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# Dechlorination of γ-hexachlorocyclohexane by zero-valent metallic iron

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ABSTRACT

This study investigated the rates and pathways of γ-hexachlorocyclohexane (γ-HCH) dechlorination by granular zero-valent iron under different pH, iron dosage and temperature conditions. It was found that γ-HCH was rapidly reduced to benzene and chlorobenzene (CB) with benzene as the major product and that the dechlorination likely follows three steps of dichloroelimination to benzene, or two steps of dichloroeliminations and one step of dehydrohalogenation to CB. The calculated pseudo-first-order rate of γ-HCH degradation was 0.0125 $\text{min}^{-1}$ at pH 6.73, 25 °C and 10 g $L^{-1}$ iron dosage, corresponding to 55.5 min of half-life. It was also found that the rate of γ-HCH dechlorination increases as a function of reaction temperature and zero-valent iron dosage and decreases as a function of solution pH. The calculated activation energy is 33.5 kJ $\text{mol}^{-1}$ at pH 6.73, which is much lower than that of dehydrohalogenation facilitated by hydroxyl under basic conditions. The study suggested that zero-valent iron could be used to effectively and efficiently transform γ-HCH.

## 1. Introduction

γ-Hexachlorocyclohexane (γ-HCH) (also called lindane), the effective component of technical insecticide HCH, had been widely used in agriculture in the mixture of technical HCH or in pure lindane throughout the world since 1940s. It is estimated that around 10 million tons technical HCH was used between 1947 and 1997 [1]. The total use of technical HCH estimated was up to about 4.46 million [2] or about 4.9 million tons [3] in China. The technical HCH has been gradually banned in developed countries since 1970s and in developing countries since 1980s due to its proven adverse effect on human and other animal health and the serious environmental problems caused by the worldwide usage of HCH [4]. However, lindane is still used in developed countries and the mixture in some developing countries [1]. For example, both technical HCH and lindane have been used in India; and lindane is currently being used for seed treatment in Canada and United States. In addition, there are tons of HCH produced over the past and are still stored in containers waiting for being disposed of [5]. It is desirable to develop remediation technologies to clean up soil, water, and waste sites contaminated by γ-HCH and to help speed up disposal of phased-out HCH products.

Over the last decade, there is a growing interest in potential use of zero-valent metals for reductive dechlorination of toxic chlorinated compounds [6–12]. Zero-valent iron is a popular metal due to its inexpensive and environmentally benign nature. Prior studies have shown that γ-HCH undergoes dehydrochlorination and hydrolysis in heterogeneous catalytic reduction systems with Pd/C, Pt/C and Raney-Ni [13] and with Pd/$Al_2O_3$ [14] to yield benzene as the major final product. However, direct application these reaction schemes for remediation may be prohibitively expensive due to the use of noble metals as the catalysts. In 1996, Schlimm and Heitz reported that lindane could be dechlorinated to benzene and CB by zero valent zinc or the bimetallic catalysts of Fe/Cu, Al/Cu, Zn/Cu, and Mg/Cu [15], but no systematic study on HCH transformation by zero-valent iron was reported. This study was initiated to investigate the reaction pathways and rates and the influence of experimental conditions on the reaction kinetics of HCH dechlorination.

## 2. Experimental

### 2.1. Chemicals and solutions

Iron powder (<100 mesh) was obtained from Fisher Scientific Co (Pittsburgh, PA) and used as received. Its specific surface area (0.1582 $m^2\,g^{-1}$) was measured in this study with the standard nitrogen adsorption method on an ASAP 2010 surface analyzer (Micromeritics Co., Norcross, GA, USA). γ-HCH, hexachlorobenzene (HCB), CB, benzene, pentane and acetone were obtained in their highest grades available from Aldrich–Sigma Co (St. Louis, MO). Sodium chloride (NaCl), acetic acid (HAc), sodium acetate

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**Table 1**
Lists of experimental conditions, molar ratio of CB to benzene, recovery efficiency mass recovery and pseudo-first-order rate constants for dechlorination of lindane by zero-valent metallic iron.

