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Applicability of alkaline hydrolysis for remediation of TNT-contaminated water

Sangchul Hwang[a,*], Timothy J. Ruff[b], Edward J. Bouwer[c], Steven L. Larson[d], Jeffrey L. Davis[d]

[a]*Department of Civil Engineering and Surveying, University of Puerto Rico at Mayagüez, PR 00680, USA*
[b]*Department of Chemical Engineering, Mississippi State University, Starkville, MS 39762, USA*
[c]*Department of Geography & Environmental Engineering, Johns Hopkins University, Baltimore, MD 21218, USA*
[d]*Environmental Laboratory, US Army Engineer Research and Development Center, Vicksburg, MS 39180, USA*

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Abstract

This study was conducted to assess the applicability of alkaline hydrolysis as an alternative ex situ technology for remediating 2,4,6-trinitrotoluene (TNT)-contaminated water. TNT reactivity had a strong dependence on the reaction pH (11–12) and initial TNT (5–25 $\mathrm{mg\,L^{-1}}$) in batch systems, resulting in pseudo first-order transformation rate, k ranging between 1.9×10^{-3} and $9.3 \times 10^{-5}\,\mathrm{min}^{-1}$. In continuous flow stirred-tank reactor (CFSTR) systems with initial TNT of 1 $\mathrm{mg\,L^{-1}}$, the highest 74% of TNT reduction was achieved at the reaction pH of 11.9 and 2-day hydraulic retention time under steady-state condition. Oxalate was produced as the major hydrolysate in the CFSTRs, indicating a ring cleavage during alkaline hydrolysis. It was also believed that TNT alkaline hydrolysis occurred through the production of color-forming intermediates via dimerization. It is concluded that alkaline hydrolysis can be an alternative treatment technology for remediation of TNT-contaminated water.

Keywords: Alkaline hydrolysis; Batch reactor; Continuous flow stirred-tank reactor; 2; 4; 6-trinitrotoluene

1. Introduction

Military activities such as the manufacturing, assembling, loading, and disposal of explosive compounds have generated widespread contaminations with explosives and their derivatives (Rosenblatt et al., 1991; Spain, 1995). Among those explosives, 2,4,6-trinitrotoluene (TNT) has been the most extensively produced nitroaromatic explosive and, therefore, has been present most abundantly in the environments (Walsh et al., 1993). Due to the adverse effects of TNT and its derivatives on humans and other natural receptors (Peres and Agathos, 2000; Won et al., 1976), a low cost means of decontaminating these areas of contamination is needed. The currently accepted method for treating groundwater contaminated with explosives is a "pump and treat" system utilizing granular activated carbon (GAC). However, spent GAC must be treated and can dramatically increase treatment costs. Bioremediation of explosives has been widely and successfully studied over the past decade. However, it is still faced with several challenges. For instance, under aerobic conditions TNT is resistant to biodegradation due to the presence of electron-withdrawing nitro groups that inhibit electrophillic attack by oxygenase enzymes (Spain et al., 2000).

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*Corresponding author. Tel.: +1 787 832 4040x3815; fax: +1 787 833 8260.
E-mail address: shwang@uprm.edu (S. Hwang).

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Batch alkaline hydrolysis has been reported to be a potential alternative remediation technology for hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) (Croce and Okamoto, 1979; Heilmann et al., 1996; Hoffsommer et al., 1977). Previous alkaline RDX hydrolysis in the authors' laboratory using a continuous flow stirred-tank reactor (CFSTR) achieved a 99% RDX reduction (i.e., $1\,\mathrm{mg\,L^{-1}}$ influent RDX$\rightarrow 0.01\,\mathrm{mg\,L^{-1}}$ effluent RDX) at the reaction pH of 11.9 and the hydraulic retention time (HRT) of 2 days (Hwang et al., 2003). A conceptual cost analysis indicated that alkaline RDX hydrolysis was more economical than GAC adsorption for long treatment periods (30 years or more). In comparison to abundance of alkaline RDX hydrolysis, alkaline treatment for TNT-contaminated water is scarce. Limited research on the determination of hydrolytic kinetics has been conducted in batch settings (Emmrich, 1999; Karasch et al., 2002).

