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Simultaneous adsorption and degradation of γ -HCH by nZVI/Cu bimetallic nanoparticles with activated carbon support

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ABSTRACT

Cu amended zero valent iron bimetallic nanoparticles were synthesized by doping Cu on the surface of iron. They were incorporated with granular activated carbon (AC) to prepare supported particles (AC–Fe⁰–Cu), which were used to remove γ -HCH. Cu on the surface of iron enhanced the dechlorination activity of Fe⁰. The dechlorination rate constant (k_{obs}) increased with the Cu loading on the surface of iron and the maximum was achieved with 6.073% Cu. AC as a support was effective for increasing the dispersion of the nanoparticles and avoiding the agglomeration of the metallic nanoparticles. The simultaneous adsorption of γ -HCH on AC accelerated the degradation rate of γ -HCH by the bimetals. After reaction for 165 min, around 99% of γ -HCH was removed by the solids of AC–Fe⁰–Cu. In addition, AC could adsorb the degradation products. The degradation of γ -HCH was mainly through dehydrochlorination and dichloroelmination based on the intermediate products detected by GC/MS.

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1. Introduction

Hexachlorocyclohexane (HCH) had been heavily used as an organochlorine insecticide since the 1940s. It was classified as a persistent organic pollutant by the Stockholm Convention due to its persistence and adverse effects on ecosystem and human beings (Walker et al., 1999). It was reported to be a potential carcinogen and teratogen (Joo and Zhao, 2008). China has a long history of production and use of HCHs. The total production of technical HCH in China was around 4 million tons from 1952 to 1984, and the total production of lindane (γ -HCH), which is the effective component of all eight HCH isomers, was approximately 11 400 tons from 1991 to 2000 (Li et al., 2001).

Due to the historically excessive application and industrial discharge, γ -HCH is widely present in water, soil and sediment. Hence, it is desirable to develop remediation technologies to get rid of the contamination of γ -HCH from the environment.

In the early 1990s, zero valent iron (ZVI) was used as an effective technique to degrade chlorinated organic compounds (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Orth and Gillham, 1995; Li and Farrell, 1999). Recently, nanoscale ZVI particles have been used extensively as an environmental remediation material, especially for treatment of halogenated hydrocarbons

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(Lowry and Johnson, 2004; Song and Carraway, 2005; Zhan et al., 2008). Compared to normal sized ZVI, nanoscale ZVI particles display higher dechlorination efficiency due to their large surface area (Zhang et al., 1998; Nurmi et al., 2005). The reactivity of nanoscale ZVI has been further advanced through deposition of a discontinuous laver of noble metals on the ZVI surface. These bimetals were used to dechlorinate several chlorinated pollutants (Elliott and Zhang, 2001; Feng and Lim, 2005; Nutt et al., 2005; Agarwal et al., 2007; Feng and Lim, 2007; Han et al., 2008; Kim et al., 2008; Lin et al., 2009; Chun et al., 2010). In most cases, the presence of the coating metal greatly enhances reaction rates as compared to uncoated iron. Among the nanoscale bimetallic particles, palladium (Pd) exhibits extremely high dechlorination efficiency (Lien and Zhang, 2005; Feng and Lim, 2007; Lien and Zhang, 2007; Yan et al., 2010), but its application is limited due to its high cost. It is desirable to investigate the catalytic effect of some cost effective alternatives of Pd, such as Cu. During the real application, nanoscale metal particles tend to agglomerate rapidly and grow into large particles in the micro to millimeter scale due to their high surface energies and intrinsic magnetic interactions. The agglomeration inhibits their mobility and reduces the chemical reactivity of nanoscale metal particles. Extensive studies reported the use of water-soluble starch, sodium carboxymethyl cellulose, natural organic matter, silica, and resin as a surfactant or support to prevent the agglomeration and stabilize the synthesized nanoscale metal particles (He and Zhao, 2005; He et al., 2007; Zhan et al., 2008; Zheng et al., 2008; Johnson et al., 2009; Lin et al., 2009). On the other hand,





