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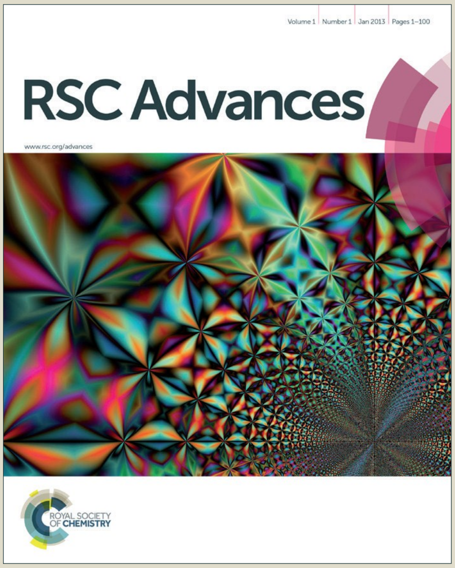

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Reductive dehalogenation of brominated disinfection byproducts by iron based bimetallic systems

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Abstract: The reductive dehalogenation of brominated disinfection byproducts (DBPs) including bromoform and tribromoacetic acid (TBAA) by iron based bimetallic systems (Cu/Fe and Pd/Fe) was investigated. In Cu/Fe bimetallic system, only 8.1% of bromoform and 20.1% of TBAA were reduced within 20 min when the particles dosage was 5 g/L, while 56.9% of bromoform and 62.7% of TBAA were removed at the same period when the dosage increased to 20 g/L. A complete removal of bromoform and TBAA was achieved within 60 min of reaction in acidic condition, while only 35.4% of bromoform and 10.8% of TBAA were removed after the whole experiment period (140 min) in alkaline condition. Similar results were observed in Pd/Fe bimetallic system. Bimetallic particles achieved high performance probably because galvanic cells were created between Fe (severed as anode) and plating elements (severed as cathode). This structure enhanced the reducibility of iron for reductive dehalogenation by facilitating the iron corrosion as well as reducing the activation barrier of H_2. Pd/Fe system showed a better performance than Cu/Fe, which attributed to a higher potential gradient (1.4 V) as compared to Cu/Fe couples (0.8 V). Furthermore, toxic assessment indicated that the toxicity of water samples had a dramatic decline after dehalogenation by bimetallic particles.

Key words: reductive dehalogenation; brominated disinfection byproducts; iron based bimetallic systems

1. Introduction

Drinking water disinfection can eliminate human health risk caused by pathogenic organisms which exist in natural water. However, potentially harmful disinfection by-products (DBPs) are generated inevitably during the disinfection process. Since chloroform was discovered by Rook in 1970, more and more attention has been paid to this area. Numerous studies have confirmed that the DBPs are generated from the reaction of disinfectant and organic matters in water. [1]

As natural anion, bromide is usually detected in the ground water of coastal areas because of seawater intrusion. [2] Although bromide ion occurs at trace concentration in drinking water sources, it has major implications regarding health effects associated with DBPs. Bromide could be oxidized to hypobromous acid (HBrO) by chlorine and this process could be very fast due to a strong nucleophilic character of bromide. [3-5] HOBr has been found to be 20 times more reactive than HOCl for the formation of haloacetic acids (HAAs) and trihalomethanes (THMs). [6] Many studies have showed that Br-DBPs are dozens to hundreds times more cytotoxic and genotoxic than traditional chlorinated analogs. Moreover, brominated DBPs also represented higher developmental toxicity and growth inhibition than their chlorinated analogs. [7-8] For example, a survey supported by USEPA in 2000 showed that bromoacetic acid (BA) and bromoform had the highest cytotoxicity and mutagenic potency than other DBPs such as chloroacetic acid or chloroform in drinking water. Furthermore, a recent study conducted in Istanbul[9] also indicated that dibromochloromethane (DBCM) contributed a higher cancer risk to residents through a dermal route than did other three chlorinated THMs. Therefore, considerable attention is currently given to the removal of

Br-DBPs in drinking waters.

The most common removal methods for organic pollutants involve mass transfer mechanisms such as adsorption by activated carbon. Although these methods are effective in removing Br-DBPs from the aqueous phase, they transfer the contaminants to another medium which still needs further treatment. In recent years, the use of zero-valent iron (ZVI) for reductive elimination of halogenated organic contaminants has received significant attention.[10-12] Gillham concluded that the reduction of halogenated compounds by ZVI is an electrochemical reaction during which iron is oxidized and halogenated compounds are reduced.[13] The ZVI is not the only reducing agents in aqueous systems, there still exist other reducing agents such as Fe (II) and H_2 which were produced from the corrosion of the iron particles. Matheson studied the reduction pathway for chlorinated methanes in Fe-H_2O system and found a sequential reductive dechlorination process. Carbon tetrachloride (CT) was first dechlorinated to chloroform, then to dichloromethane, and Helland observed that the major product during the reduction of CT by iron was CO_2. However, few studies were carried out on the reductive dehalogenation of Br-DBPs by ZVI.[14,15]

Depositing a more electropositive metallic element on the surface of iron particles (plating) is known to increase ZVI corrosion rate through the formation of a galvanic cell, which can promote the reductive degradation of contaminants.[16,17] Cheng found that the combination of Fe with Ni or Pd indeed had strong promotional effects on the reduction of trichloroethylene.[18] Schrick observed that Ni-plated Fe was more effective than the untreated Fe in degradation of trichloroethylene. [19] However, opposite results were also be found by other researchers. Ghauch demonstrated that dechlorination of clofibric acid by Pd/Fe bimetallic system was delayed while iron corrosion was accelerated by addition of MnO_2.[20] Furthermore, the degradation mechanisms between different bimetallic systems are still controversial. For palladium catalyst system such as Pd or Ni, the hydrogenation reaction is the main mechanism in the process of removing the electron withdrawing group (Cl, Br, I, NO_3) due to the strong hydrogen absorbing action of Pd series metal atoms.[21] On the contrary, for non-palladium catalyst system such as Cu or Ag, the β elimination reaction is the main mechanism due to their poor hydrogen absorption capacity.[22] Moreover, there are great differences in the removal sequence and removal degree during reductive dehalogenation reaction between palladium and non-palladium catalyst systems. Given these limited studies, additional work is required to assess the performance of different iron based bimetallic systems on the reductive degradation of halogen organic contaminants.

