Research Article

Degradation of TCE by TEOS Coated nZVI in the Presence of Cu(II) for Groundwater Remediation

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The removal of TCE by nanofer zero valent iron (nanofer ZVI) coated with tetraethyl orthosilicate (TEOS) in the presence of Cu(II) at different environmental conditions was studied. The kinetics of TCE degradation by nanofer ZVI was determined. At a dosage of 10 mg of nanofer ZVI, almost 63% of TCE was removed, when Cu(II) and TCE were present. It contrasts with 42% degradation of TCE in the absence of Cu(II). SEM/EDS images indicated that Cu(II) is reduced to form Cu^0 and Cu_2O . These formations are considered to be responsible for enhancing TCE degradation. Direct reduction involves hydrogenolysis and β -elimination in the transformation of TCE, while indirect reduction involves atomic hydrogen and no direct electron transfer from the metal to reactants. The reduction of activation energy was also noted indicating that the rate limiting step for TCE degradation in the presence of Cu(II) is surface chemical reaction rather than diffusion. Most of iron present in nanofer ZVI get dissolved causing the generation of localized positive charge regions and form metal chlorides. Local accumulation of hydrochloric acid inside the pits regenerates new reactive surfaces to serve as sources of continuous electron generation. No significant effect of TCE was noticed for Cu(II) sequestration.

1. Introduction

During the last few years, a great deal of effort has been directed to develop and improve the zero valent iron nanoparticle (nZVI) to clean groundwater contaminants. For instance, Weile [1] reviewed and classified more than three hundred publications dealing with the use of nZVI for the removal of contaminants from environmental media. This classification includes mainly studies linked to the removal of halogenated organic compounds, arsenic, radionuclides, and heavy metals. More recently, O'Carroll et al. [2] have provided a comprehensive review of the current developments of nZVI/bimetallic technology for removal of chlorinated solvents and heavy metals from water and soil media. They noted that the typical nanometal particles used for remediation tend to agglomerate to form micron size particles, which have limited stability and mobility in the porous media. To overcome this problem, various polymers and other coatings

have been used to stabilize nZVI particles, with varying degrees of success.

The direct injection of nZVI has been known as an effective process to treat organic as well as inorganic groundwater contaminants. The treatment of mixed contaminants formed by a combination of organics and inorganics poses a challenge to groundwater remediation technologies due to the vast differences in the physicochemical properties of the treated contaminants [3–5]. This is particularly true when we are dealing with aliphatic chemicals, polychlorinated biphenyls (PCBs), hydrocarbons, and polar contaminants as well as heavy metals and radionuclides. Consequently, mixed pollutants can be removed only in small quantities and this is not efficient. Several studies including those of Elektorowicz [6] have stated that removal of mixed contaminants is challenging since remediation technologies for the organic and the inorganic contaminants are different. As such, further studies are desirable in the area of treating mixed contaminants.

Although there are many studies related to the degradation mechanism comprising heterogeneous reactions, the mechanism of degradation of contaminants in the presence of iron is not fully understood [7–9]. Nowack [3] notes that the reactions occur when the metal contaminant molecules reach the surface of iron and associate with the surface sites that may be either reactive or nonreactive. Further, the reactive sites refer to those where the breaking of bonds in the reactant solute molecule occurs (i.e., chemical reaction) whilst nonreactive sites are those where only sorption interactions occur and the solute molecule remains intact.

