A continuous system for Feo reduction of nitrobenzene in synthetic wastewater.

4 AUTHORS, INCLUDING:

Keith E Taylor
University of Windsor

67 PUBLICATIONS **1,750** CITATIONS

SEE PROFILE

Nihar Biswas
University of Windsor

122 PUBLICATIONS **2,006** CITATIONS

SEE PROFILE

Jatinder K Bewtra
University of Windsor

81 PUBLICATIONS **1,718** CITATIONS

SEE PROFILE

A Continuous System for Fe⁰ Reduction of Nitrobenzene in Synthetic Wastewater

RAMKRISHNA MANTHA,[†]
KEITH E TAYLOR,*,[‡]
NIHAR BISWAS,[†] AND
JATINDER K BEWTRA[†]

Departments of Civil & Environmental Engineering, and Chemistry & Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

Nitrobenzene is a major environmental pollutant, and its degradation is difficult to achieve. Hence, a chemical reduction pretreatment is sought in this research, before the resulting aniline can be treated by enzyme-mediated oxidative polymerization. Zerovalent iron (Fe⁰) has been successfully employed to reduce nitrobenzene to aniline in synthetic wastewater in both batch and continuous flow reactors. The concentration of nitrobenzene studied was that which would be present in industrial wastewater streams (millimolar, 123 ppm), a concentration range considerably higher than those studied previously with groundwater by other researchers. Anaerobic conditions were maintained in the reactors by including Na_2SO_3 as an oxygen scavenger in the presence of $CoCl_2 \cdot 6H_2O$, which acted as a catalyst. Batch reactors exhibited adsorption of aniline on the Fe⁰, which could be described by a langmuir isotherm. A 200 g Fe⁰ (particle size: 1−2 mm) bed completely converted 1 mM of nitrobenzene flowing upward for about 600 pore-volumes before experiencing flow reduction due to clogging due to corrosion products. Green-black precipitates (Fe⁰ corrosion products) were formed at the influent end of the column which were identified as maghemite.

Introduction

Zerovalent iron (Fe⁰) is finding widespread applications in groundwater remediation techniques. Use of iron as a means to carry out reductive transformations of organic pollutants was primarily introduced by the research groups of Gillham and of Tratnyek (*1*). Reynolds et al. (*2*) while working on the suitability of various materials for construction of groundwater monitors found that metals such as aluminum, stainless steel, and galvanized steels apparently transformed compounds such as trichloroethylene (TCE), hexachloroethane, etc. They recognized that the process responsible for degradation of the chlorinated compounds by metal could be applied to the treatment of groundwater. Researchers have studied different classes of compounds: halogenated organics (*3–10*), azoaromatics (*11, 12*), and nitroaromatics (*13–16*). The earliest detailed surveys involving degradation of halocarbons by zerovalent iron in laboratory batch systems (*3, 4*) raised speculations that the dechlorination occurs

through a surface reaction leading to the ultimate degradation of the halocarbon. Weber (*11*) in a seminal paper concluded that reductive transformation by zerovalent iron is a surface-mediated process. Some of the possible mechanisms have been summarized in a recent news article (*1*). There is enough evidence to suggest that adsorption of halogenated organic compounds to the Fe⁰ surface does indeed occur (*5, 8–10*). For heterogeneous reactions to take place, it is required that the reactant molecules reach the solid surface. They then combine with either "reactive" or "nonreactive" surface sites. According to Burris et al. (*9*), reactive sites are those where the breaking of bonds in the reactant molecule takes place, while on nonreactive sites only sorption interactions occur and the solute molecule remains intact. Burris et al. (*9*) fitted the sorption data by the generalized langmuir isotherm expression. They also speculated that the bulk of sorption was to the nonreactive sites. Devlin et al. (*14*) studied the kinetics of nitroaromatic reduction on granular iron in a recirculating batch reactor. They performed static batch experiments to study sorption of different anilines on the iron and calculated the langmuir parameters. The role of surface bound Fe (II) has been studied (*17*), and it was found that Fe (II) adsorbed on surfaces might play a role in the reduction of nitroaromatics. Agrawal et al. (*13*) studied the reduction of nitrobenzene by iron under anaerobic conditions in bicarbonate-buffered batch systems. They found that the nitrobenzene reduction rate increased linearly with the available iron surface area, and the effect of solution pH was minimal on the conversion. Mass transfer to the metal surface seemed to be the rate-controlling step in the zerovalent iron reduction of nitroaromatic compounds. Tratnyek (*18*) discussed the important aspects of using iron in the form of a barrier for remediating environmental contaminants in groundwater. In a recent review article (with over 200 references), Scherer et al. (*19*) presented an overview of the mechanisms and factors controlling different processes such as sorption, precipitation, chemical reaction, etc. that are involved in permeable reactive barriers (PRBs) for in situ groundwater clean up.

