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Biodegradation of High Explosives on Granular Activated Carbon: Enhanced Desorption of High Explosives from GAC--Batch Studies

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An Interim Report on

Biodegradation of High Explosives on Granular Activated Carbon: Enhanced Desorption of High Explosives from GAC – Batch Studies

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Biodegradation of High Explosives on Granular Activated Carbon: Enhanced Desorption of High Explosives from GAC – Batch Studies

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Abstract

Adsorption to GAC is an effective method for removing high explosives (HE) compounds from water, but no permanent treatment is achieved. Bioregeneration, which treats adsorbed contaminants by desorption and biodegradation, is being developed as a method for reducing GAC usage rates and permanently degrading RDX and HMX. Because desorption is often the limiting mass transfer mechanism in bioregeneration systems, several methods for increasing the rate and extent of desorption of RDX and HMX are being studied. These include use of cosolvents (methanol and ethanol), surfactants (both anionic and nonionic), and β- and γ-cyclodextrins. Batch experiments to characterize the desorption of these HEs from GAC have been completed using Northwestern LB-830, the GAC being used at Pantex. Over a total of 11 days of desorption, about 3% of the adsorbed RDX was desorbed from the GAC using buffered water as the desorption fluid. In comparison, about 96% of the RDX was extracted from the GAC by acetonitrile over the same desorption period. Ethanol and methanol were both effective in desorbing RDX and HMX; higher alcohol concentrations were able to desorb more HE from the GAC. Surfactants varied widely in their abilities to enhance desorption of HEs. The most effective surfactant that was studied was sodium dodecyl sulfate (SDS), which desorbed 56.4% of the adsorbed RDX at a concentration of 500 mg SDS/L. The cyclodextrins that were used were marginally more effective than water. Continuous-flow column tests are underway for further testing the most promising of these methods. These results will be compared to column experiments that have been completed under baseline conditions (using buffered water as the desorption fluid). Results of this research will support modeling and design of further desorption and bioregeneration experiments.

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1. INTRODUCTION

Granular activated carbon (GAC) treatment is a well-accepted and commonly-used treatment method for removing high explosives from aqueous streams. Adsorption to GAC is currently the most widely used treatment method for RDX- and HMX-contaminated waters because it is a simple and effective technology (Wujcik, *et al.*, 1992; Henke and Speitel, 1997). A full-scale GAC system is currently in operation at the Department of Energy Pantex Plant in Amarillo, TX for treatment of HE-contaminated groundwater.

Although it is effective, adsorption simply transfers contaminants from water to the surface of the GAC and provides no permanent treatment or destruction of contaminants. Further, because GAC has a finite adsorption capacity, the carbon eventually becomes exhausted and must be replaced. Because of its reactivity, spent GAC from treating explosives wastewaters is classified as EPA-listed hazardous waste K045 (40 CFR 261.32). This may increase treatment and/or disposal costs. Spent GAC from the Pantex groundwater treatment system is currently shipped off-site and undergoes thermal regeneration (personal communication, Jimmy Rogers, Battelle Pantex). Incineration effectively destroys RDX and HMX, but is costly and does not allow for complete recycling of GAC (Sontheimer, *et al.*, 1988). Adsorption to GAC can thus have relatively high operating and maintenance costs.

Biological regeneration is a potential method for extending the service life of GAC. Bioregeneration combines adsorption to GAC with biological degradation of contaminants. Contaminants are removed from water by adsorption and/or biodegradation, and destroyed by biodegradation. Bioregeneration can potentially increase GAC service life because both adsorption and biodegradation remove contaminants. Longer GAC service life requires less frequent replacement of spent GAC, thereby reducing costs of GAC systems.

Bioregeneration systems have been developed in two general process configurations: on-line systems, in which biodegradation and adsorption occur simultaneously in a packed or fluidized bed, and off-line systems, in which contaminants are desorbed from GAC, and the regenerant solution is biologically treated in a separate reactor. This research seeks to develop an off-line bioregeneration system, which will be more feasible for this application than an on-line system due to the nutritional and dissolved oxygen requirements of the HE-degrading bacterial culture and the slow desorption of HE compounds.

Wilkie (1994) developed an off-line regeneration process for treatment of aqueous RDX and HMX, although studies were completed with RDX only. RDX was first adsorbed to GAC. After exhaustion of the bed, RDX was desorbed with a heated ethanol/water mixture. The regenerant fluid was treated in a separate bioreactor. RDX removal efficiencies of up to 80% were achieved at steady state in the biological reactor. The system was not operated continuously. No other known research has been conducted on regeneration of GAC contaminated with RDX and HMX.