The degradation hypothesis for halogenated compounds by iron is better accepted as there is a reductive dehalogenation of the contaminant coupled with the corrosion of iron [8, 11]. With a standard reduction potential ($E_h^\pm$) of -0.44 V, ZVI primarily acts as a reducing agent. Iron is oxidized while alkyl halides (RX) are reduced. At pH 7, the estimated standard reduction potentials of degradation of various alkyl halides range from $+0.50$ V to $+1.25$ V [11]. Hence, the net reaction is thermodynamically very favorable under most conditions. For example, groundwater contaminated with chlorinated solvents such as trichloromethane (TCM), trichloroethylene (TCE), and perchloroethylene (PCE) is treated using iron barriers [8, 9, 11]. The preferred electron acceptor is typically dissolved oxygen under aerobic conditions ($E_h +1.23$ V). This acceptor can compete with chlorinated hydrocarbons that have oxidizing potentials similar to oxygen. Aerobic groundwater enters the iron filling wall and causes the oxidation of metallic iron (Fe^0) to ferrous iron (Fe^{2+}), with the subsequent release of two electrons. Chlorinated solvents also react as electron acceptors, resulting in dechlorination and the release of a chloride ion. The reaction takes place in several steps resulting in reducing halogenated organic compounds through intermediate to nontoxic compounds such as ethylene, ethane, and acetylene [12]. Intermediate compounds like vinyl chloride which has a higher toxicity than the original compounds are not formed in high concentrations [13]. nZVI also reacts with water producing hydrogen and hydroxide ions resulting in an increase in the pH of water. The resulting hydrogen can also react with alkyl halides. According to Deng et al. [14] the bulk dehalogenation reaction is usually described by first-order kinetics. They found that the lower the degree of chlorination, the slower the rate of dechlorination. Batch and column tests have also indicated highly variable degradation rates due to operating conditions and experimental factors such as pH, metal surface area, concentration of pollutants, and mixing rate. Wang and Zhang [15] suggested that since the reaction is heterogeneous, the rate of reaction is proportional to a specific surface area of the iron used. Therefore adsorption, desorption, or diffusion of reactants and chemical reaction itself can limit the processes. Several limitations of this technique, including the accumulation of chlorinated by-products and the decrease in the activity of iron over time, have been reported [16]. Wang and Zhang [15] used improved methods that involved physical and chemical processes which increased the surface area of iron by reducing its particle size to enhance reactivity. Elsner et al. [17] have presented an interesting study of the dehalogenation of CCl_4 by Fe(II) on goethite including

environmental facts. They stated that specific adsorption of major anions or pH effects modify the goethite surface and stabilize short-lived radical intermediates. They also conclude that the key to predicting product formation in reductive dehalogenation of organics by Fe(II) is therefore a profound understanding of the factors that may determine the stabilization of radical intermediates at reactive Fe(II) surface sites.

Only few studies in the past have investigated the effect of organics and inorganics (mixed contaminants) on TCE degradation by nZVI. Liu et al. [18] stated that dehalogenation of TCE was not significantly affected by the presence of other organics. As stated earlier Nowack [3] observed that the reaction between metal and nZVI depends on the nonreactive surface. This implies that if mixed contaminants are present, the organics react only with the reactive sites and the metal (inorganics) gets adsorbed to nonreactive surface. Lien and Zhang [19] stated that the presence of other metals specially the ones that have standard reduction potential higher than iron may increase the reactivity and efficiency of the degradation of organic contaminants. However, intermediate reaction between metal and the organics can result in a chemical compound that is more hazardous than the original one.

In the present study, the effect of Cu(II) on the removal of TCE by nZVI coated with tetraethyl orthosilicate (TEOS) was investigated. Cu(II) was chosen since this cation is generally found in groundwater as a common pollutant. Further, Cu(II) can enhance the degradation of organics. Compared to other cations (metals) present as groundwater pollutants, Cu(II) has a higher reactivity, smaller ionic radii, and a higher electronegativity. In order to assess the applicability of coated nZVI for the degradation of TCE, batch isotherm and kinetic tests were conducted. These studies also considered the effects of environmental factors (concentration, pH, dosage, and time) on both the degradation of TCE and the adsorption of Cu(II) and identified the reaction mechanisms.