| pH | $Fe^0$ dosage ($g\,L^{-1}$) | Reaction temperature (°C) | Recovery efficiency (%) | CB/benzene | $k_{overall,obs}$ ($min^{-1}$) | $k_{1,obs}$ ($min^{-1}$) | $k_{2,obs}$ ($min^{-1}$) |
|---|---|---|---|---|---|---|---|
| 4.67 ± 0.02 | 10 | 25 | 71 | 0.09 | 0.0798 ± 0.0054 | 0.0716 ± 0.0049 | 0.0056 ± 0.0004 |
| 6.73 ± 0.02 | 10 | 25 | 88 | 0.11 | 0.0125 ± 0.0004 | 0.0098 ± 0.0003 | 0.0009 ± 0.0001 |
| 8.30 ± 0.02 | 10 | 25 | 71 | 0.31 | 0.00039 ± 0.00004 | 0.00020 ± 0.00002 | 0.000064 ± 0.000007 |
| 6.73 ± 0.02 | 5 | 25 | 61 | 0.09 | 0.0021 ± 0.0003 | 0.0013 ± 0.0002 | 0.00010 ± 0.00001 |
| 6.73 ± 0.02 | 20 | 25 | 59 | 0.11 | 0.0358 ± 0.0013 | 0.0200 ± 0.0007 | 0.0021 ± 0.0001 |
| 6.73 ± 0.02 | 10 | 35 | 67 | 0.10 | 0.0146 ± 0.0006 | 0.0091 ± 0.0004 | 0.0009 ± 0.0001 |
| 6.73 ± 0.02 | 10 | 45 | 57 | 0.15 | 0.0271 ± 0.0008 | 0.0167 ± 0.0005 | 0.0019 ± 0.0001 |

(NaAc), potassium phosphate monobasic ($KH_2PO_4$), potassium phosphate dibasic ($K_2HPO_4$), Tris–HCl ($NH_2C(CH_2OH)_3$ HCl), tris ($NH_2C(CH_2OH)_3$) were purchased from Merck Chemical Co (Gibbstown, NJ). All chemicals were used as received.

Three different pH buffer solutions were prepared from Milli-Q water using the following electrolyte mixtures: HAc + NaAc for pH 4.67; $K_2HPO_4$ + $KH_2PO_4$ for pH 6.67; Tris–HCl + Tris for pH 8.30. The ionic strength of the buffer solutions was adjusted to 0.1 M with NaCl.

### 2.2. Batch experiment

The rates of γ-HCH reactions with zero-valent iron were measured at different temperatures with a batch technique and under seven different reaction conditions (Table 1). In brief, amber glass vials (7 ml, SUPELCO, Bellefonte, PA) capped with PTFE lined septa were used as the batch reactor systems which were prepared under $N_2$ atmosphere in a glove box. The initial aqueous solution of γ-HCH was prepared by spiking 200 ml buffer solution with 2 ml γ-HCH acetone stock solution. It contained ∼1% acetone by volume and γ-HCH of about 24 μM which was below its aqueous solubility of 25.7 μM [16]. Each of the reactors contained 5 ml of the initial γ-HCH solution and a pre-determined amount of iron (25, 50, or 100 mg). The reactors were immediately capped, removed from the glove box, and placed on a shaker for mixing at desired temperature (25, 35 or 45 °C) and 180 rpm. The reaction times were recorded at the start of mixing, and the chemical analysis of the first duplicate samples at time zero was considered as the initial concentration of the reactant.

At a designated time, duplicate reactors were taken from the shaker and were centrifuged at 3000 rpm for 3 min. The reactors were uncapped, and an aliquot (4 ml) of the supernatant was withdrawn immediately from each reactor and extracted with HPLC-grade hexane (0.4 ml) in a 5-ml vial by mixing 3 min on a mixer. The hexane was pre-spiked with HCB as the internal standard for detection and quantification of the reactant and the products during sample analysis. After mixing, a portion of the hexane extract was transferred immediately to a 2-ml GC vial with a disposable glass pipette. It was immediately analyzed for the concentrations of the reactant and final products using the analytical procedure described below.

