

Kinetics of reduction of TNT by iron metal

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Abstract Although it is well known that zero-valent iron (Fe^0) rapidly reduces nitro aromatic compounds (NACs) to aromatic amines, little kinetic or mechanistic detail has been reported on the most environmentally-significant NAC: 2,4,6-trinitrotoluene (TNT). This study provides quantitative kinetics for TNT reduction by a range of reagent- and construction-grade granular irons determined in well-mixed batch systems. A representative surface-area normalized rate constant ($k_{s,A}$) for construction-grade Fe^0 is $0.050 \text{ l m}^{-2} \text{ h}^{-1}$, but reagent-grade Fe^0 can be an order of magnitude more reactive.

Key words 2,4,6-trinitrotoluene; adsorption; kinetics; nitro reduction; products

INTRODUCTION

Although research on the reduction of nitro aromatic compounds (NACs) to amines by iron metal goes at least as far back as 1927 (Lyons & Smith, 1927), recognition that this reaction might have relevance to remediation of environmental contaminants did not occur until about 1994, several years after Gillham's invention of the Fe^0 permeable reactive barrier (FePRB) had become widely known to contaminant hydrologists. All of the early work on remediation of NACs by iron metal (Agrawal & Tratnyek, 1994, 1996; Agrawal *et al.*, 1995; Burris *et al.*, 1996) focused on nitrobenzene as a model compound. Those studies showed that reduction of NACs is fast, and that the primary products are aromatic amines, with small amounts of the nitroso (and possibly hydroxylamino) intermediates.

Since then, research on nitro reduction by Fe^0 has begun to emphasize specific environmental contaminants such as TNT and RDX (Hundal *et al.*, 1997; Singh *et al.*, 1998, 1999; Wildman & Alvarez, 2001). As expected, TNT and RDX are rapidly reduced by Fe^0 in batch tests, yielding a complex mixture of products. The characterization of these products has proven to be so challenging (e.g. McGrath *et al.*, 1999) that it has delayed the appearance of a thorough, quantitative study of the kinetics of TNT reduction by Fe^0 . We recently initiated such a kinetic study, and the preliminary results are reported here.

EXPERIMENTAL DETAILS

2,4,6-trinitrotoluene was obtained in high purity from ChemService, West Chester, Pennsylvania, USA, and used as received. 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene were purchased from Sigma/Supelco, Bellefonte, Pennsylvania, 2,4-diamino-6-nitrotoluene, 2,6-diamino-4-nitrotoluene, and 2,4,6-triaminotoluene trichloride were purchased from AccuStandard, New Haven, Connecticut, and used as

received. The ten types of granular Fe⁰ used in this study were Aldrich powder (Ald), Fisher electrolytic powder (Felc), EM Science degreased filings (EMS), Fluka filings (Flk), Baker chips (Bak), Fisher filings (Ffil), Master Builders (MB), Peerless Powders and Abrasives (PL), "improved" Peerless cast iron, and Connelly aggregate (CN). To remove fines but minimize other changes, all metals were rinsed with de-ionized water, then dried with acetone before use.

Batch experiments were conducted under anoxic conditions either in 40 ml VOA vials or 60 ml serum bottles, containing varying concentrations of iron and filled with de-ionized water leaving no headspace. The bottles were spiked with 0.1 ml and 0.15 ml TNT stock solution, respectively, to get an initial concentration of 40 mg l⁻¹ and subsequently mixed end-over-end on a rotary mixer at a moderate speed (20 rpm). Approximately 200 µl samples were collected from the vials, filtered through a 0.45 µm Nalgene 4 mm nylon filter (Fisher, Pittsburgh, Pennsylvania), and analysed by HPLC.

Analysis by HPLC was performed with an Econosil C-18 column (length 250 mm, inner diameter 4.6 mm; Alltech, Deerfield, Illinois). Two mobile phases were used during different portions of the experiments; for kinetics studies we preferred 45:55 acetonitrile/water and a flow rate of 1.0 ml min⁻¹, while product studies were more successful with 50:50 methanol/water at a flow rate of 1.1 ml min⁻¹. In all cases, TNT and the products were monitored at 254 nm.

