

Effects of iron surface pretreatment on sorption and reduction kinetics of trichloroethylene in a closed batch system

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Abstract

The decline of trichloroethylene (TCE) in a metallic iron–water system results from the combination of reduction reaction and sorption onto iron surfaces. Sorption, particularly by highly impure iron, accelerates the removal of TCE from the aqueous phase, but delays the prevalence of steady-state conditions. In this case, an overly high value of reaction rate constant in the design of a treatment system would be used. In this work, the effects of an iron surface with 8.0% C, 6.1% O and 0.8% Si separately following HCl-washing and H₂-reducing pretreatment on sorption and reduction rates were examined. The amounts of both aqueous and sorbed TCE were measured using a modified solvent-extraction method. TCE sorption onto an iron surface, as quantified by the Langmuir sorption maximum, followed the trend H₂-reduced Fe⁰ > HCl-washed Fe⁰ > untreated Fe⁰ (0.887, 0.365 and 0.311 mg/g, respectively). Measurements of the concentration of sorbed TCE revealed that about 34–37% of the initial mass of TCE in the aqueous phase was removed by sorption by H₂-reduced Fe⁰, 16–19% was removed by HCl-washed Fe⁰ and 13–16% was removed by untreated Fe⁰. A combination of new and previously reported data on cast iron's capacity to sorb TCE revealed a linear relationship between this capacity and the C fraction in the surface of the iron, with the coefficient of determination (*r*²) exceeding 0.99. The first-order observed rate constants (*k*_{obs}) of the reduction of TCE in contact with Fe⁰ were obtained from the slope of a plot of total TCE loss rate ($-dC_T/dt$) versus the amount of TCE in the aqueous phase (*C*_w) using linear least-squares analysis. The *k*_{obs} values were 0.080, 0.148 and 0.191 h⁻¹ for untreated, HCl-washed and H₂-reduced Fe⁰, respectively. Normalized to iron surface area concentration, the specific rate constants (*k*_{SA}) were 2.37×10^{-3} , 2.31×10^{-3} and 5.62×10^{-3} h⁻¹ m⁻² L, respectively. The results indicated that HCl-washing approximately doubled *k*_{obs}, primarily because of the increase in the surface area of the iron, and it slightly decreased *k*_{SA} due to rapid corrosion during the rinsing process. Both the number of reactive sites and the sorption capacity per unit iron surface area through the H₂-reducing pretreatment were increased due to the reduction of iron oxide layer and the carbonization of carbon-containing subjects on the iron's surface. Hence, the H₂ reduction of cast iron promotes the removal of TCE from contaminated water by the concurrent sorption and reduction.

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Keywords: Zero valent metal; Permeable reactive barriers; Iron surface pretreatment; Acid-washing process

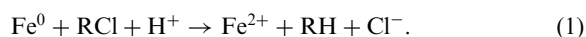
1. Introduction

The use of zero-valent metal as an electron source for the reductive dechlorination of halogenated organic

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compounds in wastewater or groundwater has been shown over the past few years to be potentially very effective (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Orth and Gillham, 1996; Agrawal and Tratnyek, 1996). Elemental iron (Fe^0) is the commonly chosen reactive metal because it is an inexpensive, nontoxic and natural material. Additionally, Fe^0 effectively destroys more complex anthropogenic chemicals, such as pentachlorophenol (Kim and Carraway, 2000), pesticides (Sayles et al., 1997) and azo dyes (Nam and Tratnyek, 2000). The typical reaction between Fe^0 and chlorinated hydrocarbons, denoted as RCl, under anaerobic conditions, in the absence of any other strong oxidants, such as carbonate, sulfate and nitrate, is as follows. (Matheson and Tratnyek, 1994; Agrawal and Tratnyek, 1996):



The process is similar to that of the corrosion of iron by chlorinated hydrocarbons substituting for oxygen as the oxidant. In this process, chlorinated hydrocarbons are transformed mostly into benign compounds such as hydrocarbons and chlorides.

Other than the reactivity of individual chlorinated hydrocarbons, Fe^0 surface characteristics, such as specific surface area, impurity, crystallinity and morphology (Su and Puls, 1999) are the most significant factors that influence the rate of reduction reaction. A pseudo-first-order rate model with respect to the aqueous phase concentration (Eq. (2)) effectively describes the disappearance of chlorinated solvents in contact with highly pure Fe^0 in a closed, well-mixed and anaerobic batch system.

$$-\frac{dC_w}{dt} = k_{\text{obs}} \times C_w, \quad (2)$$

where C_w is the concentration of contaminants in the aqueous phase; t is reaction time (h), and k_{obs} is the observed rate constant (h^{-1}). Then, k_{obs} can be expanded to (Johnson et al., 1996)

$$k_{\text{obs}} = k_{\text{SA}} \times a_s \times \rho_m, \quad (3)$$

where k_{SA} is the specific rate constant ($h^{-1} m^{-2} L$); a_s is the specific surface area of Fe^0 ($m^2 g^{-1}$), and ρ_m is the mass concentration of Fe^0 ($g L^{-1}$). Eq. (3) indicates that the amount of available surface area is the most important factor that governs the reduction rate. Studies have demonstrated the linear relationship of k_{obs} v.s. ρ_m for carbon tetrachloride (Matheson and Tratnyek, 1994), 1,2-dibromo-3-chloropropane (Siantar et al., 1996), nitrobenzene (Agrawal and Tratnyek, 1996) and trichloroethene (Su and Puls, 1999). Additionally, reducing the diameter of the iron particles to vary the a_s values also proportionally accelerates the apparent rate of dechlorination reaction (Siantar et al., 1996).