In off-line bioregeneration systems, contaminants must be desorbed to regenerate the GAC, with subsequent biological treatment of the desorbed chemicals. Desorption from GAC occurs in response to changes in global or local operating conditions of an adsorber (Thacker, *et al.*, 1983), such as (1) a decrease in the liquid phase concentration, which creates a concentration gradient that drives substrate out of the GAC and into the liquid; (2) displacement of adsorbed solutes by competitive adsorption; and (3) some other change in liquid phase concentration (such as

pH) that decreases adsorbability. Some bioregeneration studies have found slow rates of bioregeneration for contaminants that desorb slowly (Speitel *et al.*, 1989; de Jonge, *et al.*, 1996a,b; Orshansky and Narkis, 1997), but methods for improving contaminant desorption rates, and thus bioavailability, have not been pursued. In other studies, the extent of bioregeneration was limited by slow desorption kinetics and by cessation of bacterial growth at low liquid phase substrate concentrations (Goeddertz, *et al.*, 1988; Hutchinson and Robinson, 1990a,b). In these cases, adsorption performance decreased over time and complete regeneration could not be achieved because of non-zero threshold growth concentrations, which prevented complete desorption of contaminants.

Because slow desorption often limits bioregeneration of GAC, increasing the rate and extent of desorption through chemical and/or physical methods may improve bioregeneration of GAC. The research that is presented in this report seeks to develop methods for increasing the rate and extent of HE desorption, while not precluding subsequent biological treatment of desorbed chemicals. Although pure solvent extraction methods are not likely to be feasible for biological treatment, these methods are included for comparison. The methods that have been tested include synthetic surfactants, cosolvents, and cyclodextrins. Many of these methods have been utilized for soil and/or groundwater remediation, but have not been systematically compared for desorbing contaminants from GAC.

2. ENHANCED DESORPTION METHODS

2.1 Cosolvents

Cosolvents are organic solvents that are miscible in water. Cosolvents can increase contaminant solubility, increase rates of diffusion, and reduce retardation of solutes in soils by changing the properties of the bulk liquid phase (Brusseau, *et al.*, 1991, 1995; Jafvert, 1996). The net polarity of the water/cosolvent mixture is lower than for water alone; thus, the solubility of nonionic organic compounds is increased, resulting in less sorption and less retardation. Cosolvents such as methanol and ethanol undergo little sorption to solid surfaces, and are generally biodegradable at low concentrations (<1%). However, they are toxic to bacteria at higher concentrations (>3-10%). Wilkie (1994) utilized ethanol to desorb RDX from GAC. Ethanol concentrations in water of less than 30% resulted in little improvement over pure water. Solutions with 50% and 100% ethanol provided the best enhancement of RDX desorption.

2.2 Synthetic Surfactants

Surfactants, or surface active agents, are compounds that have both hydrophobic and hydrophilic regions, or moieties (Shiau, *et al.*, 1995). The four general classifications of surfactants, based on charged groups in the hydrophilic moiety, are anionic, cationic, nonionic, and amphoteric (with both positive and negative charges) (Myers, 1988). Surfactant molecules tend to migrate to interfaces where each moiety can exist in its preferred phase. At high concentrations, surfactants aggregate into micelles, which are roughly spherical and have hydrophobic interiors and hydrophilic exteriors (Myers, 1988). Micelle formation occurs at surfactant concentrations above the critical micelle concentration (CMC).

Micelles are highly soluble in water and have a hydrophobic interior, a property that can enhance solubilization and desorption of synthetic organic contaminants (SOCs). Solubilization is the increase in the apparent aqueous solubility of a contaminant due to partitioning into micelles (Myers, 1988). Enhanced solubility of neutral organic compounds is due to the partitioning of hydrophobic contaminants to the hydrophobic interior of the micelles. Above the CMC, solubility of contaminants increases linearly with surfactant concentration (Shiau, *et al.*, 1995). Below the CMC, surfactant addition usually has no effect on SOC solubility, but in some cases, SOC solubility is enhanced due to partitioning of the SOC into the nonpolar portion of dilute surfactant molecules (Kile and Chiou, 1989; Liu and Chang, 1997; Deshpande, *et al.*, 1999). SOCs with lowest solubility generally have the greatest increases in solubility in the presence of added surfactants (Liu and Chang, 1997). Ideal application would be above the CMC, but below the surfactant solubility limit to prevent surfactant precipitation.

