


Removal of 4-chlorophenol from polluted water by aluminum–iron alloys

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ABSTRACT

Chlorophenols are extremely toxic to the environment and recalcitrant to biological degradation. Herein chemical degradation of 4-chlorophenol (4-CP) from aqueous solutions by zero-valent aluminum (Al), zero-valent iron (Fe), Al and Fe mixtures (Al/Fe mass ratio 90/10, labeled as Al/Fe10) and Al-Fe alloy (Al/Fe mass ratio 90/10, labeled as Al-Fe10) were investigated. No removal was found for 50 mg·L⁻¹ 4-CP under anoxic conditions at initial pH 2.5 during a period of 10 hrs while 56%, 83%, 78% and 99% of 4-CP were removed by Fe, Al, Al/Fe10 and Al-Fe10, respectively under aeration conditions. The removal of 4-CP by Al/Fe10 mixtures was primarily in the Fe mode in the beginning 4 h and then transitioned to the Al mode. The removal of 4-CP by Al-Fe10 alloy was accomplished via two intermediate products, hydroquinone (HQ) and 4-chlorocatechol (4-CC), and it was speculated that reactive oxygen species and hydroxyl radicals ($\cdot\text{OH}$) play an important role in the degradation of 4-CP and that Al-Fe intermetallic compounds might catalyze the reactions. This study demonstrates that alloying Al with Fe offers a promising strategy for developing new materials for water and wastewater remediation.

Key words | 4-chlorophenol oxidation, aluminum alloys, water treatment, zero-valent metals

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INTRODUCTION

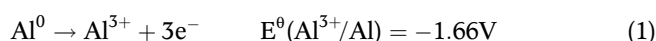
In recent years, emerging contaminants such as heavy metals (Collivignarelli *et al.* 2019a), dyes (Collivignarelli *et al.* 2019b), surfactants (Riva *et al.* 2019) and chlorinated phenols (Kadmi *et al.* 2015), in water and water waste, have become a serious problem. In particular, chlorinated aromatic compounds are widely used in chemical industries (Blázquez-Pallí *et al.* 2019). These compounds are highly toxic and have adverse impacts on the environment. Chlorophenols are a particular group of halo-aromatic compounds and have been listed as priority pollutants due to their high toxicity and non-biodegradation (Munoz *et al.* 2011).

Removal of chlorophenols from contaminated water is essential to protect water quality. Chemical degradation of a model chlorophenol, 4-chlorophenol (4-CP), using zero-valent metals (ZVM, e.g. Al⁰, Fe⁰, Mg⁰, Zn⁰, etc.) via reductive dechlorination under anoxic conditions or via oxidative dechlorination in the presence of O₂ has been investigated (Cheng *et al.* 2007; Bokare & Choi 2009; Kang & Choi 2009; Xu *et al.* 2012; Babuponnusami & Muthukumar 2014; Liu *et al.* 2014; Fan *et al.* 2016). Of ZVM, zero-valent iron (ZVI or Fe⁰) is extensively employed due to its high

abundance, low toxicity and low cost for both reductive dechlorination and oxidative degradation of chlorophenols (Cheng *et al.* 2007; Kang & Choi 2009; Babuponnusami & Muthukumar 2014). The major concern for reductive dechlorination of chlorophenols by ZVI is slow rates of degradation (Cheng *et al.* 2007). Efforts to enhance dechlorination activity of ZVI include preparation of nano-sized ZVI (Cheng *et al.* 2007) and doping a second noble or heavy metal (e.g., Pd, Pt, Ni and Cu) onto the surface of ZVI to form bimetals (Xu *et al.* 2012). However, use of nano-materials has triggered public health and environmental concerns, while doping noble and heavy metals incurs additional costs and/or risks of secondary contamination.

Oxidative degradation of chlorophenols using ZVM together with molecular oxygen/air attracts great attention (Bokare & Choi 2009; Liu *et al.* 2014). In this approach, O₂ is transformed by ZVM to reactive oxygen species (ROS, e.g. H₂O₂/ $\cdot\text{OH}$) via Fenton reaction (Kang & Choi 2009) and the resultant ROS attack chlorophenols. This approach is competitive as compared with other photochemical processes (e.g., TiO₂ photocatalysis) (Hoffmann *et al.*

1995), vacuum UV photolysis (Braun 2003), electrochemical discharge (Locke *et al.* 2006), biological reactions (e.g., metalloenzyme cytochrome P-450) (Makris *et al.* 2002), metalloporphyrins (Meunier 1992) and polyoxometalate anions (Weinstock *et al.* 2001). Nevertheless, ZVI/O₂ oxidation generates iron hydroxides, leading to an increase in solution pH and the development of surface passivation, particularly at pH > 3. In this regard, alternative ZVMs with high efficiency of producing ROS over a wide range of pH are of great interest and zero-valent aluminum (Al⁰) provides a greater thermodynamic driving force for electron transfer to produce ROS (Equations (1)–(4)) (Chen *et al.* 2008):