The production of nitrobenzene in the USA was close to 0.75 billion kg for the year 1995 (*20*). The commercial uses of nitrobenzene are reduction to aniline, solvent, metal polishes, shoe-black, perfume, dye intermediates, and as a combustible propellant (*21*). Total production-related waste for 1997 was estimated to be 3.1 million kg (*22*). A total of 320 000 kg was released on-site or was sent for off-site disposal (*22*). The remediation of nitrobenzene is of interest because it is a proven mutagen (*23*). Two reviews (*24, 25*) have discussed the biodegradation of nitroaromatics. They also provide an insight about the toxicity of nitroaromatics. Peroxidase-catalyzed coupling is an effective strategy for removal of phenols and anilines from water (*26–31*). However, nitroaromatics are outside the scope of peroxidase catalysis. The biodegradation of nitrobenzene, although known, is generally difficult to achieve. Recent reports (*32, 33*), however, indicate significant progress in this area, with complete mineralization being achieved in some instances. The transformation reaction often produces aniline, which also is an environmental contaminant. Hence, nitrobenzene must further be converted beyond the amine, whether by the microbial or the zerovalent iron reduction routes. Monsef et al. (*34*) successfully combined zerovalent iron reduction with enzyme-mediated oxidative coupling to completely remove nitrobenzene. The zerovalent iron reduction requires anaerobic conditions, and to achieve this, earlier researchers degassed the solutions prior to Fe⁰ reduction. To circumvent

* Corresponding author phone: (519) 253-3000 ext. 3526; fax: (519) 973-7098; e-mail: taylor@uwindsor.ca.
† Civil & Environmental Engineering, University of Windsor.
‡ Chemistry & Biochemistry, University of Windsor.

this, Monsef et al. (34) tried $FeSO_4$ as an O_2 scavenger. However, rather high concentrations of $FeSO_4$ were required, and its role was not clearly understood. It seemed that $FeSO_4$ did more than just scavenge O_2 in that residual nitrobenzene was converted to aniline upon raising the pH in the effluent. It was surmised (34) that this conversion was due to Fe^{2+} species deposited on the Fe^{3+} particles that had formed, a phenomenon reported by Klausen et al. (17). Gotpagar et al. (35) dehalogenated trichloroethylene using zerovalent iron in the presence of sodium bisulfite as the O_2 scavenger. However, a detailed study of the effects and concentrations of the O_2 scavenger has not been reported. In all previous works, groundwater has been the focus with concentration ranges of contaminant typically in the range of $20-50$ μM. The focus of this study is on industrial wastewater containing organic pollutants in the millimolar range (nitrobenzene aqueous solubility is ca. 20 mM). Our overall goal is to develop a continuous two-stage process following on the preliminary feasibility study reported earlier from this lab (34) where nitrobenzene in the $1-10$ mM concentration range was studied.

The objectives for the current research were (a) to continue the development of an efficient Fe^0-based process for the reduction of nitrobenzene (in the millimolar range) present in waste- or process-water; (b) to optimize the use of an O_2 scavenger so that degassing of solutions is avoided; and (c) to study adsorption of aniline on Fe^0 as a function of pH. The second reaction, in a continuous system for removing nitrobenzene from waste streams through a series of two reactions would be peroxidase-catalyzed oxidative coupling and precipitation of the aniline formed in the first reaction. Work on the second step and the combined process is in progress.

Experimental Procedure

Materials. Analytical grade aniline and nitrobenzene as well as ACS grade $NaHPO_4$, Na_2HPO_4, Na_2CO_3, and $NaHCO_3$ were purchased from BDH Inc. ACS grade Na_2SO_3 and $CoCl_2\cdot6H_2O$ were obtained from Fisher Inc. Analytical grade trinitrobenzenesulfonic acid (TNBS) (as picrylsulfonic acid 5% (w/v) aqueous solution) was obtained from Sigma Chemicals (lot no. 107H5001). Two preparations of iron metal were used in this study. The first was purchased from Fisher Chemicals (I57-500: lot no. 976195) as iron filings (about 40 mesh size). The second one was purchased from Alfa Aesar as iron granules (stock #39708, lot #D03I24) with the nominal size between 1 and 2 mm. Supplier data stated that the purity of the metal was 99.98% (on metal basis) with the major impurities being phosphorus (16 ppm), cobalt (14 ppm), nickel, and manganese (both 10 ppm).

Iron Pretreatment. Initially, the iron metal was used as received (about 40 mesh) from Fisher. However, the proportion of finer particles was comparatively much higher (particles passing through 40 mesh > 70%) than the desired size. Hence, prior to use, the Fe^0 was hand-sieved to give a size range of $30-40$ mesh. This is called Iron-I throughout this report. The other iron from Alfa Aesar (henceforth called Iron-II) was of $1-2$ mm size and was used as received. Iron was always pretreated with HCl acid as recommended (13). In the column operations, Fe^0 was pretreated in situ. The purpose of the pretreatment was to clean the surface of the iron to remove any (hydr)oxide. Subsequently, the excess HCl was removed by washing with carbonate buffer (pH 9.5), and this was followed by washing with Na_2SO_3 solution to remove any remaining dissolved alkalinity. The influent pH was between 7.2 and 7.5, while the effluent pH was between 7.4 and 7.7.