2. Experimental Section

2.1. Materials and Methods

2.1.1. Chemicals. Copper (99.0+%) and trichloroethylene (99.5±) were obtained from Fisher Scientific Canada. Polyvinylpyrrolidone (98+%) and tetraethyl orthosilicate (99.5+%) were supplied by Sigma Aldrich. TCE standard, copper standard (1000 ppm), hexane (1000 ppm), and hydrogen (1.08%) were supplied by Fisher Scientific Canada. Ultra-high-pure helium, acetylene (1000 ppm and 1%), hydrogen, and N_2 were supplied by Praxair Canada.

2.1.2. ZVI Nanoparticle. The iron suspension characterized and modified in this study was supplied by the Czech company, NANOIRON Ltd. The material was developed to overcome the limitations of Nanofer 25. The new material was produced by dry reduction of iron oxide or natural ferrihydrite [20]. The new innovative material nanofer ZVI was produced by impregnating iron oxide with polyvinylpyrrolidone (PVP) ($M_r \sim 160000$, Sigma Aldrich). This was in turn soaked and coated with TEOS (Sigma Aldrich). Detailed information about the procedure is provided by Lenka et al. [20] and Eglal

and Ramamurthy [10]. Freshly deionized water was used in all experiments.

2.2. Batch Equilibrium Experiments. Contaminant removal experiments were conducted at a fixed pH and at varied nanofer ZVI dosage and concentrations. Three different concentrations of both TCE and Cu(II) were selected as contaminants. The stock solutions containing varied concentrations of contaminant were prepared and stored in closed 1000 mL glass serum bottles. An appropriate volume of the solution was diluted with deionized water to 1000 mL. Following this, the bottles were closed and the cap was sealed with a Teflon liner to prevent leakage. The solutions were mixed using a magnetic mixer and left over night. After the mixing, the amount of nZVI and solution were added to a 40 mL bottle. The bottles were again agitated on a mechanical shaker at 250 rpm at 21°C to result in a nearly homogenous mixture. After a suitable time interval (typically 24 hours for reactions with metal species), the reaction was stopped by separating the solution and the particles with a vacuum filtration, using 0.2 μm filter (grad 42 Whatman). The particles were dried and stored in a N_2 -filled glove box ahead of solid phase analysis. The solution was acidified with 0.1 mole HCl before the analysis. After adding appropriate amounts of nanofer ZVI, the bottles were capped with Teflon Mininert valves and placed on a mechanical shaker at 250 rpm at 22°C. Both pH and temperature were measured before and after adding the nanofer ZVI to each bottle. All bottles were cleaned using 0.1 mole HCl and washed to insure that no residual contaminants could occur. After the liquid phase analyses were done, the samples were acidified to attain pH which was less than two. The bottles were stored at 4°C.

For each set of experiments, a control was performed under identical conditions in parallel, except for the case where no nanofer ZVI particles were added. Tests were conducted at 0.01, 0.1, and 0.15 M for Cu(II) and 0.01, 0.1, and 0.15 M for TCE. The nanofer ZVI dosage ranged from 5 mg/L to 30 mg/L. The equilibrium pH of the resulting suspension containing nanofer ZVI and contaminants was fixed at 6 with an increment of 0.1 units, using radiometer standard buffers (4, 7, and 10). The suspension was equilibrated for the metal adsorption for 2 hrs. A brief kinetic study was also performed using the procedure outlined above. The reaction time interval chosen was 2 hrs.

2.3. Liquid Phase Analysis. Total aqueous concentrations of Cu(II) in filtered solutions were measured with a Perkin Elmer atomic absorption spectrometer (AAS) (A Analyst 100). For analysis of each species, a five-point calibration curve was obtained with solutions prepared from the respective AAS standards (1000 mg/L standards purchased from Fisher Canada). Sample concentrations exceeding linear concentration range of the respective wavelength were diluted accordingly. The setup and selected wavelength for each metal were taken from the AAS spectrometer manual. The solution for the calibration curve was used to insure consistency after each 5th reading. After completing the reading, samples were stored at 4°C.