However, the application of Al⁰ is limited, primarily due to the protective layer of alumina on the surface of Al⁰ particles (Bokare & Choi 2009). It has been reported that a combined use of Fe⁰ and Al⁰ enhanced chemical degradation of 4-CP as compared with Fe⁰ or Al⁰ alone (Liu *et al.* 2014). Nevertheless, the combined system required addition of EDTA to increase the corrosion of Fe and a high concentration of total Fe (TFe) ions (up to 80 mg·L⁻¹) was released in the solutions (Liu *et al.* 2014).

Alloying Al with Fe increases the corrosion of Al metal (Ambat *et al.* 2006) as massive microscopic galvanic cells between Al (anode) and Fe (cathode) exist, thus enhancing the electron transfer rates. Previously, we demonstrated that Al-Fe alloys were able to rapidly reduce nitrate in the wide range of pH 2–12 (Bao *et al.* 2017; Xu *et al.* 2017) and were efficient for reductive dechlorination of chloroform, carbon tetrachloride and trichloroethylene in aqueous solutions (Xu *et al.* 2018). The objective of this study was to investigate Al-Fe alloys for the degradation of 4-CP under ambient conditions.

MATERIALS AND METHODS

Chemicals and materials

Chemicals used in this study include 4-chlorophenol (analytical grade, Xiya Reagent, China), and methanol (high-performance liquid chromatography (HPLC) grade, Tianjin Shield Specialty Chemical Ltd Co., China). All

solutions were prepared in ultrapure water prepared by a PINE-TREE purification system. Aluminum powders (200 mesh) and Fe powders (40 mesh) were purchased from Tianjin Fu Chen Chemical Reagent Factory (China). Al-Fe alloys were prepared by melting high purity Al and Fe metals (>99.99%) in mass ratios of 90/10, 80/20, 42/58 and 30/70 in a vacuum induction melting furnace (SGM, RL91/X, China). The conditions of the preparation are described elsewhere (Xu *et al.* 2017, 2018). The Al-Fe alloy ingot was crushed and particle sizes of 40–60 mesh were employed in this work. The initial pH value of the solution was adjusted by diluted solutions of H₂SO₄ (analytical grade, Beijing Chemical Works, China) and NaOH (analytical grade, Beijing Chemical Works, China).

Chemical degradation of 4-CP in aqueous solutions

The degradation experiments were conducted in a 500 mL sealed glass bottle with double holes equipped with HJ-6 magnetic stirrer (Changzhou Guohua Electric Appliance Ltd Co.) at 25 °C. The volume of 4-CP solution was 300 mL, metals or alloy concentration was 5 g·L⁻¹ and the initial pH of the solution was adjusted to pH 2.5 unless otherwise specified. The solution was aerated by an air-pump at a flow rate of 3.5 L min⁻¹ and stirred with a magnetic bar at a speed of 300 rpm for 30 min. Then, metal or alloy particles were added to the bottle and the degradation experiments were set for 10 hrs. The concentration of dissolved oxygen was measured to be 6.5–8 mg·L⁻¹ during the degradation process. Samples (1 mL) were withdrawn from the bottle at given time intervals and filtered through 0.22 μm hydrophilic polyethersulfone (PES) syringe filters (Millipore, USA). For degradation experiments under anoxic conditions, the system was continuously sparged with argon gas at a flow rate of 3.5 L min⁻¹ (the concentration of dissolved oxygen was <0.5 mg·L⁻¹). All experiments were carried out in triplicate. At the end of the experiment, the alloy particles in solutions were filtered and rinsed with deionized water, vacuum-dried for 12 hours at 30 °C and were employed for investigating the durability of the material.

Analytical and characterization methods

Determination of 4-CP and its degradation products was performed by high-performance liquid chromatography on a Thermo Fisher U3000 HPLC system (Thermo Fisher, USA) equipped with a reversed phase ZORBAX Eclipse XDB-C18 column (5.0 mm × 250 mm, 5 μm) and a diode array detector. Concentrations of total dissolved metal

ions in aqueous solutions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Thermo Jarrell Ash Corp. IRIS/AP). Al-Fe alloy particles were characterized using a JSM-6360LV scanning electron microscope (SEM) (JEOL, Japan) and X-ray powder diffraction (XRD) (D8 ADVANCE X-ray diffractometer, Bruker, Germany). The pH value was determined by a PHS-3C pH meter (Shanghai Precision & Scientific Instrument Co., Ltd, China). Dissolved oxygen (DO) was measured by JPB-607A dissolved oxygen analyzer (Shanghai Shengke Instrument Co., Ltd, China).