In fact, the disappearance of chlorinated hydrocarbons from the aqueous phase in contact with Fe^0 proceeds by concurrent sorption and reduction (Burriss et al., 1995; Kim and Carraway, 2000). Burriss et al. (1998) have demonstrated significant sorption of TCE and PCE by graphitic inclusions in a cast iron–water system. However, this effect has not usually been considered in laboratory experiments because of the use of highly pure Fe^0 . However, granular cast iron with a high content of impurities is practically used as a reductive medium in field application when economical considerations are important. The presence of impurities leads to apparent reaction orders that differ from one another (Li et al., 1999). Burriss et al. (1998) described the reaction rate model with accounting for sorption effect in a closed batch system:

$$\frac{dC_T}{dt} = -k_{\text{obs}} C_w^n, \quad (4)$$

$$\frac{dC_w}{dt} = -k_{\text{obs}} C_w^n - \frac{dC_s}{dt}, \quad (5)$$

where C_T , C_w , and C_s are the total system, aqueous phase and sorbed concentrations, respectively, of contaminants in milligram per vial and $C_T = C_w + C_s$; k_{obs} is the reaction rate constant; n represents the reaction order. Eqs. (4) and (5) state that the decline in the concentration of target contaminants in the batch system was caused only by reduction reaction at the Fe^0 surface; however, the apparent concentration in the aqueous phase was reduced by the combination of sorption and reduction reaction. Regardless of the mechanism of sorption, Eq. (5) can be simplified as Eq. (2), based on the assumption that n equals unity. However, this assumption yields an overly high k_{obs} value in the design of a treatment system. However, a material that can both sorb and reduce target contaminants, acting as a reductive medium, could reduce the risk associated with the passing of contaminants through a system. Thus, an understanding of the removal, by cast iron, of contaminants in the aqueous phase by sorption and reduction, individually, is important for designing and evaluating the performance of the treatment system.

At present, acid-washing pretreatment for virgin Fe^0 is the available method for removing the passivating oxide layer and increasing the Fe^0 surface area. The treatment of Fe^0 with dilute HCl has shown a faster reduction rate compared to the untreated one (Matheson and Tratnyek, 1994; Agrawal and Tratnyek, 1996; Su and Puls, 1999). The explanations for the effects of HCl-washing process on the apparent rate constants are (Matheson and Tratnyek, 1994; Agrawal and Tratnyek, 1996): (1) to dissolve the oxide layer on the Fe^0 surface

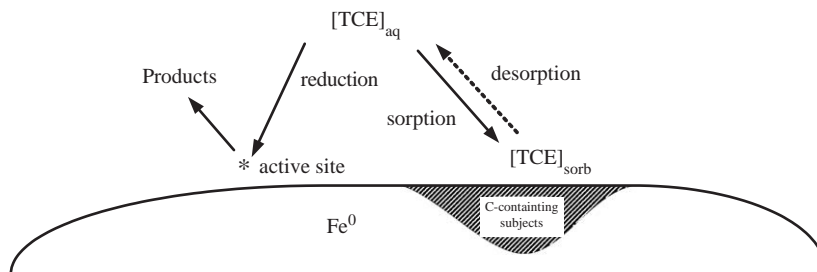


Fig. 1. A simplified conceptual model consisting of sorption/desorption and reduction for TCE by iron with graphite inclusions in a closed batch system.

and leave clean reduced Fe^0 free of nonreactive oxide or organic coatings; (2) to increase surface area due to corrosion etchings and pits; (3) to increase the density of highly reactive sites resulting from the locations of steps, edges, and kinks on the Fe^0 surface; (4) to accelerate the corrosion by sorbed H^+ and Cl^- . However, several drawbacks of this pretreatment method in practical applications have been shown and included: (1) the production of strongly acidic wastewater with a high concentration of iron ions; (2) the loss of about 15% mass of initial Fe^0 (Matheson and Tratnyek, 1994); (3) the acceleration of corrosion by sorbed H^+ and Cl^- . The above factors cause high variability in k_{obs} for different acid-washing processes and large restrictions on its application to in situ remediation.

In this study, the surface of Fe^0 was newly pretreated using reducing gas (20vol% H_2/N_2), before it was used to reductively destroy the aqueous TCE, to reduce the oxide layer and to carbonize the carbon-containing subjects on the iron's surface. This method offers many advantages over the acid-washing method for pretreating cast iron; for example, it produces no wastewater and simultaneously accelerates reduction and increases sorption capacity. The morphology and components of an exposed Fe^0 surface before and after the two pretreatments were identified using Scanning Electron Microscopy (SEM) and Energy Dispersion X-ray Spectroscopy (EDX), respectively. A simplified conceptual model consisting of the sorption/desorption and reduction of contaminants by iron with graphite inclusions in a TCE–iron–water system, is proposed (Fig. 1). The amounts of both aqueous and sorbed TCE mass were measured as functions of time to evaluate the order of the reaction rate (n) and the constant (k_{obs}) in Eq. (4). The purpose of this work was to elucidate the effects of the HCl-washing and the H_2 -reducing pretreatment of an iron surface with impurities on the reduction and sorption of TCE in a closed, anaerobic batch system.