persistent organic pollutants such as γ-HCH exhibit high affinity to the organic matters in the sediment. How to remediate the organic pollutants in the sediment seems a technical difficulty. Recently, a concept of a "reactive" capping technology has been proposed for remediation of polychlorinated diphenyls in sediment. Elliott et al (Elliott and Zhang, 2001) designed a field demonstration to remediate trichloroethene contaminated groundwater by nanoscale bimetallic (Fe/Pd) particles. The high adsorption ability of granular activated carbon (AC) was used to reduce the biovailability of the hydrophobic chemicals in the sediment. However, the adsorbed contaminants could be released in to the environment under certain conditions and pose potential risks to ecosystems. This technology was further advanced by impregnation of AC with Fe/Pd bimetallic nanoparticles (Choi et al., 2009). The simultaneous adsorption and dechlorination occurring on the impregnated materials suggest that this is a promising method for in-situ groundwater and sediment remediation for chlorinated compounds.

The primary objective of this study was to investigate the potential of using AC impregnated bimetallic nanoparticles to remediate γ -HCH in ground water and sediment. Cu-amended zero valent iron bimetallic nanoparticles were synthesized and they were in-situ incorporated with AC. The effects of Cu amendment and AC incorporation on the reaction kinetics of γ -HCH were investigated. Finally, the possible mechanisms involved in the supported nanoscale metal particles were also elucidated.

2. Experimental sections

2.1. Materials and reagents

Potassium borohydride (KBH₄) was purchased from Tianjin Aoran Fine Chemical Industry Research Institute. Polyethyleneglycol-4000 was supplied by Shanghai Tianlian Fine Chemical Company. Sodium azide (NaN₃) was purchased from Chengdu Kelong Chemical Reagents Company. Ethanol and n-hexane were purchased from Tianjin Concord Technology Company. Ferrous sulfate heptahydrate (FeSO₄-7H₂O) and anhydrous cupric sulfate (CuSO₄) were supplied by Tianjin North Tianyi Chemical Reagent Company. All solvents and reagents were analytical grade. γ -HCH was obtained from AccuStandard (New Haven, CT, USA). The activated carbon (AC) was made from tire rubber particles in our own lab and the properties of the AC were well characterized. The preparation and characterization methods were provided in Supporting Information. The AC has a graphite crystal phase with surface area of 398.5 m²/g, average pore size of 5.12 nm and pore volume 0.51 cm³/g. The mesoporous structure makes the AC as an ideal impregnation support material.

2.2. Preparation and characterization of the nanoparticles

Three kinds of nanoscale metal particles (including pure Fe⁰ nanoparticles, Fe⁰–Cu bimetallic nanoparticles and AC-supported nanoparticles) were synthesized using the liquid phase reduction method. The synthesis was conducted in N₂ atmosphere and all deionized water and solvents were degassed and saturated with N₂ before use.

Fe⁰ nanoparticles: The synthesis of nanoscale ZVI particles is based on the following reaction:

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe + 2B(OH)_3 + 7H_2$$
 (1)

The reaction was carried out at room temperature in a three–necked flask. 0.0669 mol/L KBH₄ alkaline solution was drop-wisely added into equal volume of 0.0223 mol/L FeSO₄·7H₂O ethanol aqueous solution (ethanol/water, 3/1 v/v) with vigorous stirring at 1500 \pm 50 rpm. 0.1 g of polyethylene glycol-4000 was added as a surfactant in the reaction solution. After the addition of KBH₄, the mixture was stirred continuously for another 30 min. The black solid product was washed with deionized water three times and ethanol twice, and refrigerated in ethanol in a sealed vial until use.