The purpose of this study was to investigate the performance of Pd/Fe and Cu/Fe bimetallic particles on the reductive dehalogenation of brominated DBPs including bromoform and TBAA. The influences of dosage and pH were studied in order to find an optimal reaction condition. In addition, reaction kinetics and mechanisms of brominated DBPs reduction by bimetallic particles were also proposed. Finally, toxicity test was carried out in consideration of the toxicity changes caused by incomplete degradation or intermediate products.

2. Materials and methods

2.1. Regents and standard solution preparation

Palladium (II) chloride and copper sulfate monohydrate (>99.9% trace metals basis) were purchased from Aldrich. Bromine THMs ($CHBr_3$, CH_2Br_2, CH_3Br) and HAAs (TBAA, dibromoacetic acied (DBAA), monobromoacetic acid (MBAA)) were obtained from Sigma (USA). Methanol (HPLC grade), methy-tertiary-butyl-ether (MTBE) (HP LC grade), pentane (HPLC grade) were acquired from Fisher. Deionized water was us ed for dilution and analysis. Pure nitrogen gas was used for purging solution and GC analysis.

2.2. Metallic particles preparation

Based on their standard reduction potentials, element Pd and Cu were deposited on the surface of iron particles by simple metal displacement reaction in deoxygenated solutions in order to avoid the formation of metallic oxides at an early stage before any contact with the aqueous reactive medium.

$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0$ bimetallics

$Fe^0 + Pd^{2+} \rightarrow Fe^{2+} + Pd^0$ bimetallics

Based on previous work done by Bransfield and Cwiertny,[23,24] Pd/Fe and Cu/Fe were prepared by weighing an equivalent amount of 47 μmol of each catalyst per gram of Fe^0 in order to ensure that the additive loadings were constant. After dissolution of corresponding salts in 0.1 M HCl (for $PdCl_2$) or 0.05 M H_2SO_4 (for $CuSO_4$), alkaline (20 mL 0.1 mol/L NaOH) and acid (20 mL 0.1 mol/L HCl) washed iron powder was added to the Pyrex vial to form a slurry-like material. After 5 min of mixing metal samples were then filtered, rinsed three times with deoxygenated double distilled water and transferred along to the freeze dryer for 2–3 h to remove humidity traces.

2.3. Batch Experiments

The experiments were conducted in a 500 mL conical flask reaction cell. The pH electrode, thermometer and DO electrode were clamped firmly from the top of the reaction cell. The reaction cells were set on a magnetic stirrer plate to mix the solution gently and homogeneously. All experiments were conducted at room temperature (25±1 °C).

To start an experiment, 500 mL of prepared bromoform or TBAA solution (initial concentration of 1000 μg/L) was added into a reaction cell. The reaction cell was airtight and without any head space in order to avoid the impact of volatilization. pH adjustment was prepared using high-purity 0.1 M HCl (assay: 38%, Fisher Scientific) and 0.1 M NaOH (assay: 100%, Fisher Scientific). The pre-settled pH levels were maintained constant at least 15 min before starting each experiment. After stabilization of the desired pH levels in water solution, different dosage of bimetallic particles (5 g/L, 7.5 g/L, 10 g/L, 15 g/L and 20 g/L) was added into the water samples. Temperature, DO, pH and iron ion concentration were monitored over the duration of the experiments. The samples were drawn out from reaction cell every 20 min for a total reaction period of 140 min by using syringe. The water samples were used to analysis the products generated from the reductive dehalogenation of Br-DBPs by bimetallic particles.

2.4. Bimetallic particles characterization

XRD was used to identify the crystalline phase of bimetallic particles after reaction. The particles were dried at vacuum drier for 30 minutes before the characterization. The XRD method employing a high speed Bruker D8 advanced XRD system using Cu-Ka radiation having a wavelength of 1.54 A°, tube voltage of 40 kV, and tube current of 40 mA.

2.5. GC analysis

Br-DBPs were quantified via liquid/liquid extraction and analyzed using a gas chromatograph (Agilent 7890A) with an electron capture detector based on the USEPA Method 551.1. For bromoform, pentane was used as the extracting solvent and 1,2-dibromopropane was used as an internal standard. TBAA was analyzed following derivatization with methanol. The method incorporated anhydrous sodium sulfate as a drying agent to promote complete derivatization of TBAA to its corresponding methyl ester. MTBE was used as the extracting solvent, 1,2,3-trichloropropane was used as an internal standard, and 2,3-dibromopropionic acid was used as a surrogate to monitor the derivatization efficiency. A 20 mL sample was extracted with 2 mL of extracting solvent. Two μL of the extract was then injected into GC. The column used was an HP-5 fused silica capillary column (30 m×0.32 mm, inner diameter; 0.25 μm film thickness; J&W Scientific). For bromoform, the gas chromatograph (GC) temperature program started at 40 °C for 2 min, increased to 160 °C at 10 °C /min for 2 min, and then further increased to 250 °C at 10 °C /min for 2 min. For TBAA, the GC temperature program started at 40 °C for 5 min, increased to 140 °C at 10 °C /min for 1 min, and then further increased to 250 °C at 10 °C /min for 2 min.

2.6 Toxicity assay

The toxicity of the water samples form reductive dehalogenation was evaluated using luminescent bacterium. The luminescent bacterium Q67 (purchased from Beijing Hammatsu Photon Techniques Inc., Beijing, China) freeze-dried as pellets in glass bottles were removed from -20 °C storage before the test, with recovery liquid (0.8% NaCl) added for rehydration at 20 °C for 15 min. For each test, four test tubes were prepared, three for parallel samples and one for blank control (recovery liquid). Q67 was directly exposed to the samples. Samples or control liquid (2 mL) were added into each tube, and the bacterial suspension (50 uL) was added at 10 s interval. After 15 min exposure of the bacterial to the sample at 20 °C, the relative light unit (RLU) of the luminescent bacterium Q67 was measured. Toxicity was evaluated by inhibition ratio I(%)

$$I(\%) = (1-\frac{LU}{LU_0}) \times 100\%$$

Where LU_0 was the RLU of Q67 exposed to the blank control (recovery liquid), and the LU was the RLU to the samples. Each test was repeated thrice, and the average inhibition ration was taken as the final results.

