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Chloride Effect on TNT Degradation by Zerovalent Iron or Zinc during Water Treatment

RAFAEL HERNANDEZ,* MARK ZAPPI, AND CHIANG-HAI KUO

Dave C. Swalm School of Chemical Engineering,
P.O. Box 9595, Mississippi State University,
Mississippi State, Mississippi 39762

Addition of corrosion promoters, such as sodium and potassium chloride, accelerated TNT degradation during water treatment using zerovalent zinc and iron. It was theorized that corrosion promoters could be used to accelerate electron generation from metallic species, create new reactive sites on the surface of metals during contaminated water treatment, and minimize passivating effects. The surface area normalized pseudo-first-order rate constant for the reaction of zerovalent zinc with TNT in the absence of KCl was 1.364 $L{\cdot}m^{-2}{\cdot}h^{-1}$. In the presence of 0.3 mM and 3 mM KCl, the rate constant increased to 10.5 $L{\cdot}m^{-2}{\cdot}h^{-1}$ and 51.0 $L{\cdot}m^{-2}{\cdot}h^{-1}$, respectively. For the reaction with zerovalent iron and TNT, the rate constant increased from 6.5 ($L/m^2{\cdot}h$) in the absence of KCl to 37 $L{\cdot}m^{-2}{\cdot}h^{-1}$ using 3 mM KCl. The results demonstrate that chloride based corrosion promoters enhance the rate of TNT degradation. The in-situ breakage of the oxide layer using corrosion promoters was applied as a treatment to maintain the long-term activity of the metallic species. Zinc maintained a high reactivity toward TNT, and the reactivity of iron increased after 5 treatment cycles using 3 mM KCl. Zinc and iron scanning electron micrographs indicate that TNT degradation rate enhancement is caused by the pitting corrosion mechanism.

Introduction

2,4,6-Trinitrotoluene (TNT) is a common contaminant at ammunition production facilities. Past improper wastewater disposal techniques, such as direct discharges into drainage ditches, local streams, and settling lagoons, have created soil, sediment, surface water, and groundwater contamination around these manufacturing facilities. TNT is toxic, a mutagen, and suspected carcinogen. The U.S. Environmental Protection Agency (EPA) classifies TNT as a possible human carcinogen (*1*). EPA recommended long-term drinking water health advisory concentration for TNT is 2.0 (μg/L) (*2*).

Presently, technologies for treating explosives-contaminated waters accepted by DoD consist of advanced oxidation processes (AOPs) and activated carbon adsorption. Advanced oxidation processes (AOPs), which rely on the strong oxidation capability of the hydroxyl radical ($OH^{\bullet}$), generate byproducts that are as regulated as the parent compounds (*3, 4*). For example, the reaction of TNT with chemical oxidizers generates 2,4,6-trinitrobenzene (TNB), which is as regulated as TNT. The EPA long-term drinking water advisory for TNB is also reported to be 2.0 (μg/L) (*2*). TNB is more difficult to oxidize than TNT, and its complete elimination from contaminated water, using AOPs as a stand-alone technology, requires long residence times to achieve treatment goals and, consequently, high oxidizer consumption. These factors result in high treatment costs.

Granular activated carbon (GAC) is another technology that has been applied for the treatment of explosives contaminated waters (*2*). However, GAC is a phase transfer technology. In the case of contaminated water treatment, contaminants are transferred from the liquid phase onto the solid phase. A regeneration step is necessary to remove the organic contaminants from the carbon prior to reuse of the carbon. This carbon regeneration step is performed at relatively high temperatures and pressures. Regeneration of spent carbon utilized during remediation activities (adsorbed explosives) is limited by the possibility of an explosion at the high temperature and pressure of the regeneration process. Thus, in many instances, the carbon must be discarded in a hazardous waste landfill increasing the possibility of future regulatory liability.

Zerovalent metals (ZVMs) have been used for the treatment of waters contaminated with different types of organic and inorganic compounds, such as chlorinated solvents, explosives, pesticides, and chromate (*5*−*9*). The main parameters discovered to have an effect on reaction kinetics include metal pretreatment (e.g. acid wash), metal surface area, water pH, and groundwater inorganic composition (calcium, magnesium, and carbonates). Zerovalent iron (ZVI) has been the preferred metallic species utilized in most ZVM applications because it is readily available and inexpensive. Moreover, the reaction between ZVI and many organic contaminants of concern is thermodynamically favorable. In case of TNT degradation with ZVI, the initial rate of this reaction is faster than reactions of ZVI with chlorinated solvents and pesticides (*7, 8*). However, byproducts generation and concerns about long-term stability of the iron have prevented the field application of this technology for the treatment of nitroaromatic compounds. TNT reduction byproducts include 2-amino-4,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene, 2,4-diaminonitrotoluene, 2,6-diaminonitrotoluene, and 2,4,6-triaminotoluene (*10, 11*). Various azoxytoluenes also can be formed via condensation reactions of nitroso and hydroxylamine compounds (*12*). Many of these degradation byproducts are corrosion inhibitors. Once formed, they adsorb strongly onto the iron surface, passivating and causing iron deactivation. The latter causes a decrease in the rate of TNT degradation and water treatment efficiency.