 $\rm Fe^0-Cu$ bimetallic nanoparticles: To synthesize nanoscale $\rm Fe^0-Cu$ bimetallic particles, freshly made nanoscale $\rm Fe^0$ suspension was added into 0.6265 mmol $\rm L^{-1}$ CuSO₄ solution (ethanol/water, 3/1 v/v) drop-wisely. The mixture was stirred for 15 min. The deposition of Cu onto the surface of nano-Fe⁰ particles can be described as:

$$Cu^{2+} + Fe \rightarrow Cu + Fe^{2+} \tag{2}$$

The produced nanoparticles were rinsed and preserved as described above. The content of Cu on the surface of Fe^0 was controlled by adjusting the amount of CuSO₄

added in the reaction solution. The actual Cu doping content on the surface of iron was measured with an energy disperse X-ray spectroscopy (EDX, Phoenix DX60s, EDAX, USA) in conjunction with scanning electron microscopy (SEM, 1530VP, LEO, Germany).

AC-supported nanoparticles: To synthesize carbon-supported nanoscale particles (AC–Fe⁰, AC–Fe⁰–Cu), a similar synthesis procedure described above was followed except that the activated carbon (AC, 0.025 g) was added in the solution at the begging of the synthesis reaction. This synthesis procedure had been reported previously (Ponder et al., 2000; Schrick et al., 2004).

2.3. Characterization of the nanoparticles

The size distribution of the nanoparticles was characterized by a transmission electron microscopy (TEM, JEM-2010FEF, JEOL, Japan) using 200 kV accelerating voltage. Samples were prepared by dispersing the particles in ethanol using an ultrasonicator, and the suspension was dropped on a copper grid. The morphology of nanoparticles was observed with SEM, and localized elemental information on the chosen region was viewed with an EDX in conjunction with SEM. The crystal structure of nanoparticles was examined with an X-ray diffraction (XRD, Rigaku, Japan) analysis using a RINT 2000 vertical goniometer with Cu K α (λ = 1.5406 Å) radiation at a scanning speed of 2°/min from 10° to 80°, operated at voltage of 40 kV and applied potential current of 150 mA. This scan range covered all major species of iron, copper, Cu–Fe alloy, and iron oxide peaks of our interest. X-ray photoelectron spectroscopy (XPS, PHI 5000 ESCA) with nonmonochromatized Al K α X-ray as the excitation source was employed to study the elemental composition, chemical state, and electronic state of the elements.

2.4. Sorption and degradation experiments

Batch experiments were conducted in 100 mL polytetrafluoro ethylene (PTFE)sealed headspace vials to investigate the ability of AC and nanoparticles to remove γ -HCH from water. In an anaerobic vial, a certain amount of AC or nanoparticles was added followed by the addition of 100 ml of γ -HCH aqueous solution at 5 mg/L. The amount of AC and Fe⁰ nanoparticles in the solution was 0.25 and 0.2 g/L respectively. A certain amount of supported nanoparticles was added, in which the content of Fe was 0.2 g/L. Approximately 50 mg/L of sodium azide was added to inhibit possible biodegradation of γ -HCH. The solution was shaken at a rate of 225 rpm using a reciprocal shaker at 25 \pm 1 °C. 2 ml of aqueous sample was withdrawn from the supernatant using a gastight syringe at certain time intervals. The sample was filtered through a 0.45 µm filter membrane. The filtered solution was extracted with 2 ml hexane in an 8-ml amber glass vial. The supernatant hexane phase was taken for the analysis of γ -HCH. Control experiments without AC or nanoscale particles were set up.

To measure the amount of γ -HCH and its degradation product chlorobenzene on the solids (AC and AC–Fe–Cu), sacrificed batch reactions were conducted using the same reaction conditions as described above. At predetermined time of 15, 30, 60, 90 and 165 min, reactors were taken from the shaker and sacrificed for the analysis of γ -HCH and chlorobenzene. The reaction solution was filtered and the solid was transferred to a flask. Then the solid was Soxhlet (EPA Method 3541) with solvent for 48 h and γ -HCH and chlorobenzene were measured.

2.5. Analytical methods

 γ -HCH was analyzed employing a gas chromatograph (6890N GC, Agilent Corporation, USA) equipped with an electron capture detector (GC/ECD) and an HP-5 capillary column (30 m \times 0.32 mm \times 0.25 μ m, Agilent Corporation, USA). Injection was performed in splitless mode. The temperatures of the injector and detector were 200 and 300 °C, respectively. The GC oven temperature program was as following: isothermal at 100 °C for 1 min, 30 °C/min to 180 °C, kept for 1 min, then 5 °C/min to 200 °C, and finally at 30 °C/min to 240 °C. The carrier gas and the makeup gas were ultra-pure nitrogen at a flow rate of 1 ml/min and 60 ml/min, respectively.