3. Results and discussion

3.1 Evaluating factors affecting dehalogenation of brominated DBPs by bimetallic systems

3.1.1 Dosage of bimetallic particles

Figure 1(a) and (b) depicted the dehalogenation of bromoform and TBAA under different dosage of Cu/Fe bimetallic system. A fast initial process (first 60 min) followed by a slow subsequent process (after 80 min) was found throughout the whole reaction period. 78.4% of bromoform and 81.3% of TBAA was removed within 60 min when the dosage was 10 g/L. Similar results were observed in many other surfaced-mediated processes which indicated that this reaction followed the pseudo-first-order reaction kinetic.[12] The reaction rate and reduction efficiency were increased rapidly with the increase of bimetallic particles dosages (from 5 g/L to 20 g/L). For example, only 8.1% of bromoform and 20.1% of TBAA were reduced within 20 min reaction at bimetallic particles dosage of 5 g/L. However, 56.9% of bromoform and 62.7% of TBAA were removed at the same reaction period when the dosage increased to 20 g/L. Furthermore, a complete removal of bromoform and TBAA was achieved during the whole reaction period (140 min) when the dosage exceeded 10 g/L.

Similarly to Cu/Fe system, the reaction rate and removal efficiency of bromoform and TBAA were enhanced with the increasing dosage of Pd/Fe bimetallic particles (showed in figure 1(c) and (d)). However, Pd/Fe system showed a higher reductive ability than Cu/Fe. Nearly 30% of bormoform and 35.4% of TBAA was reduced within 20min when the dosage was 5 g/L, while 71% of bormoform and 68.5% of TBAA was removed when the dosage increased to 20 g/L. This result was consistent with Ghauh who invested the removal of diclofenac by different bimetallic particles.[25] Ghauh concluded a decreasing order of bimetallic reactivity over 2h of reaction time: Pd/Fe >>> Ir/Fe > Ni/Fe ≈ Cu/Fe > Co/Fe ≈ Fe > Sn/Fe. One reason for this difference of reactivity might be that Pd had lower hydrogen over potential than Cu or other metal elements, which promoted the indirect reductive dehalogenation of bromoform.[26,27] Reductive dehalogenation at metal surfaces involved either direct or indirect reduction or both. For direct reduction, the metal itself served as a direct electron donor, while the indirect reduction involved atomic hydrogen. Atomic hydrogen was a very powerful reducing agent that reduced halogenated contaminants effectively. Because of low activation barrier for H_2 dissociation on Pd surface (2 kcal/mol), atomic hydrogen is readily formed at the Pd surface with the low hydrogen over potential.

3.1.2 pH values

The pH values had a significant influence on the metal corrosion and reactivity on halogenated compounds, so its influences were investigated. Figure 2(a) and 2(b) depicted the dehalogenation of bromoform and TBAA by Cu/Fe bimetallic system under different pH condition. In acidic condition (pH=3), the degradation rate was the fastest, followed by neutral condition, and the reaction rate in alkaline condition (pH=12) was the slowest. For example, 76.1% of bromoform and 77.9% of TBAA was removed within 20min reaction in acidic condition, while only 10.0% of bromoform and 2.9% of TBAA was removed in alkaline condition at the same reaction period. Moreover, a complete removal of bromoform and TBAA was achieved in acidic condition after 60 min of reaction, far below to what was taken in neutral condition (120 min). In contrast, the total removal efficiency of bromoform and TBAA in alkaline condition was only 35.4% and 10.8% during the whole reaction process. Similar result was observed in Pd/Fe bimetallic system in the consideration of pH effects which showed in figure 2(c) and 2(d). 61.7% of bromoform and 80.0% of TBAA were removed within 20 min of reaction in acidic condition, while only 17.2% of bromoform and 2.7% of TBAA were removed in alkaline condition at the same reaction period.

These results were in accordance with former studies by Song who reported an increase in reaction rates with decreasing pH for reductive dehalogenation of chlorinated compounds by ZVI.[28] They attributed this phenomenon to greater availability of electron form the ZVI due to dissolution of oxide layer at low pH. In addition, pH also had an effect on H_2 evolution rate (k_{H2}). Decreasing the pH values resulted in an increasing k_{H2} which promoted the indirect reductive dehalogenation by H_2.

However, low pH condition did accelerate the corrosion of zero-valent iron which resulted in the increasing concentration of iron ion in the solution. The concentration of iron ion in the solution after reaction was in the range of 5~10 mg/L under acidic condition (pH=3), while only 0.5~1 mg/L of iron ion was detected under neutral condition. Although the concentration of iron ion was higher than the drinking water quality standard (0.3mg/L in China and 0.2 mg/L in EU), this iron ion could be easily removed by subsequent aeration and coagulation-sedimentation processes. There was no need to worry about the impact of high concentration of iron ion on the drinking water quality.

3.2 Kinetics calculation

The kinetics of reductive dehalogenation of Br-DBPs was analyzed with various kinetic models. It was found that the process could be well described with the pseudo-first-order kinetic model. Therefore, the rate of reduction of Br-DBPs can be described by the following equation[29,30]

$$\frac{dc}{dt} = -k_{obs}\mathrm{C} = -k_{SA}\rho_a\mathrm{C}$$

Where C is the concentration of brominated DBPs (μg/L), k_{obs} is the pseudo-first-order rate constant (h^{-1}), k_{SA} is the specific reaction rate constant ($L/h\cdot m^2$), and ρ_a is the surface area concentration of metal in solution (m^2/L) which calculated from an average specific surface area for zero-valent iron used in this study (0.45 m^2/g). The initial reaction parameters were included: initial bromoform and TBAA concentration of 1000 μg/L, bimetallic dosage was 10 g/L and a neutral condition when calculated the reaction kinetics.

The values of the reaction rate constants were shown in Table 1. Two observation could be made from the table: (1) the specific reaction rate constant of Pd/Fe bimetallic particle was a little higher than Cu/Fe particle, but much higher than Fe alone, (2) both Cu/Fe and Pd/Fe bimetallic particles had a better reductive dehalogenation ability on TBAA than bromoform in consideration of a higher specific reaction rate constant. These calculated specific reaction rate constants were closed to former studies that investigated on dechlorination of chlorinated organics by iron or iron based bimetallic systems. Detail analysis about these differences on reaction rate constants were taken in the part of mechanism discussion.