RESULTS AND DISCUSSION

Degradation of 4-CP by reductive metals

Chemical degradation of 4-CP in water by ZVM and bimetals (e.g. Fe-Ni) involves reductive dechlorination under anoxic conditions and oxidative dechlorination in the presence of oxygen (Cheng *et al.* 2007; Bokare & Choi 2009; Kang & Choi 2009; Xu *et al.* 2012; Liu *et al.* 2014; Fan *et al.* 2016). The product of reductive degradation is phenol (Cheng *et al.* 2007; Xu *et al.* 2012), while low-molecular-weight aliphatic organic acids are the major end-products in the oxidation of 4-CP (Bokare & Choi 2009; Kang & Choi 2009; Babuponnusami & Muthukumar 2014; Liu *et al.* 2014; Fan *et al.* 2016).

Herein zero-valent Al, Fe, mixtures of Al and Fe particles (a mass ratio of Al/Fe 90/10, labeled as Al/Fe10) and Al-Fe alloy with 10% Fe (labeled as Al-Fe10) were investigated for removal of 4-CP. No removals were observed by these metal systems under anoxic conditions during the testing period of 10 h (Figure 1(a)). By contrast, the removal of 4-CP was in the range 50%–99% when each system was bubbled with air (Figure 1(b)). Of the metal systems studied in this work, Al-Fe10 alloy presented the fastest rate of 4-CP removal (90% in 3 h), the Al system showed the second fastest rate of removal (80% in 3 h) and the Fe system had the lowest rate of removal (29% in 3 h). It was noted that the Al system experienced a lag period of 1.5 h, which was most likely due to the protective layer of alumina on the surface of the Al particles. The trend of 4-CP removal by Al/Fe10 was that the first reaction period of 4 h was primarily the Fe mode and then gradually transitioned to the Al mode. This indicates that simple mixtures of zero-valent Al and Fe particles do not produce a synergistic reaction for 4-CP removal.

It has been recognized that the degradation of 4-CP by reductive metals in the presence of dissolved oxygen is a

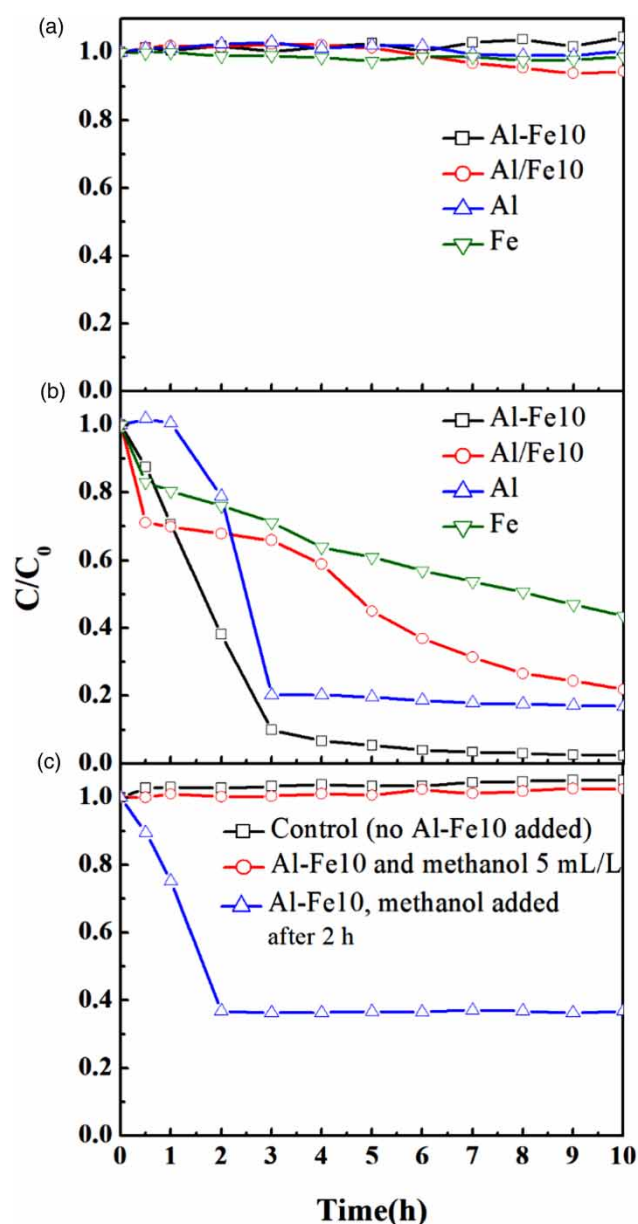


Figure 1 | Removal of 4-CP from water by Al, Fe, Al/Fe10 mixtures and Al-Fe10 alloy particles: (a) bubbled with Ar, (b) bubbled with air, (c) bubbled with air (5 mL L⁻¹ methanol added at the beginning of the reaction and after 2 h reaction). Volume of solution: 300 mL; concentration of metal or alloy particles: 5 g L⁻¹; initial concentration of 4-CP: 50 mg L⁻¹; initial pH: 2.5; temperature: 25 °C; bubbling flow-rate: 3.5 L min⁻¹; C and C₀: process and initial concentrations of 4-CP, respectively.

