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*Research Communication*

# Manufactured Coal Ash Aggregates for Aqueous TNT Sorption

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### ARTICLE INFO

## 1. Introduction

Environmental contamination with high explosives such as trinitrotoluene (TNT) and dinitrotolune has been posing a significant threat due to their toxic effects to humans, animals, agricultural produce, and other natural receptors (Peres and Agathos, 2000). Coal combustion byproducts (fly and bottom ashes) have been utilized as sorption media for remediation of hazardous compounds (Asokan et al., 2005).

Manufactured coal ash aggregates (MAs) are a solidified composite of fly and bottom ashes (2:1 by weight) that are mixed in water and then air-dried. They gain strength with time due to cementitious reactions. MAs can have better engineering properties than fly and bottom ashes in a sense that they are structurally stronger and chemically more stable (Pando and Hwang, 2006). This research was conducted to evaluate the sorption of TNT to MAs. To achieve the goals, batch sorption kinetic and isotherm tests and a sequencing batch sorption reactor (SBSR) were run at a laboratory scale.

## 2. Materials and Method

### 2.1 Manufactured coal ash aggregates and TNT solutions

MAs were sampled at a local coal-burning power plant in Puerto Rico as they were produced. The main chemical components of the MAs used were (silica + alumina + ferric oxides), lime, and sulfur trioxide, representing 51%, 30%, and 14.7% by weight, respectively. Prior to the use for the experiment, they were crushed mechanically and sieved to collect the particles sizes in the range of 1.0 (US Sieve Number 18) to 2.0 mm (US Sieve Number 10). A standard TNT solution that was purchased from Restek Corp. and the initial target TNT concentration of 1 mg/L was made with a proper dilution.

### 2.2 Sorption kinetic and isotherm experiments

Sorption kinetic study was performed to assess an equilibrium time for the TNT to sorb to the MAs. The same amounts of the MAs (2.5 g) were placed in several batch reactors and then the same amount of TNT solution (12 mL) at 1.0 mg/L TNT was added to the reactors. The reactors were prepared in duplicate. They were agitated on a slow speed end-over-end rotational shaker (Thermo-lyne Labquake Shaker) at 8 rpm in order to facilitate contacts between the MAs and TNT molecules.

For sorption isotherm study, duplicate batch reactors prepared using a different amount of the MAs (1.0 to 3.5 g) with the same volume (12 mL) at the TNT concentration of 1 mg/L. The reactors were continuously shaken for the sorption equilibrium time obtained from the kinetic experiment aforementioned (i.e., 2 hrs) and at room temperature (i.e. $23 \pm 1^\circ$C).

### 2.3 Sequencing batch sorption reactor

SBSR was tested as a treatment option for TNT-contaminated water with MAs. Initially, 12 mL of TNT solution at a concentration of 1.0 mg/L was filled in a 20 mL glass syringe reactor which had 2.5 g of the MAs. After a one hour of contact time on the shaker, the freely-drained liquid (~97% of the initial) was decanted from

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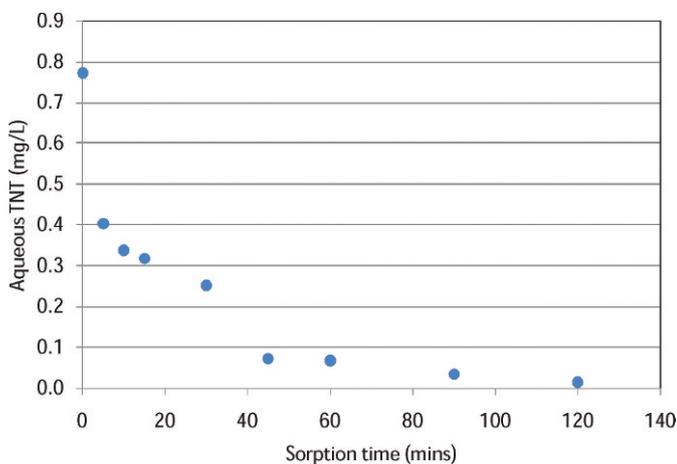
**Fig. 1.** Results from the sorption kinetic experiment. Data are the average of duplicate runs. Standard deviations were ± 5% range. A pseudo-first order sorption kinetic fit the data ($dC/dt = e{-0.05t}$, R2=0.91).



**Fig. 2.** Aqueous TNT concentration after each sequence of the SBSR. Data are the average of duplicate runs. Standard deviations were ± 5% range.

the reactor for the aqueous TNT analysis, but the spent MAs were remained in the SBSR. Then, another 12 mL of TNT at 1.0 mg/L were refilled to the SBSR and the system was shaken for another hour. This sequencing fill-reaction-decant procedure was repeated six times, totaling 72 mL of TNT solution at 1 mg/L in contact with the initial 2.5 g of MAs in the SBSR.

### 2.4 Analysis

The TNT concentration was measured with an HPLC (Perkin Elmer Series 200). Aqueous samples taken out at different time intervals were filtered with a 0.2-μm membrane filter. Sonication of the used membrane filter in acetonitrile solution and subsequent HPLC analysis showed no TNT trapped in the membrane filter. The mobile phase of the HPLC was a mixture of methanol (MeOH) and deionized (DI) water at a ratio of 70% MeOH to 30% DI water at a flowrate of 1 mL/min. The HPLC column used was a Supelco C18 (25 cm × 4.6 mm × 5 μm). The UV lamp in the HPLC was set to a wavelength at 254 nm. One microliter of sample was injected to the HPLC with a detection limit of 0.2 μg/L TNT.