The concentrations of TCE were measured by a Varian GC analyzer (3800) equipped with a flame ionization detector (FID) and a SUPELCO SPB 624 capillary column. The injection port temperature was set at 180°C. The oven temperature was set to 50°C and ramped to 200°C at 10°C/min. The detector temperature was 300°C. Helium was used as the carrier gas. A five-point calibration curve was obtained with solutions prepared from the respective standards (1000 mg/L standards purchased from Fisher Canada). The method used for the analysis selected followed the GC Varian 3800 manual for liquids. After completing the analysis, all samples were capped and stored at 4°C.

Solution pH and temperature were measured with a pH-mV meter (Hanna pH 209). Three-point calibration was performed daily using pH 4.0, 7.0, and 10.0 standard pH buffers (Fisher). Oxidation-reduction potential (ORP) was measured using the same analyzer equipped with an ORP electrode (Pt band with Ag/AgCl/saturated KCl reference cell). One-point ORP calibration was performed using a Zobel standard solution (Sigma), which gives a reading of $\sim +230$ mV at 20°C. ORP reading can be converted to the standard hydrogen electrode potential (Eh) by adding $+197$ mV at 25°C. Temperature was recorded daily before and after the analysis. For quality control, three replicate readings were obtained for each sample and the average results are reported.

3. Results and Discussion

3.1. Degradation of TCE by Nanofer ZVI Suspension in the Presence of Cu(II). It is important to study the presence of coexisting contaminants. Figure 1(a) shows the degradation of TCE by nanofer ZVI in the presence of Cu(II) at different concentrations. At the initial concentration of 10 mg/L, 70% of the TCE was removed when Cu(II) was absent. After the addition of 0.1 M Cu(II), the reaction rate improved and the removal rate of TCE increased to 98%. It is hypothesized that there are several reasons for this. The first reason relates to the electrocatalysis of copper chloride. For instance, CuCl_2 and nanofer ZVI have a replacement reaction and copper ions adhere to the surface of nanofer ZVI. The resulting numerous tiny batteries that are formed augment iron corrosion. The electrode potential of copper intensifies the electrolysis. The value of the standard electrode potential for $\text{Fe}^0/\text{Fe}^{2+}$ is -0.44 , and the corresponding value for Cu/Cu^{2+} is $+0.34$. The value of Cu/Fe is about $+0.78$ V [21]. This leads to intensified iron corrosion. Bransfield et al. [22] studied the reduction of 1-1-1 TCA by Cu/Fe and noted that the increase of Cu loading both increases the rate of reaction and yielded completely dehalogenated end-products. Further, the reaction of TCE and nanofer ZVI is a solid-liquid contact reaction. To be effective, both these components should have an effective contact during the experiments. Generally, a passivation layer easily forms on the nanofer ZVI surface. However, copper ions adhering to the nanofer ZVI can prevent the formation of a passive layer. This promotes the contact between TCE and nanofer ZVI. Finally, hydrogen production generated as result of electrolysis has an important role in

FIGURE 1: Effect of concentration on the TCE removal by nanofer ZVI in the presence of Cu(II). Nanofer ZVI dose = 10 mg, initial pH = 6, T: 21°C, and standard error: 1%.

FIGURE 2: Effect of dosage response on the adsorption of TCE by nanofer ZVI in the presence of Cu(II), initial pH = 6, T: 21°C, and standard error: 1%.

TCE dechlorination [23]. One notes that the free radicals can provide a great deal of electrons.