Zerovalent zinc (ZVZn) has also been evaluated for treating organics-contaminated waters (*13*−*18*). This metal is more thermodynamically active and reactive than iron. Experiments conducted to examine the degradation of chlorinated solvents using zerovalent zinc have shown faster degradation kinetics compared to iron (*13*−*18*). This metal has not been used for the degradation of nitroaromatic compounds in environmental media. Even though environmental and health concerns of zinc dissolution into groundwater may prevent its application in permeable reactive barriers, its higher electrochemical activity and oxide stability could result in successful ex-situ treatment of contaminated waters.

Equations 1 through 4 illustrate a simplified scheme of the reactions that occur when a metal, such as iron or zinc, is exposed to water containing TNT. The metal spontaneously oxidizes (eq 1). To maintain electroneutrality in the system, other species must be reduced. The hydrogen ion is reduced

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* Corresponding author phone: (662)325-0790; fax: (662)325-2482; e-mail: Rhernandez@che.msstate.edu.

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to form hydrogen (eq 3), and, depending on the solution pH, oxygen is reduced to form water or the hydroxide ion (eqs 4 and 5). Finally, depending on the reaction thermodynamics and kinetics of the particular metal, TNT is reduced via three 6 electron steps to aminonitrotoluene, diaminonitrotoluene, and triaminotoluene (eqs 6−8). Acceleration of electron generation from the metallic species will increase the rate of other potential reactions in solution until they become mass transfer limited.

$$M \rightarrow M^{+n} + ne^{-} \tag{1}$$

$$H_2O \leftrightarrow H^{+} + OH^{-}(WaterDissocciation) \tag{2}$$

$$2H^{+} + 2e^{-} \rightarrow H_2 \tag{3}$$

$$O_2 + 4H^{+} + 4e^{-} \rightarrow H_2O(AcidSolutions) \tag{4}$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}\ (BasicSolutions) \tag{5}$$

$$TNT + 6e^{-} \rightarrow ADNTs \tag{6}$$

$$ADNTs + 6e^{-} \rightarrow DANTs \tag{7}$$

$$DANTs + 6e^{-} \rightarrow TAT \tag{8}$$

New reactive sites or a continuous generation of electrons is necessary to maintain or increase the TNT degradation rate. This could be achieved via addition of corrosion promoters to the contaminated water. Chloride salts such as NaCl, $FeCl_3$, and $CaCl_2$ are known pitting and crevice corrosion promoters (*19−21*). These types of corrosion create acidic microenvironments inside pits and crevices. The acid inside the pits stimulates metal dissolution, generating electrons that could react with organic or inorganic species on the metal surface.

Chloride is one of the products of the reaction of zerovalent iron with chlorinated compounds. Some researchers have cited pitting corrosion as the cause of increase in chlorinated compounds degradation rate during treatment of contaminated waters using zerovalent iron (*22, 23*). Additionally, Tamara and Butler (*24*) SEM images indicate that the cause of the rate increase in carbon tetrachloride degradation rate using acid washed (HCl) versus nonacid washed ZVI is pitting corrosion. To our knowledge, this chloride autocatalytic effect has not been evaluated for the treatment of contaminated waters with non-chlorinated compounds.

This paper presents results of a study focusing on the effect of chloride addition as a method to minimize the deactivation of iron and zinc caused by adsorption of reduced byproducts onto the surface and the formation of an oxide layer. The effect of chloride on TNT degradation by iron or zinc is examined using fresh and aged metals.

Methods and Materials

The TNT test solutions were prepared by solubilizing crystalline TNT into distilled water. The TNT was purchased from Chem Service Inc., West Chester, Pennsylvania. The purity of the TNT was 99%. For safety considerations, Chem Service delivers TNT with a minimum of 30% moisture. Iron and zinc were purchased from Fisher Scientific Inc., Atlanta, Georgia.

The solutions were mixed for over 7 days to ensure complete dissolution of the TNT into the distilled water. All TNT test solutions were vacuum filtered via passage through a glass fiber filter (Pall Brand) before each experiment.

The initial pH of the TNT test solutions ranged from 6.8 to 7.8, depending on the initial TNT. The final pH after reaction generally ranged from 9.0 to 9.5. No buffers were added to control the pH to avoid chemical interactions between the buffers and the metal surfaces. Buffers based on borates, phosphates, or carbonates have been known to interact with zerovalent metal surfaces, forming precipitates that may adversely affect the degradation of the compounds of interest (*12*, *25*).