2. Experimental Section

2.1. Chemicals

The chemicals used were trichloroethylene (99+%, Aldrich, Milwaukee, WI), n-hexane (HPLC grade, Fisher), *N*-[2-hydroxyethyl]piperazine-*N'*-[2-ethanesulfonic acid] acid (HEPES, Sigma) and iron powder (Wako Co., Japan). All aqueous solutions were made in water purified with a Milli-Q system (18.2 M Ω /cm). The desired concentrations of TCE in Ar-saturated water were prepared by dilution of a saturated TCE stock solution (1100 mg/L, 25 °C), which was made by stirring excess TCE with Ar-saturated water. Prior to use, the iron powders were hand-sieved to constrain particle size to a 325–400 mesh screen. The nominal purity of the cast iron was 95%. However, the elemental analysis by EDX revealed 85.1% Fe, 8.0% C, 0.8% Si and 6.1% O by average weight on the iron's surface.

2.2. Pretreatment methods for iron surface

2.2.1. Acid-washing process

The iron was pretreated by washing in Ar-sparged 10% HCl with periodic shaking for 30 min, then rinsed five times with vigorous shaking in Ar-sparged Milli-Q water to remove residual acidity and chloride, a method which is similar to that described previously (Matheson and Tratnyek, 1994; Agrawal and Tratnyek, 1996; Su and Puls, 1999). The HCl-washed iron was dried by vacuum freeze-drying technique (200×10^{-3} Torr and -56 °C for 24 h) before use.

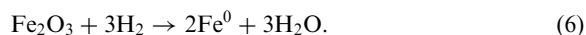
2.2.2. H_2 -reducing process

The iron was heated in a flow of H_2/Ar (20 Vol%, 60 ml/min) from ambient to 400 °C, keeping at 400 °C for 4 h to completely reduce the iron oxide. After cooling down to room temperature, the flow of H_2/Ar was then replaced by He (60 ml/min) to purge the reduced sample

for 10 min. The H₂-reduced Fe⁰ must be stored in a drying box.

2.3. Characterization of iron surface

Surface areas were determined by BET N₂ adsorption analysis on a Coulter SA3100 surface area analyzer (Coulter Co., Hialeach, FL). The morphology and size of the surface of the iron was viewed with SEM and localized elemental information from the chosen region with EDX in conjunction with SEM. Temperature programmed reduction (TPR) studies were performed to determine the required temperature for reducing iron oxide and the quantity of iron oxide with the apparatus similar to that described previously (Bond and Namijo, 1989). In that, a flow of H₂/Ar (20 vol%, 100 mL/min) was used as reducing gas. The oven temperature was programmed from ambient to 450 °C at 10 °C/min and keeping it at 450 °C for 1 h. The peak of H₂ consumption was assigned to Fe(III)→Fe⁰, represented as Eq. (6)



The quantity of H₂ consumption was obtained by comparing the area of this peak to that of 1 mL H₂ (40.9 μmol at 1 atm, 298 K) passing through the reactor of TPR. Simultaneously, the total number of Fe₂O₃ atoms was calculated by multiplying by a factor (1/3), consistent with the stoichiometry of Eq. (6).

2.4. Batch experiments

2.4.1. Reactor system

All experiments as functions of time were performed with 15 mL serum bottles. In each bottle, 0.3 g iron and 14.9(±0.1) mL Ar-purged buffered Milli-Q water (10 mM HEPES) were added with zero headspace. The use of HEPES as pH buffer avoids the effect of the variability in pH on the reaction rate over the duration of a typical experiment. Matheson and Tratnyek (1994) had demonstrated that HEPES interacted weakly with the iron and controlled the solution pH well. A 100 μL aliquot of TCE (1100 mg/L) was then added under the water level to cause the initial concentration of TCE at 7.3 mg/L. Immediately after TCE addition, the vials were capped with Teflon silicone septa and aluminum seals and then mixed on a rotary shaker (50 rpm) at room temperature (25 °C) in the dark.

2.4.2. Extraction

Aqueous phase and total system concentration of TCE were determined by liquid–liquid and liquid–solid extraction using n-hexane as a solvent. Firstly, 5 mL aqueous solution was sampled from the reactor system by a gas-tight syringe through the septa, and simultaneously another disposable needle of 13 mL He was

spiked through the septa to displace the liquid volume. Then, the 5 mL sample was extracted with 5 mL n-hexane by axial rotation on a roller drum at 20 rpm, and at room temperature in the dark for 15 min. Successive withdrawal of aqueous solution with the second gas-tight syringe was done for 9 mL aqueous solution, which was then thrown it away. Another syringe of 5 mL pentane was spiked through the septa to extract TCE of residual aqueous phase and sorbed phase in the vial. The extraction was achieved by axial rotation on a roller drum using the same extraction conditions.