 γ -HCH and its possible degradation products were identified using a gas chromatograph coupled with mass spectrometer (7890A GC-5975C MSD, Agilent corporation, USA). The temperatures of the injector, interface and MS source temperatures were 200, 150 and 230 °C, respectively. The GC oven temperature program was as following: isothermal at 35 °C for 1 min, 15 °C/min to 150 °C, kept for 4 min, then 6 °C/min to 225 °C, kept for 2 min, and finally at 15 °C/min to 250 °C. Automatic injections of 1 µl sample solution were made in splitless mode. The carrier gas was ultra-pure nitrogen at a flow rate of 1 ml/min. Full scan mode was used to obtain the mass spectra of the chemicals.

3. Results and discussion

3.1. Characterization of the nanoparticles

Fig. 1a, b compares the TEM images of the Fe^0 -Cu and AC-Fe⁰-Cu nanoparticles. The size of the Fe^0 -Cu nanoparticles



Fig. 1. TEM images of Fe^0 -Cu (a) and $AC-Fe^0$ -Cu (b); SEM image of $AC-Fe^0$ nanoparticles (c) and the XRD images of the nanoparticles (d-1) nano-Fe⁰; (d-2) nano-Fe⁰/Cu; (d-3) $AC-Fe^0$; (d-4) $AC-Fe^0$ -Cu.

was <30 nm, and they clustered in the medium. The agglomeration was attributed to the magnetic interactions between the metallic particles, resulting reduced available reactive surface area for contaminant degradation. In Fig. 1b, the large gray sheets are AC supports, while the smaller and black particles are metal particles. The TEM images of Fe⁰ and AC–Fe⁰ are similar to those of the Cu amended nanoparticles (which are not shown). Apparently, the immobilization of metallic particles with AC prevents their agglomeration and thus maintains their high surface area and reactivity. Schrick et al. prepared hydrophilic carbon-supported iron nanoparticles by similar methods and confirmed that there was a strong association between the carbon support and the iron particles using TEM image (Schrick et al., 2004). Fig. 1c shows the SEM image of the impregnated AC–Fe⁰ nanoparticles. The white globular clusters are nanoscale metal particles and the large gray sheets are AC. It is clear that the metal particles are well attached to the surface and also incorporated in the mesopores (dark area in Fig. 1c) of AC.

Fig. 2 illustrates the elemental distribution of $AC-Fe^{0}-Cu$ particles using SEM-EDX. The AC as a background material is covered by Fe. Fe and Cu elements are evenly deposited on the surface of the AC support. In addition, O element is also present, indicating the presence of Fe₂O₃ or Fe₃O₄, which could be formed due to the oxidation of Fe during the transfer and processing of the material for the characterization analysis. But the signal of O is very weak, implying that most Fe element is present as ZVI. The Cu content on the surface of ZVI particles characterized by SEM-EDX is 1.628, 2.558, 3.411, 6.073 and 8.599% in Cu/Fe w/w respectively.

The XRD of the unsupported and supported nanoscale particles are illustrated in Fig. 1d (1–4). The apparent peak at the 2θ of 44–45° in all samples indicates the presence of α -Fe⁰. Because of the small size of the particles, the peaks in the XRD pattern are relatively broad (Nurmi et al., 2005; Wang et al., 2009b). A small peak at 2θ of 35–40° also suggests that Fe⁰ was partially oxidized to α -Fe₂O₃ or Fe₃O₄ (Wang et al., 2009a). Due to the low content of crystal Cu in the bimetallic nanoparticles, the characteristic peak of Cu is not observed in the XRD pattern of Fe⁰–Cu (Fig. 1d (2)) and AC–Fe⁰–Cu (Fig. 1d (4)). However, Cu element which deposited on the iron surface is observed in Fig. 2 by SEM-EDX. An obvious diffraction peak (\blacklozenge) at the 2 θ of 22–26° in the XRD patterns of supported nanoparticles (Fig. 1d (3, 4)) indicates the crystalline nature of graphite, which is due to the graphite structure of the AC (Hsieh et al., 2009).