3.2. Effect of Cu(II) on the Degradation of TCE by Nanofer ZVI. Figure 2(a) represents the degradation of TCE in the presence of Cu(II) and nanofer ZVI dosages. Preliminary study had

indicated the optimum TCE concentration to be in the vicinity of 0.1 M, for a dosage of 10 mg nanofer ZVI. Hence, three different TCE concentrations were selected around the edge of the optimum concentration (0.1 M). At a dosage of 10 mg of nanofer ZVI about 64% of TCE was removed when 0.1 M Cu(II) and 0.15 M TCE were present. This contrasts with

43% degradation of TCE in the absence of Cu(II). Due to several reasons mentioned earlier, the presence of Cu(II) is very effective in TCE degradation. Zhang et al. [24] studied the effect of Cu(II) and carbon (C) on TCE degradation over the surface of micro ZVI and found that Cu(II) increases TCE degradation by 72%, when the molar ratio of Cu(II) to TCE was 10 : 1. In the case of C, they stated that the addition of an appropriate mass of C may maximize TCE removal due to adsorption as well as the synergetic role of Fe/C. Their results are in agreement with Zhou and Yang [25].

It is well accepted that metal mediated dechlorination is mainly a surface reaction [19, 26]. The surface reaction usually involves steps in the overall reaction including diffusion of a reactant to the surface, a chemical reaction on the surface, and the diffusion of the product back into the solution. The rate limiting step (i.e., the slow step reaction requiring great activation energy) determines the overall kinetics of a reaction. In general, a typical minimum value of the activation energy for chemical controlled reaction is ~ 29 kJ/mole [27]. The activation energy for the nanofer ZVI is estimated to be in the range of 35 to 45 kJ/mole [20]. The decrease of the activation energy indicated that the dechlorination by nanofer ZVI is a catalytic reaction. The Cu(II) in this case served as a catalyst. Furthermore, the reduction of the activation energy also indicates that the rate limiting step for the TCE degradation in the presence of Cu(II) is surface chemical reaction rather than diffusion.

In general, TCE degradation by metal involved either direct reduction or indirect reduction of both. Direct reduction such as hydrogenolysis and β -elimination in the transformation of TCE by nanofer ZVI may occur via formation of an organic chemisorption complex at the metal surface. Here, the metal itself serves as a direct electron donor [26]. However, indirect reduction involves atomic hydrogen and no direct electron transfer from metals to reactants. Atomic hydrogen is a very powerful reducing agent that reductively dechlorinates contaminants effectively. It is probable that TCE degradation follows both direct and indirect pathways. However, the results of dechlorination by iron may result in many intermediate compounds that could be hazardous [26]. Lien and Zhang [27] investigated the effect of palladium on the dechlorination of TCE. It was found that the use of catalytic metal may lead to a lesser amount of chlorinated intermediates. Their molecular structures may be responsible for the different surface intermediate products.

3.3. Effect of Cu(II) on the Degradation Kinetics of TCE by Nanofer ZVI. The combined effect of nanofer ZVI and Cu(II) on TCE degradation is presented in Figure 3. It shows the effect of time on the degradation efficiency of TCE as well as the adsorption of sequestering Cu(II). As stated earlier, Cu(II) and TCE were added to the deionized water at the same time and at a fixed concentration (1 mM). The value of pH was set at 6. Addition of 10 mg of nanofer ZVI was followed after the solution was mixed for 2 hrs. In the initial period (0–5 minutes), the presence of Cu(II) increased the dechlorination of TCE considerably. At 120 minutes, the increase in the degradation of TCE was only marginal. The images of SEM/EDS (Figure 4) indicated that

FIGURE 3: Effect of time on the adsorption of Cu(II) by nanofer ZVI in the presence of TCE (40 mL), Conc. 0.1 mM, 0.05 mM, and 0.15 mM, initial pH = 6, T: 21°C, and standard error: 1%.