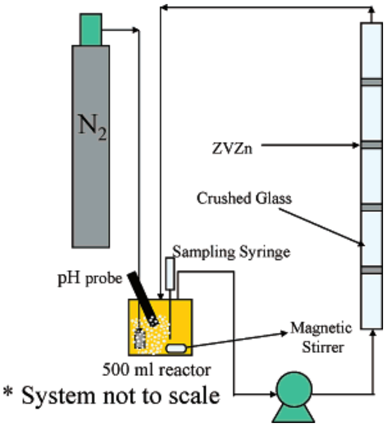


FIGURE 1. Reactor configuration (drawing not to scale).

Reactor System. Most of the experiments were conducted using a reactor system such as the one illustrated in Figure 1 with the experiments run in duplicate. The reactors were purchased from Ace Glass Inc., Vineland, New Jersey, and had a 500 mL working volume. The glass column shown in Figure 1 was also purchased from Ace Glass Inc. and had a length of 30 cm and an internal diameter of 1 cm. The column was connected on the outlet side of the reactor using Nalgene 890 Teflon tubing (Fisher Scientific, Inc.). The tubing has 0.25 in. outside diameter. The inlet side of the column was connected to a Cole Palmer Inc. pump (Model 7553-20). The MasterFlex pump head (Model 7518-10) used was also purchased from Cole Palmer Inc. as well as the Tygon extended life silicon tubing used with the pump head. The pump and the reactor were connected to complete a closed loop. Teflon fittings were used for all the connections in contact with the test solution, except for the small piece of Tygon extended life silicon tubing used within the pump head. This type of tubing allows for the continuous recirculation of solution for more than 6 h without leakage or breakage.

The reactor was equipped with five openings. Two were used as an inlet and outlet for introduction and removal of TNT solutions. One was used as a port for a Corning brand plastic combination pH electrode with sealed Ag/AgCl reference electrode. This electrode was 10 in. long. As for the other two openings: one served as a sample port using a septum adapter, and the other was used for sparging nitrogen during the anaerobic experiments by immersion of a glass gas dispersion tube with a fritted cylinder.

During the experiments, 500 mL of the TNT test solution was mixed and sparged with high purity nitrogen for 30 min prior to beginning the experiment to obtain anaerobic conditions, which is defined for these experiments as less than 0.5 mg/L of dissolved oxygen in the solution. Concentrations of dissolved oxygen were measured with an Orion DO probe and an Orion meter (Model 842). Mixing within the reactor was accomplished through the use of a magnetic stir bar placed on the reactor bottom and the whole unit placed onto a stir plate. The column was filled with glass beads, crushed glass, and a thin layer of metal used as received. The glass beads were purchased from Fisher Scientific, Inc. The crushed glass was prepared by crushing the glass beads with a DAKE hydraulic press manufactured by DAKE Corporation, Grand Haven, Michigan. The column was loaded with crushed glass and glass beads using a glass funnel.

The metal layer was placed between two crushed glass layers approximately 3 cm of height. The crushed glass layers were held in place using hollow glass beads.

Once the column was prepared, it was connected to the pump and the reactor. Thus, the column was also flushed with nitrogen during the removal of oxygen from the test solutions. After 30 min of sparging with nitrogen, the glass gas dispersion tube was removed from the reactor, and this opening was closed with a solid Teflon stopper. Then, a sample from the reactor solution was collected, and the experiment was initiated by turning the pump on at a specified set point. Samples were collected at predetermined time intervals for TNT analysis. At the end of the experiment, the metal was extracted via recovering the metal from the column and immersing it in 10 mL of methanol in a beaker, which was then placed in a Branson ultrasonic bath (Model 3510) for ten minutes. A sample of the extract was then collected for TNT and its reaction byproduct analysis (the analysis of the extract indicates the amount of TNT and byproduct adsorbed onto the metal).

In experiments that required the addition of sodium chloride, the salts were added five minutes before the end of the sparging period. A 3 M potassium chloride solution was purchased from Fisher Scientific Inc. and used as received. In the case of sodium chloride, a 3 M solution was prepared in the laboratory by mixing the proper amount of ACS grade sodium chloride (Fisher Scientific, Inc.) with distilled water.

A control experiment was conducted to determine the amount of TNT adsorbed by the reactor configuration (no metallic species). A 20 mg/L TNT solution was recirculated throughout the system for 2 h. Initial and final samples were collected and analyzed for TNT. This experiment demonstrated that the glass beads, crushed glass, Teflon tubing, and Tygon tubing (extended life silicon) adsorbed a negligible amount of TNT from the 20 mg/L solution (3.54%). A similar control experiment was conducted to determine the disappearance of TNT in the presence of potassium chloride (no metallic species present). In this experiment, 3 mM of potassium chloride was added into the TNT solution, which was then recirculated throughout the system for 2 h. In this case, 5.79% (by weight) of the initial TNT was removed from the system. The TNT removed during this experiment was likely due to adsorption. It was concluded that no reaction occurs between TNT and KCl.