RESULTS

Products

In all cases, the batch data show rapid disappearance of TNT and transient appearance of various degradation products (Fig. 1). In general, the largest intermediate was an unidentified peak (which is most likely to be one of the nitroso or hydroxylamine intermediates for which we were not able to obtain standards). Lesser amounts of the aminodinitrotoluenes (ADNTs), diaminonitrotoluenes (DANTs), and other unknowns, were also observed. The amount of product appearance was generally least with the construction-grade iron samples (MB, PL, and CN). Long-term batch experiments (not shown) showed that many of the products eventually disappeared, presumably due to a combination of further transformation and sequestration on the particle surfaces.

Kinetics

The kinetics of TNT disappearance turned out to be more complex than has generally been observed in the batch experiments with other contaminants. Rather than fitting all the disappearance data to a pseudo first-order kinetic model, as is usually done (Johnson *et al.*, 1996), we found that some experiments were best described as transitional from zero-order to first-order, much like what was reported recently by (Wüst *et al.*, 1999) for trichloroethylene (TCE). The analysis is illustrated in Fig. 2.

For the purposes of this study, it is convenient to express our mixed-order kinetic model for site saturation limited kinetics in terms that are commonly used for enzyme

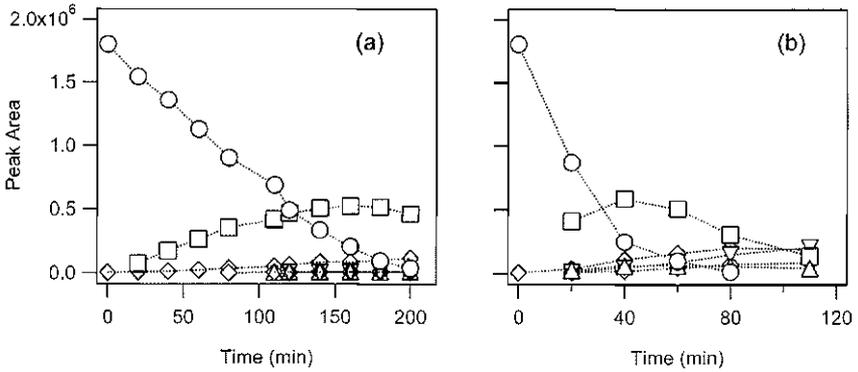


Fig. 1 Selected results from batch experiments for removal of TNT (circles) by: (a) reagent-grade Fluka iron, and (b) construction-grade Connelly iron. Products observed include ADNT (both isomers, triangles) and DANT (both isomers, inverted triangles), an early-eluting unidentified product (squares), and other later-eluting unidentified products (diamonds). These data correspond to experiment numbers 7 and 18 in Table 1.

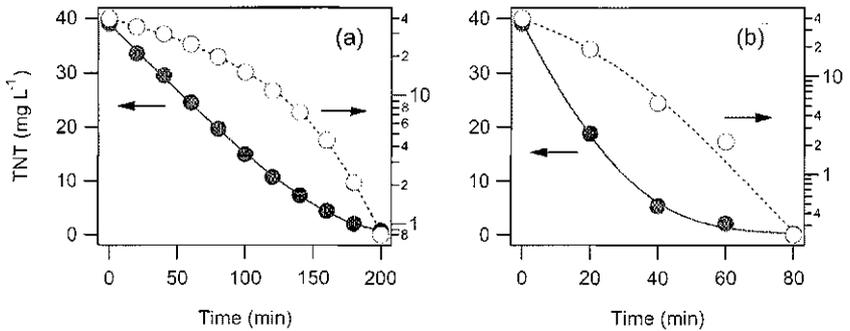


Fig. 2 Kinetics of reduction of TNT by: (a) Fluka, and (b) Connelly iron. Progress curves on linear (left) and log (right) axes are shown. Smooth curves reflect fits to the mixed-order kinetic model. These data correspond to experiment numbers 7 and 18 in Table 1.