Surfactant solubilization affects adsorption of SOCs to a variety of surfaces. Increased solubility of SOCs in surfactant solutions reduces adsorption to soil and aquifer material (Jafvert, 1996), and competitive adsorption between surfactants and contaminants may displace surfactants from soil surfaces (Liu and Chang, 1997). Hawari, *et al.* (1996) tested the ability of several surfactants to extract RDX from soil. Extraction with water was limited by the low water solubility of RDX. Three anionic surfactants were tested at concentrations of 1% w/v (CMC of the test surfactants was not stated). These solutions removed 1.2 to 2.0 times more RDX from soil as compared to water.

Surfactant solutions can also effectively desorb SOCs from GAC, a potential method for GAC regeneration that

was first proposed by Blakeburn and Scamehorn (1989). They introduced the concept of surfactant-enhanced carbon regeneration (SECR), in which a concentrated surfactant solution is passed through a bed of spent GAC. The process has been utilized to regenerate GAC loaded with amyl acetate and toluene adsorbed from the gas phase (Roberts, *et al.*, 1989); 4-tert-butyl-phenol adsorbed from the aqueous phase (Blakeburn and Scamehorn, 1989); and phenol adsorbed from the aqueous phase (Bhummasobhana, *et al.*, 1996). In many cases, multiple regeneration cycles did not affect the adsorption capacity of the GAC. However, some portion of the adsorption capacity may not be regenerated due to irreversible adsorption of SOCs or surfactant adsorption (Bhummasobhana, *et al.*, 1996). The surfactant concentration must be above its CMC for significant contaminant solubilization to occur (Blakeburn and Scamehorn, 1989), and the amount of SOC desorbed from the GAC increases as the surfactant concentration is increased (Bhummasobhana, *et al.*, 1996).

2.3 Cyclodextrins

Cyclodextrins (CDs) are cyclic oligosaccharides that are formed by bacterial degradation of starch (Szejtli, 1982). The general molecular shape of these compounds is a toroidal, hollow, truncated cone. CDs exist in three forms (α, β, and γ), corresponding to progressively larger molecular size. The interior cavity of a CD molecule is hydrophobic; thus, they behave somewhat like surfactant micelles and can solubilize low polarity or nonionic SOCs (Murai, *et al.*, 1998). CDs solubilize SOCs by forming 1:1 inclusion complexes through non-specific chemical interactions between the solute and the hydrophobic cavity of the CD (Cahill and Bulusu, 1993). Some dissolved CD is inevitably complexed with highly soluble, non-target organic compounds, reducing the amount of CD available for complexation of target SOCs (Wang and Brusseau, 1993). CDs do not form emulsions, are sorbed very little to soils, and are nontoxic and biodegradable (Wang and Brusseau, 1993). According to Brusseau, *et al.* (1995), cyclodextrins can solubilize organics to a greater degree than miscible cosolvents, but to a somewhat lesser degree than synthetic surfactants. Adsorption of CDs to GAC is unknown.

Cahill and Bulusu (1993) studied interactions between cyclodextrins and RDX and HMX. They found that both of these HEs are bound to cyclodextrins in aqueous solutions, and that both compounds are most strongly bound to the larger γ-CDs. Hawari, *et al.* (1996) utilized cyclodextrins to improve RDX extraction from spiked soil. Two cyclodextrins (hydroxypropyl-β-cyclodextrin and methyl-β-cyclodextrin) at concentrations of 0.1% w/v increased RDX removal by 1.5 to 2.4 times that of water, comparable to removal by synthetic surfactants. A more concentrated (10% weight/volume) solution of hydroxypropyl-β-cyclodextrin extracted 95% of the RDX from the spiked soil, but was considered to be uneconomical.

3. MATERIALS AND METHODS

Initials testing focused on screening several possible methods for enhancing desorption. Batch tests were first used to screen potential chemical treatments. Each of these treatments was compared to desorption under baseline conditions (i.e., water buffered at pH 7). A limited number of the most promising methods will then be tested in further detailed experiments.