For the aging experiments, an identical 6 h experiment was conducted over the course of 4 or 5 days using the same metal specimen. In other words, the same metal was exposed to a fresh TNT solution every day. At the end of each day, the column containing the metal was flushed with methanol. The column containing the reacted metal was left overnight under a nitrogen atmosphere. During selected experiments, the metal was collected, and the surface was characterized by scanning electron microscopy (SEM). This technique was also used to characterize the initial metal surface in terms of elemental composition and morphology.

Analytical Methods. *TNT and Byproducts.* TNT was analyzed using high performance liquid chromatography (HPLC) as described by USEPA Analytical Method 8330 (*26*). The equipment consisted of a Hewlett-Packard Model 1100 system equipped with a quarternary pump (Model G1311A), degasser (Model G1322A), auto sampler (Model G1313A), and UV diode array detector (Model G1315A). The HPLC was controlled by computer using the Chem Station software marketed by Agilent.

A Hypersyl-BDS C18 (Agilent) was used for the separations. TNT was identified by comparison with the retention times of a certified standard, and concentrations were determined from peak areas by comparison to standard curves. Standard curves were prepared by diluting a standard mixture of explosives with a certified concentration of 100 mg/L. This mixture (Mix A EPA 8330) is prepared and marketed by Supelco. The amount of sample injected for analysis was 10 μL. The Hypersyl column was eluted with a methanol/water solvent gradient. The initial concentration of the eluent phase was 30% (v/v) methanol. The analysis ran for 30 min. The final concentration of the eluent was 80% methanol. The elution rate was 0.72 $\text{mL}\cdot\text{min}^{-1}$. The detection limit was taken as the lowest concentration of a standard that resulted in a measured signal. For TNT, the detection limit was 0.193 mg/L.

SEM. A scanning electron microscope (Stereoscan 360, Cambridge Instruments Ltd., Cambridge, England) was used to generate micrographs of metal samples. This equipment is located in the Entomology Department of Mississippi State University. The samples were mounted on aluminum specimen mounts with double-sided conductive adhesive carbon tape. The samples were sputter coated for 3 min with gold or palladium. A Polaron Model E5100 Series II, manufactured by Polaron Equipment Limited, Watford Hertfordshire, England, was used to sputter the samples.

Surface Area. The surface area of the metals was measured using an Accelerated Surface Area and Porosimetry (ASAP) 2405 Analyzer. The analyses were conducted by Micromeritics Instrument Corporation (Norcross, Georgia) on all the metals examined during the study. The low surface area option, which uses krypton as the adsorbate was performed due to the very low surface area of the metallic species.

Results and Discussion

The surface area of iron and zinc used in this study was 0.0060 and 0.0110 m^2/g, respectively. These low values of surface area indicate that the metallic species are nonporous with few surface irregularities. The higher surface area for zinc is indicative of its smaller particle size compared to iron. Figure 2 illustrates scanning electron micrographs for both metals. The SEMs corroborate that the metals surface morphology is relatively smooth and nonporous.

The effect of chloride concentration in solution on the degradation of TNT using ZVZn is presented in Figure 3. In the absence of chloride, the reaction rate of TNT with ZVZn is significantly slower compared to solutions containing 300 μM and 3 mM KCl (Figure 3). In the absence of potassium chloride, 28% of the initial TNT concentration disappeared in 6 h of treatment. The addition of 3 μM and 3 mM potassium chloride degraded 100% of the initial TNT within 4 and 3 h, respectively. It also can be observed that an initial potassium chloride concentration of 3 μM requires approximately 15 min before acceleration of the TNT degradation. This activation period could be associated with the breakage of the inhibiting oxide layer on the zinc surface. Previous work indicates that pitting corrosion is initiated after the oxide layer has grown to a critical thickness (*27*). This oxide layer formation activation period can be reduced via increasing chloride concentration (*19*). Relatively high chloride concentrations chemically depassivates the oxide layer and accelerates pitting corrosion (*28*). As the results indicate, higher concentrations of chloride seem to break this protective oxide layer faster.