General Reaction Conditions. All reactions were carried out at room temperature, $18-22$ °C, except where noted. Buffers, whenever used, were prepared following the recommendations of Gomori (36). Batch reactor runs were carried out typically in 30-mL vials sealed by screw-cap. The vials were shaken on a Burrell model 75 shaker at maximum setting (Burrell, Pittsburgh, PA). This provides a wrist-like action to the vials for proper mixing. Solutions were made anaerobic by adding Na_2SO_3 along with $CoCl_2\cdot6H_2O$ as catalyst at 0.1 wt %, except where noted otherwise. In general, all the vials received 1 g of Iron-I, unless noted otherwise. Standing the vial on a magnet for a few minutes facilitated settling of iron particles after the reaction.

Column operation of the Fe^0 reduction step was initially investigated with 50 g of Iron-I in a 15×150-mm column (Fe^0 bed depth was 110 mm). After pretreatment, iron was maintained in Na_2SO_3 solution. An upward flow of the solution through the column was executed using a peristaltic pump (Auto Analyzer) supplied by Technicon Corp., Tarrytown, NY. The columns used were purchased from Bio-Rad Inc. Mississauga, ON. A continuous flow of $2.8-3.1$ mL/min was maintained which resulted in complete conversion of 1 mM nitrobenzene. The effluent from the column was analyzed at regular intervals for aniline. However, most of the column operations were subsequently studied with 200 g Fe^0 (Iron-II) in a 15×300-mm size column under similar flow conditions. Fe^0 bed depth, in this case, was about 280 mm. Complete conversion of nitrobenzene to aniline was sustained for almost 600 pore volumes. To estimate the corrosion products, the vertical column was back-washed at high flow rate with Na_2SO_3 solution and the precipitates were collected on a filter paper and the precipitate mass was determined. Also, another method was followed to confirm these results. The iron filings from the influent end of another column, that had not been back-washed, were collected in a beaker and thoroughly washed with Na_2SO_3 solution to dislodge the precipitates. The wash liquid (along with the precipitates) was treated with concentrated acid, digested, and then analyzed by the direct coupling plasma (DCP) technique.

Analysis. The concentration of the reaction product, aniline, was determined by TNBS test. In a final volume of 1.0 mL, 100 μL of 10 mM TNBS, 100 μL of 0.5 M phosphate buffer of pH 6.4, and 800 μL of sample plus water were added. Samples were allowed to stand for 30 min and then absorbance was measured at 384 nm against a reagent blank. Solution absorbance was measured using Hewlett-Packard diode array spectrophotometer models 8451A and 8452A. The results showed that there was a linear relationship between the absorbance and the concentration. Concentrations were calculated using an experimentally determined extinction coefficient (molar absorptivity) of $13\,200\,M^{-1}\,cm^{-1}$. It is known that TNBS readily forms an adduct with SO_3^{2-} that affects the analysis (37). This complication was overcome by preparing a calibration curve for authentic aniline solution doped with Na_2SO_3 and measuring the peak at 398 nm at a slightly higher extinction coefficient ($14\,000\,M^{-1}\,cm^{-1}$) than for pure aniline. UV−Vis spectra measurements and multicomponent analysis (MCA) software was used with authentic standards to determine nitrobenzene and aniline concentration in reaction solutions. Dissolved oxygen measurements were done on an oxygen meter (model 57) supplied by YSI, Inc., Yellow Springs, Ohio. Fe^0 filings taken from the influent end of the column were dried in a stream of N_2 and then examined by scanning electron microscopy (SEM) (JEOL 5800-LV) with energy-dispersive X-ray spectrometry (EDS) analysis (Kevex) for surface morphology and elemental composition. An accelerating voltage of 15 kV was used under low vacuum at room temperature. The filings were later characterized by X-ray diffraction (XRD) analysis (Rigaku DMAX/1200). Direct coupling plasma (DCP) technique was employed to analyze the effluent water stream and Fe^0 corrosion precipitates for total Fe and total Co. A SpectraSpan
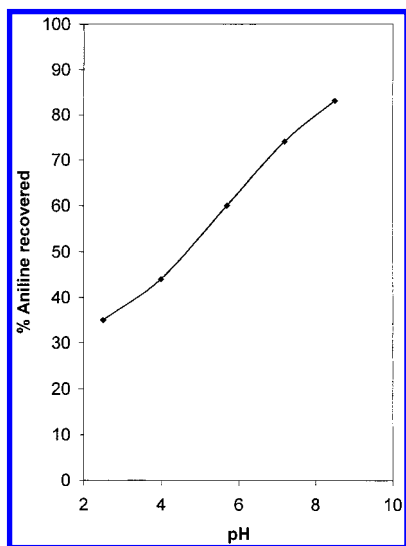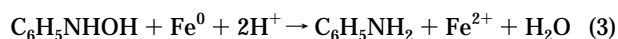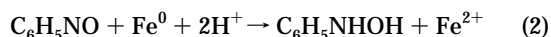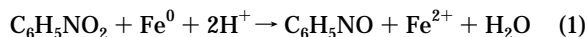
FIGURE 1. Product (aniline) recovery under different solution pH. One gram of Fe^0 (Iron-I) completely reduced 1 mM nitrobenzene to aniline in 30-mL batch reactors in 1 h. 5 mM Na_2SO_3 was used to make the solutions anaerobic.
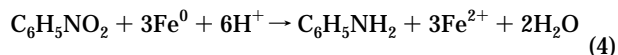
V System (supplied by SpectraMetrics Inc., Andover, MA) was employed to analyze the samples, prepared according to Standard Methods no. 3030E (*38*).