catalysed reactions, as we have in several previous publications (Johnson *et al.*, 1996, 1998; Nam & Tratnyek, 2000). This model has usually been written as:

$$-\frac{dC}{dt} = \frac{V_m C}{K_{1/2} + C} \tag{1}$$

where V_m is the maximum reaction rate and $K_{1/2}$ is the concentration of contaminant, C , where $-dC/dt = V_m/2$. Note that V_m is equivalent to the rate constant for the zero-order portion of the progress curve and that $V_m/K_{1/2}$ approximates the rate-constant for the first-order portion (represented by k_0 and k_1 , respectively, in Wüst *et al.* (1999)). To apply this model, we used the bisection method (Press *et al.*, 1988) to solve the integrated form of equation (1) for C as a function of V_m , $K_{1/2}$, C_0 , and t , and this result was fit to experimental data by chi-square minimization. Details of the justification and computations for this analysis will be presented elsewhere (Miehr *et al.*, 2001; Tratnyek *et al.*, 2001).

Table 1 Conditions and results of batch experiments with TNT and Fe⁰.

Iron type	Iron α_s (m ² g ⁻¹)	Iron mass (g)	Solution vol. (ml)	TNT C_0 (mg l ⁻¹)	Equil. (h)	Kinetic model	k_{obs} (min ⁻¹)	k_{SA} (l m ⁻² h ⁻¹)
Ald	0.0941	3.50	43.92	40	0	Mixed ^b	1.84e-2	1.48e-1
Ald	0.0941	3.50	43.92	40	0	Mixed	5.74e-2	4.59e-1
Felc	1.27	4.00	43.88	40	0	Mixed ^c	1.74e-1	9.00e-2
Felc	1.27	6.00	43.67	40	0	Mixed ^c	--	--
EMS	0.075	5.00	43.74	40	0	Mixed	3.84e-6	2.76e-5
EMS	0.075	8.00	43.41	40	0	Mixed	2.16e-5	9.38e-5
Flk	0.229	4.00	43.83	40	0	Mixed	5.77e-2	1.66e-1
Flk	0.229	5.00	43.72	40	0	Mixed ^c	7.56e-2	1.73e-1
Bak	0.0401	4.00	43.88	40	0	Mixed	2.77e-3	4.55e-2
Bak	0.0401	6.00	43.67	40	0	Mixed	4.76e-2	5.19e-1
Ffil	4.09	0.50	44.24	40	0	Mixed	2.34e-2	3.04e-2
Ffil	4.09	0.50	44.24	40	0	Mixed	3.29e-2	4.27e-2
MB	1.45	0.50	44.23	40	0	Mixed ^b	7.25e-3	2.65e-2
MB	1.45	0.50	44.23	40	0	Mixed ^b	4.50e-3	1.65e-2
PL	1.54	0.50	44.23	40	0	Mixed	8.77e-3	3.02e-2
PL	1.54	0.50	44.23	40	0	Mixed	1.12e-2	3.88e-2
CN	4.94	0.50	44.23	40	0	Mixed	2.31e-2	2.48e-2
CN	4.94	1.00	44.17	40	0	Mixed	8.57e-2	4.60e-2
PL ^a	1.54	0.75	59.90	40	164	First ^b	1.11e-3	3.45e-3
PL ^a	1.54	0.75	59.90	40	211	First	1.89e-4	5.89e-4
PL ^a	1.54	0.75	59.90	40	24	First	5.03e-4	1.56e-3
PL ^a	1.54	2.00	59.73	40	24	First	1.69e-2	1.96e-2
PL ^a	1.54	2.90	59.61	20	24	First	1.54e-1	1.24e-1
PL ^a	1.54	2.90	59.61	40	24	First	5.70e-2	4.57e-2
PL ^a	1.54	2.90	59.61	70	24	First	7.64e-3	6.12e-3
PL ^a	1.54	3.75	59.49	40	24	First	7.03e-2	4.34e-2
PL ^a	1.54	5.00	59.32	40	24	First	8.65e-2	4.00e-2
PL ^a	1.54	7.50	58.99	40	24	-- ^d	-- ^d	-- ^d
PL ^a	1.54	15.0	57.97	40	24	-- ^d	-- ^d	-- ^d

^a Special lot of "improved" iron aggregate provided by Peerless. For this material, we assumed that the specific surface area and specific gravity was the same as for the conventional Fe⁰ from Peerless.

