An integrated two-stage process for effective dechlorination of polychlorinated biphenyls in subcritical water in the presence of hydrogen donors

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HIGHLIGHTS

- Corrosion of Fe⁰ and dechlorination are conducted at different temperature, respectively.
- Corrosion of Fe⁰ conducted at 150 °C favors product of reactive hydrogen species.
- Slight addition of oxalic acid enhances utility efficiency of Fe⁰ without dislodgment of Ni from Ni/Fe.

GRAPHICAL ABSTRACT

Effect of residence time on dechlorination during two-stage reaction process. X axis: residence time at first stag, C_{PCBs} = 5.25 mg/L, C_{Ni/Fe(s)} = 6.25 g/L, T_{first stage} = 150 °C, T_{second stage} = 330 °C.

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ABSTRACT

In this study, a novel two-stage process, i.e. first stage for hydrogen species generation at 150 °C and second stage for PCB dechlorination at 330 °C, was developed for efficient PCB degradation in subcritical water with nanoscale Ni/Fe particles. The obtained results showed that over 92% of PCBs was completely converted into 1-alkyl-benzenes during this process. The addition of hydrogen donors could greatly enhance PCB dechlorination in descending order: oxalic acid $\approx$ HAc > NaH₂PO₄ $\approx$ KH₂PO₄. The anion introduced along with H⁺ played the crucial role in overall dechlorination process due to the undesired reaction between anion and reactive nanoscale Ni/Fe. Oxalic acid was quite effective for the generation of hydrogen species by supply more available H⁺ without undesired side reaction. In contrast, phosphate could react with Ni/Fe rapidly to form complex precipitates on particle surface and thereby block the reactive sites of particle following suspension of dechlorination. In addition, low 150 °C at first stage as compared to 330 °C at second stage favored the dissolution and adsorption of hydrogen on Ni surface for catalyzing to form more reactive hydrogen species used for rapid dechlorination.

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1. Introduction

In recent years, reductive dehalogenation with iron-based particles in subcritical water has attracted more attention due to the absence of undesired by-products such as polychlorinated

dibenzo-*p*-dioxins and dibenzofurans in this process. As hydrogen donor, water under subcritical state can supply more available H₃O⁺ and energy for accelerating rate constant as compared to ambient water during this process [1–5]. Meanwhile, the solubility of organics is enhanced greatly in subcritical water, and therefore the limits of mass transfer between water phase and organic phase decline remarkably. As electron donor, Fe⁰ provides electron via corrosion to reduce H⁺ to molecular hydrogen which was used

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for subsequent hydrodehalogenation. Hence, corrosion of Fe^0 and generation of hydrogen species are always considered as the key steps during the whole dehalogenation process [6,7]. However, the low utility efficiency of Fe^0 due to the low H^+ concentration and formation of passivation layer always presents as obstacle to effective dehalogenation, especially in the case of complicated composition of PCBs mixture, such as commercial Aroclor [5,8].

Studies have aimed at enhancing utility efficiency of Fe^0 by introduction hydrogen donors in order to increase available H^+ concentration, such as inorganic and organic acid [9–13]. Meanwhile, addition of acid can also retard the formation of passivation layers on particles surface because the precipitates of iron oxide is dependent on the pH of water in terms of mechanisms depicted as follows [6,10,13].

But further discussion about the role of these hydrogen donors at high temperature such as in subcritical water is still scarce.

It should be noted that the high temperature in subcritical water not only favors the dehalogenation but also facilitates the formation of passivation layer. However, batch experiments in previous reports were conducted with improper consideration that the optimum reaction temperature for dehalogenation was also best suitable for corrosion of Fe^0 and catalysis of hydrogen species. This ignored that each section reaction involved in whole dehalogenation process, such as dehalogenation, corrosion of Fe^0 , generation of hydrogen species, has its own optimum reaction conditions. Zhu et al. [4] found that the presence of PCBs could not affect the chemical behavior of Ni/Fe particles in subcritical water, implying that corrosion of Fe^0 and subsequent generation of hydrogen species are independent of the presence of PCBs. Therefore, corrosion of Fe^0 for production of hydrogen species and subsequent dechlorination can be carried out separately in terms of reaction temperature and time in order to optimize each section reaction and thereby enhance overall dechlorination efficiency significantly. It has been reported that the hydrogen species in aqueous phase other than gas phase is used for dechlorination [14]. Hence, corrosion of Fe^0 at low temperature other than at high temperature cannot only result more hydrogen species dissolve in aqueous phase because the solubility of hydrogen species in aqueous phase increase as the decrease of temperature in subcritical water but also retard the formation of passivation layer on particle surface.

