

Explosives Sorption to Coal Ash Aggregates

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INTRODUCTION

Sorption is a process where a dissolved substance is transferred to and becomes associated with solid sorption materials. Synthetic polymeric materials and activated carbons have been used most widely for the treatment purposes [1]. Waste materials also have been used as sorption media in many studies, such as rice bran and rice husk for triazophos sorption [2], basic oxygen furnace slag for phosphate sorption [3], and papaya seeds for methylene blue sorption [4].

2,4,6-trinitrotoluene (TNT) had been the predominant high explosives (HEs) for military purposes before its production was ceased in the mid 1980s in the United States. TNT environmental contamination still exists because of both military activities before that time and demilitarization afterwards. For example, 28% of 1,155 soil samples from 46 sites were found to be contaminated with one or more explosives. Of those samples, 97% contained TNT, hexahydro-1,3,5-trinitro-1,3,5-triazine and/or 2,4-dinitrotoluene [5]. Environmental contamination with HEs has been posing a significant threat due to their toxic effects to humans, animals, agricultural produce, and other natural receptors [6].

Coal ash aggregates (CAAs) are solidified mixtures of coal combustion residues. This material has many potential for applications in the field of environmental engineering. An example is use of the CAAs as a sorption media utilizing their high surface area and void ratio. The high void ratio content of the coarse CAAs was found to be related to a structure of an agglomerate of particles [7].

The goal of this research was to evaluate the sorption and desorption behaviors of TNT with low-cost industrial byproducts CAAs. To achieve the goals, both batch kinetic and isotherm studies were performed. This study would not only provide useful technical information for remediation of TNT-contaminated water, but also offer guidance for environmental management and utilization of industrial byproducts CAAs.

MATERIALS AND METHODS

Coal Ash Aggregates

Coal ash aggregates (or commonly called manufactured aggregates) are solidified mixture of fly (FA) and bottom ashes (BA). This material gains strength with time due to

cementitious reactions and physiochemical properties of the CAAs can be found in a previous study [7]. Bulk CAAs were sampled at a local coal burning power plant in Puerto Rico. Since the particle sizes are in a wide range, they were crushed and sieved in the laboratory. The CAA particles used in the current study were those passes the sieve numbers 10 (i.e., mesh size 2.0 mm) but retained on the sieve number 18 (i.e., mesh size 1.0 mm).

Sorption/Desorption Experiments

Sorption kinetic study was performed to assess an equilibrium time for the TNT to sorb to the CAAs. The reactors for this experiment were in a batch setting in duplicate. They were agitated using a slow speed end-over-end rotational shaker (Thermolyne Labquake Shaker) at 8 rpm in order to provide enhanced contact between the CAAs and the TNT molecules. The same amounts of the CAAs (2.5 grams) 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 them. The batches were continuously shaken for the length of the experiment. They started at the same time and each duplicate was “sacrificed” at a different time, while the rest of the batch reactors were remained on the shaker.

Sorption isotherm study was performed using a similar procedure as the kinetic study. Each duplicate batch was prepared using different amount of the CAAs with the same volume and concentration of TNT solution. The initial TNT concentration for this isotherm experiment was 1.0 mg/L and the volume of the TNT solution was 12 mL. Therefore, the initial mass of TNT present in the system was 0.012 mg (i.e., $1.0 \text{ mg/L} * 12 \text{ mL} * 10^{-3} \text{ L/mL} = 0.012 \text{ mg TNT}$). The amount of CAAs added was in the range of 1 g to 3.5 g with 0.5 g increments. The experiment was conducted at room temperature (i.e. $23 \pm 1^\circ\text{C}$). As in the kinetic study, the batch reactors were continuously shaken for the sorption equilibrium time obtained from the previous kinetic experiment.

Desorption kinetic experiment consisted of using the vials that had been used for the sorption kinetic experiment. Liquid portion remaining in the reactors was carefully withdrawn as much as possible and 12 mL of pure water was added. Liquid withdrawal rate was in the range of 95% to 97 % of the original volume. Again, the systems were put on the shaker and duplicate reactors were “sacrificed” at a different time interval for sampling. Similar to the desorption kinetic study, desorption isotherm experiment was also done. Difference is in that desorption isotherm study used the reactors that had been used for the sorption isotherm study.

Sequential Batch Sorption Reactor

A sequential batch sorption reactor (SBSR) was tested to provide an engineering management guideline of TNT-contaminated water via sorption with the CAAs. Initially, 12 mL of TNT solution at a concentration of 1.0 mg/L was introduced in a syringe reactor which had 2.5 g of the CAAs. The SBSR was put on the shake for an hour. After one hour, the liquid was emptied from the syringe as much as possible for the aqueous TNT analysis, but the spent CAAs were left in the SBRR. 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 procedure was repeated for six consecutive hours totaling 72 mL of TNT solution in contact with the initial 2.5 g of CAA in a sequential manner.