Other researchers have determined the surface area normalized reaction rate constant for reactions of chlorinated solvents with ZVMs using the pseudo-first-order model given by (*7*, *29*)

$$-\frac{d[P]}{dt} = k_{SA} a_s \rho_m [P]$$

where $[P]$ = pollutant concentration, <fr>mg<fd>L<frx>, k_{SA} = specific reaction rate constant, <fr>L<fd>h·m^2<frx>,

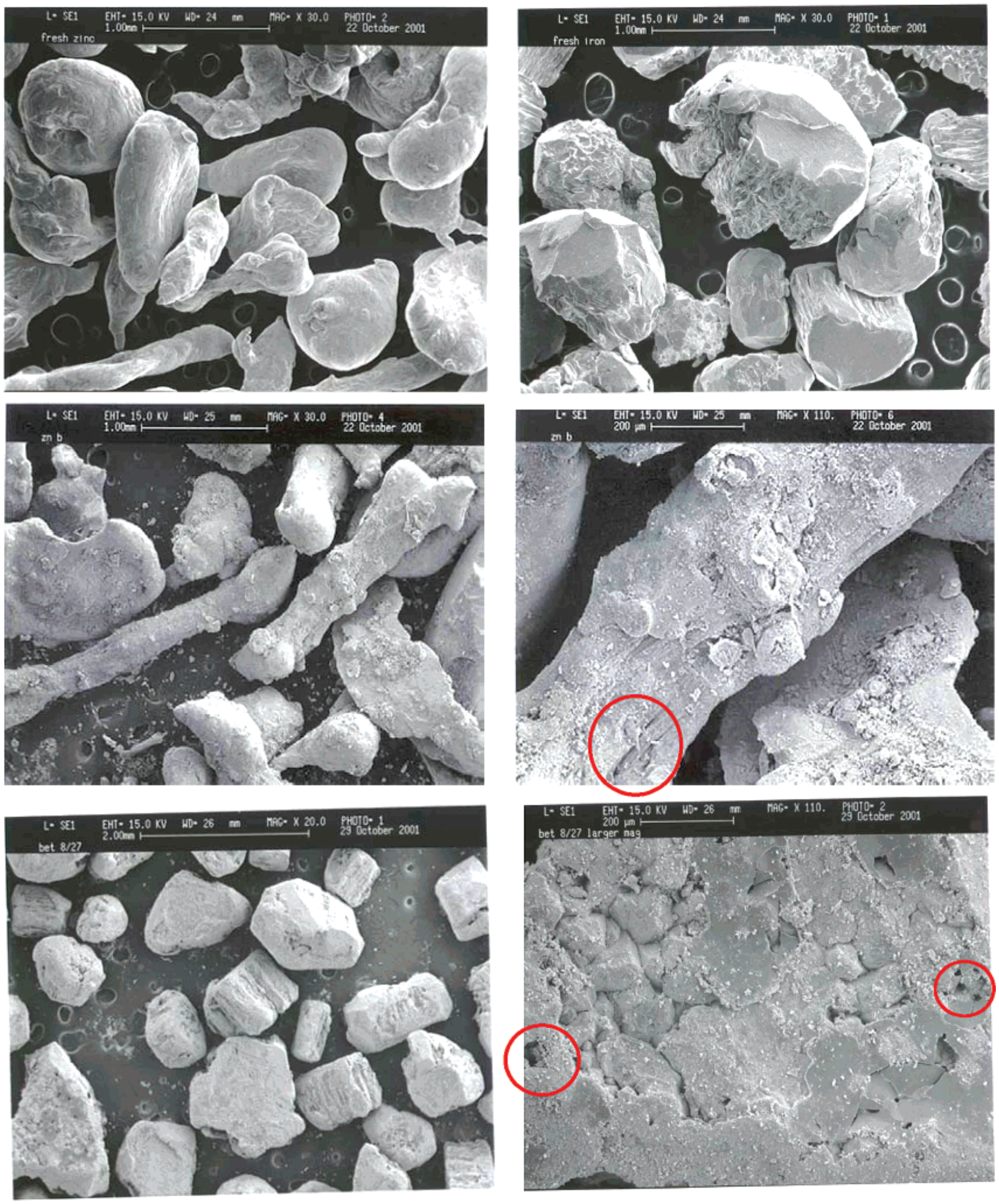


FIGURE 2. (TOP) SEM micrographs of fresh zinc (Left) and iron (Right). (MIDDLE) Micrographs of zinc after reaction with TNT in the presence of KCl (The magnifications were 30 and 110 for the left and right micrographs, respectively.). (BOTTOM) Micrographs of iron after treatment of TNT contaminated water with addition of KCl (The magnifications were 20 and 110 for the left and right micrographs, respectively.).

a_s = specific surface area of metal, <fr>m^2<fd>g<frx>, and ρ_s = metal mass concentration, <fr>g<fd>L<frx>.

A value of 1.364 $L \cdot m^{-2} \cdot h^{-1}$ ($r^2 = 0.88$) was obtained for this study using this model for the reaction in the absence of chloride. The chloride effect on TNT degradation also was measured by calculating the pseudo-first-order surface area normalized rate constants. Values of 10.5 ($r^2 = 0.95$) and 51.0 $L \cdot m^{-2} \cdot h^{-1}$ ($r^2 = 0.99$) were obtained for the 300 μM and 3 mM KCl experiments, respectively. The rate of TNT degradation increased by a factor of approximately 35 in the presence of 3 mM KCl indicating a significant acceleration in TNT degradation when chloride was added to the test solutions. Similar results were obtained using 3 mM NaCl suggesting that the identity of the cation accompanying chloride does not have an effect on TNT degradation.