In present study, the whole dechlorination process was divided into two stages in term of reaction temperature. The corrosion of Fe^0 was conducted at first stage below 200 °C in the both presence of hydrogen donors, and following PCB dechlorination was carried out at second stage as increase of temperature from first stage to 330 °C. The primary objective of this study is to elucidate the effect of hydrogen donor on Fe^0 corrosion and generation of hydrogen species at first stage. And the comprehensive influence of hydrogen donor on whole PCB dechlorination under this two-stage process was also investigated.

2. Experimental

2.1. Materials

PCB-contained capacitor oil was obtained from a certificated PCBs disposal company located in north-east China. The stock solution used for each dechlorination run was prepared by diluting raw capacitor oil with hexane and stored in a refrigerator. Analytical grade chemical reagents involved in this study were: acetic acid,

oxalic acid, ethanol, NaH_2PO_4 , KH_2PO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Ni}(-\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, NaOH , NaBH_4 , Na_2SO_4 . HPLC grade n-hexane and acetone were supplied by Jackber Company, USA. Deionized water used in the study was adequately purged with N_2 before use to create an anoxic aqueous environment. Aroclor 1242 standards (1000 $\mu\text{g}/\text{mL}$ in hexane) used as calibration standard and PCB209 (1000 $\mu\text{g}/\text{mL}$ in hexane) used as surrogate standard were obtained from AccuStandard, USA.

2.2. Preparation of bimetallic Ni/Fe nanoparticles

Ni/Fe particles were synthesized in ethanol/water solution by reducing Fe^{2+} and Ni^{2+} to Fe^0 and Ni^0 using BH_4^- . Detailed preparation and collection procedure were described in previous report [4]. The Ni was selected as the catalytic candidate in bimetallic particles rather than other precious metals such as Pd, Pt, Rh because it is a more cost-effective alternative. The ratio of Fe:Ni was adjusted to 9:1 (w/w) corresponding theoretical 10% (wt.%) Ni in bimetallic particles. The resultant black particles were stored in a sealed container filled with acetone and then placed in a refrigerator. Before each experiment, black particles were dried in vacuum to remove acetone for use.

2.3. Characterization of Ni/Fe particles

Transmission electron microscope (TEM) images were obtained using a Hitachi H-7500 microscope. X-ray diffraction (XRD) analysis was carried out using Philips PW 1700 X-ray diffractometer. Inductively coupled plasma-optical emission spectrometry (Perkin Elmer OPTIMA 2000, USA) was used to determine the actual Ni:Fe ratios of synthesized Ni/Fe samples and concentration of metal ions in aqueous phase after reaction.

2.4. Batch experiments

Batch tests were conducted in a 100 mL autoclave constructed from 316L materials. Before experiment, 0.5 g of vacuum-dry Ni/Fe particles was placed into the autoclave. Then 1 mL (420 $\mu\text{g mL}^{-1}$ of PCBs) stock solution of capacitor oil was quickly spiked onto particles directly to form an 840 mg kg^{-1} PCBs uptake in the particles. In order to protect particles from oxidation in the air, hexane in the autoclave was dried by gentle nitrogen stream. Due to a small amount used, each hydrogen donor was dissolved in 80 mL deionized water to form homogenous solution for use. After complete evaporation of hexane, 80 mL homogenous solution containing hydrogen donor was decanted into the autoclave gently to result in a Ni/Fe concentration of 6.25 g L^{-1} and initial PCBs concentration of 5.25 mg L^{-1} . Subsequently, the autoclave was screw down immediately and then pure Ar gas was flushed through interior of the autoclave to discharge the unwanted air. After purge with Ar gas, the sealed autoclave was heated by electrical rod-like heater to a desired temperature and hold for a certain time. After termination of reaction, the hot autoclave was cooled down by electrical fan in atmosphere. All experiments were carried out in triplicate and each data point reported in all figures is mean of triplicates with standard deviation.