ANALYSIS

The equipment used to determine the aqueous TNT concentrations was a Perkin elmer Series 200 HPLC. The mobile phase mentioned above was a mixture of methanol (MeOH) and deionized (DI) water at a ratio of 70% MeOH to 30% DI water. The HPLC column used was a Supelco C18 with dimensions of 25 cm x 4.6 mm x 5 μ m. The flow used for the analysis was 1 mL/min. The UV lamp in the HPLC was set to wavelength amplitude at 254 nm.

EXPERIMENTAL RESULTS

Sorption/Desorption

The initial aqueous TNT concentration of 1.0 mg/L (nominal) was reduced to 0.02 mg/L after 2 hours of sorption contact time. Pseudo-equilibrium of TNT sorption to the CAAs was assumed to be achieved after 2 hours of sorption equilibrium time.

At high pH levels greater than 11.0, some TNT degradation could be achieved via an alkaline hydrolysis [8]. However, the value of pH in the batch settings used in the current study was not developed high enough to provoke an alkaline hydrolysis. Throughout the sorption experiments, the reaction pHs were in the range of 9.50 ± 0.25 . Therefore, it is construed that TNT alkaline hydrolysis did not take place, but that the sorption to the CAAs played a key role in TNT reduction during the entire experiments.

Several models have been proposed to mathematically represent the sorption isotherms. The most frequently used ones are the Freundlich ($q_e = K_f \cdot C_e^{1/n}$) and the Langmuir ($q_e = (Q^0 \cdot b \cdot C_e) / (1 + b \cdot C_e)$) equations. 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, C_e is the equilibrium concentration of the compound in liquid, Q^0 is the maximum sorption capacity, and b is the Langmuir sorption coefficient.

The sorption isotherm data were fit to the Freundlich sorption model very accurately ($R^2=0.999$) as shown in [Figure 1](#). The Freundlich constant (k_f) was 25.7 mg TNT/kg CAA with $1/n = 0.379$. The Freundlich exponent ($1/n$) less than 1 shows that TNT sorption to the CAAs was favorable. It also implied that the sorption sites with the highest binding energies were used first and then followed by the weaker sites [9].

The Langmuir sorption model also fit the data well ($R^2=0.987$) as shown in [Figure 1](#). In this case, the Q^0 of the CAAs for TNT was calculated to be 25.7 mg TNT/kg CAAs, which was the same for the Freundlich sorption model as described above. The coefficient, b , was calculated to be 6.5 which implies that the rate of TNT sorption to the CAAs was 6.5 times faster than that of TNT desorption from the CAAs.

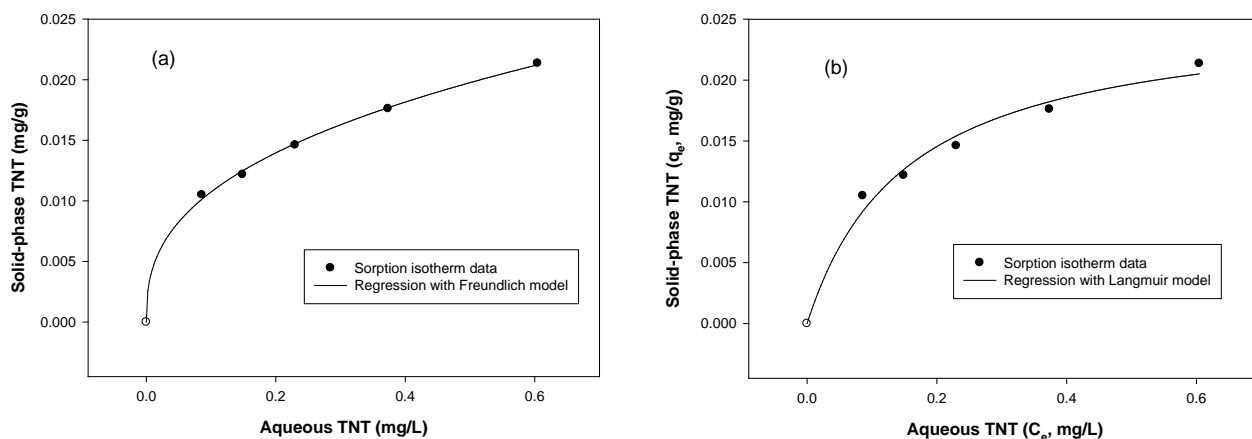


Figure 1. Sorption isotherm data and regression with the Freundlich (a) and Langmuir (b) sorption models. Data are the average of duplicate runs. Standard deviations were +/- 5% range.