2.4.3. Sample analysis

Two separate 0.5 mL samples of liquid–liquid and liquid–solid extraction were measured using a HP5890 GC equipped with a 30 × 0.53 mm (I.D) × 3.0 μm (thickness), DB-624 capillary column (J&W) and an electron capture detector operated in the splitless mode. Temperature conditions were programmed as follows: oven temperature at 50 °C; injection port temperature at 280 °C; detector temperature at 300 °C. Ultrapure nitrogen was the carrier gas for GC, and at a flow rate of 4.16 mL/min. The method detection limit for TCE was 0.2 μg/L. The total TCE mass (mg/vial) comes from the sum of both the measured masses in liquid–liquid and liquid–solid extraction. The sorbed TCE mass (C_s, mg/vial) was determined by the difference of total and aqueous TCE mass as follows:

$$C_s = C_T - C_w \times V_w \quad (7)$$

where C_T donates the total mass; C_w is the aqueous phase concentration; V_w is the volume of aqueous solution.

3. Results and discussion

Preliminary test was done using TPR to determine the required temperature for reducing iron oxides at the oven in flowing H₂/Ar (20 vol%, 60 ml/min). The TPR profile of the iron oxides on the untreated iron surface was shown in Fig. 2. A peak of hydrogen consumption appeared at 390–410 °C, which assigned to Fe(III)→Fe⁰. Thus, the pretreatment for Wako iron in a flow of 20 vol% H₂/Ar was set to be heated at 400 °C for 4 h (Table 1).

3.1. Characteristics of iron surface

The characteristics of exposed iron surfaces, washed with dilute HCl, reduced by H₂ and untreated, were compared. The specific surface areas obtained using N₂ adsorption by BET analysis were 1.8, 3.4 and 4.9 m²/g (Table 2) for untreated, HCl-washed and H₂-reduced Fe⁰, respectively. HCl-washing and H₂-reducing pre-

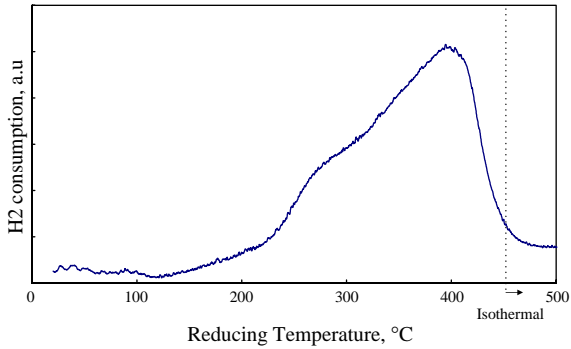


Fig. 2. The TPR profile of untreated Fe^0 in flowing 20 vol% H_2/Ar , heating from room temperature to 450 °C at 10 °C/min and then keeping it for 1 h.

treatment clearly increased the specific surface area. The morphology and contents of these three iron surface were analyzed using SEM and EDX. The H_2 -reduced Fe^0 in Fig. 3c yielded the same results as the untreated Fe^0 surface in Fig. 3a. However, the HCl-washed Fe^0 surface, depicted in Fig. 3b, exhibited many folds. This change was due to pitting or etching corrosion by HCl (Agrawal and Tratnyek, 1996), and increasing in the surface area. Table 1 presents the relative mass percentage of elements on the iron surface, including Fe, C, Si and O. The mass percentage of C element on the H_2 -reduced Fe^0 surface was much higher than that on the surface of untreated Fe^0 . The source of the C mass on the H_2 -reduced Fe^0 surface was the graphitic inclusions and the organic coating which were carbonized in flowing 20 vol% H_2/Ar . Accordingly, a greater C mass on the H_2 -reduced Fe^0 surface than on the untreated Fe^0 surface corresponded to a higher surface