Fenton or Fenton-like reaction, owing to the generation of ROS (e.g. ·OH radicals) by electrons transferring from metals to dissolved oxygen (Bokare & Choi 2009; Kang & Choi 2009; Babuponnusami & Muthukumar 2014; Liu *et al.* 2014; Fan *et al.* 2016). Therefore, ROS plays a critical role in 4-CP degradation while scavenging ROS inhibits the degradation (Ai *et al.* 2005; Bokare & Choi 2009; Kang

& Choi 2009; Babuponnusami & Muthukumar 2014; Liu *et al.* 2014; Fan *et al.* 2016). This mechanism has been proved by adding methanol as an $\cdot\text{OH}$ scavenger in the degradation of 4-CP by an Al/Fe + O_2 system (Liu *et al.* 2014; Fan *et al.* 2016). In this study, methanol was added to the Al-Fe alloy + O_2 system at the beginning of the experiment and after 2 h of the reaction and the results show that no degradation occurred when methanol (5 mL L^{-1}) was added at the beginning and the degradation was completely stopped upon the addition of methanol at 2 h when 4-CP removal efficiency had reached 60% (Figure 1(c)).

The concentrations of Al and TFe ions during the degradation of 4-CP by the Al-Fe10 alloy and Al/Fe10 mixtures are shown in Figure 2. Al concentration increases rapidly with reaction time and reaches $32 \text{ mg}\cdot\text{L}^{-1}$ at 4 h of the reaction in the Al-Fe10 alloy system while almost no Al ions are released in the Al/Fe10 mixture system ($[\text{Al}^{3+}] < 0.3 \text{ mg}\cdot\text{L}^{-1}$) during the 5 h of the reaction. In comparison, TFe ion concentration surges quickly to $80 \text{ mg}\cdot\text{L}^{-1}$ within 30 min in the Al/Fe10 mixture system while it increases slowly to $16 \text{ mg}\cdot\text{L}^{-1}$ in 5 h in the Al-Fe10 alloy system. Clearly, a rapid release of Al ions is a consequence of the fast corrosion of Al-Fe alloys, indicating that Al-Fe alloys are capable of transferring electrons to oxygen efficiently to generate ROS and $\cdot\text{OH}$ radicals.

Effect of Fe content of Al-Fe alloys

It has been reported that the rate of 4-CP degradation dropped with the ratio of Fe increasing from 1% to 20% in the mixtures of zero-valent Al and Fe particles (Liu *et al.* 2014) and it was proposed that this trend happened as a

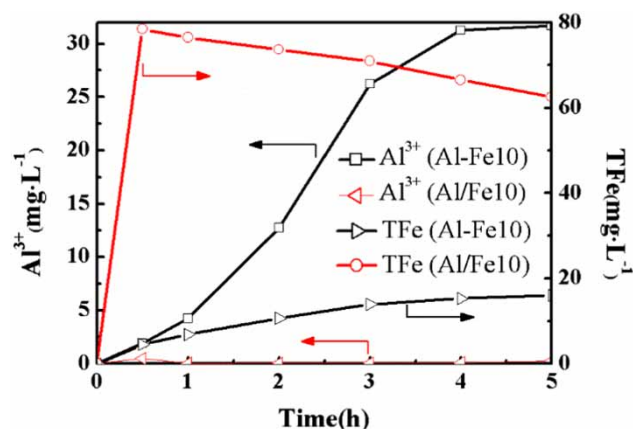


Figure 2 | Al and total Fe (TFe) ion concentrations during 4-CP degradation by Al-Fe10 alloy and Al/Fe10 mixtures in the experiment of Figure 1(b).

result of the reaction between ferrous Fe ions and $\cdot\text{OH}$ radicals (Equation (5)):



A similar trend was also observed in the present Al-Fe alloy system where the degradation rate declined with the Fe content of the alloy increasing from 10% to 70% (Figure 3).