The XPS spectrum of the AC impregnated nanoparticles is shown in Fig. 3. The binding energies obtained in XPS analysis are corrected with the reference of C1s (284.6 eV). The characteristic binding energies at 707.49 and 720.50 eV for Fe $2p_{3/2}$ and $2p_{1/2}$ peaks confirm the presence of Fe⁰. The two intense peaks observed at 711.08 and 725.50 eV indicate that Fe₂O₃ is also present on the surface of the material. The sharp and intense peaks $2p_{3/2}$ and $2p_{1/2}$ observed at 933.01 and 952.90 eV are ascribed to the metallic copper. The result of XPS suggests that Fe is in zero and tri-valent electronic states, while Cu is in zero valent electronic state.

3.2. Effect of Cu loading on dechlorination efficiency

The following pseudo first-order reaction kinetic model may be used to describe the dechlorination reaction of γ -HCH using the nanoparticles (Matheson and Tratnyek, 1994; Johnson et al., 1996)

$$C_{\gamma-\text{HCH,t}}/C_{\gamma-\text{HCH,0}} = e^{-k_{\text{obs}}t}$$
(3)

where $C_{\gamma-\text{HCH}, t}$ is the concentration of γ -HCH in aqueous phase (mg/L), $C_{\gamma-\text{HCH}, 0}$ is the initial concentration of γ -HCH (mg/L), k_{obs} is the pseudo first-order rate constant (min⁻¹) and t is the reaction time (min). The pseudo first-order reaction kinetic model fitted the experimental data very well with regression coefficient $R^2 > 0.96$ in all cases. A linear fitting of $\ln(C/C_0)$ and t would give the reaction rate constant k_{obs} . The k_{obs} s of the reactions with bimetallic nanoparticles containing different loading of Cu are listed in Table 1. The



Fig. 2. Energy dispersive X-ray spectroscopy of AC-Fe⁰-Cu. (a) The chosen region of AC-Fe⁰-Cu particles for EDX. (b) Typical energy peaks of EDX.

 $k_{\rm obs}$ s of the reactions using bimetallic particles are all greater than that of using mono Fe⁰ particles. The dechlorination efficiency increased as Cu content increased from 0 to 6.073 wt% and then slightly decreased as the content further increased to 8.599%. The maximum $k_{\rm obs}$, which was achieved at copper loading of 6.073%, was 5 times of the reaction using pure Fe⁰ particles. It is widely reported that the deposition of a small amount of a secondary metal, such as Pd, Pt, Ag and Ni, on the surface of ZVI may enhance the dechlorination efficiency (Grittini et al., 1995; Feng and Lim, 2005; Agarwal et al., 2007; He et al., 2007; Lien and Zhang, 2007; Liou et al., 2009; Wang et al., 2009c; Chun et al., 2010). When Fe⁰ is used alone in a reaction, the halogenated compounds might be reductively degraded by the electrons transferred from iron metal or ferrous iron; or by hydrogen resulting from corrosion of Fe, on the surface of ZVI (Matheson and Tratnyek, 1994). The standard potential of Fe/Fe²⁺ is -0.44 V, making Fe a good reducing agent. The standard potential of Cu/Cu^{2+} is 0.337 V. As Cu is deposited on the surface of ZVI, many tiny galvanic cells are formed and the relative potential difference drives the electrons from Fe to Cu. The adsorbed hydrogen ions accept electrons and are then converted to adsorbed atomic hydrogen gas (H_{ads}) on the surface of Cu. H_{ads} acts as a good reducing agent and it reductively degrade the halogenated chemicals (Liou et al., 2009). Other studies also reported that hydrogen was produced on the surface of the second metal (Grittini et al., 1995; Cheng et al., 1997; Agarwal et al., 2007). Increasing the loading of Cu on the surface could increase the number of catalytic metal islands and/or the total cathodic areas on the Fe surface, leading to higher dechlorination efficiency. The doping of Cu of the surface of Fe accelerates the corrosion of iron metal and thus the removal of γ -HCH. However, over abundance of Cu coating on Fe⁰ might hinder the corrosion of iron and the formation of hydrogen on the surface, and result in the decrease of degradation rate. Deposition of iron corrosion products on the surface of Cu could also reduced the activity of Cu. Our result agrees