Therefore, this study was conducted to assess alkaline hydrolysis as an efficient alternative "pump and treat" technology for treating TNT-contaminated water. The study consisted of two phases. Phase I examined the kinetics of TNT removal by alkaline addition as a function of the reaction pH and initial TNT concentration in a series of batch titration studies. Phase II was a proof-of-concept study using a CFSTR to examine the feasibility and applicability of TNT alkaline hydrolysis as a function of pH and the HRT.

2. Materials and methods

2.1. Chemicals

TNT was obtained from the Halston Army Ammunition Plant, Kingsport, TN. The calibration standards for TNT and potential transformation products such as nitrobenzenes and nitrotoluenes were purchased from SUPELCO (EPA 8330 Energetic Materials Kit). Sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), acetonitrile (CH_3CN), HPLC-grade water, and other chemicals used during the experiment were purchased from Fisher Scientific.

2.2. Batch reactor

Alkaline solutions at three different pH levels (11.0, 11.5, and 12.0) were placed in 250 mL beakers, to which was added an aqueous TNT solution to make 100 mL of three different initial TNT concentrations (25, 10, and $5\,\mathrm{mg\,L^{-1}}$). Constant pH levels were maintained during the batch experiments at room temperature ($25\pm1\,^{\circ}\mathrm{C}$) using pH controller (Systemics Inc., Bristol, RI) connected to metering pumps (Barnard Co., Barrington Hills, IL) that dispensed 0.1N HCl and 0.1N NaOH solutions into the reactor. Samples were analyzed for concentrations of TNT and its transformation products over time.

2.3. Continuous flow stirred-tank reactor

The reactor (BioFlo® 3000, New Brunswick Scientific) was filled with 10 L of reverse osmosis water, and was stirred at 200 rpm. The solution was initially dosed with 50% NaOH solution to raise the starting solution pH to 11.0, 11.5, and 11.9. The highest pH in the CFSTR was limited to 11.9 because the maximum controllable pH by the BioFlo pH controller was pH 12, with a dead band of 0.1 pH unit. The reaction temperature was kept constant at $25\pm1\,^{\circ}\mathrm{C}$ with a PolyScience Chiller (Model 6305). TNT solution ($1\,\mathrm{mg\,L^{-1}}$) was continuously added to the reactor at flowrates of 5.0, 10.0 and $14.3\,\mathrm{L\,day^{-1}}$, corresponding to HRTs of 2, 1, and 0.7 days, respectively. During the experiment, the reaction pH was maintained constant by the automatic addition of 0.1N H_2SO_4 and 0.2N NaOH solutions by the pH controller. Liquid samples were collected in short-term intervals and analyzed for TNT and transformation products as described below. The reaction was continued until three reactor volumes (30 L) had been flushed through the reactor. To enhance the possibility for detection of reaction intermediates, two elevated initial TNT concentrations (10 and $25\,\mathrm{mg\,L^{-1}}$) were treated at reaction pH of 11.9 and 2-day HRT.

To assure complete mixing, a non-reactive chloride (Cl^-) tracer was flushed through the reactor under the same experimental condition as that used for the alkaline hydrolysis. The OH^- concentration in the reactor decreased due to dilution with the influent water. Therefore, blank systems (i.e., without TNT) at three different pH levels (11.0, 11.5, and 11.9) were run in order to quantify the amount of OH^- added to the reactor to counteract dilution effects only. To ensure that TNT was transformed by alkaline hydrolysis only, a control system was run at the reaction pH of 6 and 1-day HRT with the initial TNT concentration of $1\,\mathrm{mg\,L^{-1}}$.

2.4. Approach for the kinetics of TNT alkaline hydrolysis

The kinetics of alkaline TNT transformation in the batch experiments can be described by the second-order rate expression as follows:

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = KXC, \tag{1}$$

where C is the TNT concentration ($\mathrm{mg\,L^{-1}}$), t the time (min), K the second-order TNT transformation rate constant ($\mathrm{L\,mg^{-1}\,min^{-1}}$), and X the OH^- concentration ($\mathrm{mg\,L^{-1}}$). Since the OH^- concentration was kept constant during the experiment, Eq. (1) can be