Effect of initial pH

Solution pH plays a critical role in oxidative degradation of 4-CP by Al and the mixtures of Al and Fe because pH values influence the formation of metal hydroxides and the surface passivation of metals (Bokare & Choi 2009; Liu *et al.* 2014). Figure 4(a) shows the effect of initial pH on the degradation of 4-CP. The degradation of 4-CP quickly reaches 98.5% in 5 h at initial pH 2 but it is only 45.1% at initial pH 3. The degradation is negligible at initial pH 4–9 during the whole period of the experiment (10 h). This result is consistent with the general trend of oxidative degradation of 4-CP by zero-valent aluminum and ZVI (Bokare & Choi 2009; Liu *et al.* 2014; Fan *et al.* 2016). Figure 4(b) shows the variation of pH values during the course of the degradation process. The solution pH slowly increases to near 7 by the end of the experiment (10 h) from both initial pH 4 and 6. By contrast, the pH drops from initial pH 9 to 7.2 in half an hour and then remains relatively steady at pH 7.5 by the end of the experiment. The pH increases to 3.7 from initial pH 2 in 4 h and then remains unchanged in the following 6 h while it increases to pH 4.1 from initial pH 3 in 2 h and remains steady in the next 8 h.

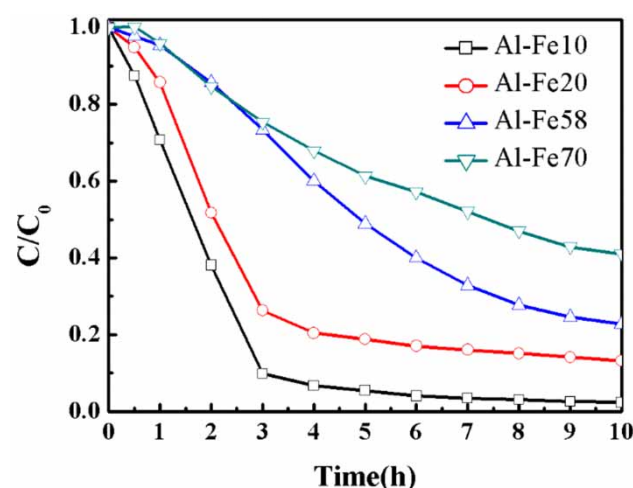


Figure 3 | Effect of Fe content (10%, 20%, 58% and 70%) of Al-Fe alloys. Volume of solution: 300 mL; Al-Fe alloy particles: $5 \text{ g}\cdot\text{L}^{-1}$; initial concentration of 4-CP: $50 \text{ mg}\cdot\text{L}^{-1}$; initial pH: 2.5; temperature: 25°C ; air bubbling flow-rate: $3.5 \text{ L}\cdot\text{min}^{-1}$.

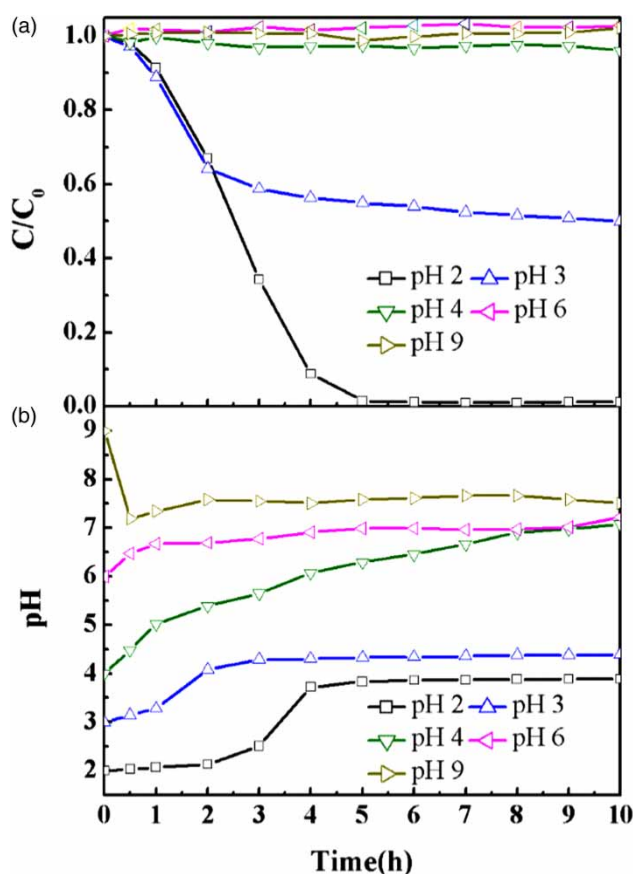


Figure 4 | (a) Effect of initial pH on removal of 4-CP and (b) pH variation during the removal process. Volume of solution: 300 mL; Al-Fe10 alloy particles: 5 g·L⁻¹; initial concentration of 4-CP: 50 mg·L⁻¹; temperature: 25 °C; air bubbling flow rate: 3.5 L min⁻¹.