3.3 Mechanism discussion

As a strong reducing agent, iron reduced bromoform by reductive dehalogenation while being oxidized:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad (1)$$

$$RX + e^- + H^+ \rightarrow RH + X^- \qquad (2)$$

The sequential dehalogenation of halogenated compounds with Fe^0 as electron donor was thermodynamically very favorable. However, Iron could react with water producing hydrogen gas, which could act as a reductant. Dehalogenation with hydrogen as direct electron donor often required a catalyst since H_2 alone was not a good reductant:

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \qquad (3)$$

$$2RX + H_2 \rightarrow 2RH + 2X^- \qquad (4)$$

This reaction could lead to the formation of iron (hydr)oxide precipitates ($Fe(OH)_2$), resulted in the formation of a surface layer on ZVI particles. Fe^{2+} could also be oxidized to Fe $^{3+}$, which produced equivalents for dehalogenation:

$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$

This was a slow process and often required the presence of ligands.

The combination of Cu or Pd with Fe significantly enhanced the reaction rates of the reductive dehalogenation of reactants. The poor performance of iron alone was a consequence of the formation of oxide layer on the iron surface that blocked reaction site. However, metallic Cu or Pd was incapable of serving as an effective reductant because of their low reduction potential. In contrast, galvanic cells were created by coupling active metal (Fe) with inert metal (Cu or Pd) in bimetallic system. Element Fe served as the anode and became preferably oxidized in the galvanic cells while plating elements (Cu or Pd) served as the cathode. In other words, the bimetallic structure enhanced the reducibility of iron for reductive dehalogenation by facilitating the iron corrosion. On the other hand, because of low activation barrier for H_2 dissociation on Pd surface, atomic hydrogen was easily generated at the surface of plating elements which had the low cathodic hydrogen overpotentials. The dissolution of water by iron lead to the hydrogen evolution and was followed by the formation of atomic hydrogen at the plating elements surface. Atomic hydrogen acted as the reducing agent which broke the Br-C bond and replaced the halogen atom with a hydrogen atom through a surface-mediated process (Figure 5). It is likely that enhanced hydrogenation as well as hydrogen production is the main cause for the increase reaction rates in Pd/Fe bimetallic system compared to Cu/Fe bimetallic system. This proposed model was consistent with previous researches.[31,32]

3.4 Characterization of bimetallic systems

XRD measurement was carried out to investigate the structure of bimetallic particles after reaction. Figure 4 illustrated the XRD patterns of Cu/Fe and Pd/Fe. The characteristic peak of Fe metal appeared at 42.5° as indicated by a solid square symbol, the peaks assigned to Cu were at 50.5° and 74.1° as indicated by a solid triangle and the characteristic peak of Pd was at 52.5° as indicated by a solid diamond. Magnetite (Fe_3O_4) was the dominate corrosion products in both Cu/Fe and Pd/Fe bimetallic systems after reaction. The characteristic peaks of magnetite were assigned to 13.5°, 27.1°, 36.5° and 47.2° as indicated by solid circle. None characteristic peaks of Cu oxide or Pd oxide were determined, which offered direct evidence to support the catalytic functions of the plating elements in the dehalogenation of Br-DBPs.

3.5 Variation of toxicity during dehalogenation process

One significant concern of any remediation technology was the formation of daughter products that were more toxic than the parent compounds. Although former results demonstrated that Cu/Fe and Pd/Fe bimetallic systems effectively degraded Br-DBPs, it was critical to establish the biological activity of the resulting treated solution or the individual breakdown products.[33] In general, dehalogenations of bromoform and TBAA by bimetallic system occurred sequentially and lead to low halogenated products. It was a daunting task to isolate the individual reaction byproducts and assess their individual biological activities. Therefore, luminescent bacteria were chosen to assess the toxicities of the treated water samples, which would help to assess the eco-toxicity changes of the treated water samples during the dehalogenation process by bimetallic systems.[34,35] The toxicity was expressed in luminescence inhibition rate and the results were showed in Table 2. 83.12% and 75.89% of luminescent inhibition occurred at the initial concentration (1000 μg/L) of bromoform and TBAA, respectively. As the removal of brominated DBPs during the reductive dehalogenation process in Cu/Fe system, a notable decrease in toxicity was observed. The inhibition rate of bromoform and TBAA decreased to 31.14% and 30.84% within 60 min reaction. However, a complete removal of both bromoform and TBAA were achieved after the reaction period (140 min) according to previous results, whereas 20.19% and 15.04% of inhibition rates were still detected in water samples at the end of the reaction. Dehalogenation of multi halogenated compounds such as bromoform or TBAA by bimetallic system usually occurred sequentially. Several low brominated byproducts such as dibromomethane (CH_2Br_2), bromomethane (CH_3Br), dibromoacetic acid (DBAA) and monobromoacetic acid (MBAA) were generated inevitably during this process. Part of these low brominated byproducts could be further reduced to nontoxic products such as methane or acetic acid with a longer reaction period, while some others could be hardly removed by bimetallic system. Although these low brominated intermediate products had relative low toxicities than bromoform or TBAA, they were toxic to luminescent bacteria and accounted for the residual inhibition rate in water samples at the end of the reaction.[36] Similarly to Cu/Fe, a significant decrease in toxicity was also observed in Pd/Fe system. Moreover, the residual inhibition rates of bromoform and TBAA in Pd/Fe system after 140 min were 7.84% and 7.85% respectively, far more below to what was in Cu/Fe system. This result was in accordance with previous studies that Pd/Fe bimetallic system obtained a better performance on the reductive dehalogenation of brominated DBPs than Cu/Fe.