2.5. Extraction, cleanup and analysis procedure

The extraction, cleanup and analysis procedures were performed according to literatures and EPA methods [4,15–17]. After cooling, the autoclave was opened carefully and the surrogate standard of PCBs 209 was added into the autoclave for quality control. Aqueous phase was subjected to liquid–liquid extraction with hexane. The solid particles were separated from aqueous phase with strong magnet and allowed to air-dry for subsequent ultrasonic

extraction with mixture of acetone and hexane (1:1, v/v). Then all organic extracts were combined and concentrated with rotary evaporator to approximate 2 mL for solvent exchange with hexane. The received hexane phase was concentrated again with rotary evaporator to approximate 1 mL for concentrated sulfuric acid cleanup in a separatory funnel. After washing the sulfuric acid with deionized water in separatory funnel, the hexane phase passed through a cleanup column consisted of 1 cm sodium sulfate, and then 5 cm of PR Grade Florisil (60–100 mesh) topped with 1 cm of sodium sulfate. Then the cleanup column was eluted with 50 mL hexane, and the received eluate in a ball flask was concentrated to 1 mL for GC–MS analysis using an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass spectrometry and autosampler (USA). Chromatographic separation were accomplished with a HP-5 capillary column (30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m film thickness) using splitless injections. The initial oven temperature was set at 50 °C and ramped to 150 °C at 20 °C min⁻¹, then to 200 °C at 2 °C min⁻¹, finally to 250 °C hold for 1 min. Injector and detector temperatures were 280 and 300 °C, respectively. Ultrahigh pure helium was used as the carrier gas at a constant flow rate of 1 mL min⁻¹.

Quantification of total PCBs in capacitor oil was based on the calibration with Aroclor 1242 using eight major congeners following EPA method 8270 and previous literatures [4,16,17] due to the equivalence of congener distribution between capacitor oil and Aroclor 1242. The Arabic symbols in order labeled in Fig. 3 denoted the selected PCB peaks for quantification. The work of Frame et al. [18] was used as a reference for composition of the Aroclor 1242. In separate control experiments, the recoveries for PCB 209 were found to be 85–105%, which can meet the accuracy of quantification.

2.6. Data interpretation

Total PCB conversion ratio is defined as follows:

$$\text{Total conversion ratio (\%)} = \frac{c_0 - c_{\text{product}}}{c_0} \quad (4)$$

where c_0 and c_{product} are PCBs concentration in stock solution of capacitor oil and product mixture, respectively (mg L⁻¹).

3. Results and discussion

3.1. Characterization of Ni/Fe particles

TEM image of fresh particles in Fig. 1a shows that particles exhibited an average diameter of 20–80 nm and formed aggregated structure due to the magnetic dipole interactions [19]. As for spent particles, a slight expansion of particle is observed after reaction in Fig. 1b. This might be ascribed to the buildup of passivation layer on particle surface [20,21].

Fig. 2a presents the XRD patterns of different particles before and after reaction. No characteristic peaks are associated with crystals of Fe⁰ and Ni⁰ for fresh Ni/Fe particles, which implies that amorphous structure was formed in the synthesis process. Only iron oxides (Fe₃O₄/γ-Fe₂O₃) appeared after reaction in the presence of acetic acid and oxalic acid, resembling that observed in pure subcritical water [4]. This means that the presence of acetic and oxalic acid did not affect the reaction behavior of nanoscale Ni/Fe remarkably in subcritical water. In contrast, many characteristic peaks of iron phosphates emerged besides faint iron oxides peaks when dihydrogen phosphates used as hydrogen donors. The formation of iron phosphates might be attributed to the reaction of phosphates with Fe⁰ or released iron from initial corrosion of Fe⁰ [22,23]. It indicates that the phosphates might compete for reactive sites on nanoscale particle surface with water and conse-

quently affect the PCB dechlorination. Results of EDX analysis in Fig. 2b and c show that the Ni percentage at the outer layer of particles after reaction decreased with increase of amount of organic acid used as compared to that without hydrogen donor. This suggests that partial dislodgement of Ni from bimetallic Ni/Fe might occur due to the dissolution of Fe into liquid phase especially in the presence of organic acid [10,11], which could impair the catalytic function of Ni/Fe particles.