### 2.3. Analytical procedure

The analyses of hexane extracts were performed using a gas chromatography (GC) with flame ionization detector (FID) (HP 6890 II, Agilent, Santa Clara, CA, USA). Chromatographic separations were accomplished using a Chrompack CP-sil 5CB column with a 50 m length, 0.25 mm i.d. and 0.25 μm film thickness. The detector temperatures were preset at 280 °C. Oven temperature was initially isothermal at 35 °C for 2 min, ramped from 35 to 150 °C at a rate of 15 °C $min^{-1}$, then ramped at 6 °C $min^{-1}$ to 300 °C. The total run time was 21.5 min. $N_2$ gas at 99.99% purity was used as both the carrier at a flow rate of 1 ml $min^{-1}$ and the makeup gas at 60 ml $min^{-1}$. In addition, selected samples were analyzed on a GC–MS (Finnigan model GC 8000$^{TOP}$ voyager) equipped with an HP-5 column (50 m × 0.32 mm × 0.25 μm, J&W Scientific, Folsom, CA) for further identification of possible intermediates and products. The conditions set for GC–MS were similar to those mentioned above for GC-FID.

The concentrations of γ-HCH and the final products in the hexane extracts were calculated from their respective GC peak areas against six-point standard curves established using external hexane solution standards. The concentrations of the reactant and the products in the aqueous solutions were calculated based on the volumetric ratio of the aqueous and hexane solutions.

## 3. Results and discussion

### 3.1. Products and their distributions

Benzene and CB were identified as the two final products of the reaction. They were confirmed using their respective external standards on GC-FID and GC–MS. No intermediate product was detected with the GC-FID technique. Further analysis of selected samples with GC–MS did not detect any additional product. Among the two final products, benzene was the major and CB was the minor product in all the systems tested. The product distribution pattern is consistent with previous studies of HCH reduction with zinc, iron [15], Pd/C, Pt/C and Raney-Ni [13], Pd/$Al_2O_3$ [14] as reductants or catalysts. It should be noted that benzene and CB were also the final two products of HCH biodegradation under the methanogenic conditions, but CB was the dominant product, whereas benzene was the minor [17,18]. CB was also detected as a product in FeS-containing system [19].

Fig. 1 presents a typical concentration profile of the reactant and the final products versus time for the batch systems of 10 g $L^{-1}$ $Fe^0$ tested at pH 6.73 and 25 °C. It clearly shows that the concentrations of the two products increase as the concentration of γ-HCH decreases. The figure also indicates that benzene is the major final product, whereas CB is the minor product. The molar ratio of CB to benzene is 0.11. The mass balance (on molar basis) of the reactant and the products shown in the figure indicates about 88% of recovery. The remaining mass might be lost due to adsorption and volatilization during reaction and subsequent extraction procedure.

The results observed for other reaction systems are listed in Table 1. For instance, the molar ratio of CB to benzene and the recovery efficiency were respectively 0.09 and 71% for the system tested at pH 4.67, 25 °C and 10 g $L^{-1}$ iron dosage, 0.31 and 71% at pH 8.30, 25 °C and 10 g $L^{-1}$ iron dosage, and 0.10 and 67% at pH 6.73, 35 °C and 10 g $L^{-1}$ iron dosage.