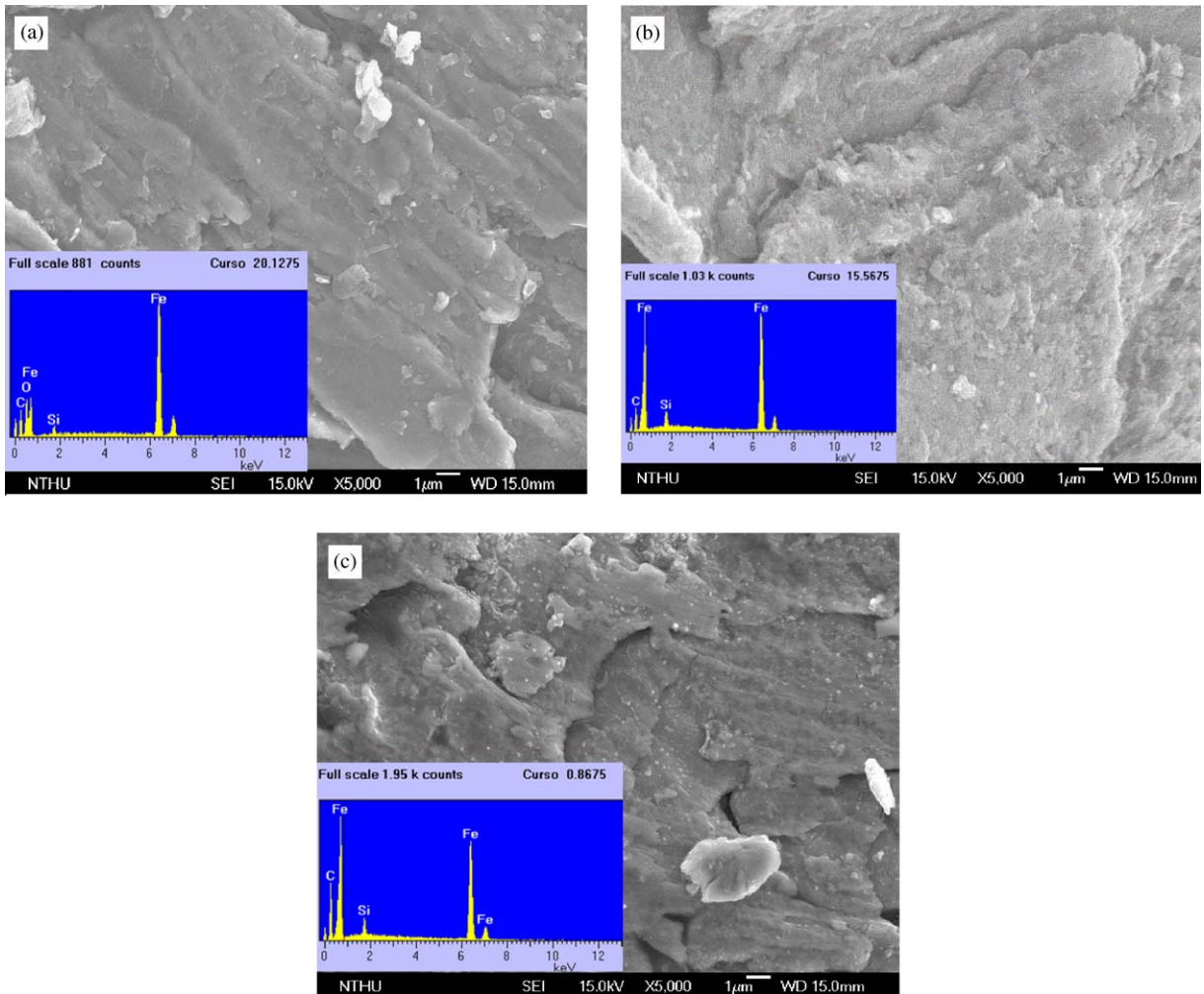


Fig. 3. The SEM and EDX images of iron surface at 5000 × magnification. (a) untreated Fe^0 , (b) HCl-washed Fe^0 , (c) H_2 -reduced Fe^0 .

Table 1
element analysis on the iron surface by EDX

Elemental Name	Untreated Wako Fe ⁰ (n = 5) ^a	HCl-washed Wako Fe ⁰ (n = 4)	H ₂ -reduced Wako Fe ⁰ (n = 4)
	Elemental wt%	Elemental wt%	Elemental wt%
Fe	85.1 ± 2.4 ^b	86.7 ± 3.2	82.0 ± 3.3
C	8.0 ± 0.8	8.3 ± 1.1	15.1 ± 2.6
Si	0.8 ± 0.1	2.2 ± 0.4	2.0 ± 0.4
O	6.1 ± 0.7	2.8 ± 0.2	0.9 ± 0.1
Total	100	100	100

^aThe value of *n* refers to the number of random analyses for the iron surface at 5000 × magnification.

^bAverage ± standard deviation.

area, even though no morphological change was observed. This fact was also evidenced by a dramatic difference between the TCE adsorption onto H₂-reduced Fe⁰ and that onto the untreated Fe⁰, considered in the next section. Additionally, the O fraction of HCl-washed iron surface components quickly rose to 2.7% (the rusted Fe fraction was 7.2%, see Table 2), due to corrosion during the rinsing process. In summary, the increase of the iron surface area (BET analysis) comes from the morphological change of HCl-washed Fe⁰ surface, but comes from the increase in the C fraction on H₂-reduced Fe⁰ surface.

The amount of H₂ consumed by the samples of iron (untreated, HCl-washed and H₂-reduced Fe⁰) was obtained by TPR; the total number of Fe₂O₃ atoms was calculated by multiplying by a factor consistent with the stoichiometry of Eq. (6). Then, the total mass of Fe₂O₃, which is 30% O and 70% Fe, on the surface of the iron was normalized to the specific surface area in the units of milligrams per meter square. The total Fe mass on the iron surface was calculated by multiplying the total O mass by the ratio of the mass percentages of Fe and O, given in Table 2. The fraction of the iron's surface that had rusted is thus represented as the ratio of the Fe mass bonded to O atoms to the total Fe mass on the surface. Table 2 shows the relevant values. The fraction of untreated Fe⁰ that rusted reached 16.7%. This sample had been unsealed for 6 months and then stored in a drying box. After pretreatment by washing with dilute HCl, the iron quickly combined with the O atoms, by oxidation reaction, during the rinsing process. In contrast, few O atoms remained on the H₂-reduced Fe⁰ surface after reducing by H₂.