3.1 Selection of Methods

Numerous possibilities exist for methods that can potentially enhance desorption of RDX and HMX from GAC. The methods that were examined in this research were those that could potentially enhance desorption of RDX and HMX, that would result in minimal fouling of the GAC, and which would be compatible with biological treatment of the desorption fluid. Cationic and amphoteric surfactants tend to strongly sorb to surfaces (Jafvert, 1996), making them impractical for SECR. Thus, only anionic and nonionic surfactants were considered. Several surfactants that are commonly used in soil remediation research were chosen for this study due to the availability of CMC data for these compounds. The anionic surfactant chosen was sodium dodecyl sulfate (SDS). The three nonionic surfactants chosen were Tween 80 (polyoxyethylene (20) sorbitan monooleate; CAS number: 9005-65-6); Brij 30 (polyoxyethylene(4) lauryl ether; CAS number: 5274-68-0), and Triton X-100 (polyoxyethylated octyl phenol; CAS number: 9002-93-1). Table 1 summarizes information about these surfactants.

Cosolvents were chosen on the basis of biodegradability and lack of adsorption to GAC. Methanol and ethanol are both biodegradable and do not adsorb well to GAC. Additionally, the solubility of RDX and HMX are much higher in these alcohols than in water (USAMC, 1971). Wilkie (1994) determined a relationship between RDX solubility and ethanol concentration at 26°C:

$$\text{RDX (mg/L)} = 0.19015 + 10.053(\%\ \text{Ethanol})$$

Cyclodextrins were chosen based on limited research conducted with RDX. Hawari, *et al.* (1996) found that some β-CDs could extract RDX from soil, and Cahill and Bulusu (1998) found that RDX and HMX bind more strongly to γ-CD as compared to β-CD.

Table 1: Surfactants Used in Enhanced Desorption Research and Published CMCs

Surfactant	Type of Surfactant	CMC (mg/L)	Reference
SDS	Anionic	2420	Deshpande, *et al.* (1999)
		2360	Van Os, *et al.* (1993)
Tween 80	Nonionic	32.7	Park, *et al.* (1998)
		13	Yeh, *et al.* (1998)
Brij 30	Nonionic	12.7	Park, *et al.* (1998)
		16.7	Van Os, *et al.* (1993)
Triton X-100	Nonionic	115	Park, *et al.* (1998)
		159	Van Os, *et al.* (1993)

3.2 Chemicals

Surfactants, solvents, and cyclodextrins were obtained from various sources. SDS powder and Tween 80 liquid were obtained from Fisher. Brij 30 and Triton X-100, both as liquids, were from Sigma. Absolute ethanol (Aaper Alcohol & Chemical) and HPLC-grade methanol (Fisher Optima) were used as cosolvents. Both cyclodextrins (β and γ) were donated by Cerestar, USA (Hammond, IN). All surfactants and cyclodextrins were used as received, without further purification. All solutions were prepared with distilled water (steam condensate) from a laboratory water tap.

3.3 Analytical

RDX and HMX concentrations in liquid samples were determined using high performance liquid chromatography (HPLC) according to EPA Method 8330 (USEPA, 1994), with slight modifications. Analytes were quantified with a Waters 2960 HPLC system with a photodiode array detector. The mobile phase consisted of 45% water and 55% methanol, which was filtered, degassed, and pumped isocratically at 0.9 mL/min. A Phenomenex Ultracarb C18 reversed-phase column was used for analyte separation. Under these conditions, HMX eluted at approximately 4.9 minutes and RDX at about 6.6 minutes. The detection limit for both HMX and RDX was 20 μg/L. HMX and RDX standards (Supelco) were obtained as 1,000 μg/mL solutions of each compound in acetonitrile.

3.4 Batch Tests

Each of the potential enhanced desorption methods were screened in batch experiments, similar to bottle point isotherm tests (Randtke and Snoeyink, 1983). For batch enhanced desorption experiments, 0.15 g of washed 200×325 mesh size Northwestern LB-830 GAC was loaded with RDX in 500 mL amber glass bottles. The initial RDX concentration was about 20.7 mg/L. After loading for one week, the GAC was separated from the solution by filtering through a 0.5-μm glass fiber filter (Gelman). The filter, with GAC, was placed in the bottle, and the bottle was filled with a solution for desorbing HEs from the GAC. HEs were desorbed for four days, after which the desorption fluid was replaced with a clean solution by a procedure identical to the filtering that was done after initial loading. Desorption continued for another seven days, for a total of eleven days of enhanced desorption. Liquid samples were taken and analyzed after loading and after each of the two desorption cycles to determine the distribution of RDX over the course of each experiment. All enhanced desorption solutions were tested in duplicate, with the exception of acetonitrile, which was tested in a single bottle.