Fig. 3. XPS spectrum of AC–Fe⁰–Cu nanoparticles. (a) Fe; (b) Cu.

with those in other reports (Nutt et al., 2005; Lien and Zhang, 2007; Wang et al., 2009c).

3.3. Removal of γ -HCH by supported nanoscale particles (AC-Fe⁰ and AC-Fe⁰-Cu)

The disappearance kinetics of γ -HCH in the aqueous phase is shown in Fig. 4a. The supported nanoscale particles provide faster reaction rates toward γ -HCH than the corresponding unsupported nanoscale particles. The removal of γ -HCH by supported nanoparticles might be the results of simultaneous adsorption of γ -HCH on AC and dechlorination on nanoscale particles. The adsorption kinetic on AC also follows pseudo first-order kinetic model ($R^2 = 0.9932$) and its adsorption rate constant is also expressed as k_{obs}

Table 1 Reaction rate constants and half lives for reduction of γ -HCH by (supported) nanoscale metal particles.

Serial number	$k_{\rm obs}({\rm min}^{-1})$	$t_{1/2}$ (min)	R^2
Fe ⁰ (0%)	0.0128	54.4	0.9633
Fe ⁰ —Cu (1.628%)	0.0168	41.4	0.9908
Fe ⁰ —Cu (2.558%)	0.0294	23.6	0.9900
Fe ⁰ —Cu (3.411%)	0.0338	20.5	0.9892
Fe ⁰ —Cu (6.073%)	0.0565	12.3	0.9927
Fe ⁰ —Cu (8.599%)	0.0415	16.7	0.9779
AC-Fe ⁰	0.0141	49.2	0.9796
AC-Fe ⁰ -Cu (6.073%)	0.1065	6.5	0.9979
AC	0.0911	7.6	0.9932



Fig. 4. (a) Removal kinetics of γ -HCH by AC, unsupported and supported nanoscale metal particles; (b) The variation of γ -HCH in the solids (AC, AC–Fe⁰ and AC–Fe⁰–Cu) with time. C_0 is the initial mass concentration of γ -HCH. The total amount of γ -HCH and its degradation products in the liquid and solid phases should be equal to C_0 . Reaction conditions: pH 7.0; AC 0.25 g/L; γ -HCH initial concentration at 5 mg/L. The solid inc in Fig. 4a show the first-order kinetic fits.

for easy comparison. The disappearance kobs decreases in the order of $AC-Fe^{0}-Cu$ particles (0.1065 min⁻¹) > AC (0.0911 min⁻¹) > $Fe^{0}-Cu$ $(0.0565 \text{ min}^{-1}) > \text{AC}-\text{Fe}^0 (0.0141 \text{ min}^{-1}) > \text{Fe}^0 (0.0128 \text{ min}^{-1}, \text{See})$ Table 1). It is interesting that AC alone provided high removal efficiency for γ -HCH. However, the contaminants remain intact and would pose potential threat to the environment. During the first 60 min of the reaction, the supported nanoparticles displayed significantly faster reaction rate than the neat nanoparticles without support, indicating that incorporation the nanoparticles to AC accelerated the removal of γ -HCH from the solution. It was reported that the degradation of halogenated compounds by Fe⁰ happens at the interface of Fe⁰/H₂O (Matheson and Tratnyek, 1994; Grittini et al., 1995). The strong adsorption capacity of AC enhances mass transfer of γ -HCH in the solution and the contact of target compounds with Fe⁰. In addition, the carbon support enhances the dispersivity of Fe⁰ particles, resulting more available reactive sites. As a result, the reactivity of the impregnated particles is promoted. The stabilizing effect of AC support in enhancing reaction rate was also reported in previous studies (He and Zhao, 2005).