3.2. TCE sorption onto cast iron

Sorption of TCE from solution onto the iron surface was observed by simultaneously measuring the amount

of both sorbed and aqueous TCE mass, described by the Langmuir isotherm. The form of the Langmuir isotherm is represented by

$$S = \frac{K_L S_m C}{(1 + K_L C)}, \quad (8)$$

where *S* is the amount sorbed on the iron surface at equilibrium (mg/g); *C* is the equilibrium aqueous concentration (mg/L); *S_m* is the sorption capacity (mg/g); *K_L* is the sorption intensity (L/mg). The sorption isotherms for TCE onto various iron surfaces (untreated, acid-washed and H₂-reduced Fe⁰) are presented in Fig. 4 and well described by the linear form of Langmuir isotherm (Eq. (9)) with coefficients of determination (*r*²) exceeding 0.97

$$\frac{C}{S} = \left(\frac{1}{K_L S_m} \right) + \left(\frac{C}{S_m} \right). \quad (9)$$

Table 3 indicates that the observed maxima were 0.311, 0.365 and 0.889 mg/g for TCE mass onto untreated, acid-washed and H₂-reduced Fe⁰, respectively. All these observed values are larger than the value of 0.116 mg/g of Fisher cast iron (3.1% C) reported by Burris et al. (1995). TCE sorption onto iron was increased proportional to the carbon fraction of iron on the surface (Fig. 5), but not related to the fraction of the iron's surface that had rusted (Table 1). In consequence, TCE predominantly was sorbed onto the carbon-containing subjects rather than iron oxide on the iron's surface, consistent with the conclusion proposed by Burris et al. (1998). Obviously, the H₂-reducing pretreatment for iron dramatically increased the TCE sorption, attributed to the increase in the carbon content on the iron's surface. The highly TCE sorption also gave evidence that the sharp increase in the specific surface area of H₂-reduced Fe⁰, 4.9 m²/g, compared with the untreated one, 1.8 m²/g, mainly attributed to the N₂ adsorption by the carbon content on the iron's surface. Thus, the reasonable specific surface area of exposed H₂-

Table 2
Specific surface area and the fraction of rusted Fe⁰ on the surface with different pretreatment

Surface area (m ² /g) (1)	H ₂ consumption of 0.45 g various iron sample (μmol) (2)	H ₂ consumption per unit exposed iron surface area (mole/m ²) (3) = $\frac{(2)}{(1) \times 0.45}$	Fe ₂ O ₃ mass per unit exposed iron surface area (mg/m ²) (4) = $\frac{(3) \times 10^{-6} \times 55.8 \times 10^3}{3}$	The mass of Fe-fraction of Fe ₂ O ₃ per unit exposed iron surface area (W _{rust, Fe}) (mg/m ²) (5) = (4) × 70%	Total Fe mass per unit exposed iron surface area (W _{surf, Fe}) (mg/m ²) (6)	$\frac{W_{rust, Fe}}{W_{surf, Fe}} \times 100\%$ (7) = $\frac{(5)}{(6)}$
Untreated Fe ⁰ 1.8	112.5	139.0	7.39	5.17	31.02	16.7
HCl-washed Fe ⁰ 3.4	96.5	56.4	3.35	2.35	32.39	7.2
H ₂ -reduced Fe ⁰ 1.8(4.9) ^a	18.6	22.9	1.22	0.85	33.73	2.5

^aThe value in the bracket is the surface area of H₂-reduced Fe⁰ measured by BET analysis, but that mainly comes from carbon-containing subjects rather than the exposed elemental Fe⁰.

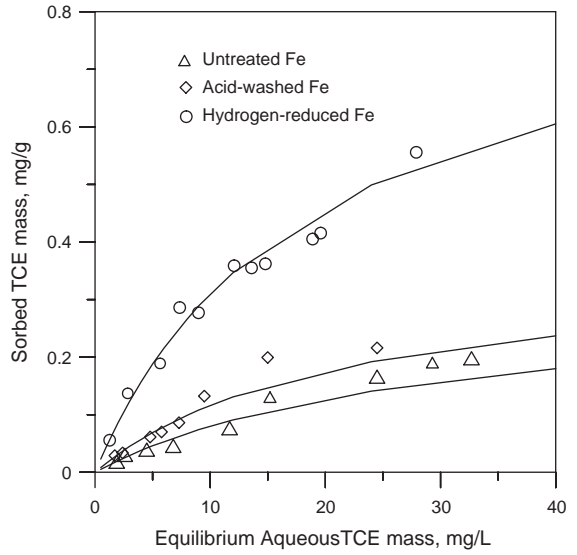


Fig. 4. Sorption isotherms for TCE on the iron with different pretreatments. Fitted lines are based on the Langmuir equation using the parameters in Table 3.

Table 3
Fitted langmuir parameters for sorption of TCE by iron with different pretreatment

	Untreated Fe ⁰	HCl-washed Fe ⁰	H ₂ -reduced Fe ⁰
S _m (mg/g)	0.311	0.365	0.887
K _L (L/mg)	0.035	0.046	0.054
r ²	0.966	0.976	0.989

reduced Fe⁰ was 1.8 m²/g the same as that of untreated Fe⁰.