Cu(II) is reduced to Cu^0 and Cu_2O . These formations on the surface of nanofer ZVI are considered to be responsible for the enhancing the dechlorination of TCE. Henderson and Demond [28] studied the effect of Pb II, As V, and Cr VI on the dechlorination of carbon tetrachloride by zero valent iron powder. They found that the addition of Pb II favored the production of toxic substances such as dichloromethane. The influence of As V was insignificant while the influence of Cr VI was negative. Figure 3 also presents the adsorption and reduction of Cu(II) and TCE in a single adsorption test. On the other hand, TCE was noted to have no effect on Cu(II) removal. This may be due to the fact that Cu(II) moves faster to the surface of nanofer ZVI and acts as an intermediary between nanofer ZVI and TCE. The result is in agreement with Shih et al. [29] who found that the deposition of Cu on iron particles resulted in a significant increase in dechlorination of pentachlorophenol by Pd/Fe in the presence of Cu(II).

When TCE particles dissociate, chloride ions are produced (Figure 5). Chloride serves as a corrosion promoter and whenever present, it accelerates electron generation from metallic species and creates new reactive sites on the surface of metals [30]. Chloride also destabilizes the passive films present on the nanofer ZVI surface. This can also induce corrosion pit formation (Figure 5). The nanofer ZVI contains almost 98% pure iron (α -Fe) as shown in Figure 6. It could get dissolved faster causing the generation of localized positive charge regions and form metal chlorides to maintain electroneutrality in the system. After hydrolysis of the chlorides to form metal hydroxides and hydrochloric acid, local accumulation of hydrochloric acid inside the pits regenerates new reactive surfaces to serve as sources of continuous electron generation (Figure 5). Such effects have been hypothesized by Johnson et al. [30] and Gotpagar et al. [31] earlier to elucidate the rate enhancements observed for the reduction of TCE and carbon tetrachloride by iron metal.

The structures of the fresh and the aged (after experiments) nanofer ZVI were also examined using XRD

FIGURE 4: EDS analysis of nanofer ZVI after the experimental test, pH = 6, T = 21°C. (a) TCE concentration (1 mM) and Cu(II) concentration (1 mM): iron, oxygen, carbon, copper, copper, carbon, oxygen, iron, copper, and carbon. (b) Nanofer ZVI in deionized water; the peaks appear in the following sequence (left to right): iron, oxygen, copper, chlorine, copper, chlorine, and iron.

FIGURE 5: Schematic diagram illustrating the effect of cations on degradation of TCE by nanofer ZVI in the presence of Cu(II) and the formation of corrosion pit.

(Figure 7). The % of pure iron α -Fe (blue pattern) decreased to about 59.9% when TCE (40 mL) was introduced, compared to % α -Fe present in fresh nanofer ZVI (98%, red patterns). However, in the case of Cu(II) (0.1 mL) and TCE (40 mL) experiments (blue pattern), the % of α -Fe decreased to about 35.5%. This clearly indicated that when Cu(II) was introduced to the solution containing TCE, it helped to increase TCE degradation. Several of expected XRD peaks for Fe, Cu, and iron oxide phases are within close proximity and therefore had overlaps. As such, there was an evidence of an overall decrease of iron nanoparticles which might form a different

metal speciation due to the presence of Cu(II), Cl, and O_2 in solutions.

3.4. Sequestration of Cu(II) by Nanofer ZVI in the Presence of TCE. Figures 1(b) and 2(b) show the results for the removal of Cu(II) by nanofer ZVI in the presence of TCE. Figure 1(b) outlines the effect of TCE (0.01 M) on the removal of Cu(II) at different concentrations (0.01 to 0.1 M). Other factors such as pH, temperature, and nanofer ZVI dosage were kept constant in all tests. The results indicated that TCE had no significant effect on the removal of Cu(II) at all concentrations tested.

FIGURE 6: XRD nanofer ZVI of α -Fe; the particle size 50–100 nm and high content of iron in range of 70–90 wt.% ($\lambda = 1.5418 \text{ \AA}$ = 40 Kv, and $I_{30} = 30 \text{ mA}$); composition: FeO_3 , 2.1% (green), and α -Fe, 97.9% (red), taken after Eglal and Ramamurthy [10].