3.2. Dechlorination products

Fig. 3 shows the GC–MS chromatograms of the raw capacitor oil and products after reaction with and without hydrogen donors, respectively. Fig. 3g–i are the magnification of Fig. 3f, d, and e with the purpose of convenient description of degradation products. Fig. 3a indicates that all revealed PCB congeners comprised of different positional isomers, including *ortho*-, *para*- and *meta*-chlorine substituted PCBs. As compared to GC–MS profile of products without hydrogen donor in Fig. 3f, oxalic acid and acetic acid caused significant dechlorination shown in Fig. 3d and e but only trace amounts of new mon- and dichlorobiphenyls were observed as dechlorination products in the presence of dihydrogen phosphates shown in Fig. 3b and c.

Positive dechlorination products mainly consisted of 1-alkyl-benzenes along with a little biphenyl and cyclohexyl-benzene in the presence of organic acids in Fig. 3h and i. Besides these positive dechlorination products, alkanes also emerged as products in Fig. 3h and i. The appearance of these alkanes might be ascribed to the further reductive hydrogenation of 1-alkyl-benzenes because no unsaturated hydrocarbons are observed in raw capacitor oil as shown in Fig. 3a. After reaction without hydrogen donor, however, dechlorination products were mainly composed of biphenyl, 1-alkyl-benzenes and other lower chlorinated biphenyls in Fig. 3g. However, there were little alkanes observed as degradation products in the absence hydrogen donor, which suggests that further hydrogenation of 1-alkyl-benzenes was mainly ascribed to the employment of organic acid as hydrogen donor. The notable difference in distribution of dechlorination products among different hydrogen donors shows that the H⁺ from dissociation of oxalic acid and acetic acid could play similar role as H⁺ from self-dissociation of H₂O and be used for dechlorination in subcritical water. However, H⁺ from dihydrogen phosphates could not counterbalance the negative effects of PO₄³⁻ on reactivity of nanoscale Ni/Fe towards to PCB dechlorination, which resulted in inferior dechlorination performance.

3.3. Optimization of dechlorination parameters

3.3.1. Effects of different hydrogen donors

Fig. 4 compares the total PCB conversion ratio in the presence of NaH₂PO₄, KH₂PO₄, HAc and oxalic acid, respectively. Taking into account the different dissociation constant, mass of each donor used was calculated according to the same amount of H⁺ dissociated from each donor based on dissociation constant. Total conversion ratio decreased with increasing mass of hydrogen donor in all cases. As shown in Fig. 4c and d, PCB conversion ratio of 83.4% with 0.5 mg oxalic acid was almost same as that 82.8% with 1 mg oxalic acid, but the same PCB conversion ratio of 82.0% with 1 mg acetic acid and 81.37% with 5 mg acetic acid were superior to that 75.64% with 10 mg acetic acid. Accordingly, 0.5–1 mg of oxalic acid and 1–5 mg of HAc can be regarded as optimal mass range used as hydrogen donor for PCB dechlorination respectively under this experimental condition. Taking into account the statistical error and cost of each hydrogen donor, addition of hydrogen donors enhanced PCB dechlorination with an increasing order of KH₂PO₄ $\approx$ NaH₂PO₄ < HAc $\approx$ oxalic acid.

Fig. 1. Transmission electron microscope (TEM) images of (a) fresh Ni/Fe particles and (b) spent Ni/Fe particles after reaction used oxalic acid as hydrogen donor.

Fig. 2. (a) XRD patterns of fresh particles and spent particles after reaction with hydrogen donors. EDX images of spent particles after reaction in the presence of (b) oxalic acid, and (c) HAc. PCBs concentration in water $C_{\text{PCBs}} = 5.25$ mg/L, dosage of Ni/Fe particles in water $C_{\text{Ni/Fe(s)}} = 6.25$ g/L, $T = 330$ $^\circ\text{C}$, $t = 3$ h.

Previous studies reported that enhanced dechlorination in the presence of sodium hypophosphite was attributed to the formation of reductive hydrogen gas via sodium hypophosphite decomposition [24,25]. However, dihydrogen phosphates used in this study could not be decomposed to form hydrogen gas but supply H^+ for corrosion of Fe^0 to generate hydrogen species which subsequently were used to hydrodechlorination. Although the pH (<5.5) of water was lower than that maximum of pure subcritical water (pH ≈ 5.5) [26] due to the addition of dihydrogen phosphates, the total conver-

sion ratios for both dihydrogen phosphates were below 65% which is lower than that ($>75\%$) achieved in pure subcritical water without hydrogen donor [4]. The inferior dechlorination efficiency for both dihydrogen phosphates was mainly attributed to the complex precipitation of iron phosphates on particles surface as shown in Fig. 2a. It has been demonstrated that phosphates could react with reactive functional groups on the zerovalent iron (ZVI) surface or released iron to form insoluble inner-sphere complexes on particle surface, which then caused the suspension of dechlorination

