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Degradation of high energetic and insensitive munitions compounds by Fe/Cu bimetal reduction

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ABSTRACT

A reductive technology based on a completely mixed two-phase reactor (bimetallic particles and aqueous stream) was developed for the treatment of aqueous effluents contaminated with nitramines and nitro-substituted energetic materials. Experimental degradation studies were performed using solutions of three high energetics (RDX, HMX, TNT) and three insensitive-munitions components (NTO, NQ, DNAN). The study shows that, on laboratory scale, these energetic compounds are easily degraded in solution by suspensions of bimetallic particles (Fe/Ni and Fe/Cu) prepared by electro-less deposition. The type of bimetal pair (Fe/Cu or Fe/Ni) does not appear to affect the degradation kinetics of RDX, HMX, and TNT. The degradation of all components followed apparent first-order kinetics. The half-lives of all compounds except NTO were under 10 min. Additional parameters affecting the degradation processes were solids loading and initial pH.

1. Introduction

The production of energetic materials results in the generation of explosives-laden waste streams which require treatment prior to discharge into the environment. Such waste streams often contain a multitude of high-explosive and insensitive-munitions compounds, and degradation products thereof. Some of these compounds may be ecotoxic and persistent in the environment, and some have been classified as class C "Possible Human Carcinogen" by the United States Environmental Protection Agency.

Hexahydro-1,3,5-trinitro-1,3,5-triazine (Royal Demolition Explosive, RDX) is a white crystalline solid, soluble in acetone and acetonitrile, but very poorly soluble in water (about 35–45 mg/L at room temperature). RDX is the most important high explosive for military applications in the United States. RDX is a heterocyclic nitramine with chemical stability similar to that of trinitrotoluene (TNT) but sensitivity to mechanical impact and explosive power superior to those of TNT and other explosives. Since World War II, RDX has been used widely in a variety of military and civil activities around the world, resulting in the contamination of groundwater, surface water, sediments, and soils [1]. There are estimated 12,000 sites in the United States contaminated by high explosives owing to production activities, field usage, and disposal of munitions materials or their combustible products. Soil concentrations often exceeding 3000 mg/kg [2] and levels of 11–14 mg/L in groundwater [3] surrounding munitions plants are reported for RDX and High Melt Explosive (HMX). Chemically, HMX is a higher nitramine homolog of RDX. HMX has similar energetic properties to those of RDX, and can form as a by-product during RDX manufacture. HMX also dissolves very slightly in water; it is photodegradable and relatively non-volatile.

TNT is a white, slightly yellowish crystalline solid, poorly soluble in water (100–200 mg/L at room temperature), but soluble in acetone and benzene [4]. It is a widely used high explosive, both alone and, because of its low melting point (80 °C), as a matrix binder for other explosives, often RDX and HMX. The abiotic transformation of TNT in anaerobic soil environments has been demonstrated in buffered batch tests with montmorillonite and Fe^{2+} [5]. Reduction

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products of TNT have been assessed to possess comparable toxicity to that of the parent compound [6].

Nitrotriazolone (3-nitro-1,2,4-triazol-5-one, NTO) is a white crystalline compound soluble in water (12.8 g/L at 19 °C) producing yellow solutions. Its high aqueous solubility renders adsorption-based technologies ineffective for the treatment of wastewater generated during NTO manufacturing. Several alternative methods have been reported, focusing on advanced oxidation processes and/or biodegradation [7–10]. Preliminary batch experiments conducted in our laboratory, using 0.5 N solutions of NaOH, proved alkaline hydrolysis ineffective for NTO removal for treatment times up to 2 h.

Nitroguanidine (NQ) is a nitramine compound that serves as an oxidizer in triple-base propellants, and also reduces flash and temperature during deflagration. Nitroguanidine has an aqueous solubility ranging between 2.6 and 5.0 g/L, depending on the reporting source. In aqueous solution NQ hydrolyzes to NH_3, N_2O, and CO_2 at pH greater than 10. Alkaline hydrolysis is strongly pH dependent, and at 25 °C the NQ half-life ranges from 8 years to 7.5 h between pH 7 and 13, respectively. NQ has been reported to be non-degradable aerobically but partially degradable through anaerobic co-metabolism [11]. Carbon adsorption and ion exchange have also been reported as potential treatments for NQ [12].

2,4-dinitroanisole (DNAN) is a nitroaromatic compound poorly soluble in water (632 mg/L) and readily soluble in various organic solvents (ethanol, ether, acetone, benzene). Boddu et al. [13] have reported the removal characteristics of DNAN through adsorption on variably treated activated carbons. Reportedly, DNAN is converted to diaminoanisole in anaerobic fluidized bioreactors [14]. Experiments in our laboratory have shown that DNAN can be degraded successfully to dinitrophenol by alkaline hydrolysis. An Arrhenius expression was obtained for the apparent first-order rate constant (k') with a pre-exponential constant (A) of $2.24 \times 10^{18}\ \text{min}^{-1}$ and activation energy (E_a) of 121.8 kJ/mol.