The concentrations of γ -HCH and its degradation products in the solids were monitored and carbon mass balance in the reaction system was calculated. The results are illustrated in SI Fig. S2. Mass balance was calculated on the basis of concentrations of γ -HCH and

its degradation products (Tetrachlorocyclohexene (TeCCH) and chlorobenzene (CB)) detected in both liquid and solid phases. As shown in SI Fig. S2, the mass balance was in the range of 88–114% in the system using neat nanoparticles of Fe⁰–Cu. As a comparison, the mass balance in the system with AC–Fe⁰–Cu was slightly lower. It decreased with reaction time and was in the range of 75–100%. The lower recovery in the system of AC–Fe⁰–Cu could be explained in two aspects: 1) The strong affinity of γ -HCH and its degradation products to AC–Fe⁰–Cu particles makes incomplete extraction recovery of these compounds from the solids. 2) Due to the strong degradation capability of AC–Fe⁰–Cu, γ -HCH was further degraded to smaller molecules beyond TeCCH and CB, which were not identified and quantified by the GC/MS analysis.

The time evolution of γ -HCH in the solids is shown in Fig. 4b. The disappearance of γ -HCH in the AC system is solely due to the adsorption. The adsorption of γ -HCH on AC reached equilibrium in 90 min and around 93.4% of γ -HCH was adsorbed at equilibrium. In the solution with AC-Fe⁰ and AC-Fe⁰-Cu, 89.3% and 98.4% of γ -HCH was removed after reaction for 165 min (Fig. 4a). This is the result of adsorption and degradation by the particles. In addition, it was reported that Fe corrosion in the pH range of natural waters vielded an obstructive oxide film of corrosion products on the metal surface. Therefore, adsorption and co-precipitation of γ -HCH and its degradation products with the corrosion products might contribute partially to the removal of γ -HCH from the solution (Noubactep, 2008, 2010; Noubactep and Caré, 2010). However, only 12.8% and 0.49% of γ -HCH and negligible degradation products were found in the solids of AC–Fe⁰ and AC–Fe⁰–Cu at the end of reaction (Fig. 4b), indicating that most adsorbed γ -HCH was degraded immediately by the supported metal. Interestingly, the time evolution of γ -HCH in the AC–Fe⁰ and AC–Fe⁰–Cu solid phase is different. γ -HCH in AC–Fe⁰ increased gradually during the whole reaction while it increased shortly after the reaction and then decreased to very low level in AC–Fe⁰–Cu. This implies that the adsorbed γ -HCH could be degraded by AC–Fe⁰. However, its degradation efficiency is not high enough, leading the accumulation of γ -HCH in the solid. After 165 min reaction, around 76.5% of γ -HCH was degraded and 12.8% was adsorbed on the solid. In the case of AC-Fe⁰-Cu, the enhanced dechlorination capacity resulted in almost complete degradation of γ -HCH while it was adsorbed. At the end of reaction, almost 99% of γ -HCH was destroyed.