Figure 4 shows the effect of chloride on TNT degradation by ZVI. In the absence of chloride the reaction of ZVI with TNT came to a halt after 180 min. This phenomena could have been caused by two factors. First, formation of nitroamines on the surface of the iron acted as corrosion inhibitors, stopped the iron oxidation, and consequently, TNT degradation. These compounds adsorb strongly to the iron oxide layer (*5*, *12*). The standard electrode-reduction potential of 2-amino-4,6-dinitrotoluene is more negative than that of iron (*30*). This compound was identified (not quantitated) in the metal samples extracted with methanol. This nitroamine can cathodically protect the iron surface and stop its corrosion. Second, the surface of the iron is covered with a protective oxide layer and has few reactive sites available. TNT could have adsorbed irreversibly on these reactive sites. The effect of chloride addition on TNT degradation suggests that the second factor is the main cause of the halted TNT degradation. Fontana (*20*) indicates that pit anodic reactions activate the rest of the metal surface.

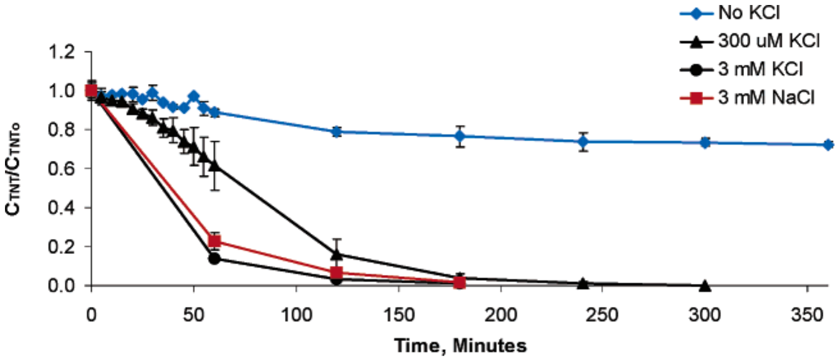


FIGURE 3. Effect of the KCl or NaCl concentration on the TNT degradation by ZVZn (conditions: anaerobic, 12 mL/s, 4 g/L Zn, $[TNT]_o = 30$ ppm).

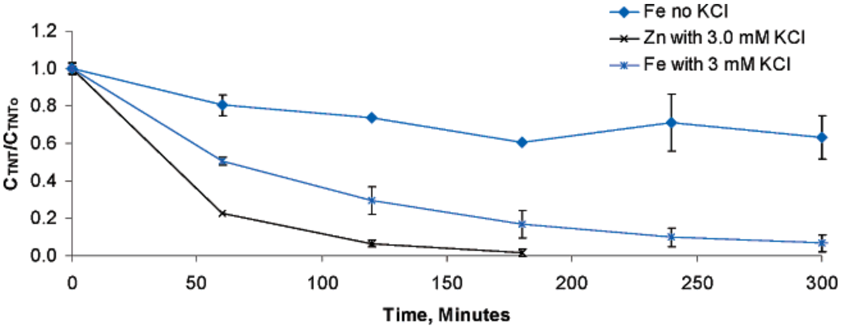


FIGURE 4. Effect of the KCl concentration on the TNT degradation by ZVI (conditions: anaerobic, 4 g/L Fe, $[TNT]_o = 10$ or 20 ppm (Fe) or 30 ppm (Zn) for the no added and added KCl experiments, respectively).