4. Conclusions

This paper investigated the performance of Pd/Fe and Cu/Pd bimetallic particles on the reductive dehalogenation of brominated DBPs included bromoform and TBAA. Besides, the influence factors, reaction kinetics, reaction mechanisms and toxicity assessment were also conducted to lead to the conclusions:

1) Dosage of bimetallic particles had a significant influence on the dehalogenation of Br-DBPs. Only 8.1% of bromoform and 20.1% of TBAA were reduced during the initial reaction period (20min) when the bimetallic particles dosage was 5 g/L, while 56.9% of bromoform and 62.7% of TBAA were removed when the dosage increased to 20 g/L. As the dosage of Cu/Fe particles increased from 5 g/L to 20 g/L, the removal efficiency of bromoform and TBAA increased from 8.1% to 56.9% and 20.1% to 62.7% within 20 min, respectively. A similar result was observed in Pd/Fe system. Nearly 30% of bromoform and 35.4% of TBAA were reduced within 20min when the dosage of Pd/Fe was 5 g/L, while 71% of bromoform and 68.5% of TBAA were removed when the dosage increased to 20 g/L.
2) Acidic condition was favorable for dehalogenation of brominated DBPs with bimetallic systems, while alkaline condition had an adverse effect on this process. A complete removal of bromoform and TBAA was achieved by Cu/Fe bimetallic particles within 60 min of reaction in acidic condition, while only 35.4% of bromoform and 10.8% of TBAA was removed after the whole reaction (140min) in alkaline condition.
3) Bimetallic particles achieved high performance on the dehalogenation of brominated DBPs probably because galvanic cells were created between Fe (severed as anode) and plating elements (severed as cathode). This structure enhanced the reducibility of iron for

reductive dehalogenation from two aspects: facilitating the iron corrosion and reducing the activation barrier of H_2. Furthermore, Pd/Fe system showed a better performance, which attributed to a higher potential gradient (1.4 V) as compared to Cu/Fe couples (0.8 V).

4) The results of toxic assessment indicated that the toxicity of water samples had a significant decline during the dehalogention of brominiated DBPs. The luminescence inhibition rate of bromoform and TBAA in initial reaction was 83.12% and 75.89%, and decreased to 20.19% and 15.04% after a 140 min of reductive dehalogenation by Cu/Fe. However, Pd/Fe achieved a better performance on reducing the toxicity represented by a residual luminescence inhibition rate of 7.84% (bromoform) and 7.85% (TBAA) in water samples.

Acknowledgements

This study was supported by Supporting Program of the “Twelfth Five-year Plan” for Sci & Tech Research of China (No. 2013BAC01B01) and National Science Foundation of China (No. 51078091).

Reference:

1 O. A. Ali and S. J. Tarek, *Desal Water Treat.,* 2009, **1,** 229-289.

2 A. K. Adamantia and G. S. Euripides, *Water Res.,* 2012, **36,** 2596-2606.

3 K. Kumar and D. W. Margerum, *Inorg. Chem.,* 1987, **26,** 2706-2711.

4 M. Deborde and U. von Gunten, *Water Res.,* 2008, **42,** 13-51.

5 H. Y. Zhai, X. R. Zhang, X. H. Zhu, J. Q. Liu and M. Jin, *Environ Sci Technol.,*2014, **48,** 2579-2588.

6 V. Uyak and I. Toroz, *J. Hazard. Mater.,* 2007, **149,** 445-451.

7 M. T. Yang and X. G. Zhang, *Environ Sci Technol.,*2013, 47, 10868-10876.

8 J. Q. Liu and X. R. Zhang, *Water Res.,* 2014, **65,** 64-72.

9 V. Uyak, *Environ. Int.,* 2006, **32,** 12-21.

10 L. J. Matheson and P. G. Tratnyek, *Environ. Sci. Technol.,* 1994, **28,** 2045-2053.

11 T. Li, and J. Farrel, *Environ. Sci. Technol.,* 2000, **34,** 173-179.

12 L. Zhang, W. A. Arnold, and R. M. Hozalski, *Environ. Sci. Technol.,* 2004, **38,** 6881-6889.

13 W. S. Orth and R. W. Gillham, *Environ. Sci. Technol.,* 1996, **30,** 66-71.

14 L. Xie and C. Shang, *Chemosphere.,* 2006, **64,** 919-930.

15 G. A. Loraine, D. R. Burris, L. Li, J. Schoolfied, *J. Envrion. Eng.,* 2002, **128,** 85-93.

16 H. L. Lien, and W. X. Zhang, *Chemosphere.,* 2002, **49,** 371-378.

17 H. L. Lien and W. X. Zhang, *Appl. Catal. B: Environ.,* 2007, **77,** 110-116.

18 S.F. Cheng and S.C. Wu, *Chemosphere.,* 2000, **41,** 1263-1270.

19 B. Schrick, J. L. Blough, A. D. Jones and T. E. Mallouk, *Chem. Mater.,* 2002, **14,** 5140-5147.

20 A. Ghauch, H. A. Assi and S. Bdeir, *J. Hazard. Mater.,* 2010, **182,** 64-74.

21 Y. H. Tee, E. Grulke and D. Bhattacharyya, *Ind Eng Chem Res.,* 2005, 44, 7062-7070.

22 H. L. Lien and W. X. Zhang, *J Environ Eng-ASCE.,* 2005, **131,** 4-10.

23 S. J. Bransfield, D. M. Cwiertny, K. J. T. Livi, D. H. Fairbrother, *Appl. Catal. B: Environ.,* 2007, **76,** 348-356.

24 D. M. Cwiertny, S. J. Bransfield, K. J. T. Livi, D. H. Fairbrother, A. L. Roberts, *Environ. Sci. Technol.,* 2006, **40,** 6837-6843.

25 A. Ghauch, *Chemosphere.,* 2001, **43,** 1109-1117.

26 P. G. Tratnyek, T. L. Johnson, M. M. Scherer, G. R. Eykholt, *Ground Water Monitor.,* 1997, **17,** 108-114.

27 Y. Shih, M. Y. Chen and Y. F. Su, *Appl. Catal. B: Environ.,* 2011, **105,** 24-29.

28 H. Song and E. R. Carraway, *Appl. Catal. B: Environ.,* 2008, **78,** 53-60.

29 T. L. Johnson, M. M. Scherer and P. G. Tratnyek, *Environ. Sci. Technol.,* 1996, **30,** 2634-2640.

30 J. Feng and T. T. Lim, *Chemosphere.,* 2005, **59,** 1267-1277.

31 Y. H. Tee, L. Bachas and D. Bhattacharyya, *J. Phys. Chem. C.,* 2009, **22,** 9454-9464.

32 J. N. Xiao, B. Y. Gao, Q. Y. Yue, Y. Gao, Q. Li, *Chemical Engineering Journal.,* 2015, **262,** 1226-1236.

33 H. Yu, E. Nie, J. Xu, S. W. Yan, W. L. Cooper, W. H. Song, *Water Res.,* 2013, **47,** 1909-1918.

34 L. L. Zhang, Q. Li, L. Chen, A. Zhang, J. N. He, Z. H. Wen, L. L. Wu, *Ecotoxicology and Environmental Safety.,* 2015, **112,** 137-143.