Desorption kinetic experiment was conducted during 2 hours and showed that the sorbed TNT was not desorbed out of the CAAs within the given desorption time. The same phenomenon occurred for the desorption isotherm experiment where 2 hours of desorption time was provided. A previous work reported that desorption of a 4-ring polycyclic aromatic hydrocarbon pyrene from a natural soil was influenced significantly by different lengths of desorption time [10]. Likely, the results shown in the current study could be attributed to possibility that the rate of TNT desorption was too slow to be measured in the liquid due probably to a mass transfer limitation, or that the TNT was sorbed irreversibly to the CAAs.

Sequential Sorption Reactor

Figure 2 shows the results from the SBSR experiment. The result showed that 2.5 grams of CAA could completely sorb all the TNT present on the liquid during the first 3 sequences. This was a total of 36 mL of TNT solutions at a nominal concentration of 1.0 mg/L. Actual measured initial TNT concentration was 0.96 mg/L. Therefore, total 0.035 mg of TNT was applied up to the 3rd sequence and completely sorbed to 2.5 grams of the CAAs (i.e., 14.4 mg TNT/kg CAAs).

Although the CAAs were still able to sorb additional TNT applied during the last three sequences, the residual TNT concentrations were getting increasing upon reaching the maximum sorption capacity of the CAAs from the 4th sequence. The residual TNT concentration was measured to be 0.08, 0.09 and 0.12 mg/L, respectively, after the 4th, 5th and 6th sequence. These were corresponding to the TNT reduction of 91%, 90% and 87%, respectively. Increasing trend of the residual TNT concentration from the 4th sequence indirectly implies that CAAs had a fixed number of sorption site available for TNT (i.e., Langmuir sorption model), or that sorption did not take place with equilibrium time.

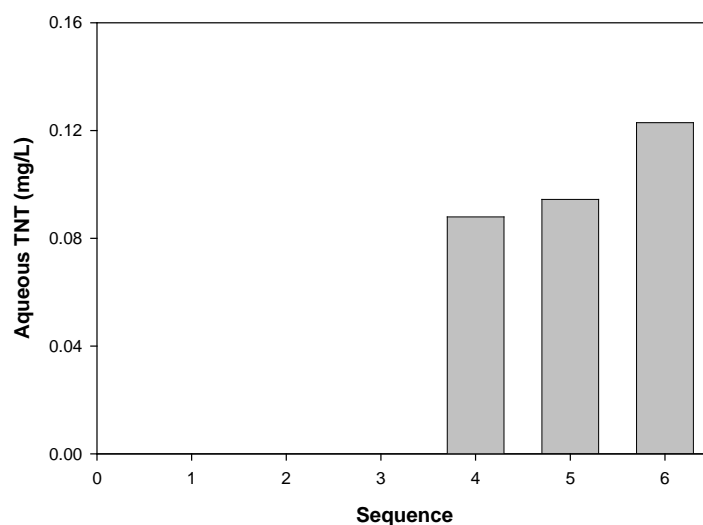


Figure 2. Aqueous TNT concentration after each sequence of the sequential batch sorption reactor. Data are the average of duplicate runs. Standard deviations were +/- 5% range.

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 to underestimation of the extent of compound's sorption [11]. Nevertheless, overall sorption capacity of the SBSR was calculated to be 28.8 mg TNT/ kg CAAs after completion of the 6th sequence. This value was very close to 25.7 mg TNT/kg CAAs that was obtained to be the maximum sorption capacity of CAAs for TNT from the Freundlich and Langmuir sorption models. A blank system without the CAAs was run for the same period of experiment time and showed a minimal reduction (~3%) of decrease in TNT concentration at the end of the experiment.

CONCLUSIONS

Pseudo-equilibrium sorption was attained after 2 hours of contact time. Both the Freundlich and Langmuir sorption models revealed that the CAAs could sorb 25.7 mg of TNT per gram of the CAAs. The CAAs completely sorbed all the TNT up to the 3rd sequence of sorption in an SBSR where the application rate was 4.8 mg TNT/kg CAAs per each sequence. Desorption of the TNT from the CAAs was not measurable during this investigation. This was due probably to the rate of TNT desorption was too slow to be measured within the given desorption time (2 hours), or the TNT was sorbed irreversibly to the CAAs. Overall, the research presented in this manuscript shows that the CAAs could be used as sorption media for remediation of TNT-containing water. Therefore, utilization of the CAAs for remediation of TNT-contaminated water can be an alternative management of the industrial byproducts CAAs.

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