### 3.2. Possible reaction mechanisms

According to Liu et al. [19], HCH may be reduced via two major reaction mechanisms, dichloroelimination (–2Cl) and

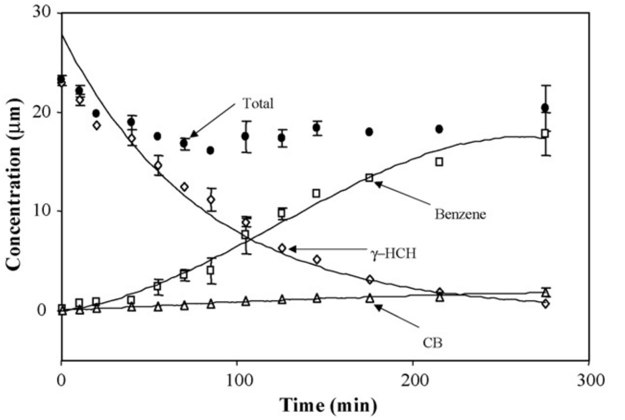

**Fig. 1.** The evolution of γ-HCH and its products in $Fe^0$ system at pH 6.73, 25 °C, and the iron dosage of 10 g/L. Symbols represent mean values of duplicate experimental data. Error bars indicate standard error of duplicate samples. Some error bars are smaller than data symbols. The lines represent the smooth lines of the data. Total (●), γ-HCH (◊), benzene (□), CB (△).

dehydrohalogenation (–HCl). It is expected that whether a reaction follows either dehydrohalogenation or dichloroelimination depends largely on the reactivity of the reactant and the relative positions of chlorines on the cyclic structure [19]. Fig. 2 schematically shows a possible degradation pathway of γ-HCH based on the identified final products and the reaction mechanisms of γ-HCH reduction. In the presence of $Fe^0$ surfaces, electrons provided by the solid may attack γ-HCH or intermediate products (polychlorinated cyclohexenes), forming a double bond by eliminating two $Cl^-$ or one HCl from each of these molecules. As shown in Fig. 2, γ-HCH likely undergoes dichloroelimination to form tetrachlorocyclohexene (TeCCH), followed by dichloroelimination to dichlorocyclohexadiene (DCDD), which can be further degraded to benzene via dichloroelimination. In parallel, γ-HCH may also be transformed to CB via three sequential steps; i.e., two steps of dichloroelimination and one step of dehydrohalogenation. The dehydrohalogenation step could be the first, the second or the third step of the three sequential steps of the reaction. It is assumed that the pathway involves two intermediates of TeCCH and DCDD, or three intermediates of TeCCH, DCCD and trichlorocyclohexadiene (TCCD), or four intermediates of TeCCH, DCDD, pentachlorocyclohexene (PCCH) and TCCD which were not identified in our batch experiments. It seemed that these intermediates are not stable in the $Fe^0$–$H_2O$ system. As formed on the surface of iron, these intermediates may not have returned to the solution phase as they were further degraded immediately on the iron surface. The intermediates of TeCCH and DCCD were detected at low concentration levels in other studies of biological or abiotic transformation of HCH under methanogenic conditions [17,18] or in the presence of iron sulfide [19]. The PCCH was also observed in the reductive dechlorination of lindane catalyzed by iron sulfide [19].