3.5 Column Tests

Two or three of the most effective enhanced desorption experiments will be tested in column experiments similar to those that have been previously used to estimate the adsorptive characteristics of Pantex groundwater (Henke and Speitel, 1997). A known mass of 80x100 mesh LB-830 will be placed in a glass chromatography column and will be loaded with HEs. After equilibration (i.e., column effluent concentration is equal to column influent concentration), influent will be switched to clean desorption fluid. The mass of RDX that is desorbed by these enhanced methods will be determined by monitoring effluent concentrations over time. Results of enhanced desorption will be compared to desorption at baseline conditions (i.e., desorption using distilled water buffered at pH 7). After the GAC is regenerated, adsorption capacity may be tested to determine alterations in adsorption capacity of regenerated GAC.

4. RESULTS AND DISCUSSION

4.1 Batch Screening Tests

Different methods that were screened for enhancing desorption of RDX and HMX are discussed below. For comparison, water was used as the desorption fluid to represent the lower limit of HE desorption, and acetonitrile represents the upper limit of HE desorption. All results are the average of two bottles, with the exception of acetonitrile, which is the result of a single bottle.

4.2 Water

Distilled water, buffered at pH 7, desorbed only 3% of adsorbed RDX over a total of 11 days of desorption. As expected, water was the least effective solution for desorbing RDX of all the methods that were tested.

4.3 Acetonitrile

Acetonitrile, which is the solvent used in Method 8330 (USEPA, 1994) for extraction of HE compounds from soil, was very effective in desorbing HEs from GAC. Over 11 days, this solvent desorbed a total of 95% of sorbed RDX. This was the highest efficiency for all methods tested and is expected to be the upper limit of desorption efficiency. However, acetonitrile will not be used to desorb contaminants in a full-scale system due to toxicity and safety concerns.

4.4 Cosolvents

Ethanol and methanol were tested at five concentrations in solutions with water. At all concentrations, ethanol desorbed a higher percentage of adsorbed RDX than methanol. At 100% ethanol, the total RDX that was desorbed (92.6%) approached the desorption that was achieved by acetonitrile. The 100% methanol solution also performed well, desorbing 92% of the RDX over 11 days. At fairly low ethanol concentrations (5% ethanol with 95% water), more than 20% of the adsorbed RDX was desorbed over the 11 day desorption period. Results for ethanol and methanol are summarized in Table 2, and compared graphically in Figure 1. Results of desorption with buffered water are included for comparison.

Table 2: RDX Desorption for Cosolvents (Ethanol and Methanol)

Solvent	RDX desorption 4 days	RDX desorption 7 days	Total RDX Desorption
Water Alone (Baseline)	1.8%	1.2%	3.0%
5% Solvent/95% Water			
Ethanol	11.5%	8.8%	20. 3%
Methanol	3.9%	3.7%	7.6%
10% Solvent/90% Water			
Ethanol	19.8%	11.5%	31.3%
Methanol	7.7%	5.4%	13.1%
25% Solvent/75% Water			
Ethanol	46.2%	13.9%	60.1%
Methanol	22.3%	11.7%	34.0%
50% Solvent/50% Water			
Ethanol	76.5%	7.5%	84.0%
Methanol	59.1%	14.4%	73.5%
100% Solvent			
Ethanol	89.9%	2.7%	92.6%
Methanol	90.9%	1.1%	92.1%
Acetonitrile	93.8%	1.2%	95%