35 X. F. Zhou，W. J. Sang, S. S. Liu, Y. L. Zhang, H. L. Ge, *J. Environ. Sci.,* 2010, **22,** 433-440.

36 S. J. Jiao, S. R. Zheng, D. Q. Yin, L. H. Wang, L. Y. Chen, *Chemosphere.,* 2008, **73,** 377-382.

Table 1 Values of rate constants for reductive dehalogenation of bromoform and TBAA by iron based bimetallic systems

Metal particles	Parameters	Bromoform	TBAA
Fe alone	$k_{obs}(h^{-1})$	0.64	0.75
	$k_{SA}(L/h·m^2)$	$2.9×10^{-2}$	$3.4×10^{-2}$
	$ρ_a(m^2/L)$	22.22	22.22
	R^2	0.976	0.987
Cu/Fe	$k_{obs}(h^{-1})$	1.52	1.84
	$k_{SA}(L/h·m^2)$	$6.8×10^{-2}$	$8.3×10^{-2}$
	$ρ_a(m^2/L)$	22.22	22.22
	R^2	0.962	0.998
Pd/Fe	$k_{obs}(h^{-1})$	1.63	2.18
	$k_{SA}(L/h·m^2)$	$7.3×10^{-2}$	$9.8×10^{-2}$
	$ρ_a(m^2/L)$	22.22	22.22
	R^2	0.959	0.999

Table 2 Varation of luminescence inhibition rate (%) during the dehalohagenation of brominated DBPs by iron based bimetallic systems

Time	Cu/Fe		Pd/Fe	
（min）	Bromoform	TBAA	Bromoform	TBAA
0	83.12±6.52	75.89±6.87	83.12±6.52	75.89±6.87
20	53.41±4.38	53.71±5.24	46.43±4.12	53.25±4.68
60	34.16±3.96	30.84±3.26	33.45±3.79	35.88±3.96
100	28.81±2.76	21.37±2.58	16.80±2.83	19.02±2.75
140	20.19±2.33	15.04±2.03	7.84±1.24	7.85±1.52

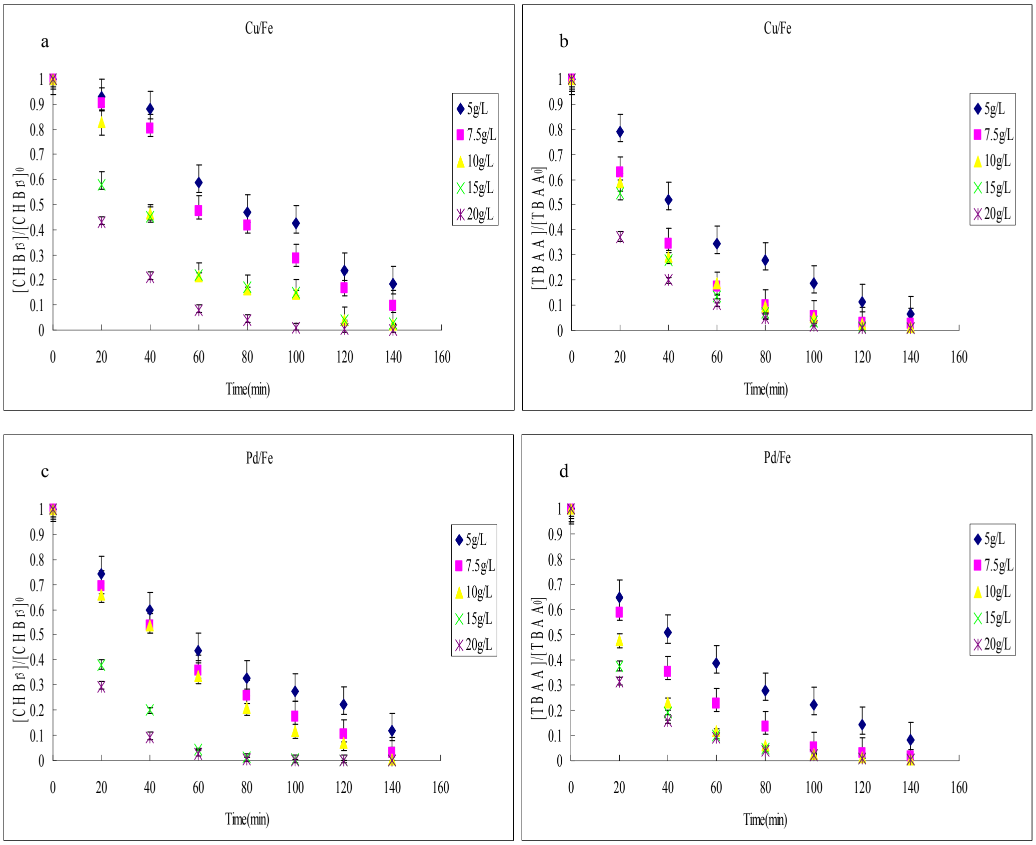


Figure. 1 (a) effects of Cu/Fe dosage on the reductive dehalogenation of bromoform; (b) effects of Cu/Fe dosage on the reductive dehalogenation of TBAA; (c) effects of Pd/Fe dosage on the reductive dehalogenation of bromoform; (d) effects of Pd/Fe dosage on the reductive dehalogenation of TBAA.