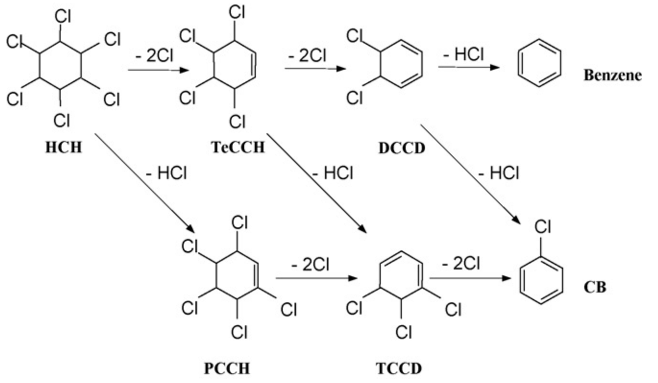

**Fig. 2.** Proposed possible pathways of γ-HCH dechlorination by zero-valent iron.

Other reaction schemes were not considered in this study. For instance, there would be three schemes for HCH dechlorination to form chlorinated benzene. They include: (i) HCH would undergo triple dehydrohalogenation to form 1,2,4-trichlorobenzene (1,2,4-TCB) [13]; (ii) HCH would be first transformed to PCCH *via* dehydrohalogenation, and then to TCBs *via* simultaneous eliminations of two chlorine and two hydrogen atoms [19]; and (iii) γ-HCH would undergo dichloroelimination to form TeCCH as shown in Fig. 2, and then TeCCH would be further degraded to dichlorobenzene (DCB) *via* double dehydrohalogenation [19]. Moreover, TCBs or DCBs would theoretically be dechlorinated to CB and to benzene. These schemes, however, are not likely because TCBs and DCBs were not detected in our batch systems. Xu and Zhang reported that HCB was dechlorinated by zero-valent iron to tetrachlorobenzenes (TeCBs), TCBs and DCBs within 24 h, but neither CB nor benzene was detected even after 200 h of mixing [20]. Their study suggested that CB in our batch systems was unlikely formed from TCBs or DCBs.

### 3.3. *Kinetics of γ-HCH dechlorination*

It is expected that the first step of γ-HCH dechlorination on iron surface is a second-order reaction, i.e., first order with respect to both γ-HCH and $Fe^0$ concentration. In systems initiated at a constant dosage of $Fe^0$, the surface activity of $Fe^0$ could be assumed constant at time zero. The reaction can be simplified to a pseudo-first-order reaction with respect to γ-HCH concentration. Mathematically, the rates of the disappearance of γ-HCH could be given below:

$$\frac{\partial C_{\gamma-\mathrm{HCH}}}{\partial t} = -k_{\mathrm{overall,obs}} C_{\gamma-\mathrm{HCH}} \tag{1}$$

or

$$C_{\gamma-\mathrm{HCH}} = C_{\gamma-\mathrm{HCH},0} e^{-k_{\mathrm{overall,obs}} t} \tag{2}$$

where $C_{\gamma\text{-HCH}}$ and $C_{\gamma\text{-HCH},0}$ are the time-dependent and the initial concentrations of γ-HCH, respectively; $k_{\mathrm{overall,obs}}$ is the overall rate constant for the disappearance of γ-HCH; $t$ is the reaction time.

Formation of the benzene and CB can be simplified as two parallel pathways since the intermediates were highly reactive and could be dechlorinated rapidly on the surface of iron as discussed above. In such a simplified model, the time-dependent concentrations of benzene and CB can be estimated with the following two expressions [21]:

$$C_{\mathrm{B}} = \frac{k_{1,\mathrm{obs}}}{k_{\mathrm{overall,obs}}} C_{\gamma-\mathrm{HCH},0}(1 - e^{-k_{\mathrm{overall,obs}} t}) \tag{3}$$

$$C_{\mathrm{CB}} = \frac{k_{2,\mathrm{obs}}}{k_{\mathrm{overall,obs}}} C_{\gamma-\mathrm{HCH},0}(1 - e^{-k_{\mathrm{overall,obs}} t}) \tag{4}$$

where $C_{\mathrm{B}}$ and $C_{\mathrm{CB}}$ are the time-dependent aqueous concentrations of benzene and CB, respectively; $k_{1,\mathrm{obs}}$ and $k_{2,\mathrm{obs}}$ are the observed pseudo-first-order rate constants for the formation of benzene and CB, respectively.

By inserting Eqs. (2)–(4) can be further reduced to:

$$C_{\mathrm{B}} = \frac{k_{1,\mathrm{obs}}}{k_{\mathrm{overall,obs}}}(C_{\gamma-\mathrm{HCH},0} - C_{\gamma-\mathrm{HCH}}) \tag{5}$$

$$C_{\mathrm{CB}} = \frac{k_{2,\mathrm{obs}}}{k_{\mathrm{overall,obs}}}(C_{\gamma-\mathrm{HCH},0} - C_{\gamma-\mathrm{HCH}}) \tag{6}$$

The values of $k_{\mathrm{overall,obs}}$, $k_{1,\mathrm{obs}}$ and $k_{2,\mathrm{obs}}$ were obtained by fitting each experimentally measured dataset into Eqs. (2), (5), (6) using a nonlinear least squares regression approach. The resulting $k_{\mathrm{overall,obs}}$, $k_{1,\mathrm{obs}}$ and $k_{2,\mathrm{obs}}$ values are listed in Table 1.