## 3. Results and Discussion

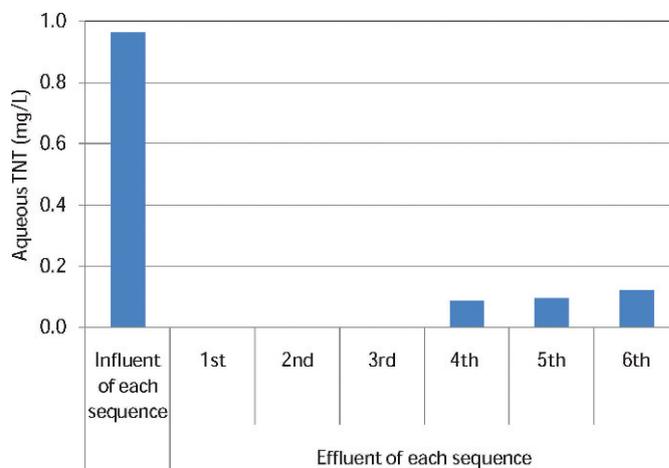### 3.1 Sorption equilibrium time and isotherms

As shown in Figure 1, a pseudo-equilibrium of TNT sorption to the MAs was assumed to be achieved after 2 hours of sorption equilibrium time. The initial aqueous TNT concentration of 1.0 mg/L was reduced to 0.02 mg/L after 2 hours of sorption contact time. It was reported that TNT sorption equilibrium was achieved with the seven organoclays within 2 hours (Upson and Burns, 2006).

Sorption kinetic data were modeled using pseudo-first order kinetics as follows:

$$\frac{d[TNT]}{dt} = -k_{obs}[TNT] \qquad (1)$$

where $k_{obs}$ is the observed pseudo first-order sorption rate constant. The value of $k_{obs}$ was calculated to be 0.05 min$^{-1}$ with a regression coefficient of $R^2 = 0.91$.

For sorption isotherms, the TNT concentrations sorbed to the solids was plotted against the aqueous TNT concentrations. The difference between the initial and final aqueous TNT concentra-

tions was used for calculation of the TNT amount sorbed to the MAs. The blank system without the MAs was run simultaneously to assess any losses of TNT during the experiment. It showed <2% loss of the TNT concentration after 2-hour experiment due probably to sorption to the reactor wall. Therefore, the reductions of TNT concentration in the sorption reactors were due to TNT sorption to MAs.

The sorption isotherm data were fit to the Freundlich sorption model:

$$q_e = K_f \cdot C_e^{1/n} \qquad (2)$$

where $q_e$ is the equilibrium concentration of the compounds sorbed to the solids, $k_f$ is the Freundlich sorption constant, $1/n$ is the Freundlich exponent, and $c_e$ is the equilibrium concentration of the compound in liquid. The Freundlich constant ($k_f$) was 25.7 mg/kg (L/mg)$^{1/n}$ with $1/n = 0.379$. The Freundlich exponent ($1/n$) less than 1 implies that TNT sorption to the MAs was favorable.

### 3.2 Sequencing batch sorption reactor

As shown in Figure 2, MAs completely sorbed all the TNT present on the liquid during the first three sequences of the SBSR. This was a total of 36 mL of TNT solutions at a nominal concentration of 1.0 mg/L (actual measured initial TNT concentration = 0.96 mg/L). Therefore, total 0.035 mg of TNT during three sequences completely sorbed to 2.5 g MAs (i.e., 14.4 mg TNT/kg MAs). The MAs were not saturated with the TNT even after the 6$^{th}$ sequence. However, the residual TNT concentration was measured to be 0.08, 0.09 and 0.12 mg/L after the 4$^{th}$, 5$^{th}$, and 6$^{th}$ sequence, respectively. These were corresponding to 91%, 90% and 87%, respectively, of the TNT reduction by sorption.

It should be noted that the SBSR was run for 1 hour of sorption contact time for each sequence. A shorter sorption contact time than equilibrium sorption time could lead underestimation of the extent of compound's sorption (Hwang and Cutright, 2004). Nevertheless, overall sorption capacity of the SBSR was calculated to be 28.8 mg TNT/ kg MAs after completion of the 6$^{th}$ sequence. A blank SBSR system without the MAs was also run and showed a minimal decrease (<2%) in TNT concentration at the end of the experiment.

Aqueous TNT degradation was reported at high pH levels greater than 11.0 via an alkaline hydrolysis (Hwang et al., 2005). However,

the reaction pHs were in the range of 9.5 ± 0.3 throughout the sorption experiments. Therefore, it is construed that TNT alkaline hydrolysis did not take place, but that the sorption to the MAs played a key role in TNT reduction during the experiments.

Sorbed TNT was not desorbed out of the MAs within 2 hours of desorption time. This could be attributed to a very slow rate of TNT desorption or an irreversible TNT sorption to the MAs (Hwang and Cutright, 2002). Further investigation is warranted to elucidate the rate and mechanism of TNT desorption from the MAs.

## 4. Summary

Pseudo-equilibrium sorption of TNT to the MAs was attained after 2 hours of contact time at a $k_{obs}$ of 0.05 min$^{-1}$. The Freundlich sorption model fit well the sorption isotherm data with $k_f$ being 25.7 mg/kg (L/mg)$^{1/n}$ and $1/n$ being 0.379. The MAs completely sorbed all the TNT up to the 3$^{rd}$ sequence of sorption in an SBSR where the application rate was 4.8 mg TNT/kg MAs per each sequence. The sorbed TNT was not desorbed from the MAs under the given desorption conditions of this investigation.

Overall, the research presented in this manuscript shows that the MAs could be used as sorption media for remediation of TNT-containing water. However, care should be given for their potentials to introduce other contaminants to water in various environmental conditions (e.g., pH, hydrologic characteristics, and temperature), although the MAs are already solidified aggregates and would not have secondary contamination as much as fly and bottom ashes.

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