Results and Discussion

The zerovalent iron reduction of nitrobenzene yields aniline via nitrosobenzene and phenylhydroxylamine as intermediates (*13*) according to the following reactions:

$$C_6H_5NO_2 + Fe^0 + 2H^+ \rightarrow C_6H_5NO + Fe^{2+} + H_2O \quad (1)$$

$$C_6H_5NO + Fe^0 + 2H^+ \rightarrow C_6H_5NHOH + Fe^{2+} \quad (2)$$

$$C_6H_5NHOH + Fe^0 + 2H^+ \rightarrow C_6H_5NH_2 + Fe^{2+} + H_2O \quad (3)$$

Formally, the overall reaction can be written as:

$$C_6H_5NO_2 + 3Fe^0 + 6H^+ \rightarrow C_6H_5NH_2 + 3Fe^{2+} + 2H_2O \quad (4)$$

Previous studies demonstrated the need for anaerobic conditions and iron pretreatment. Anaerobic conditions were necessary to achieve the complete reduction of nitrobenzene to aniline. Under aerobic conditions, 100% conversion of nitrobenzene was never achieved in preliminary work from this lab (*34*). In groundwater treatment with zerovalent iron, generally anaerobic conditions exist. Also, the concentration of organic pollutants is extremely low as compared to wastewater. This provides a very high surface area/mass of pollutants removed in groundwater as compared to the conditions in this study. Also, the rates of reduction were faster after acid treatment of iron. This confirmed the findings of Agrawal et al. (*13*) that acid pretreatment does in fact accelerate the rate of reduction. Scherer et al. (*7*) also experienced rate enhancement with surface cleaning.

Effect of pH. Owing to direct involvement of H^+ ions in the reduction of nitrobenzene, it was thought that changes in pH might affect the nitrobenzene reduction. The pH range studied was from 2.5 to 8.5. In a 30-mL vial, 1 g of Fe^0 completely reduced 1 mM nitrobenzene. However, depending on the prevalent pH, product recovery varied widely (Figure 1). Since no nitrobenzene was detected in the final analysis of the batch reactor, it was thought that protonation of the aniline formed ($pK_a = 4.6$) prevented its desorption
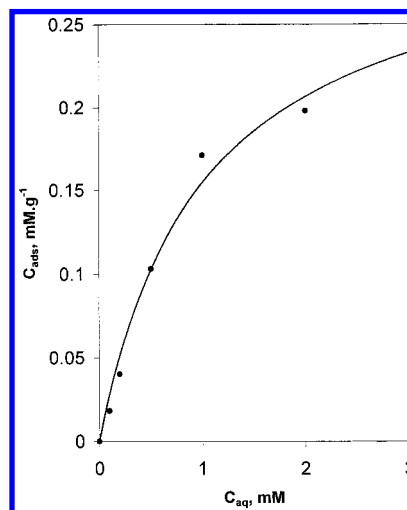

FIGURE 2. Adsorption isotherm for aniline on Iron-I. Curve is fit to eq 5 with parameters given in the text. 5 mM Na_2SO_3 was used. Batch reactors were of 30 mL capacity at pH 7.3. Each batch received 1 g of Fe^0 (Iron-I).

from the iron surface completely. Ionizable nitrophenols exhibited a strong pH dependence of the distribution coefficient value in the pH region corresponding to the pK_a of the compound (*39*). This is similar to what was observed for aniline. It is also possible that the amino group of aniline (in the neutral, free-base form) acts as a ligand in complex formation with the metal as indicated by Vasudevan and Stone (*40*). No analysis was done to ascertain the presence of any intermediates (phenylhydroxylamine or nitrosobenzene), since it is known from the literature (*13*, *34*) that their presence was negligible in the final stages of conversion.

Adsorption Isotherm. Batch experiments were conducted to evaluate the sorptive properties of aniline on Fe^0. Typically, 30-mL vials received 1 g of Fe^0 (Iron-I) and 1 mM of aniline. The vials were shaken as before, and the contents analyzed after 3 h. The data are presented in Figure 2. Different plots were generated at different pH values. The isotherms plotted are nonlinear over the range tested and are described by the langmuir equation:

$$C_{ads} = \frac{K_L \cdot C_{aq}}{1 + K_L \cdot C_{aq}} [C_{ads}]_{max} \quad (5)$$

Here C_{ads} and C_{aq} are the concentrations of aniline on Fe^0 and in solution, respectively. K_L is the langmuir constant, and $[C_{ads}]_{max}$ is the saturation concentration.