As shown in Table 1, the $k_{\mathrm{overall,obs}}$ values appeared to be rather great. For instance, it is up to $0.0146 \pm 0.0006\,\mathrm{min}^{-1}$ for the system tested at pH 6.73, 25 °C and $10\,\mathrm{g\,L}^{-1}$ iron dosage, and $0.0798 \pm 0.0054\,\mathrm{min}^{-1}$ at pH 4.67, 25 °C and $10\,\mathrm{g\,L}^{-1}$ iron dosage, suggesting the zero-valent iron is an efficient candidate for rapidly reducing γ-HCH. The reaction rate of γ-HCH by zero-valent iron is far greater than γ-HCH hydrolysis rates [19,22,23], transformation rate of γ-HCH using FeS as a reductant [19], and its biodegradation rates [24,25].

Since benzene is the major product of the reaction, the rate constant for the formation of benzene ($k_{1,\mathrm{obs}}$) is far greater than the rate of formation CB ($k_{2,\mathrm{obs}}$) for the same reaction system (Table 1). According to the above simplified model, the sum of $k_{1,\mathrm{obs}}$ and $k_{2,\mathrm{obs}}$ values would be equal to the $k_{\mathrm{overall,obs}}$ value; but it is less than the $k_{\mathrm{overall,obs}}$ value. The difference may be due to that fact that the mass balance is less than 100%.

### 3.4. *Effects of temperature*

As shown in Table 1 and Fig. 3, the dechlorination rate ($k_{\mathrm{overall,obs}}$) depends strongly on reaction temperature conditions. The best fit $k_{\mathrm{overall,obs}}$ values are 0.0125, 0.0146 and $0.0271\,\mathrm{min}^{-1}$ at temperature of 25, 35, and 45 °C, respectively, indicating that increasing of reaction temperature results in a faster dechlorination of γ-HCH. The dependence of the reaction rates on temperature can be delineated with the Arrhenius equation

$$k_{\mathrm{overall,obs}} = A \exp\left(\frac{-E_a}{RT}\right) \qquad (7)$$

or

$$\ln(k_{\mathrm{overall,obs}}) = \frac{\ln(A) - E_a}{RT} \qquad (8)$$

where $k_{\mathrm{overall,obs}}$ is the observed pseudo-first-order reaction rate constant ($\mathrm{min}^{-1}$), $A$ is the pre-exponential factor, $E_a$ is the reaction activation energy ($\mathrm{kJ\,mol}^{-1}$), and $R$ and $T$ are the universal gas constant and the absolute temperature ($K$), respectively. A linear regression of the rate constants against temperature yielded an $E_a$ value of $33.50\,\mathrm{kJ\,mol}^{-1}$ for γ-HCH transformation. This value is much lower than $84.6\,\mathrm{kJ\,mol}^{-1}$ reported by Ngabe et al. [22], $69\,\mathrm{kJ\,mol}^{-1}$ reported by Kubátová et al. [26], or $67.7\,\mathrm{kJ\,mol}^{-1}$ reported by Ren et al. [23] for base dehydrochlorination. The lower activation energy observed for our system is consistent with the faster rates of γ-HCH reaction with zero-valent iron.