The trend of pH variation observed above is different from that in nitrate reduction by the same Al-Fe alloy material under anoxic conditions, where the solution pH values were all increased to pH 9–11 from initial pHs of 2–8 (Bao *et al.* 2017; Xu *et al.* 2017). The increase of pH in aqueous nitrate reduction by Al-Fe alloy under anoxic conditions was attributed to a continuous reaction between Al and water, which produced hydroxides. Under air aeration conditions as observed here, the thin layer of Al₂O₃ on the surface of the Al-Fe alloy particles was dissolved by hydrogen ions or hydroxide ions, bringing the pH to near neutral. Then, the fresh surface of the Al-Fe alloy particles was quickly re-passivated in the presence of dissolved oxygen, leading to relatively stable pH near neutral.

Effect of Al-Fe alloy concentration

The effect of Al-Fe alloy concentration between 1 and 20 g·L⁻¹ is shown in Figure S1 (Supplementary Data). In

general, the rate of 4-CP removal increased with the alloy concentration. The degradation rate was increased by 20% when the alloy concentration varied from 1 g·L⁻¹ to 2 g·L⁻¹. However, no significant differences were observed for alloy concentrations of 5, 10 and 20 g·L⁻¹. Liu *et al.* (2014) investigated the effect of Al⁰ and Fe⁰ mixture (100:1) concentrations (1–20 g·L⁻¹) on the oxidative degradation of 4-CP and found that 5 g·L⁻¹ had the highest rate of degradation. They explained that increasing Fe concentration could accelerate the decomposition of in-situ generated H₂O₂ and ROS radicals.

Effect of 4-CP concentration

The effect on 4-CP concentrations between 5 and 200 mg·L⁻¹ of 5 g·L⁻¹ Al-Fe alloy particles is shown in Figure S2 (Supplementary Data). For 5 and 10 mg·L⁻¹ 4-CP, greater than 95% are removed in 2 h. For 50 mg·L⁻¹ 4-CP, a reaction time of 3 h is required to remove 90%. For 100 and 200 mg·L⁻¹ 4-CP, the removals are less than 55% in 3 h. The oxidative degradation of 4-CP is a process of consuming H⁺ and therefore higher concentrations of 4-CP mean more H⁺ consumption, leading to the increase of pH during the degradation process. The degradation would cease when solution pH increased to 4. For a complete removal of 4-CP higher than 50 mg·L⁻¹, the solution pH is required to remain below 4.

The durability of Al-Fe alloy

Figure 5 shows that the Al-Fe alloy particles possess relatively stable performance for 4-CP degradation through five times of use. The SEM images and XRD patterns of Al-Fe10 alloy before use and after the first and fifth use are presented in Figure 6. After use, the surface of the Al-Fe alloy particles becomes porous (Figure 6(a)–6(c)) while the XRD patterns do not change (Figure 6(d)). The alloy consists of three phases: Al, Fe and an intermetallic compound Al₁₃Fe₄, which has been proved to be an alternative catalyst to Pd (Armbrüster *et al.* 2012; Piccolo & Kibis 2015). This intermetallic compound probably plays an important catalytic role in the degradation of 4-CP when the performance of the Al-Fe10 alloy is compared with that of Al/Fe10 mixtures (see Figure 1(b)). Further characterizations of the material (e.g. surface properties, composition, structure), particularly in a long-term experiment, are required to investigate the durability of the material.

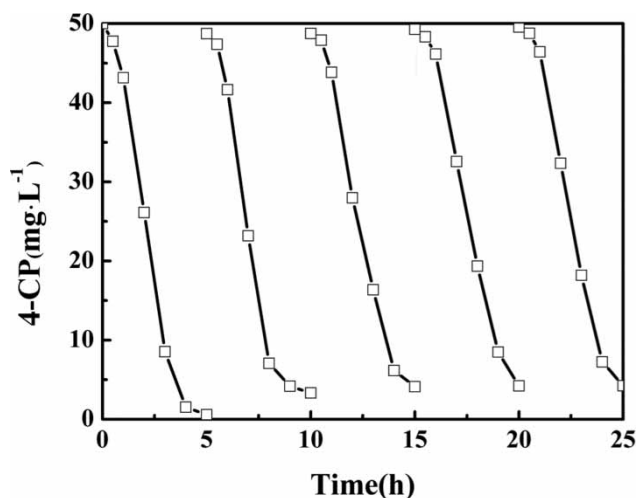


Figure 5 | Concentration profiles of 4-CP by repeated use of Al-Fe10 alloy particles. Volume of solution: 300 mL; Al-Fe10 alloy particles: 5 g·L⁻¹; initial pH 2.5; temperature: 25 °C; air bubbling flow-rate: 3.5 L min⁻¹.

