI [43,44]. Cu was not consumed during the reaction since no Cu^{2+} was detected in the whole treatment process (Table SM2), a small amount of Cu could catalyze the corrosion of iron continuously, thereby providing electrons for halogenation of HACams. When excess Cu existed, it might occupy the reaction sites on the surface of ZVI, which resulted in less contact between ZVI and HACams, and affected the mass transfer efficiency.

Fig. 1b and c display the change in the concentration of DCACam and MCACam during the reaction. As seen, DCACam and MCACam changed similarly in the use of Cu/Fe bimetal with different molar ratios. DCACam concentration reached the peak at 0.5 h, followed by a decrease and then reached complete degradation at 12 h. The increase of DCACam before 0.5 h was due to the reaction of TCACam and ZVI, as the step (1) in Fig. 2. At the same time, since the amount of metal particles was excessive, the activity of the reaction system was very high, and the DCACam produced from TCACam was further reduced, as the step (2) in Fig. 2. Similarly, the process of increasing and decreasing

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