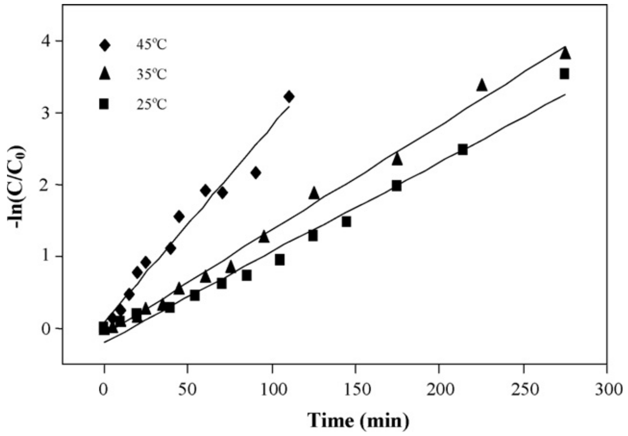

**Fig. 3.** Effect of different temperature value on the degradation of γ-HCH by iron.

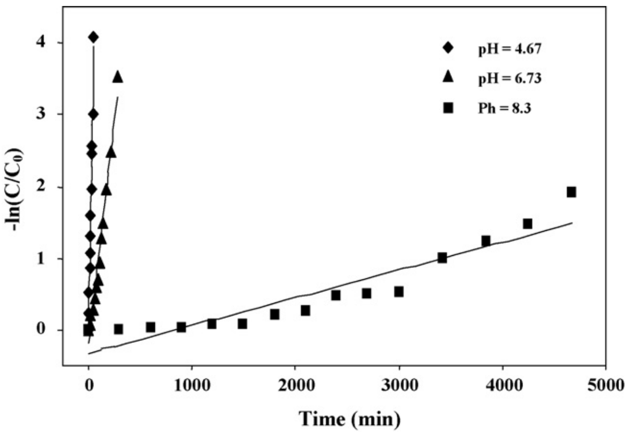

**Fig. 4.** Effect of initial solution pH on the degradation of γ-HCH by iron.

### 3.5. *Effects of initial pH*

The major reactions for degradation of halogenated organic compounds in oxygen-free $\mathrm{Fe}^0$–$\mathrm{H_2O}$ systems may be summarized as below [6,7,27]:

$$\mathrm{Fe}^0 \rightleftharpoons \mathrm{Fe}^{2+} + 2\mathrm{e} \qquad (8)$$

$$\mathrm{RCl} + \mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{RH} + 2\mathrm{Cl}^- \qquad (9)$$

As illustrated by Eq. (9), $\mathrm{H}^+$ ion (proton) and the electron play a very important role in the dechlorination reaction. Lower pH conditions favor higher activities of both proton and electron and hence speed up the overall reaction rates of chlorinated compounds. In addition, Fe(II) and Fe(III) precipitates often block surface sites and hence slower the reaction rate. Lower pH also increases the aqueous solubilities of Fe(II) and Fe(III), yielding less iron hydroxide precipitates on the surface of zero-valent iron. As shown in Table 1, the best-fit rate constants were 0.0798, 0.0125, and $0.00039\,\mathrm{min}^{-1}$, respectively, at pH 4.67, 6.78, and 8.3. Obviously, a lower initial solution pH value results in much faster dechlorination of γ-HCH as shown in Fig. 4. Matheson and Tratnyek [6], Agrawal and Tratnyek [9] and Agrawal et al. [10] and Lu et al. [28] also found that the reduction rates of $\mathrm{CCl_4}$, nitro-aromatic compounds and HCB by iron decreased with increasing pH. Matheson and Tratnyek [6] obtained a linear relationship between the pseudo-first-order rate constant $k_{\mathrm{obs}}$ and the pH values of buffer solutions ($k_{\mathrm{obs}} = -0.018\ (\pm 0.001)\ \mathrm{pH} + 0.20\ (\pm 0.01)$). However, similar linear relationship was not obtained for our study because the reaction was examined only in three pH conditions.

### 3.6. *Effects of iron content*

The effect of the zero-valent iron dosage on the dechlorination of γ-HCH was studied at pH 6.73 and 25 °C. The data are shown in Table 1 and the best-fit $k_{\mathrm{overall,obs}}$ values are 0.0021, 0.0125 and $0.0385\,\mathrm{min}^{-1}$ at the iron dosage of 5, 10 and $20\,\mathrm{g\,L}^{-1}$, respectively. Clearly, a higher iron dosage leads to faster dechlorination of γ-HCH as shown in Fig. 5. It is possible that the dechlorination of γ-HCH by iron particles occurs at the metal surface. The more available metal surface areas at higher iron dosage should increase the apparent rate of dechlorination.