The degradation mechanism of 4-CP by Al-Fe alloys

Practitioners have proposed two pathways of 4-CP degradation through the intermediates hydroquinone (HQ)/p-benzoquinone (BQ) and 4-chlorocatechol (4-CC) to the end products of aliphatic organic acids (e.g. maleic acid, iminodiacetate, succinic acid and formic acid) by a titanium dioxide photocatalytic system or Al/Fe + O₂ catalytic system (Stafford *et al.* 1994, 1997; Li *et al.* 1999a, 1999b; Liu *et al.* 2014). Both 4-CC and HQ pathways occurred in the titanium dioxide photocatalytic system, but the former predominated (Stafford *et al.* 1994, 1997; Li *et al.* 1999a, 1999b). The pathway was 4-CC and it turned to HQ when EDTA was added in the Al/Fe + O₂ catalytic system (Liu *et al.* 2014). In this work, both 4-CC and HQ were also identified during the course of reaction where 4-CC concentration increased to 15 mg·L⁻¹ in 2.5 h and the

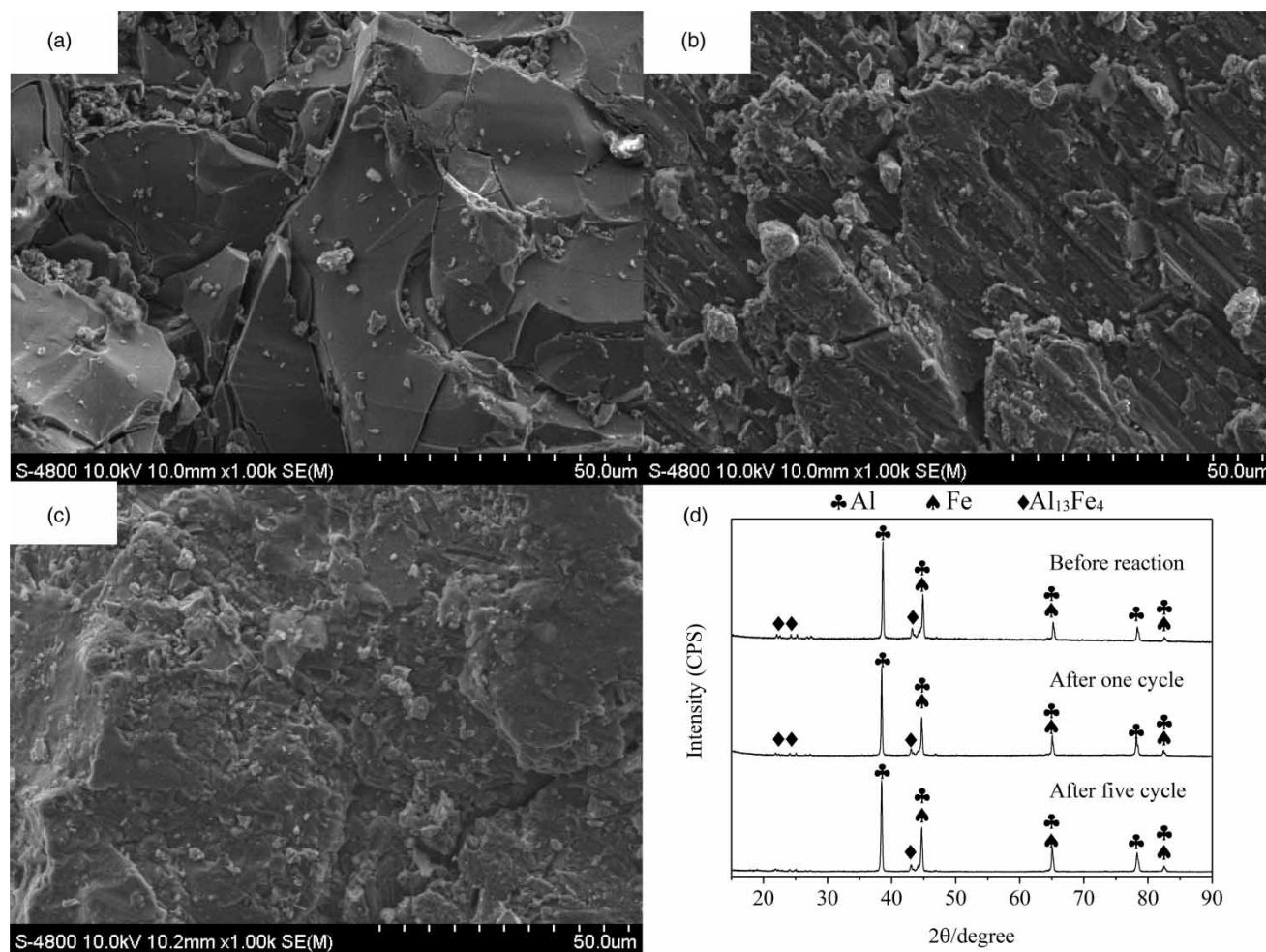


Figure 6 | SEM images of Al-Fe10 alloy particles (a) before use, (b) after the first use (5 h), (c) after fifth use and (d) the XRD patterns of Al-Fe10 before and after the first and fifth uses.

