ALKALINE HYDROLYSIS IS AN EFFECTIVE TREATMENT TECHNOLOGY FOR RDX-CONTAMINATED GROUNDWATER

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Introduction

The great concern to the USEPA and the DoD is the potential spreading of the explosives and their toxic effects to humans, animals, agricultural produce, and other natural receptors [1]. Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) poses a particular environmental concern due to its high potential of leaching due to its low partitioning characteristics, despite a relatively low aqueous solubility. 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. Alkaline hydrolysis has been known as a potential alternative treatment technology [2,3].

This study was, therefore, conducted to develop an efficient alternative "pump and treat" method for treating RDX-contaminated groundwater using alkaline hydrolysis. The study was conducted in two phases. Phase I examined the kinetics of RDX removal by alkaline addition as a function of pH and RDX concentration. This was accomplished by completing a series of batch titration studies. Phase II was a proof of concept study using a continuous flow stirred-tank reactor (CFSTR) to examine the feasibility and applicability of alkaline RDX hydrolysis as a function of pH and the mean hydraulic retention time (HRT).

Materials and Methods

Batch Reactor: Four different initial RDX concentrations (10, 5, 2 and 1 mg/L) were challenged with the reaction pH of six different pH levels (11, 11.5, 12, 12.2, 12.6, and 13) at room temperature (25 ± 1°C). The pH controllers equipped with pumps for acid and base solutions maintained the reaction pH constant.

Continuous Flow-Stirred Tank Reactor: One mg/L RDX solution was continuously added to the 10 L reactor, of which the reaction pH was set at 11.0, 11.5, or 11.9 prior to the initiation of the experiment. The reaction temperature was kept constant at 25°C and the HRT was set at 2, 1, or 0.54 days. During the experiment, the reaction pH was maintained constant by an automatic addition of acid and base solution.

Analysis: The effluent was sampled at a specific time and quenched immediately to make aliquots acidic (pH ~3). Analysis for RDX and RDX transformation products was performed by a DIONEX high-performance liquid chromatography (HPLC). The potential hydrolysis byproducts nitrite (NO_2^-), nitrate (NO_3^-), and formate ($HCOO^-$) were analyzed using a DIONEX ion chromatograph (IC).

Results and Discussion

Alkaline RDX Hydrolysis in Batch Reactor: The pseudo first-order model was used to get the RDX transformation rate constant, k. The value of k was obtained to be faster with an increase in the reaction pH, thereby indicating that the OH^- strength was involved in the rate-limiting step. The obtained values of k's were fit with the following Monod-type equation. As shown in Figure 1, a dissimilar trend in k and subsequent k_{max} was obtained depending on the initial RDX concentration. For 1 and 2 mg/L of the initial RDX concentration, the rate was enhanced with an increase in the reaction OH^- range (1 to 100 mM), resulting in approximately 0.1 min^{-1} of k_{max}. On the contrary, an increase in k_{max} was not continued after 40 mM of the reaction OH^- for 5 and 10 mg/L of the initial RDX concentration, which resulted on about 0.03 min^{-1} of k_{max}. This implied that the effectiveness of alkaline RDX hydrolysis also depended on the initial RDX concentration.

Alkaline RDX Hydrolysis in CFSTR: As shown in Figure 2 as a representative plot, the best alkaline RDX transformation in the CFSTR was achieved at the longest 2-day HRT and the highest reaction pH of 11.9, resulting in approximately 99% RDX reduction. On the contrary, only 23% RDX destruction was observed when the shortest 0.54-day HRT and the lowest reaction pH of 11. At steady-state conditions, the values of k's were determined to be in the range of 0.02 to 1.47 hr^{-1} with being greater at a longer HRT and greater pH.