A nonlinear regression yielded the coefficients: $K_L = 9.8 \times 10^{-4}$ M and $[C_{ads}]_{max} = 0.312$ M kg^{-1} (for a solution pH of 7.3). The standard error was 0.012, while the correlation coefficient was 0.992. The data converged in 3 iterations with a tolerance of 0.006. In general, at different pH values and under different C_{aq} ranges, the values of K_L and $[C_{ads}]_{max}$ were different (data not shown) indicating that the behavior was not truly langmuir in nature. Once the product loss due to adsorption was accounted for, a complete mass balance for nitrobenzene reduction was obtained. The nature of the langmuir isotherm is consistent with the past literature (*8*–*10*, *13*, *14*, *18*, *19*). However, sorption constants differ sharply from the results presented by ref *14*. The sorption constants reported here are for a solution pH of 7.3, while ref *14* have their data at pH 10. It is expected that at such a high pH, aniline adsorption would be quite low. Also, the type of iron in their study was different (particle size > 0.3 mm), and it was not pretreated. It has been shown (*13*) that acid wash increased the surface area by 7.6 times. Thus, it is expected
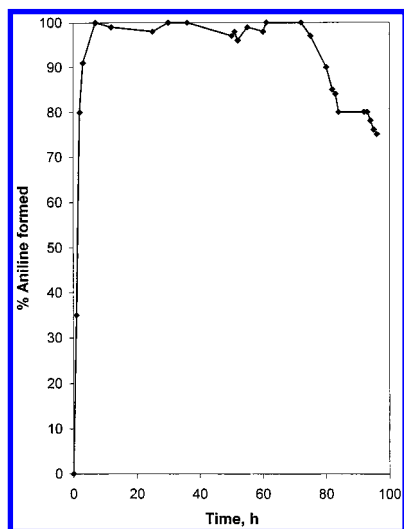
FIGURE 3. Conversion of nitrobenzene to aniline with time. Continuous column operation at a flow rate of 3.1 mL/min and pH 7.4. Na_2SO_3 in the inlet solution was kept at 1 mM. Two hundred grams of Fe^0 (Iron-II) was used. The column was abandoned after 72 h of operation. The effluent pH was about 7.4–7.7.
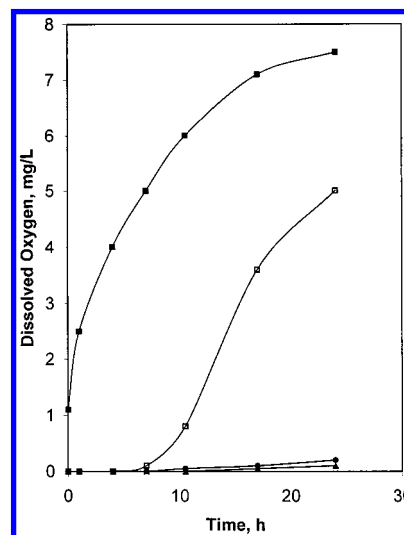

FIGURE 4. Amount of O_2 absorbed into the influent solution. Na_2SO_3 was used in various concentrations in the feed reservoirs, open to atmosphere at room temperature: 0.5 mM (■), 1.0 mM (□), 2.0 mM (●), and 5.0 mM (▲). pH was around 7.3–8.0.

that the iron used in this study had a lot more sites amenable for aniline adsorption.

Continuous Column Operation. Loss of nitrobenzene due to volatilization from the feed reservoir was found to be about 8% over a 24-h period. This was accounted for while calculating the rates of formation of aniline in the reduction step. A typical conversion plot vs time is depicted in Figure 3. It can be seen that it took several hours to reach the 100% conversion level. This was due to both the time required to flush out the original solution and to saturate the available sites during sorption of aniline on to the Fe^0 bed. However, once the sites were saturated, complete product recovery was obtained and persisted until the column became clogged. It was shown by Burris et al. (15) that in a continuous flow-through system, the extent of reaction is not affected by sorption to nonreactive sites under steady-state conditions. The data after 72 h were collected to show the drop in conversion efficiency. However, this reduction in efficiency will not be acceptable in actual practice. Also, since Iron-II has lower surface area per unit mass as compared to Iron-I (actual surface areas were not measured), the sorption over the former iron was much lower. In some experiments, aniline desorption curves were recorded (not shown) which confirmed that aniline had deposited on the Fe^0 bed as expected from the batch studies. Desorption experiments were carried out by flushing with water containing 1 mM Na_2SO_3 at pH 8 or higher.

Effect of Na_2SO_3. It was indicated by Monsef et al. (34) that an oxygen scavenger could be used instead of degassing the solutions. Literature (41, 42) shows that Na_2SO_3 is capable of scavenging O_2 effectively and has long been used in the presence of a catalyst ($CoCl_2$) to scavenge O_2 for boiler-feedwater (42). It was suggested that the amount of $CoCl_2$ used should be about 0.1% of Na_2SO_3 by weight (42). Therefore, all Na_2SO_3 solutions used in this study contained $CoCl_2$ in this proportion. Stoichiometrically, the amount of Na_2SO_3 needed to scavenge O_2 from tap water at room temperature (20–22 °C) is about 0.5 mM. However, the literature (42) suggests a much higher ratio of Na_2SO_3/O_2 is required for complete removal of O_2. Initially, 5 mM Na_2SO_3 along with the recommended proportion of $CoCl_2$ as a catalyst was used in all of the experiments. In the absence of the catalyst, scavenging of O_2 was very slow. It was decided to optimize the amount of Na_2SO_3 required for the reaction to