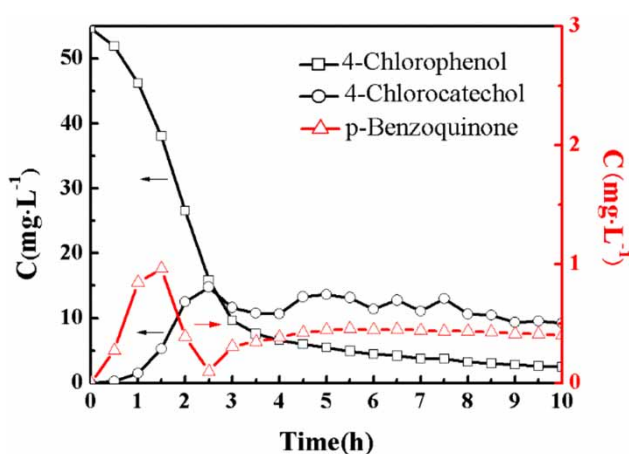


Figure 7 | Concentrations of 4-CP, 4-CC (4-chlorocatechol) and BQ (*p*-benzoquinone) as a function of reaction time during the degradation of 4-CP. Volume of solution: 300 mL; Al-Fe10 alloy particles: 5 g·L⁻¹; initial pH 2.5; temperature: 25 °C; air bubbling flow-rate: 3.5 L min⁻¹.

highest concentration of BQ was 1.0 mg·L⁻¹ at 1.5 h (see Figure 7). The concentration of 4-CP decreased from 50 mg·L⁻¹ to ~10 mg·L⁻¹ (i.e. 80% removal) in 3 h and then very slowly to 2.5 mg·L⁻¹ in the following 7 h, where 4-CC and BQ were relatively stable at 11 mg·L⁻¹ and 0.4 mg·L⁻¹, respectively. The proposed mechanism of 4-CP degradation by Al-Fe alloy particles in the presence of dissolved oxygen is shown in Figure 8. HQ is transformed to BQ and then degraded to aliphatic organic acids while chlorine of 4-CC is replaced by hydroxyl and then the replacement is further degraded. The degradation was rapid in the first 3 h and then became almost stagnant. This phenomenon was likely due to the pH of the system in the first 3 h being increased from the initial pH 2.5 to pH ~4 (refer to Figure 4), at which the degradation did not occur.

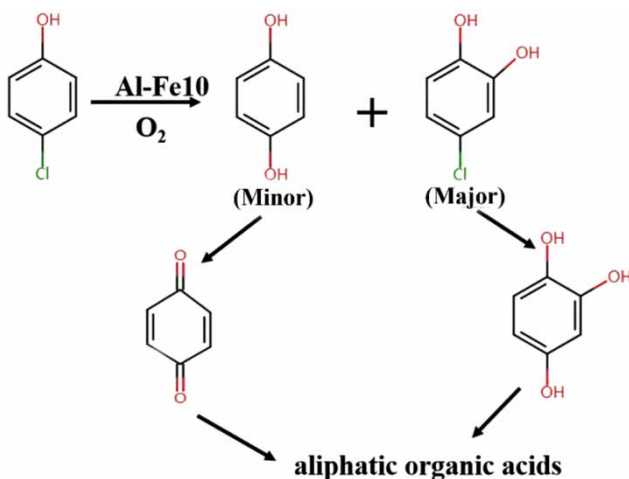


Figure 8 | The proposed pathway of 4-chlorophenol degradation by the Al-Fe10/O₂ system.

CONCLUSIONS

No chemical removal was observed for 4-chlorophenol from water by zero-valent Al, zero-valent Fe and their mixtures, and Al-Fe alloys under anoxic conditions during a testing period of 10 hrs while appreciable removals were detected in the presence of dissolved oxygen. Of these metal systems, Al-Fe alloys presented the best performance. The pollutant was quickly removed by Al-Fe10 alloy of 5 g·L⁻¹ from an initial concentration of 50 mg·L⁻¹ to 2.7 mg·L⁻¹ in 5 h (a removal rate of 95%) at initial pH 2.5 and an air aeration rate of 3.5 L min⁻¹. An acidic pH below 4 was required to effectively degrade the pollutant and the degradation was accomplished by oxidative dechlorination with ROS and hydroxyl radicals generated by transferring electrons from Al to dissolved oxygen via the intermediates hydroquinone and 4-chlorocatechol. The rate of 4-chlorophenol degradation by Al-Fe alloy particles increased with the decreases of initial pH and the content of Fe in the alloy and the performance of 4-chlorophenol degradation did not change significantly through five times of use.

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NOTES

The authors declare no competing financial interest.

SUPPLEMENTARY DATA

The Supplementary Data for this paper are available online at <http://dx.doi.org/10.2166/wst.2019.349>.

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