^b Excluded initial data that were dominated by adsorption.

^c Excluded initial data that exhibited a lag phase.

^d Disappearance of TNT was too fast to measure.

For comparison with previously reported kinetic data, the results have been reduced to surface area normalized rate constants, k_{SA} , by equating V_m/K_{12} with k_{obs} and dividing by the surface area concentration, ρ_u (m² of Fe⁰ per litre of solution). Note that normalization for surface area gives relatively small values of k_{SA} for the Fe⁰ samples that contain a large amount of iron oxide (MB, PL, CN, and Ffil) because the iron oxide has a comparatively high specific surface area and low reactivity.

The comparison presented in Fig. 3 shows that the values of k_{SA} measured in this study fall within the range of previously reported values for nitro aromatics (TNT, ArNO₂, 4Cl-ArNO₂, and parathion). It can also be seen that these compounds react considerably more rapidly than most chlorinated hydrocarbons, including TCE and vinyl chloride (VC). In general, highly reactive contaminants such as the NACs are more prone to give mass transport limited kinetics. In fact, we have recently shown

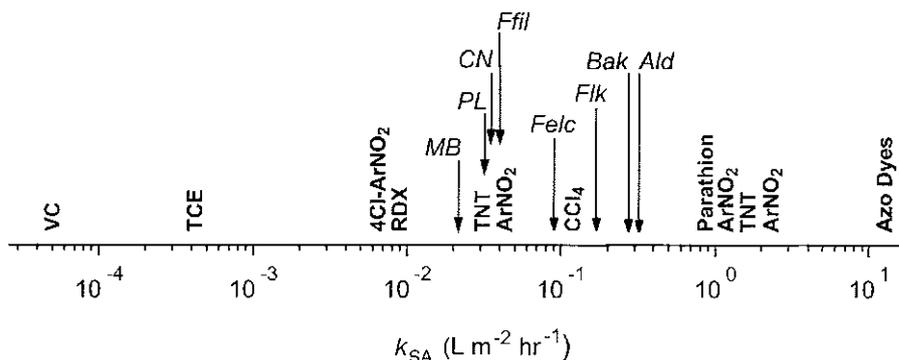


Fig. 3 Comparison of k_{SA} from batch studies with TNT and eight types of iron (arrows with italic labels) vs rate constants for other contaminants obtained from the literature. This figure is adapted from Scherer *et al.* (2001), where the sources of all the data are identified. New data are average values from experiment numbers 1–18 in Table 1.

that nitrobenzene (ArNO_2) exhibits kinetics that reflect a mixture of reaction and mass transport effects, and that this has a variety of important implications for the design of PRBs to treat such reactive contaminants (Scherer *et al.*, 2001). It appears that TNT is comparable to ArNO_2 in reactivity, so we expect that some of the kinetic data reported here (and previously by others) reflect at least some influence of mass transport.

Treatment effects

The most important design variable that can be used to influence k_{obs} is the amount of Fe^0 exposed to the contaminant, or more precisely, the amount of Fe^0 surface area per unit volume of aqueous solution (Johnson *et al.*, 1996; Tratnyek *et al.*, 1997). This parameter (usually designated ρ_a) is readily calculated from the mass, specific gravity, and specific surface area of the Fe^0 used, and the total volume of the reaction vessel. As has been shown for many other contaminants, increasing ρ_a causes a linear increase in k_{obs} for TNT (Fig. 4(a)). The slope obtained by fitting such data gives a reliable estimate of the surface area normalized rate constant, k_{SA} , if all other experimental variables are held constant. This was the case for the data represented in Fig. 4(a) and regression of these data gave a slope from which we estimated $k_{SA} = 0.050 \pm 0.007 \text{ l m}^{-2} \text{ h}^{-1}$ for the Peerless iron metal used in these experiments. This sample of Fe^0 was from a custom batch prepared by Peerless to give more rapid degradation of chlorinated solvents. Superimposing the k_{SA} we obtained for this Fe^0 on Fig. 3 shows that “improved” Peerless iron removed TNT more rapidly than other construction-grade Fe^0 materials, but still more slowly than the high-purity reagent-grade Fe^0 . The enhanced reactivity could reflect improvements in the metal, but could also be due to the 24 h “equilibration” time prior to addition of TNT. This step was added to our procedure for experiment numbers 21–29 (Table 1) because it consistently produced first-order, rather than mixed-order, disappearance kinetics. This phenomenon may reflect activation of the surface as oxides are reduced (Odziemkowski *et al.*, 1998), and further investigation of such effects is clearly needed.