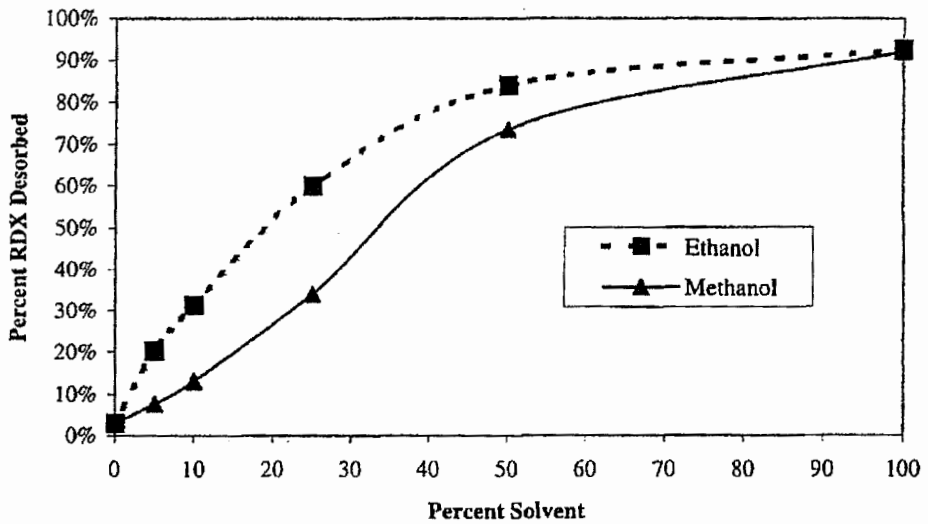

Figure 1: Percent RDX Desorption for Different Solvent Concentrations

4.5 Surfactants

One anionic and three nonionic surfactants were tested at three concentrations each. One concentration was below the CMC, while the other two were above the CMC. In Figure 2, results for the four surfactants are presented as percent RDX desorbed over 11 days, as a function of normalized surfactant concentration (the ratio of the actual surfactant concentration to its CMC. The CMC value that was used for this calculation was the average of published values as cited in Table 1). All data are tabulated in Table 3, which includes both the normalized and actual surfactant concentrations.

SDS, the anionic surfactant, was the most effective surfactant tested in these experiments. At concentrations above the CMC, SDS solutions desorbed nearly 70% of the adsorbed RDX. At a concentration of 500 mg SDS/L (about 20% of the CMC), about 56% of the adsorbed RDX was desorbed. Although SDS was highly effective in desorbing RDX, SDS may not be an appropriate choice for enhanced desorption because of the high concentrations required, which may cause significant surfactant adsorption and fouling of the GAC.

The three nonionic surfactants that were tested were also able to desorb a significant amount of RDX, but none performed as well as SDS. However, all of the nonionic surfactants have much lower CMC values than SDS; therefore, to achieve solubilization of RDX above the CMC, much less nonionic surfactant would be required. At sub-CMC concentrations, Brij 30 and Tween 80 performed poorly, desorbing less than 5% of adsorbed RDX (only slightly better than water). In contrast, Triton X-100 desorbed more than 35% of the RDX at a concentration of about 40% of its CMC. Above their respective CMCs, the nonionic surfactants desorbed significantly more RDX than below their CMCs. Tween 80 desorbed about 25% of the RDX at a concentration of just 50 mg/L (twice its CMC). At an even higher concentration (4.5 times the CMC), Tween 80 desorbed 44% of the RDX. Brij 30 desorbed more than 40% of the RDX at a concentration of 2.7 times its CMC.