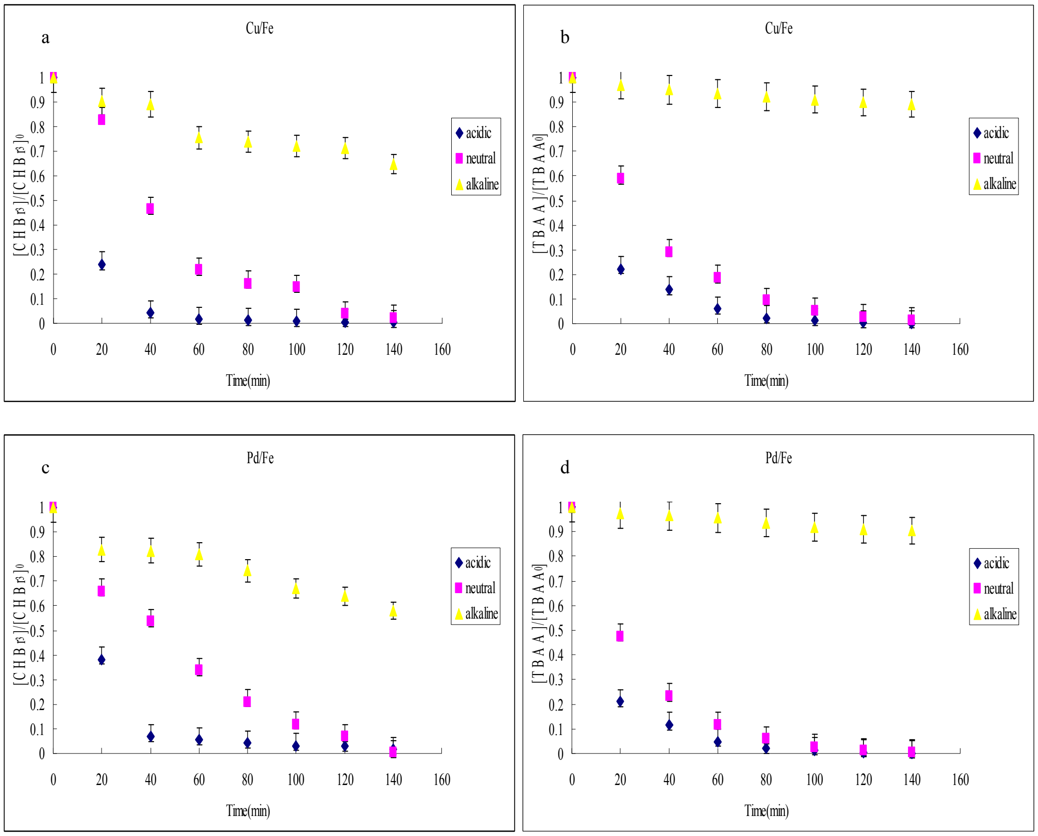


Figure. 2 (a) effect of pH on the reductive dehalogenation of bromoform by Cu/Fe; (b) effect of pH on the reductive dehalogenation of TBAA by Cu/Fe; (c) effect of pH on the reductive dehalogenation of bromoform by Pd/Fe; (d) effect of pH on the reductive dehalogenation of TBAA by Pd/Fe.

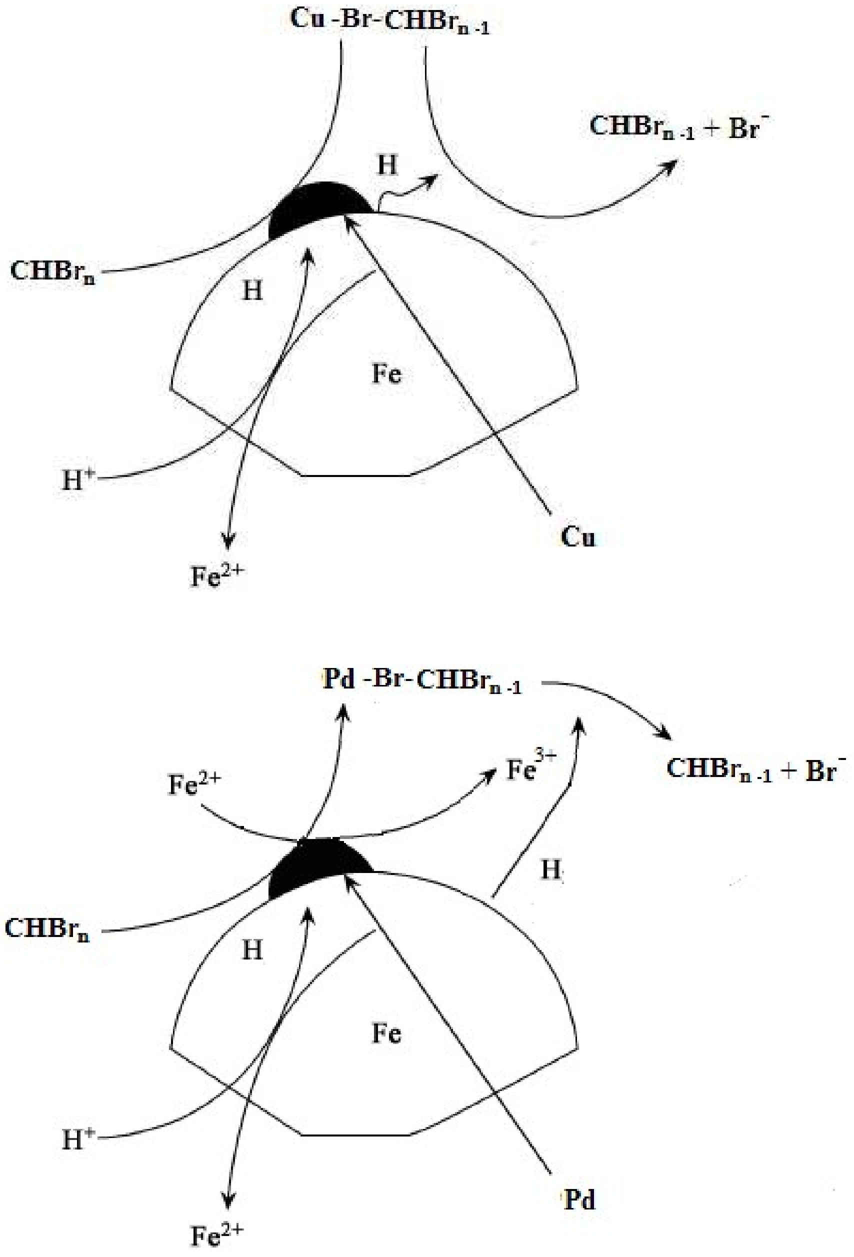


Figure. 3 The mechanisms of reductive dehalogenation by Cu/Fe and Pd/Fe bimetallic systems.