The removal of Cu(II) was attributed to its deposition on the nanofer ZVI surface. This was confirmed by SEM-EDS analysis (Figure 4). The two copper species (CuO and Cu^0) identified at the surface of nanoparticle indicated that the reduction of Cu(II) by iron nanoparticle is involved as noticed in Figure 5(a). The standard reduction potential E^0 for $\text{Cu}^{2+}/\text{Cu}^0$ and $\text{Fe}^{2+}/\text{Fe}^0$ couple is +0.34 and -0.44 V , respectively (Figure 5(a)). Hence, the overall E^0 for the reaction is +78 V, which indicates thermodynamically favorable reaction. The formation of Cu_2O could be attributed to the reaction between the Fe II and Cu(II) in the aqueous solution. These are in agreement with the results of Maithreepala and Doong [32]. Li et al. [33] suggested that any metal with a standard reduction potential higher than iron can be immobilized at the surface of iron nanoparticle by adsorption and chemical reduction. This mechanism supports the results shown in Figures 1(b) and 2(b). Whenever organics and a metal with a higher standard reduction potential than iron are present, the process of metal adsorption to the surface of nanofer ZVI will be much faster than the degradation rate of the organic (TCE).

Figure 3 shows the effect of time on Cu(II) reduction and TCE degradation by nanofer ZVI. Although a moderate increase in the TCE degradation was noticed due to the presence of Cu(II), the presence of TCE had insignificant effect on Cu(II) removal. This is due to the effect of copper getting adsorbed to the surface and acting as an intermediate (catalyst). Similar conclusions were drawn by Lien and Zhang [19] who studied the catalytic effects of palladium on hydrodechlorination and by Doong and Lai [21] who studied the effect of heavy metals on dechlorination of carbon tetrachloride by iron nanoparticles.

4. Conclusions

The study indicated the rapid degradation of TCE by nanofer ZVI in the presence of Cu(II). Increasing pH was found to reduce degradation due to the formation of the hydroxyl group which created a passive film around the nanoparticle.

FIGURE 7: XRD image of nanofer ZVI before and after the experiments ($\lambda = 1.5418 \text{ \AA}$, = 60 Kv, and $I_{30} = 30 \text{ mA}$); green line represents the TCE experiment; TCE Conc. 40 mL; blue line represents Cu(II) Conc. 0.1M and TCE Conc. 40 mL; red line represents the nZVI before the experiment. Time: 3 hrs. T: 22°C .

At a dosage of 10 mg of nanofer ZVI, almost 63% of TCE was removed, when Cu(II) and TCE were present. This contrasts with 42% degradation of TCE in the absence of Cu(II). Although copper gets adsorbed faster to nanofer ZVI, its role in the intermediate catalysis enhances TCE degradation.

The images of SEM/EDS showed that reduction of Cu(II) leads to the formation of Cu^0 and Cu_2O . These formations on the surface of nanofer ZVI were responsible for enhancing the degradation of TCE. TCE degradation by nanofer ZVI involved both direct and indirect reduction. Direct reduction such as hydrogenolysis and β -elimination in the transformation of TCE formed an organic chemisorption complex at the metal surface where the metal itself serves as a direct electron donor. The indirect reduction involved atomic hydrogen and no direct electron transfer from the metal to reactants. The reduction of the activation energy was also noted indicating that the rate limiting step for the TCE degradation in the presence of Cu(II) is surface chemical reaction rather than diffusion.

Almost 98% of iron (α -Fe) present in nanofer ZVI could get dissolved faster causing the generation of localized positive charge regions. They formed metal chlorides to maintain electroneutrality in the system. Hydrolysis of chlorides gave rise to metal hydroxides and hydrochloric acid. Possibly, local accumulation of hydrochloric acid inside the pit regenerated new reactive surfaces to serve as source of continuous electron generation. However, no significant effect of TCE was noticed for either increasing or decreasing Cu(II) sequestering on the surface of nanofer ZVI.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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