Most of the available technologies for the treatment of soil and water contaminated with high explosives employ biological and physical/chemical methods. The effectiveness of these methods varies. Anaerobic treatment rarely leads to the full degradation of the parent compounds, and frequently the daughter products are, in terms of toxicity, of equal or higher concern than the parent compound. Adsorption-based treatment technologies are rather expensive because the spent carbon must be disposed of as a hazardous waste.

Bimetallic particles with iron as the principal metal have been effective in degrading various organic and inorganic compounds. While treatment with bimetallic particles has not been thoroughly studied, it is believed to have several potential advantages over traditional zero-valent iron (ZVI) treatment, including faster reaction kinetics and slower deposition of corrosion products on the particle surface [15]. Several studies have indicated that iron-palladium bimetallic particles have been effective in treating nitroso- and nitro-compounds at ambient pressure and temperature [16,17]. The secondary metals used – copper, nickel, palladium, etc. help to catalyze the reaction and decrease oxide formation on the iron surface [15]. Transition metals, e.g. copper, are effective at inducing and promoting iron corrosion by forming a galvanic couple between the iron (anode) and the respective metal (cathode) with ambient water acting as the salt bridge [15]. Dissolution of the metal occurs at the anodic sites, releasing ions that can then form rust on the iron surface [18]. A thin film of oxyhydroxides develops on the ZVI and results in a cycle of oxidation, recrystallization, and precipitation [19]. The effectiveness of ZVI is strongly influenced by the formation of precipitates on the iron surface [19]. When the film of oxyhydroxides grows on the iron surface, the iron becomes less effective because there are fewer active sites and the galvanic cell loses its strength. It is believed that the addition of halide salts extends the life of the ZVI and makes it more effective as the halide ions are able to penetrate the pores in the oxide layer, dispersing it and making it more permeable [18]. Ghauch and Tuqan [15] were able to fit kinetic data using a pseudo-first-order model for the degradation of chlorothalonil, with copper and palladium being the most effective. Increasing the concentration of palladium to 10% (w/v), i.e. above catalytic amounts, caused a very large drop in the k_{obs} value. This was attributed to an "over-coating" of the iron particle which effectively turned the iron particle into a palladium particle with an iron core – this was analogous to what was observed during our studies with nanoscale iron (data not shown). Ghauch and Tuqan's study found the most effective dosing level to be 1% Cu and 1% palladium. Additionally, chloride and bromide salts have been shown to be pitting and corrosion promoters [18]. Kim et al. [18] examined the hypothesis that halide salts promote degradation of high explosives and extend the life of ZVI. Degradation of RDX and HMX in aqueous solutions was significantly faster with the addition of chloride and bromide salts. RDX showed complete degradation within 12 h when halide salts were added, and only 30% degradation after 12 h when ZVI was used alone. HMX degraded completely within 48 h with the addition of halide salts, and showed little to no change in the same amount of time when ZVI was used alone. Additionally, at any given salt concentration, Cl^- was more effective than Br^-, most likely due to the lower pH of the $CaCl_2$ solutions attributed to ion pairing and greater acidification. Fuller [20] obtained similar results to Kim [18] using nickel catalysts to degrade explosives in water solutions, and found that RDX and HMX rapidly degraded to below detection under acidic conditions.

The goal of this research was to study the degradation of high explosives and insensitive-munitions components using bimetal-particle reduction that degrades the target compounds within reasonable treatment time. This study (a) evaluates the feasibility of bimetallic zero-valent iron–copper (Fe/Cu) and iron–nickel (Fe/Ni) particles for the treatment of three high explosives (in laboratory prepared solutions and industrial pinkwater samples) and three insensitive munitions, and (b) investigates the reaction kinetics and the factors affecting the degradation rates during treatment.

2. Materials and methods

The experimental program involved the following steps: (a) preparation and characterization of the bimetal substratum: micron-sized iron particles were plated with secondary metals (Cu and Ni) by cold electrolytic deposition. The surface loading was controlled by the strength of the plating solution and the contact time. Bimetallic particles were characterized using BET surface area, and metal content. (b) Bench-scale experiments: this phase focused on determining the reaction kinetics of RDX, HMX, TNT, NTO, DNAN and NQ and sought to identify the various factors affecting their decomposition. Standards for TNX (>99.0% pure), DNX (59% pure), and MNX (99.5% pure) were purchased from SRI International (Menlo Park, CA). Work standards for RDX, MNX, DNX, and TNX were prepared by diluting stock solutions with acetonitrile to desired concentrations. All stock and work solutions were stored at 4 °C.

2.1. Materials

RDX (90% purity, 10% HMX) and HMX were supplied by US ARMY TACOM/ARDEC (Picatinny Arsenal, NJ). Industrial grade iron particles HC-200 (70–80 μm particle size, 2.8–3.2 g/cm³ bulk density) were obtained from Hepure Technologies (Wilmington, DE). Dissolved explosives calibration standards in acetonitrile were purchased from Restek Corporation (Bellefonte, PA). All compounds were 98% pure. RDX standards (99.4% purity) dissolved in methanol