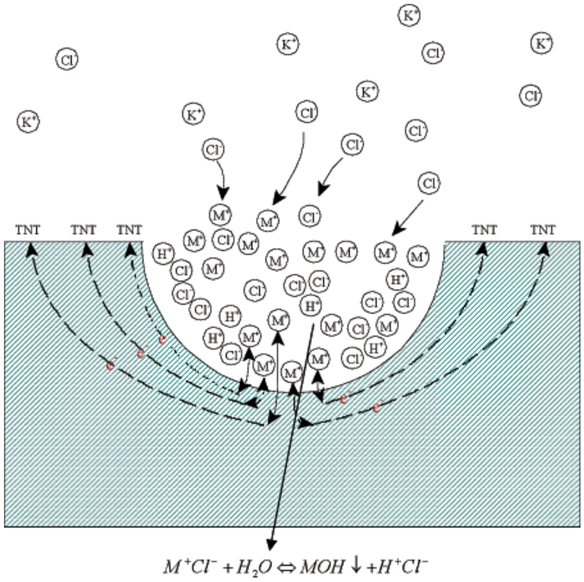


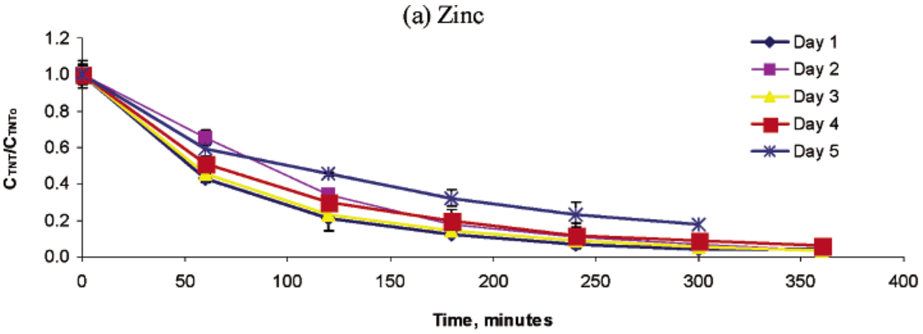
FIGURE 5. Pitting corrosion during the degradation of TNT by ZVMs in the presence of chloride (*20*).

Additionally, relatively high chloride concentrations chemically depassivates the oxide layer (*28*). This depassivation creates new reactive sites for pitting and reaction of organic and inorganic species adsorbed onto the metal surface.

Generation of new reactive sites via chloride addition enhanced TNT degradation significantly. In this case, k_{SA} in the absence and presence of 3 mM KCl was 6.5 and 37.0 L·m^{2}·h, respectively. No TNT degradation occurred after 180 min in the absence of potassium chloride. Therefore, the TNT degradation within this period was used to determine the rate constants. The results presented in Figures 3 and 4 indicate that, in the absence of chloride, iron is more reactive than zinc toward TNT in contaminated water (k_{SA} for zinc was 1.364 L·m^{-2}·h^{-1} vs 6.5 L·m^{-2}·h^{-1} for iron). This result indicates that the oxide layer formed on the zinc surface via interaction with oxygen in air and water, is more passivating than a ferric oxide layer. Additionally, surface associated Fe(II) has been shown to reduce nitroaromatics (*22*, *31*). To our knowledge, Zn(II) associated to zinc oxides have not shown reactivity toward nitroaromatic compounds. The chloride ion minimizes the resistance to electron transfer caused by the oxide layer formed on the metal surface via the mechanism of pitting corrosion. Pits break the oxide layer and generate new reactive sites. Once the oxide layers breaks, zinc is more reactive toward TNT than iron as indicated by their respective k_{SA} in the presence of 3 mM KCl (k_{SA} for zinc was 51 L·m^{-2}·h^{-1} vs 37 L·m^{-2}·h^{-1} for iron).

Figure 5 illustrates the proposed mechanism of pitting corrosion associated with TNT degradation via the reaction with a zinc or iron surface. This mechanism is consistent with the theory of pitting corrosion in aerated chloride solutions (*19*–*21*). Metal surface irregularities dissolve faster than the rest of the surface causing generation of localized positive charge regions on the zinc surface. To maintain electroneutrality in the system, the chloride ion is attracted to these regions and forms metal chlorides. Hydrolysis of these chlorides form a metal hydroxide and hydrochloric acid. Local accumulation of hydrochloric acid inside the microscale pits serves as a source of continuous generation of electrons, which react with the TNT and partially reduced byproducts adsorbed on the zinc surface.

Figure 2 (MIDDLE) shows scanning electron micrographs of the zinc surface after exposing the metal to TNT contaminated water with a 3 mM potassium chloride concentration. Initially the zinc surface morphology was relatively smooth (see TOP of Figure 2). In contrast, flakes, crevices, and pits can be observed on the metal surface after 3 h of TNT degradation. The hydrochloric acid formed during pitting corrosion accumulates inside the crevices and pits, auto catalyzing the generation of electrons, and thus, TNT degradation. Fontana (*20*) describes the autocatalytic nature



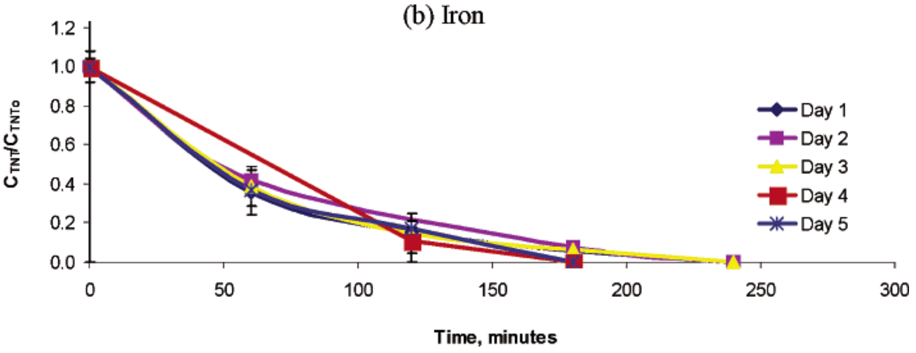


FIGURE 6. Effect of chloride on zinc and iron aging during TNT degradation (condition: 4 g/L zinc or iron, anaerobic, [KCl] = 3 mM KCl, and $[\mathrm{TNT}]_o$ = 25 mg/L for Zn and 10 mg/L for zinc and iron experiments, respectively).