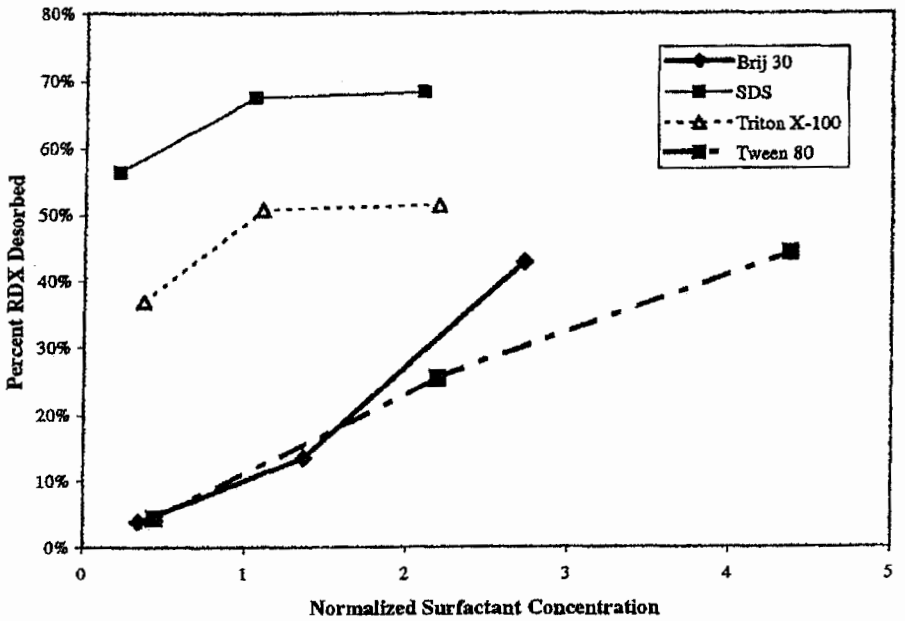

Figure 2: Enhanced Desorption of RDX by Surfactants

Table 3: RDX Desorption by Surfactants

Surfactant	Concentration (mg/L)	Normalized Concentration	4 Day RDX desorption	7 Day RDX desorption	Total RDX Desorption
Water Alone	--	--	1.8%	1.2%	3.0%
	500	0.21	42.4%	14.0%	56.4%
SDS	2500	1.05	51.5%	16.0%	67.5%
	5000	2.09	52.9%	15.4%	68.3%
	5	0.34	1.6%	2.3%	3.8%
Brij 30	20	1.36	5.0%	8.6%	13.5%
	40	2.72	11.8%	31.0%	42.9%
	50	0.36	11.2%	25.7%	36.9%
Triton X-100	150	1.09	34.9%	15.8%	50.8%
	300	2.19	37.2%	14.2%	51.3%
	10	0.44	1.7%	2.7%	4.4%
Tween 80	50	2.19	7.4%	18.1%	25.5%
	100	4.38	22.9%	21.3%	44.3%

Triton X-100 appeared to be the best performing nonionic surfactant. At a concentration of just 0.36 times its CMC, X-100 desorbed more then 35% of the RDX. At concentrations above the CMC, its performance appeared to be uniform. At a concentration of about 1.1 times the CMC, Triton X-100 was able to desorb about 50.8% of the RDX; at a concentration of 2.2 times the CMC, 51.3% of the RDX was desorbed.

Two of the surfactants will be tested further. The criteria for selection include effectiveness in desorbing RDX from GAC, the potential toxicity and biodegradability of the surfactant, and the adsorption of each surfactant to the GAC. To determine these

questions, additional research will be conducted to determine the adsorption and biodegradation characteristics of each of these surfactants. Two of the surfactants will be tested in continuous flow column studies. One of these will be SDS, which desorbed the greatest percent of RDX of the surfactants that were tested. One of the nonionic surfactants will be tested further based on adsorption and biodegradation testing.

4.6 Cyclodextrins

Two cyclodextrin (CD) compounds, β-CD and γ-CD, were tested for their ability to enhance desorption of HE compounds from GAC. Each CD was used in solution at three different concentrations; two of the concentrations were similar to provide a direct comparison between the two different CDs.

Neither of the cyclodextrins performed as well as the surfactants, although this may simply be a function of the CD concentrations that were tested. Water was able to desorb 3% of the RDX over 11 days. In comparison, β-CD at 1 g/L (0.1%) desorbed just 5.3% of the RDX, and β-CD at 10 g/L desorbed 8.1% of the RDX (1.8 and 2.7 times that of water, respectively). In studies with RDX-contaminated soil, Hawari, *et al.* (1996) found that a 0.1% w/v solution of hydroxypropyl-β-CD extracted 1.5 to 2.4 times the mass of RDX that was desorbed by water. γ-CD desorbed just 4.4% of the RDX at a concentration of 1 g/L and just 4.8% of the RDX. In both cases, increased CD concentrations appear to slightly increase the amount of RDX that was desorbed. Because of the poor performance of these cyclodextrins, and the high concentrations that would be required to achieve adequate desorption of HEs, use of cyclodextrins for enhanced desorption from GAC will not be explored further.

5. ADDITIONAL EXPERIMENTS AND EXPECTED RESULTS

Further testing must be completed to demonstrate the effectiveness of enhanced desorption methods. Several of the methods that were most effective in batch systems will be tested in continuous-flow columns. Results of these experiments will be compared to continuous flow desorption of RDX by buffered water. Eventually, existing computer models will be modified to accurately model the enhanced desorption process. This will require not only modification of existing adsorption models but a determination of relevant modeling parameters.

To complete biological regeneration of GAC and destroy the desorbed high explosives, effluent from enhanced desorption of RDX in continuous flow column tests must be treated in a separate bioreactor. Both RDX and HMX have been successfully biodegraded in sequencing batch reactors; however, the effects of different enhanced desorption methods (i.e., presence of surfactants or higher concentrations of ethanol) is currently unknown. Some of the methods that are expected to enhance desorption rates may also improve biodegradation rates.