3.4. Mechanism of the dechlorination of γ -HCH

TeCCH and CB were identified as the major intermediate and final products of γ -HCH in most batch experiments by GC/MS. In addition, in the reaction system with AC–Fe⁰–Cu, trace amount of pentachlorocyclohexane and pentachlorocyclohexene were observed while they were not present in the system of AC–Fe⁰. Liu et al. reported that HCH may be degraded via two major reaction mechanisms: dechloroelimination (-2Cl) and dehydrohalogenation (-HCl) (Liu et al., 2003). As discussed above, hydrogen was involved as a reducing reagent in the degradation reaction by AC–Fe⁰–Cu. H_{ads} might reduce γ -HCH by hydrogenation and sequential dehydrohalogenation or by direct dehydrohalogenation to produce pentachlorocyclohexane and pentachlorocyclohexene. Then they were continuously degraded to TeCCH by further dehydrohalogenation, which is a reactive intermediate and might be further degraded to dichlorocyclohexadiene (DCCD) by further dichloroelimination. TeCCH had been detected as a major intermediate in the anaerobic biodegradation of β -HCH (Middeldorp et al., 1996; van Doesburg et al., 2005). In this study, sodium azide was added to inhibit the microbial activity. Therefore, the degradation reaction was due to the reduction by nanoscale metal particles. DCCD was not detected as an intermediate in the reaction solution because it is a very reactive intermediate and may disappear quickly. DCCD may be degraded quickly to CB via dehydrochloration. Elliott et al. studied the degradation of γ -HCH using non-stabilized Fe⁰ and identified TeCCH and benzene. They proposed a degradation pathway of γ -HCH to TeCCH to DCCD and finally to benzene. In their study, a relatively low level of benzene was observed with high initial γ -HCH concentration (300–600 mg/L) in ethanol (Elliott et al., 2009). The formation of benzene cannot be ruled out in our study since the initial concentration of γ -HCH was only 5 mg/L. But it seems that CB is the major final product while benzene is a minor one. This is different from the result reported by Wang et al. who only detected CB and benzene with granular Fe⁰ as a reductant. In their study, benzene was a major product but CB was a minor one (Wang et al., 2009d).

The variation of γ -HCH and the major products formed in the solution are shown in Fig. 5. It was found that the amount of TeCCH and CB increased with the decrease of γ -HCH. TeCCH concentration increased shortly after the reaction got started and then decreased. It was almost zero after reaction for 165 min (Fig. 5). However, the concentration of CB increased continuously during the experiments, suggesting that CB might be one of the final products. TeCCH was not accumulated in the course of the reaction. Thus, it is more likely that it was further degraded to CB or benzene.



Fig. 5. Evolutions of γ -HCH and its major dechlorination products with reaction time in the liquid with (a) Fe⁰ and AC-Fe⁰; (b) Fe⁰-Cu and AC-Fe⁰-Cu as reducing reagents. C_0 is the same as described in Fig. 4.



Fig. 6. The possible pathways of γ -HCH degradation by Fe/Cu bimetallic nanoparticles.

Fig. 5 also compares the variation of the major intermediates using unsupported and supported nanoparticles. The concentrations of the major products, such as TeCCH and CB, in the solution using supported nanoscale particles were lower than that using unsupported ones. This might be due to the strong adsorption of γ -HCH and its degradation products on AC support. It also further confirms the concurrence of adsorption and dechlorination of γ -HCH on supported nanoparticles. The existence of AC prevents the release of these organic chemicals into water solution and diminishes their potential adverse effects to aqueous bioorganisms.

Based on the above discussion, Fig. 6 illustrates the degradation pathway of γ -HCH by AC–Fe⁰–Cu. It was degraded to form TeCCH by three reaction pathways: dechloroelimination (–2Cl), dehydrohalogenation (–HCl) and hydrogenation followed by dehydrohalogenation. TeCCH was degraded successively to DCCD by dechloroelimination, and then presumably further degraded to CB or benzene.

4. Conclusions

In this study, it was demonstrated that the amendment with Cu could enhance the dechlorination efficiency of nano Fe⁰ toward γ -HCH. The removal efficiency of γ -HCH was further improved when the nanoscale metal particles were incorporated in the mesopores of AC. The AC support has several functions: 1) It diminishes the agglomeration of nanoscale particles and maintains

their high reactivity; 2) it can adsorb γ -HCH and its degradation products, reducing the concentrations of these chemicals in the aqueous solution and their ecological risks in water; 3) it increases the contact of γ -HCH with the nanoparticles and accelerates the reaction rate of the degradation of contaminants. The AC-supported bimetallic nanoparticles could be used as a potential material to remediate γ -HCH in water. Further research is needed to investigate its application in real world.

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Appendix. Supplementary data

Preparation of activated carbon (AC); Characterization methods for AC; Characterization results; Elemental composition and ash content of tire rubber and the obtained AC; Properties of the AC determined from nitrogen adsorption; TEM image of the AC; Carbon mass balance of the systems with Fe–Cu and AC–Fe–Cu. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.envpol.2011.06.021.

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