proceed under anaerobic conditions. Replicate, open feed reservoirs (of the type to be used in continuous operation) were set up that contained 1 mM of nitrobenzene and Na_2SO_3 in various concentrations at room temperature. The pH was maintained between 7.3 and 8.0. An oxygen meter was used to measure the amount of residual O_2 left in the feed reservoirs after the addition of Na_2SO_3. Concentration of O_2 in the reservoir due to reabsorption from the atmosphere was also followed as a function of time (Figure 4). It is apparent from the plot that the stoichiometric amount of Na_2SO_3 (0.5 mM) could not scavenge dissolved O_2 completely. On the basis of these observations, 1 mM Na_2SO_3 was used for the continuous-column operations, and the feed from an open reservoir was changed after every 7 h. This was followed as a standard protocol for all subsequent runs. UV–Vis spectra measurements of the influent solution containing nitrobenzene and Na_2SO_3 confirmed that the aromatic was not transformed by Na_2SO_3. Also, presence of Na_2SO_3 did not shift the λ_{max} or change the molar extinction coefficient (ϵ) for nitrobenzene.

pH Effect. The overall process of corrosion in anaerobic Fe^0-H_2O systems may be depicted by the following reactions (13):

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{6}$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{7}$$
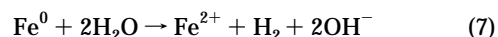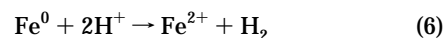
Early experiments in batch reactors resulted in the expected pH rise of nearly 2 units due to aqueous corrosion of the metal (eq 7). However, the same effect was not observed in the continuous flow system. The effluent pH was more or less comparable to the inlet solution pH. There was a general lack of dependency of conversion on pH as found by Agrawal et al. (13). Hence, most of the column studies were conducted at pH of about 7–7.5.

Iron (Fe^0) Corrosion Products. A 200 g of Fe^0 (Iron-II) bed completely converted 1 mM of nitrobenzene flowing upward at 3.1 mL/min for almost 72 h on a continuous basis. However, the operation had to be discontinued at this point due to formation of a dark green-black precipitate (corrosion products) at the influent end of the column. The zone of the precipitates had risen to almost one-third of the bed height. Figure 5 shows the change in height of the precipitate front from the influent end of the column with time. It is a linear
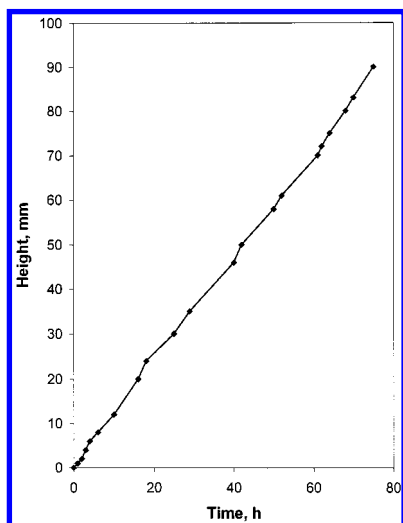
FIGURE 5. Change in height of precipitate front from influent end of the column (15 × 300 mm). Continuous flow at 3.1 mL/min and pH 7.4. Na_2SO_3 in the inlet solution was kept at 1 mM. Two hundred grams of Fe^0 (Iron-II) was used with a bed depth of 280 mm.
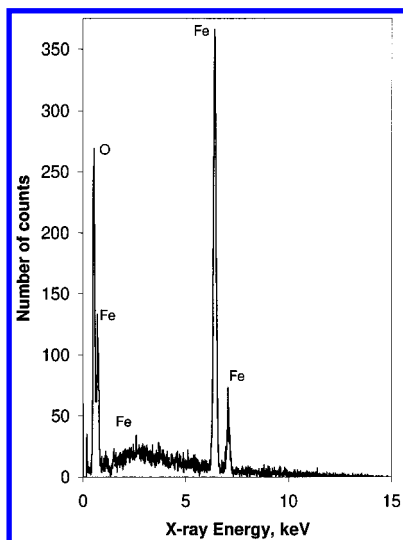

FIGURE 6. EDS analysis indicating the presence of only Fe and O in the precipitates. The precipitate was collected from the influent end of the column after 72 h of operation.