To illustrate the iron content (i.e., the total surface area) dependence of the reaction rates, we plotted the $k_{\mathrm{overall,obs}}$ values in Fig. 6 against the iron dosage. The figure shows a linear correlation between the apparent reaction rate and the amount of iron present in the batch experiments. This is consistent with the surface mediated reaction [6,29]. Assuming a constant specific surface area of

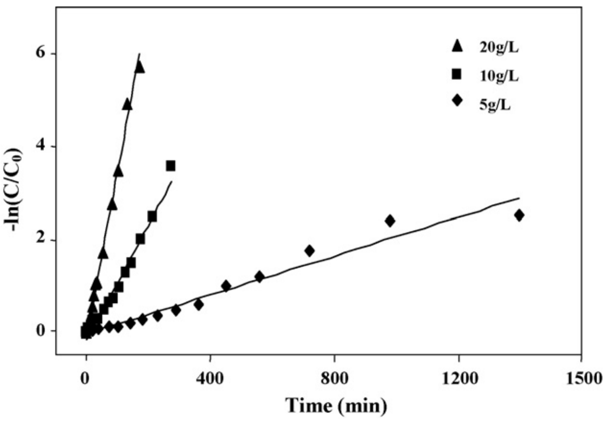

**Fig. 5.** Effect of initial concentration of zero-valent iron on the degradation of γ-HCH by iron.

0.1582 $m^2 g^{-1}$, a more general relationship between the rate constant ($k_{\text{overall,obs}}$) and the reactive surface area concentration [SA], can be regressed, yielding

$$k_{\text{overall,obs}} = 0.0143 \times [\text{SA}] - 0.0096 \qquad (10)$$

with $r^2 = 0.9993$ for $n = 3$. As shown in above equation and also in Fig. 6, the regressed line does not go through the origin, suggesting that the reactivity of the zero-valent iron particles changes with iron mass loading [30]. The negative intercept indicates that the granular iron reactivity increases with increasing iron loading in our batch systems. A possible explanation may be that phosphate added as the pH buffer may react with Fe(II) to precipitate at the surfaces, hence decreasing ZVI reactivity [31]. At lower ZVI loadings and hence higher phosphate to iron ratios, the majority of the ZVI surfaces may be covered with iron phosphate, resulting in lower reactivity of ZVI surface with lindane.

In summary, zero-valent iron is shown to effectively transform γ-HCH to benzene and CB. The reduction of γ-HCH is pseudo-first-order with respect to γ-HCH concentration and the transformation rate was strongly dependent on the pH values, iron dosage and temperature. The apparent rate of γ-HCH dechlorination is higher at higher reaction temperature, higher zero-valent iron dosage and lower solution pH. The study suggests that zero-valent iron is a suitable candidate for reducing γ-HCH.

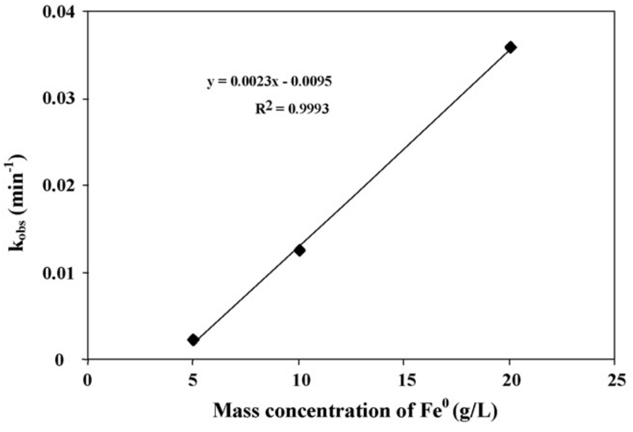

**Fig. 6.** The observed pseudo-first-order constants for γ-HCH transformation vs. $Fe^0$ dosage at 25 °C and pH 6.73.

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