Fig. 3. GC-MS chromatograms of (a) raw capacitor oil and products after reaction with hydrogen donors, (b) NaH_2PO_4 , (c) KH_2PO_4 , (d) oxalic acid, (e) HAc and (f) without hydrogen donor. (g–i) are enlargements of (f), (d) and (e). Peaks of I–V were identified as follows: I = monochlorobiphenyl; II = dichlorobiphenyl; III = trichlorobiphenyl; IV = tetrachlorobiphenyl; V = pentachlorobiphenyl. $C_{\text{PCBs}} = 5.25 \text{ mg/L}$, $C_{\text{Ni/Fe(s)}} = 6.25 \text{ g/L}$, $T = 330^\circ\text{C}$, $t = 3 \text{ h}$.

significantly in ambient water [22,23,27]. In present batch tests, higher reaction temperature ($>250^\circ\text{C}$) as compared to ambient water could speed up the reaction of phosphates with functional groups considerably, and hence resulted in the rapid formation of insoluble iron phosphates. These insoluble iron phosphates precipitated and blocked the reactive site on particles surface, and consequently caused the suspension of PCB dechlorination significantly. Although the concentration of H^+ increased with the mass of phosphates added, the increase of amount of PO_4^{3-} caused more rapid formation of iron phosphates which were insoluble even at lower pH. Hence, the particles were quickly covered by complex precipitates following the drop of dechlorination efficiency.

Acids, regardless of whether it is organic or inorganic, not only play the role of reaction enhancer by supplying H^+ for generation of hydrogen species but also act as reaction retarder in point of causing the corrosive dislodgment of catalyst from bimetallic particles [11,28]. The results in Fig. 4c and d indicate that water under weak

acid condition favored the hydrodechlorination at subcritical state. Schrick et al. [29] found nickel and iron needed to be in electronic contact in order to facilitate the catalysis of hydrogen species to generate active hydrogen species. In weak acidic water, the amount of H^+ is sufficient to produce hydrogen species via corrosion of Fe^0 but not enough to cause the break of electronic contact between Fe^0 and Ni^0 as shown in Fig. 1b, which was also observed by Bokare et al. [10,11]. Meantime, lower pH caused by the addition of organic acid could prevent formation of passivation layer to a certain extent in ambient water [13]. Unlike to PO_4^{3-} , CH_3COO^- and $^- \text{OOC}-\text{COO}^-$ could not react with released iron to form iron oxalates or iron acetates but form iron oxides as passivation layer, which is confirmed by XRD patterns of spent particles in Fig. 2a. Increase of amount of organic acid could promote the corrosion of Fe^0 significantly as well as the increase of production of hydrogen species, but the electronic contact between Fe^0 and Ni^0 was also damaged due to the serious corrosion of Fe^0 . Subsequently, the partial Ni was dislodged from surface of integrated Ni/Fe particles which was confirmed by the decrease of Ni percentage in Ni/Fe particles as increase of organic acids added shown in Fig. 2b and c as EDX results of spent particles after reaction with organic acids. Therefore, the catalytic function of Ni/Fe was impaired, which caused that the bimetallic particles were disabled from catalysis to generate reactive hydrogen species following the drop of dechlorination efficiency.