relationship suggesting that the rate of formation of corrosion products is directly proportional to the rate of conversion reaction. Corrosion of the metal in anaerobic aqueous media, in absence of the nitroaromatic compound, was too slow to be a significant contributor to material damage by corrosion as observed in a control experiment where the feed had no nitrobenzene. The flow rate also dropped drastically (3-fold) due to clogging. These results are consistent with previous studies that indicated plugging and porosity reduction as a result of precipitation of corrosion products (*43*). It is known that the first corrosion product of Fe^0 under anaerobic conditions is $Fe(OH)_2$, which may be further oxidized to magnetite Fe_3O_4 (*44, 45*). Prior to the formation of magnetite, mixed-valent Fe(II) + Fe(III) salts, known as green rusts, may form under neutral pH conditions (*43–45*). The oxidation of mixed-valent salts commonly leads to the formation of maghemite (γ-Fe_2O_3) (*45*). An EDS spectrum of N_2-dried iron filings, taken from the inlet end of the column, indicated the presence of only Fe and O (Figure 6). Also, X-ray diffraction analyses of the same filings confirmed that they were coated with maghemite, which could only have formed by oxidation of the corrosion product magnetite. The corrosion products

in this study were similar to those reported in the literature (*43, 44*). These precipitates were removed by using 1.2 M HCl to regenerate the bed. Preliminary studies indicated that a more dilute acid could not remove the precipitates completely (data not shown). It was found that the same bed could be used again and again with the same efficiency as before, once it was regenerated.

There is a net dissolution of Fe^0 following the reduction reaction (eq 4). Stoichiometrically, this amount is 2.244 g (for a flow rate of 3.1 mL/min for 72 h, and nitrobenzene concentration of 1 mM). Analyses of the combined effluent stream and the precipitates by the direct coupling plasma (DCP) technique, accounted for almost 94% (2.11 g) of the Fe^0 reacted. DCP results indicated that, although most of the corrosion products had precipitated in the column itself (68.4%), the effluent stream still contained corrosion products above the detection limit (concentration of the corrosion products was about 0.05 g/L). Total Fe detected in the effluent stream under the above conditions was about 0.667 g. DCP analyses were also done on the effluent to ascertain the fate of $CoCl_2 \cdot 6H_2O$, being added as a catalyst to scavenge O_2 in the feed. Analyses indicated that most of the Co (as total Co) was getting plated out in the column itself. From an initial 126 μg/L of $CoCl_2 \cdot 6H_2O$ (31.2 μg/L as Co) in the feed, only 1.96 μg/L of Co could be detected in the effluent stream. It might be speculated that in this deposition we would be creating a bimetallic zerovalent metal phase. However, a bimetallic bed of the Co/Fe system was ruled out as the effective agent, since even with 100% Co plating out in the bed it would only amount to an additional 2 ppm in the Fe^0 bed (over the 600 pore-volume operating lifetime). However, to achieve bimetallic systems researchers have used between 200 and 500 ppm of metal doping (*46, 47*).

Na_2SO_3 is used as an O_2 scavenger. An optimum value of 1 mM has been used in this study. This is equivalent to 126 mg/L. At this level of discharge, Na^{2+} and SO_4^{2-} (since SO_3^{2-} either gets oxidized in the feed or upon elution from the column by atmospheric O_2) are not a problem. They are within the accepted levels of discharge, even from a drinking water point of view.

The system presented here for oxygen-scavenging in Fe^0 reduction of nitrobenzene is more practical than that used in the preliminary communication from this lab (*34*). We are, therefore, currently investigating the coupling of this process to the enzyme-catalyzed oxidative polymerization of the resulting aniline.

Acknowledgments

Literature Cited

(1) *Chem. Eng. News* **1995**, *July 3*, pp 19–22.
(2) Reynolds, G. W.; Hoff, J. T.; Gillham, R. W. *Environ. Sci. Technol.* **1990**, *24*, 135–142.
(3) Matheson, L. J.; Tratnyek, P. G. *Environ. Sci. Technol.* **1994**, *28*, 2045–2053.
(4) Gillham, R. W.; O'Hannesin, S. F. *Ground Water* **1994**, *32*, 958–967.
(5) Orth, W. S.; Gillham, R. W. *Environ. Sci. Technol.* **1996**, *30*, 66–71.
(6) Johnson, T. L.; Scherer, M. M.; Tratnyek, P. G. *Environ. Sci. Technol.* **1996**, *30*, 2634–2640.
(7) Scherer, M. M.; Westall, J. C.; Ziomek-Morz, M.; Tratnyek, P. G. *Environ. Sci. Technol.* **1997**, *31*, 2385–2391.

(8) Wust, W. F.; Kober, R.; Schlicker, O.; Dahmke, A. *Environ. Sci. Technol.* **1999**, *33*, 4304−4309.

(9) Burris, D. R.; Campbell, T. J.; Manoranjan, V. S. *Environ. Sci. Technol.* **1995**, *29*, 2850−2855.

(10) Arnold, W. A.; Roberts, A. L. *Environ. Sci. Technol.* **2000**, *34*, 1794−1805.

(11) Weber, E. J. *Environ. Sci. Technol.* **1996**, *30*, 716−719.

(12) Nam, S.; Tratnyek, P. G. *Water Res.* **2000**, *34*, 1837−1845.

(13) Agrawal, A.; Tratnyek, P. G. *Environ. Sci. Technol.* **1996**, *30*, 153−160.

(14) Devlin, J. F.; Klausen, J.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1998**, *32*, 1941−1947.

(15) Burris, D. R.; Hatfield, K.; Wolfe, N. L. *J. Environ. Eng.* **1996**, *122*, 685−691.