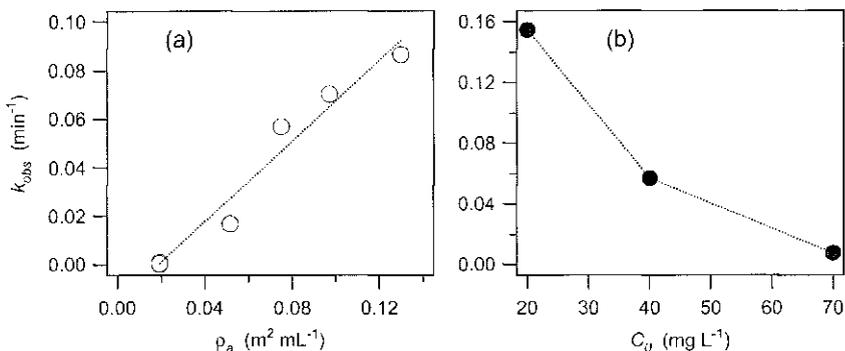


Fig. 4 Effects of reaction variables on the rate constant for TNT reduction using "improved" Peerless iron. (a) Reaction variable is the amount of iron used, ρ_a , expressed as m² of iron surface area per ml of solution volume. The regression line from these data has slope = 0.8 ± 0.1 , intercept = -0.02 ± 0.01 , and $r^2 = 0.95$. (b) Reaction variable is the initial concentration of TNT. These data correspond to experiment numbers 19–27 in Table 1.

Varying the initial concentration of TNT (at constant ρ_a) gave a notable result: both rates (not shown) and rate constants (Fig. 4(b)) decrease with increasing initial concentration of TNT. These results are not consistent with the site saturation effects that have been observed for many chlorinated solvents (Johnson *et al.*, 1998; Arnold & Roberts, 1999; Wüst *et al.*, 1999; Devlin *et al.*, 2000; Tratnyek *et al.*, 2001), but they are consistent with inhibition by accumulation of adsorbed products of nitro reduction (Devlin *et al.*, 1998). This effect may also be responsible for the slower disappearance rate of TNT in one experiment where we re-spiked with TNT (experiment 20, Table 1). In future work, we hope to develop a kinetic model for the disappearance of TNT by Fe⁰ that resolves adsorption, desorption, and reduction into independently calibrated processes.

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REFERENCES

- Agrawal, A. & Tratnyek, P. G. (1994) In: Abiotic remediation of nitro-aromatic groundwater contaminants by zero-valent iron In: *Proc. 207th National Meeting American Chemical Society* (San Diego, California), vol. 34(1), 492–494.
- Agrawal, A. & Tratnyek, P. G. (1996) Reduction of nitro aromatic compounds by zero-valent iron metal. *Environ. Sci. Technol.* **30**, 153–160.
- Agrawal, A., Tratnyek, P. G., Stoffyn-Egli, P. & Liang, I. (1995) Processes affecting nitro reduction by iron metal: mineralogical consequences of precipitation in aqueous carbonate environments In: *Proc. 209th National Meeting American Chemical Society* (Anaheim, California), vol. 35(1), 720–723.
- Arnold, W. A. & Roberts, A. L. (1999) Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reactions with Fe(0). In: *Proc. 218th National Meeting American Chemical Society* (New Orleans), vol. 39(2), 158–160.