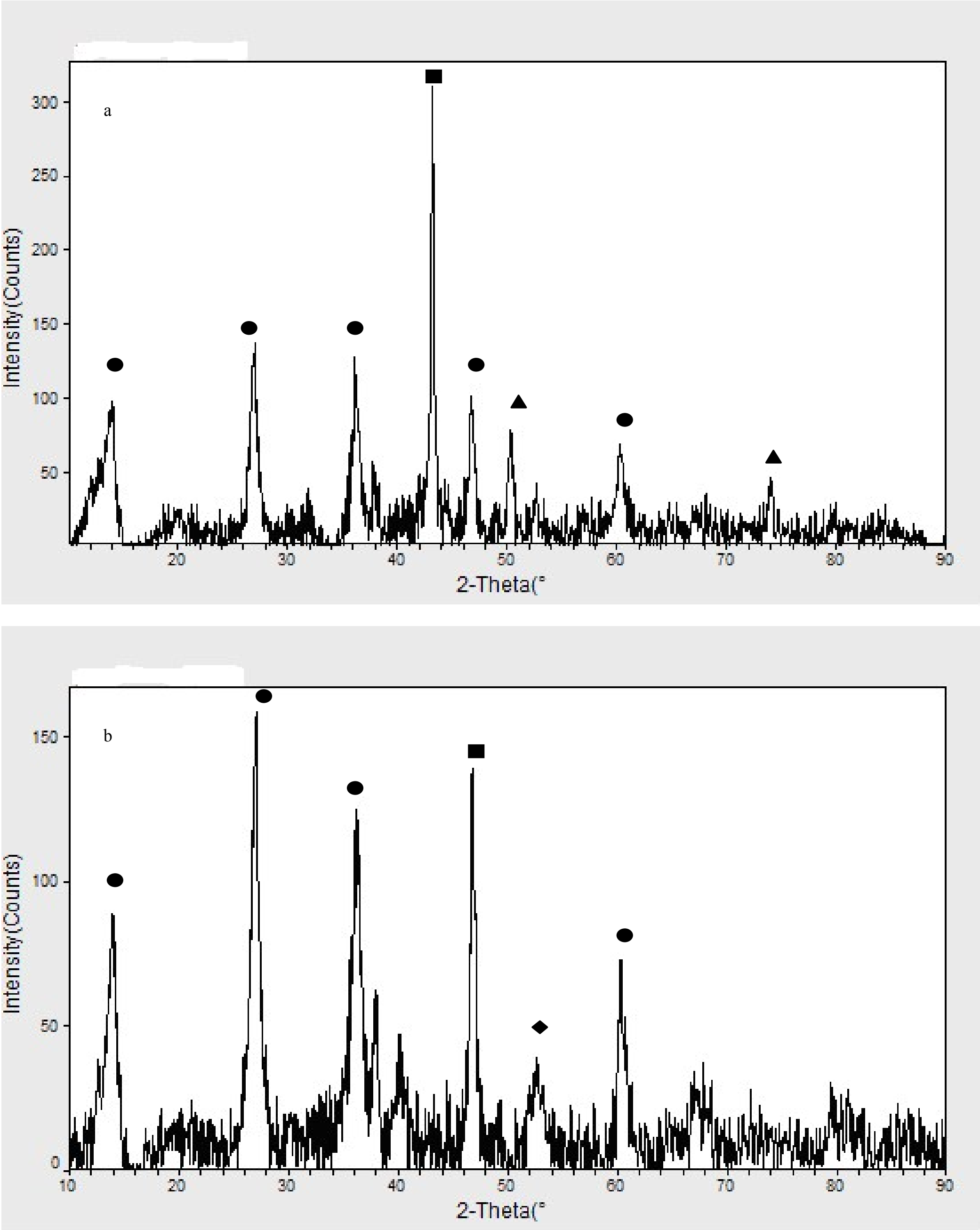
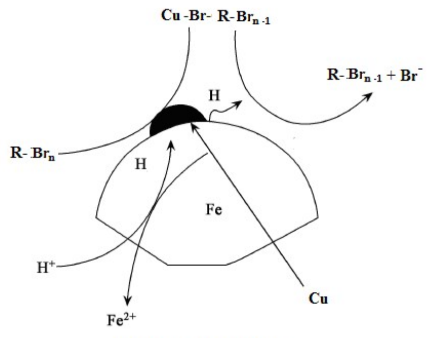
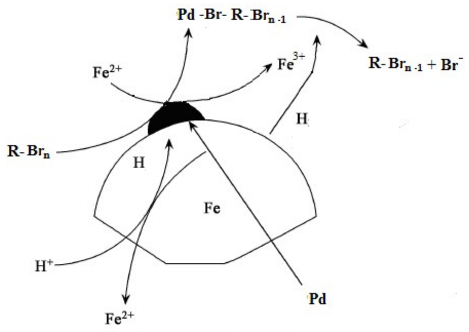


Figure. 4 X-ray diffractogram of bimetallic particles after reductive dehalogenation reaction (a) Cu/Fe and (b) Pd/Fe. Solid square represent Fe^0, solid triangle represent Cu, solid diamond represent Pd and solid circle represent magnetite (Fe_3O_4).



Cu/Fe bimetallic system



Pd/Fe bimetallic system

Abstract: The reductive dehalogenation of brominated disinfection byproducts (DBPs) including bromoform and tribromoacetic acid (TBAA) by iron based bimetallic systems (Cu/Fe and Pd/Fe) was investigated. In Cu/Fe bimetallic system, only 8.1% of bromoform and 20.1% of TBAA were reduced within 20 min when the particles dosage was 5 g/L, while 56.9% of bromoform and 62.7% of TBAA were removed at the same period when the dosage increased to 20 g/L. A complete removal of bromoform and TBAA was achieved within 60 min of reaction in acidic condition, while only 35.4% of bromoform and 10.8% of TBAA were removed after the whole experiment period (140 min) in alkaline condition. Similar results were observed in Pd/Fe bimetallic system. Bimetallic particles achieved high performance probably because galvanic cells were created between Fe (severed as anode) and plating elements (severed as cathode). This structure enhanced the reducibility of iron for reductive dehalogenation by facilitating the iron corrosion as well as reducing the activation barrier of H_2. Pd/Fe system showed a better performance than Cu/Fe, which attributed to a higher potential gradient (1.4 V) as compared to Cu/Fe couples (0.8 V). Furthermore, toxic assessment indicated that the toxicity of water samples had a dramatic decline after dehalogenation by bimetallic particles.

Key words: reductive dehalogenation; brominated disinfection byproducts; iron based bimetallic systems