(16) Singh, J.; Comfort, S. D.; Shea, P. J. *J. Environ. Qual.* **1998**, *27*, 1240−1245.

(17) Klausen, J.; Trober, S. P.; Haderlein, S. B.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1995**, *29*, 2396−2404.

(18) Tratnyek, P. G., *Chem. Ind.* **1996**, *1 July*, 499−503.

(19) Scherer, M. M.; Richter, S.; Valentine, R. L.; Alvarez, P. J. J. *Crit. Rev. Environ. Sci. Technol.* **2000**, *30*, 363−411.

(20) *Chem. Eng. News* **1996**, *June 24*, p 41.

(21) U. S. Environ. Prot. Agency, *Ambient Water Quality Criteria for Nitrobenzene*, EPA 440/5-80-061, 1980, October.

(22) Toxic Release Inventory (TRI) data, 1997, http://www.rtk.net

(23) Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile for Nitrobenzene (draft), U. S. Public Health Service, U. S. Department of health and human services, Atlanta, GA, 1989, http://www.epa.gov/ttn/uatw/hlthef/nitroben.html

(24) Higson, F. K.; *Adv. Appl. Microbiol.* **1992**, *37*, 1−19.

(25) Haderlein, S. B.; Schwarzenbach, R. P.; *Biodegradation of Nitroaromatic Compounds*; Spain, J. C.; Ed; Plenum: New York, 1995; pp 199−225.

(26) Klibanov, A. M.; Alberti, B. N.; Morris, E. D.; Felshin, L. M. *J. Appl. Biochem.* **1980**, *2*, 414−421.

(27) Saunders: B. C., *Peroxidase*; Butterworths: London, 1964; pp 10−24.

(28) Chang, C. W.; Bumpus, J. A. *FEMS Microbiol Lett.* **1993**, *107*, 337−342.

(29) Caza, N.; Bewtra, J. K.; Biswas, N.; Taylor, K. E. *Water Res.* **1999**, *33*, 3012−3018.

(30) Wu, J.; Taylor, K. E.; Bewtra, J. K.; Biswas, N. *Water Res.* **1993**, *27*, 1701−1706.

(31) Al-Kassim, L.; Taylor, K. E.; Bewtra, J. K.; Biswas, N. *Enz. Microb. Technol.* **1994**, *16*, 120−124.

(32) Boopathy, R.; Manning, J. F. *Can. J. Microbiol.* **1996**, *42*, 1203−1208.

(33) Widrig, D. L.; Boopathy, R.; Manning, J. F. *Environ. Toxicol. Chem.* **1997**, *16*, 1141−1148.

(34) Monsef, H. R.; Michels, D. A.; Bewtra, J. K.; Biswas, N.; Taylor, K. E. in *Emerging Technologies in Hazardous Waste Management 8*; Tedder, D. W., Pohland, F. G., Eds; Kluwer Academic/Plenum Publishers: New York, 2000; pp 141−152.

(35) Gotpagar, J.; Grulke, E.; Tsang, T.; Bhattacharyya, D. *Environ. Prog.* **1997**, *16*, 137−143.

(36) Gomori, G. *Methods Enzymol.*, Vol I.; Colowick, B. D.; Kaplan, N. D.; Eds.; Academic Press: New York, 1955; pp 138−146.

(37) Means, G. E.; Congdon, W. I.: Bender, M. L. *Biochemistry* **1972**, *11*, 3564−3571.

(38) *Standard Methods for the Examination of Water and Wastewater*; 19th ed.; American Public Health Association, 1995; pp 3−5.

(39) Haderlein, S. B.; Schwarzenbach, R. P., *Environ. Sci. Technol.* **1993**, *27*, 316−326.

(40) Vasudevan, D.; Stone, A. T. *Environ. Sci. Technol.* **1996**, *30*, 1604−1613.

(41) Babbitt, H. E.; Doland, J. J.; Cleasby, J. L. *Water Supply Engineering*, 6th ed.; McGraw-Hill Book Company Inc.: New York, 1975; pp 565−567.

(42) Brandvold, D. C. *Water Treatment: Industrial & Municipal*; Vantage Press Inc.: New York, 1975; pp 55−57.

(43) Gu, B.; Phelps, T. J.; Liang, L.; Dickey, M. J.; Roh, Y.; Kinsall, B. L.; Palumbo, A. V.; Jacobs, G. K. *Environ. Sci. Technol.* **1999**, *33(13)*, 2170−2177.

(44) Farrell, J.; Kason, M.; Melitas, N.; Li, T. *Environ. Sci. Technol.* **2000**, *34(3)*, 514−521.

(45) Cornell, R. M.; Schwertmann, U. *The Iron Oxides*; VCH Publishers: New York, 1996; pp 445−450.

(46) Kim, Y.-H.; Carraway, E. R. *Environ. Sci. Technol.* **2000**, *34,* 2014−2017.

(47) Liang, L.; Korte, N.; Goodlaxson, J. D.; Clausen, J.; Fernando, Q.; Muftikian, R. *Ground Water Monitoring Remediation* **1997**, *Winter*, 122−127.