- Burris, D. R., Hatfield, K. & Wolfe, N. L. (1996) Laboratory experiments with heterogeneous reactions in mixed porous media. *J. Environ. Engng* **122**, 685–691.
- Devlin, J. F., Klausen, J. & Schwarzenbach, R. P. (1998) Kinetics of nitroaromatic reduction on granular iron in recirculating batch experiments. *Environ. Sci. Technol.* **32**, 1941–1947.
- Devlin, J. F., Morkin, M. & Repta, C. (2000) Incorporating surface saturation effects into iron wall design calculations. In: *Chemical Oxidation and Reactive Barriers* vol. C2-6 (ed. by G. B. Wickramanayake, A. R. Gavaskar & A. S. C. Chen) (Proc. Second Int. Conf. on Remediation of Chlorinated and Recalcitrant Compounds, May 2000, Monterey, California), 393–400. Battelle Press, Columbus, Ohio, USA.
- Hundal, L. S., Singh, J., Bier, E. L., Shea, P. J., Comfort, S. D. & Power, W. L. (1997) Removal of TNT and RDX from water and soil using iron metal. *Environ. Poll.* **97**, 55–64.
- Johnson, T. L., Fish, W., Gorby, Y. A. & Tratnyek, P. G. (1998) Degradation of carbon tetrachloride by iron metal: complexation effects on the oxide surface. *J. Contam. Hydrol.* **29**, 377–396.
- Johnson, T. L., Scherer, M. M. & Tratnyek, P. G. (1996) Kinetics of halogenated organic compound degradation by iron metal. *Environ. Sci. Technol.* **30**, 2634–2640.
- Lyons, R. E. & Smith, L. T. (1927) Die Reduktion von Nitroverbindungen mit Eisen und Löslichen Chloriden. *Chem. Ber.* **60**, 173–182.
- McGrath, C. J., Davis, W. M. & Porter, J. E. (1999) In: Reactivity of TNT and RDX on zero-valent iron. In: *Proc. 218th National Meeting American Chemical Society* (August 1999 New Orleans), vol. 218, 96.
- Michr, R., Tratnyek, P. G., Bandstra, J. Z., Scherer, M. M., Alowitz, M. & Bylaska, E. J. (2001) The diversity of contaminant reduction reactions by zero-valent iron: role of the reductate (in prep.).
- Nam, S. & Tratnyek, P. G. (2000) Reduction of azo dyes with zero-valent iron. *Wat. Res.* **34**, 1837–1845.
- Odziemkowski, M. S., Schuhmacher, T. T., Gillham, R. W. & Reardon, E. J. (1998) Mechanism of oxide film formation on iron in simulating groundwater solutions: Raman spectroscopic studies. *Corr. Sci.* **40**, 371–389.
- Press, W. H., Flannery, B. P., Teukolsky, S. A. & Vetterling, W. T. (1988) *Numerical Recipes in C: The Art of Scientific Computing*. Cambridge University Press, Cambridge, UK.
- Scherer, M. M., Johnson, K., Westall, J. C. & Tratnyek, P. G. (2001) Mass transport effects on the kinetics of nitrobenzene reduction by iron metal. *Environ. Sci. Technol.* **35**, 2804–2811.
- Singh, J., Comfort, S. D. & Shea, P. J. (1998) Remediating RDX-contaminated water and soil using zero-valent iron. *J. Environ. Qual.* **27**, 1240–1245.
- Singh, J., Comfort, S. D. & Shea, P. J. (1999) Iron-mediated remediation of RDX-contaminated water and soil under controlled Eh/pH. *Environ. Sci. Technol.* **33**, 1488–1494.
- Tratnyek, P. G., Bandstra, J. Z., Agrawal, A., Ferguson, W. J. & Christ, J. (2001) Effects of carbonate on contaminant reduction by zero-valent iron (in prep.).
- Tratnyek, P. G., Johnson, T. L., Scherer, M. M. & Eykholt, G. R. (1997) Remediating groundwater with zero-valent metals: kinetic considerations in barrier design. *Ground Water Monitor. Remed.* **17**, 108–114.
- Wildman, M. J. & Alvarez, P. J. J. (2001) RDX degradation using an integrated Fe(0)-microbial treatment approach. *Wat. Sci. Technol.* **43**, 25–33.
- Wüst, W. F., Köber, R., Schlicker, O. & Dahnke, A. (1999) Combined zero- and first-order kinetic model of the degradation of TCE and cis-DCE with commercial iron. *Environ. Sci. Technol.* **33**, 4304–4309.