FIGURE 1

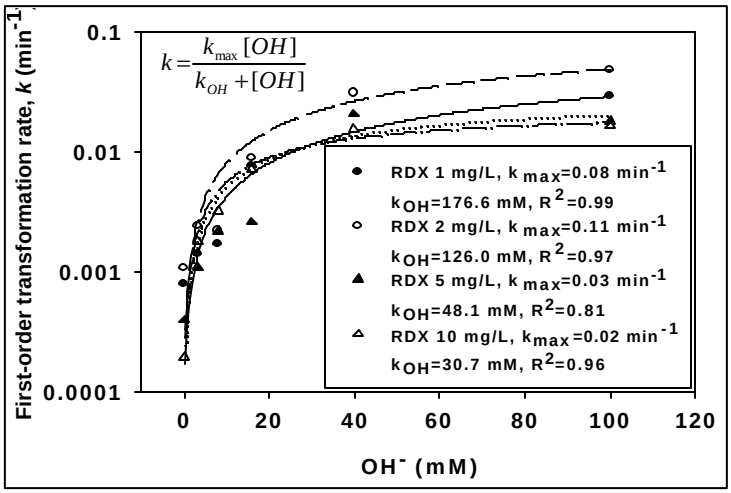
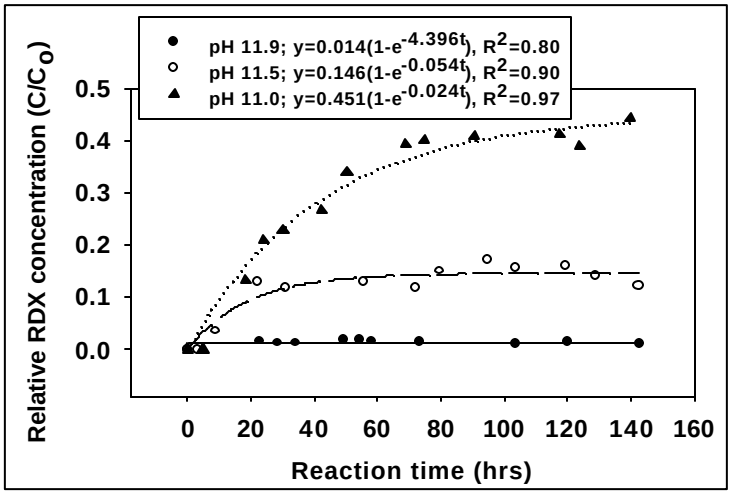


FIGURE 2



Production of Formate and Nitrite in CFSTR: Neither heterocyclic byproducts such as TNX, DNX and MNX nor NO_3^- were not detected. Instead, $HCOO^-$ and NO_2^- were produced. The production of $HCOO^-$ implied that RDX ring cleavage occurred. Such production of $HCOO^-$ and NO_2^- was consistent with the results of others [4,5]. At the 2-day HRT, molar yield was found to be 2.09 M $HCOO^-$ and 0.20 M NO_2^- /M RDX_{rem} at pH 11.0, 1.40 M $HCOO^-$ and 0.17 M NO_2^-/M RDX_{rem} at pH 11.5, and 1.88 M $HCOO^-$ and 0.18 M NO_2^-/M RDX_{rem} at pH 11.9. A bimolecular mechanism was proposed for the alkaline RDX hydrolysis, by which a proton abstraction by OH^- from the relatively acidic methylene hydrogens and a simultaneous loss of NO_2^- ion from the adjacent ring nitrogen occurred in a concerted elimination process [6].

Hydroxide Demand in CFSTR: Alkaline demand was calculated in two ways: net OH^- demand and total OH^- demand. The former was obtained by subtracting the OH^- amount demanded by the influent dilution from the latter. When the CFSTR was operated at pH 11.5, approximately 390 M OH^- was demanded per M $RDX_{removed}$. Such demand was three times greater than approximately 130 M OH^- demand when operated at pH 11.0. However, when the RDX hydrolysis was conducted at pH 11.9, only about 1.5 M OH^- was used for removing one mole of RDX. On the other hand, the total OH^- demand was obtained to be 3030, 1440, and 580 M/M $RDX_{removed}$, on average, for the reaction pH of 11.9, 11.5, and 11.0, respectively.

Therefore, the results of this research suggest that alkaline hydrolysis be an effective alternative "pump and treat" method for treating RDX contaminated groundwater. However, further study is warranted for more enhanced kinetics and subsequent treatability before the facility of alkaline treatment for RDX contaminated groundwater is constructed on-site.

References

1. McLellan, W., Hartley W.R. and Brower, M. (1988). Health advisory for hexahydro-1,3,5-trinitro-1,3,5-triazine. Technical Report No. PB90-273533. Office of Drinking Water, US Environmental Protection Agency. Washington, DC.
2. Bishop, R.L., Flesner, R.L., Dell'Orco, P.C., Spontarelli, T., Larson, S.A. and Bell, D.A. (1999). *Ind. Eng. Chem. Res.* **38**, 2254-2259.
3. Croce, M. and Okamoto, Y. (1979). *J. Org. Chem.* **44**, 2100-2103.
4. Heilmann, H.M., Wiesmann, U. and Stenstrom, M.K. (1996). *Environ. Sci. Technol.* **30**, 1485-1492.
5. Hoffsommer, J.C., Kubose, D.A. and Glover, D.J. (1977). *J. Phys. Chem.* **81**, 380-385.
6. Jones, W.H. (1954). *J. Am. Chem. Soc.* **76**, 829-835.