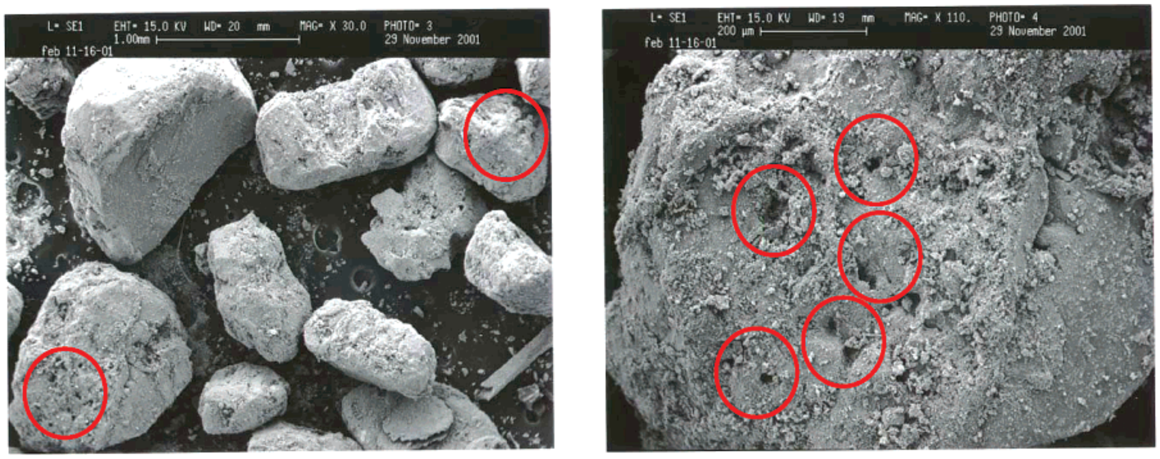


FIGURE 7. SEM micrographs of iron used for treating TNT contaminated water containing KCl for 5 days.

of pitting as follows: inside the pit "both hydrogen and chloride ions stimulate the dissolution of most metals and alloys, and the entire process accelerates with time". Since after breakage of the oxide layer iron is less reactive than zinc, more localized pitting is observed on its surface (see Figure 2 (BOTTOM)). This localized pitting and relatively slower reaction of TNT with ZVI in the presence of chloride makes iron more structurally stable compared to zinc during long-term operation.

Figure 6 (a and b) illustrates the effect of chloride on the rate of TNT degradation using aged zinc or iron. The same zinc or iron was used for a period of 5 days and fresh TNT test solutions were reacted each day. In the case of zinc, the figure shows that there were no losses in the activity of the metal during the first 4 days of experiments and similar rates of TNT degradation were observed each day. The rate of TNT degradation decreased during Day 5 compared to the other days. The zinc reactivity decreased because of changes in zinc metallic structure. At the end of Day 5, the metal was a white powder with no metallic appearance.

In the case of iron (see Figure 6[b]), TNT degradation rate was maintained nearly constant during the first 3 days of treatment with a slight rate increase during Days 4 and 5. Figure 7 illustrates a SEM micrograph of the iron collected from the column after Day 5. It can be observed that iron maintained its metallic structure during the whole 5 days of experiments. The figure also shows the appearance of well developed pits. The rate acceleration during Days 4 and 5 could have been caused by accumulation of hydrochloric acid inside the formed pits. Once the pits are formed, the continuous dissolution of metal inside the pits provide a continuous source of electrons for oxidizing agents adsorbed onto the metal surface.

Summarizing, the use of pitting corrosion promoters accelerates the degradation of TNT by both zerovalent zinc and iron. In the absence of KCl, TNT degradation of TNT by ZVI is faster than TNT degradation by ZVZn. The experimental data suggested that the oxide layer formed on the zinc surface has more resistance to electron transfer than the iron oxide layer. Breakage of these oxide layers via the use of pitting corrosion promoters minimizes this resistance and zinc becomes more reactive than iron toward TNT. Elimination of the oxide layers in metals allows for the full utilization of their electrons electromotive force, which predicts that the reaction of zinc with TNT is more thermodynamically feasible than the reaction with iron. A polishing treatment step to remove potentially dissolved zinc down stream from the ZVM step could be required during ex-situ water treatment operations.

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