3.3.2. Effect of reaction time

Due to the remarkable retardant effects of dihydrogen phosphates on dechlorination, acetic acid and oxalic acid were chose for investigating the effects of reaction time on dechlorination at 330°C without residence at low temperature. As shown in Fig. 5, total conversion ratio increased with time but appeared a plateau after 3 h for all cases. Compared results demonstrate that little addition of organic acid as hydrogen donor could facilitate dechlorination notably. In terms of optimal amount used, the enhanced dechlorination efficiency caused by oxalic acid is almost equivalent to that caused by acetic acid, which is also indicated in Fig. 4c and d. As prolonging of reaction time, the corrosion of Fe^0 proceeded fast and then slowed down along with release of iron and generation of active hydrogen species for catalytic hydrodechlorination of PCBs. During this process, the released iron reacted with hydroxyl to form insoluble iron oxides (Fig. 2a) which then precipitated on particle surface and covered the reactive sites. After all fresh particle surfaces were covered by insoluble precipitates, the corrosion of Fe^0 ceased and thereby dechlorination slowed down to termination with time, which is confirmed by the appearance of plateau after 3 h in Fig. 5. This indicates that higher dechlorination efficiency could not be achieved even with considerable increase of reaction time of dechlorination at 330°C despite the addition of organic acid. Although the reactivity of passivation bimetallic particles could be partially restored via HCl wash for eliminating the oxides layer on particle surface [21], retard of the passivating rate during dechlorination process is more economical in terms of the operation cost of HCl wash after reaction. It is undoubted that residence at low temperature for a moment can be regarded as a favorite alternative to retard passivation during dechlorination process.

3.3.3. Effect of temperature at first stage

In this section, the whole dechlorination process was divided into two stage in terms of reaction temperature: first stage for corrosion of Fe^0 at low temperature ($<250^\circ\text{C}$) and subsequent second stage for PCB dechlorination at 330°C . Fig. 6 presents the effects of temperature at first stage on whole dechlorination and corrosion of selected metals with residence at second stage for 1 h. As shown in Fig. 6a, total conversion ratio increased with decline of temperature at first stage. With 1 mg oxalic acid, the total conversion ratio

Fig. 4. Effect of mass of hydrogen donor (a) NaH_2PO_4 , (b) KH_2PO_4 , (c) oxalic acid, (d) HAC on dechlorination. $C_{PCBs} = 5.25 \text{ mg/L}$, $C_{Ni/Fe(s)} = 6.25 \text{ g/L}$, $T = 330^\circ\text{C}$, $t = 3 \text{ h}$.

Fig. 5. Effect of reaction time on dechlorination in the presence of oxalic acid and HAC. $C_{PCBs} = 5.25 \text{ mg/L}$, $C_{Ni/Fe(s)} = 6.25 \text{ g/L}$, $T = 330^\circ\text{C}$.

for 150°C and 200°C are 89.7% and 82.6%, respectively, which were superior or equal to that in Fig. 5 without residence at first stage. This indicates that lower temperature at first stage might favor the following dechlorination at 330°C . Apparently, the corro-

sion and passivation of Ni/Fe particles would be completed rapidly in subcritical water owing to the high temperature above 250°C in previous reports [2,3]. Low temperature at first stage in this study might retard the corrosion of Fe^0 and formation of insoluble iron oxides, which hence enhanced the utility efficiency of Fe^0 and yield of hydrogen species used for dechlorination. Total conversion ratios for both 150°C and 200°C dropped drastically when the amount of oxalic acid was beyond 2 mg. This might be resulted from the corrosive dislodgment of Ni from Ni/Fe particles due to the strong acidity with 2 mg or more oxalic acid added into water ($\text{pH} < 4.1$).

Ni, Cr, Cu, Fe, Mn were chose as preferred monitored metals in respect that they were the main composition elements of constructed materials of the autoclave as well as constitutes of bimetallic particles. Apparently, the concentration of all monitored metal ions except for Fe in aqueous phase after reaction was almost constant regardless of addition of oxalic acid in Fig. 6b and c. Iron concentration increased as the increase of oxalic acid amount to 1 mg, after that, it declined with the increase of amount to 3 mg, and then increased again. The change tendency of iron concentration both in Fig. 6b and c shows that the affect of temperature on corrosion of iron was sharper than that on other metals. It should be noted that iron and nickel ions in the aqueous phase after reaction were the combined results of the corrosion of Ni/Fe particles and constructed materials of the autoclave. As compared to Fe, however, element Ni is more resistant to acid corrosion even

Fig. 6. Effect of temperature at first stage on (a) PCBs conversion ratio and metal dissolution at (b) 150 °C, (c) 200 °C. $C_{\text{PCBs}} = 5.25 \text{ mg/L}$, $C_{\text{Ni/Fe(s)}} = 6.25 \text{ g/L}$, $T_{\text{second stage}} = 330 \text{ °C}$, $t_{\text{first stage}} = 1 \text{ h}$, $t_{\text{second stage}} = 3 \text{ h}$.