3.3. Kinetics of reduction of TCE by Cast iron

As presented in Fig. 6, both total and aqueous TCE mass declined substantially. The rate of loss of total TCE mass obtained using acid-washed Fe⁰ resembled that of H₂-reduced Fe⁰, and both losses were significantly faster than that obtained using untreated Fe⁰. This finding implies acid-washing or H₂-reducing pretreatment enhances the destruction of TCE in a metallic iron–water system. The steep slope of the curve for the aqueous TCE loss due to H₂-reduced Fe⁰ persisted for a few hours, and then declined over the long-term as the reaction continued because a very large amount of TCE mass was initially eliminated by concurrent reduction and sorption, finally, the sorbed TCE mass was released

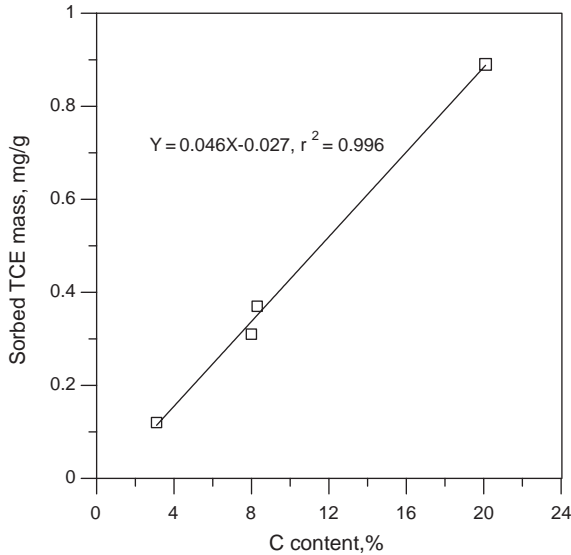


Fig. 5. Relationship between sorbed TCE mass and the C content on the surface of the iron. The data of (3.1, 0.116) is quoted from Burris et al. (1995).

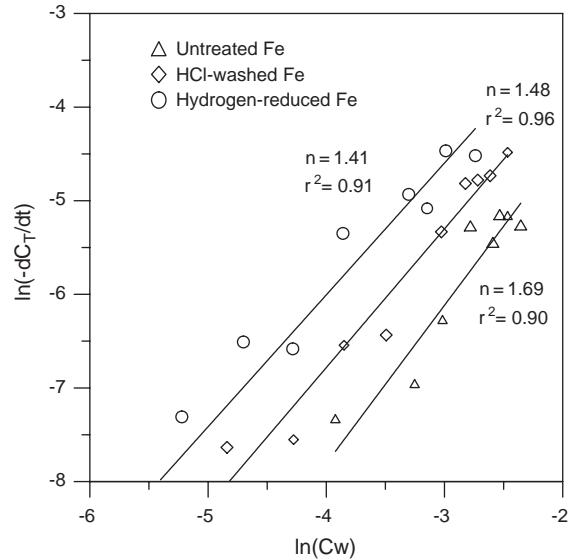


Fig. 7. Reaction order plots for TCE in contact with various iron surfaces including untreated Fe^0 , HCl-washed Fe^0 and H_2 -reduced Fe^0 .

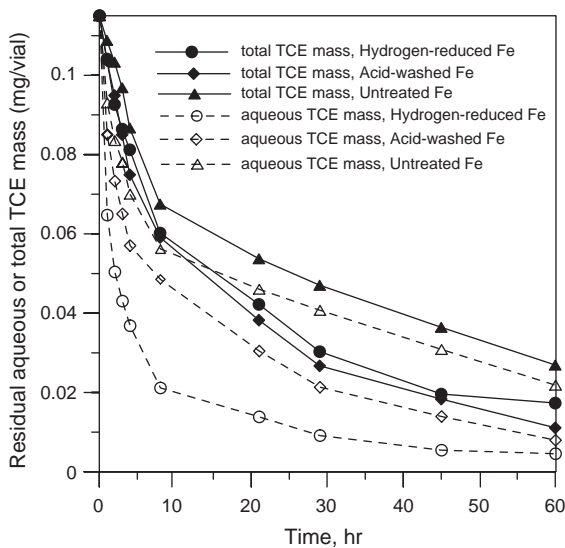


Fig. 6. The loss of total and aqueous TCE as function of time in contact with various iron surfaces with different pretreatment. The initial mass of TCE: 0.11 mg/vial. The initial concentration of TCE was 7.3 mg/L.

into the aqueous phase in a rate-limiting process. Measurements of the concentration of sorbed TCE over 2 h indicated that approximately 34–37% of the initial mass of TCE was removed from the aqueous phase by

sorption by H_2 -reduced Fe^0 , 16–19% was removed by acid-washed Fe^0 and 13–16% was removed by untreated Fe^0 .