in subcritical water according to the metal activity order, which resulted that the strong acid corrosion in acid solution mainly occurred on Fe surface other than Ni surface although these two metals contact closely in Ni/Fe. Therefore, the dissolution of Fe was predominant in subcritical water in the presence of organic acid, which resulted that iron ions were main composition in aqueous phase after reaction. But Ni almost kept stable during whole reaction even in the presence of organic acid and hence the leaching of Ni could hardly be observed with the increase of acid mass added. Meantime, nickel was also prevented from corrosion via cathodic protection by Fe^0 in bimetallic particles, which was also observed in previous report [29]. As for other monitored metals, such as Cr, Cu, Mn, their resistance to acid leaching were mainly ascribed to their alloy state existed in constructed materials of the autoclave. As compared to the high reactive nanoscale Ni/Fe, these alloy metals could hardly compete for H^+ with Ni/Fe and hence were protected from acid corrosion. Therefore, the high concentration of iron ions in aqueous phase after reaction was mainly resulted from the corrosion of Fe^0 of Ni/Fe particles, which also indirectly confirmed that addition of oxalic acid could enhance utility efficiency of Fe^0 . Considering the dechlorination performance and corrosion of Ni/Fe, 150 °C was regarded as optimal temperature adopted at first stage.

3.3.4. Development of the two-stage process

In order to optimize the whole process, 150 °C was chose as optimum temperature for Fe^0 corrosion at first stage on the basis of results in Fig. 6 and 330 °C was still regarded as optimum temperature for PCB dechlorination according to our previous report [4]. Fig. 7 shows the change tendency of the total conversion ratio with residency time at different stage. Apparently, total conversion

ratio increased gradually with time at first stage under the same residency time at second stage. And total conversion ratios for all batch experiments conducted at second stage for 2 h were greater than that only conducted at second stage for 3 h, indicating that Fe^0 corrosion at first stage could promote dechlorination. It should be noted that the conversion ratio with only residency at first stage for 3 h is 46.5% (Fig. 7). The remarkable difference in dechlorination efficiency with and without residency at second stage shows that the main dechlorination was achieved at the second stage under

Fig. 7. Effect of residence time on dechlorination during two-stage reaction process. X axis: residence time at first stage, $C_{\text{PCBs}} = 5.25 \text{ mg/L}$, $C_{\text{Ni/Fe(s)}} = 6.25 \text{ g/L}$, $T_{\text{first stage}} = 150 \text{ °C}$, $T_{\text{second stage}} = 330 \text{ °C}$.

330 °C. The first stage was mainly used for conducting Fe⁰ corrosion and generation of hydrogen species. It has been reported that the relative resistance of positional isomers increased from *para*- to *meta*- to *ortho*-positions, which resulted in chlorines in the *para*- and *meta*-position were predominantly removed over chlorines in the *ortho*-position during the dechlorination process [7,30–33]. Therefore the total conversion ratio of 46.5% with only residency at first stage in Fig. 7 might be attributed to the removal of chlorines in the *para*- or *meta*-position attached to biphenyl rings. It is well known that the solubility of hydrogen species generated from corrosion of Fe⁰ increased with the decrease of temperature in hot water, thereby 150 °C at first stage might conduce to more dissolved hydrogen species in comparison to that at second stage under 330 °C. Since the catalysis of hydrogen species to form active hydrogen species happened on the surface of catalytic metals [10,34], more dissolved hydrogen species could result that more hydrogen species were adsorbed on Ni⁰ surface and then catalyzed to form active hydrogen species. The active hydrogen species generated at first stage were then used to hydrodechlorinate the PCBs at second stage.

4. Conclusions

The results of this study demonstrate that the PCB dechlorination efficiency depends strongly on the property of hydrogen donors in subcritical water. The anion introduced along with the hydrogen donor plays a key role in overall dechlorination process. Phosphates inhibit the dechlorination remarkably via undesired competitive reaction with Ni/Fe to form thick passivation layer on particle surface. In contrast, oxalic and acetic anions cannot compete for reactive nanoscale Ni/Fe with H⁺. Meanwhile, the two-stage process combined with addition of oxalic acid can enhance utility efficiency of Fe⁰ and yield of active hydrogen species such as atomic H[•] and metal hydride Ni–H, thereby improve subsequent PCB dechlorination significantly. The obtained conclusions also pose a precaution that it is necessary to perform pH adjustment and desalination when dehalogenation using nanoscale iron-based particles is carried out in subcritical water.

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