The loss of total TCE mass was fitted with an n th-order rate equation (Eq. (1)), and then converted to Eq. (10) with the natural logarithm

$$\ln\left(\frac{-dC_T}{dt}\right) = n \ln C_w + \ln k_{\text{obs}}, \quad (10)$$

where C_T and C_w donate the total and aqueous TCE mass in milligrams per vial, respectively. n was obtained by plotting $\ln(-dC_T/dt)$ vs $\ln C_w$ in a linear regression. Fig. 7 shows the resulting values of n , k_{obs} and the coefficients of determination (r^2). The orders of degradation reaction (n) were 1.7, 1.5 and 1.4 for untreated, acid-washed, and H_2 -reduced Fe^0 , respectively. The orders of degradation reaction are not relatively close to unity, reflecting the complexity of the reaction mechanisms. The order of degradation reaction was assumed to unity to facilitate comparison among reaction rate constants for the various irons (untreated, acid-washed and H_2 -reduced Fe^0). Hence, Eq. (4) was simplified to Eq. (11) which differs from the first-order mode (Eq. (2)) that has been commonly used in other studies

$$-\frac{dC_T}{dt} = k_{\text{obs}} C_w. \quad (11)$$

The first-order observed rate constants (k_{obs}) of the dechlorination of TCE in contact with Fe^0 were obtained from the slope of a plot of total TCE loss rate

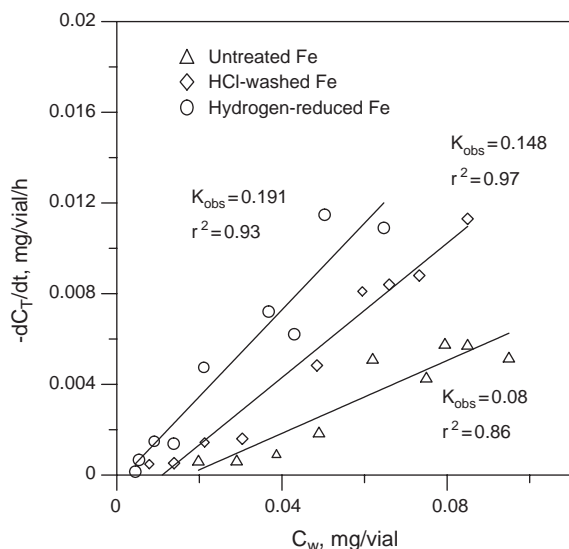


Fig. 8. Observed reaction rate constant plots for TCE in contact with various iron surfaces including untreated Fe^0 , HCl-washed Fe and H_2 -reduced Fe^0 .

$(-dC_T/dt)$ vs TCE concentration in the aqueous phase, C_w in mg-TCE/vial, using linear least-squares analysis. Fig. 8 shows the resulting values of k_{obs} and the coefficients of determination (r^2). The k_{obs} values were 0.080, 0.148 and 0.191 h^{-1} for untreated, acid-washed and H_2 -reduced Fe^0 , respectively. Washing with dilute HCl approximately doubled the rate constant of the reduction of TCE by Fe^0 . Moreover, the increase due to the H_2 -reducing pretreatment exceeds that due to HCl-washing pretreatment. Both the pretreatments of the iron surface clearly increased k_{obs} . However, the rate of loss of total TCE mass $(-dC_T/dt)$, depended not only on k_{obs} but also C_w , and trended toward slack in H_2 -reduced Fe^0 -water system because the sorbed TCE was slowly released in the final reaction period. Normalized to iron surface area, the specific rate constants (k_{SA}) were 2.37×10^{-3} , 2.31×10^{-3} and $5.62 \times 10^{-3} \text{ h}^{-1} \text{ m}^{-2} \text{ L}$, respectively. Notably, a specific surface area of $1.8 \text{ m}^2/\text{g}$, the same as that of the untreated Fe^0 , was used to calculate k_{SA} for H_2 -reduced Fe^0 , because the morphology of its surface was similar to that of untreated Fe^0 , using SEM analysis. These findings indicated that acid-washing approximately doubled k_{obs} mainly because of an increase in the Fe^0 surface area, but it slightly decreased k_{SA} because of the rapid corrosion during the rinsing process. After H_2 -reducing pretreatment, both k_{obs} and k_{SA} were increased due to the increase in the number of reactive sites per unit surface area. Meanwhile, the carbonization of carbon-containing subjects increased the sorption capacity for TCE.

4. Conclusion

Significant sorption of TCE by highly impure iron was observed. Sorption capacity was increased by HCl-washing and H_2 -reducing pretreatment of the iron, resulting from the increase in the C fraction in the iron's surface. The results revealed that approximately 34–37% of the initial mass of TCE was removed from the aqueous phase by sorption by H_2 -reduced Fe^0 , 16–19% was removed by HCl-washed Fe^0 and 13–16% was removed by untreated Fe^0 . HCl-washing approximately doubled k_{obs} , mainly because of the increase in the surface area of iron, but it slightly decreased k_{SA} because of rapid corrosion during the rinsing process. H_2 reduction reduces the fraction of rusted iron, increases the number of the reactive sites and increases the sorption capacity in relation to those values obtained when iron is, as is common, pretreated by acid washing. Additionally, no wastewater or sludge was generated. Therefore, pretreatment by H_2 reduction is a promising alternative means of promoting the removal of TCE from contaminated water.

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