6. CONCLUSIONS

Several methods for enhancing desorption of high explosives compounds were tested in batch reactors. Methods that were tested included four surfactants, two cosolvents, and two cyclodextrins. Over a total of 11 days of desorption, buffered water desorbed about 3% of the adsorbed RDX. In contrast, about 96% of the RDX was extracted from the GAC by acetonitrile over the same desorption period. Ethanol and methanol were both effective in desorbing RDX and HMX. These cosolvents desorbed more than 90% of RDX when used alone. At lower concentrations, ethanol was more effective than methanol. Surfactants varied widely in their abilities to enhance desorption of HEs. The most effective surfactant that was studied was sodium dodecyl sulfate (SDS), which desorbed 56.4% of the adsorbed RDX at a concentration of 500 mg SDS/L. Triton X-100, a nonionic surfactant, was also fairly effective, desorbing more than 50% of the RDX at concentrations above its CMC. The cyclodextrins that were used were marginally more effective than water, and thus will not be studied further.

Additional column tests using cosolvents and surfactants are underway. Ethanol, which desorbed 20% of adsorbed RDX in a 5% ethanol/95% water solution, will be tested further. SDS, an anionic surfactant that was the most effective of the four surfactants that were included in this research, will be tested further at sub-CMC concentrations to minimize surfactant adsorption to the GAC. In batch tests, SDS at about 20% of its CMC desorbed more RDX than any of the other surfactants. Additionally, one of the nonionic surfactants will be included in column experiments based on results of additional adsorption and biodegradation studies.

REFERENCES

1. Bhummasobhana, A., J.F. Scamehorn, S. Osuwan, J.H. Harwell, and S. Baramee. 1996. "Surfactant-Enhanced Carbon Regeneration in Liquid-Phase Application." *Separation Sci. And Tech.* 31(5):629-641.

2. Blakeburn, D.L., and J.F. Scamehorn. 1989. "Surfactant-Enhanced Carbon Regeneration" in *Surfactant-Based Separation Processes,* ed. by J.F. Scamehorn and J.H. Harwell. Surfactant Science Series Vol. 33. Marcel Dekker, New York.

3. Brusseau, M.L., R.M. Miller, Y. Zhang, X. Wang, and G.-Y. Bai. 1995. "Biosurfactant- and Cosolvent-Enhanced Remediation of Contaminated Media." *Surfactant-Enhanced Subsurface Remediation: Emerging Technologies,* ed. by D.A. Sabatini, R.C. Knox, and J.H. Harwell, pp. 82-94. ACS Symposium Series No. 594. American Chemical Society, Washington, DC.

4. Brusseau, M.L., A.L. Wood, and P.S.C. Rao. 1991. "Influence of Organic Cosolvents on the Sorption Kinetics of Hydrophobic Organic Chemicals." *EST* 25:903-910.

5. Cahill, S., and S. Bulusu. 1993. "Molecular Complexes of Explosives with Cycoldextrins. I. Characterization of Complexes with the Nitramines RDX, HMX, and TNAZ in Solution by ^{1}H NMR Spin-Lattice Relaxation Time Measurements." *Mag. Res. Chemistry* 31:731-735.

6. de Jonge, R.J., A.M. Breure, and J.G. van Andel. 1996a. "Bioregeneration of Powdered Activated Carbon (PAC) Loaded with Aromatic Compounds." *Water Research* 30(4):875-882.

7. de Jonge, R.J., A.M. Breure, and J.G. van Andel. 1996b. "Reversibility of Adsorption of Aromatic Compounds onto Powdered Activated Carbon (PAC)." *Water Research* 30(4):883-892.

8. Deshpande, S., B.J. Shiau, D. Wade, D.A. Sabatini, and J.H. Harwell. 1999. "Surfactant Selection for Enhancing *Ex Situ* Soil Washing." *Water Research* 33(2):351-360.

9. Goeddertz, J.G., M.R. Matsumoto, and A.S. Weber. 1988. "Offline Bioregeneration of Granular Activated Carbon." *J. Env. Eng.* 114(5):1063-1076.

10. Hawari, J., L. Paquet, E. Zhou, A. Halasz, and B. Zilber. 1996. "Enhanced Recovery of the Explosive Hexahydro-1,3,5-Trinitro-1,3,5-Triazine (RDX) from Soil: Cyclodextrin Versus Anionic Surfactants." *Chemosphere* 32(10):1929-1936.

11. Henke, J.L. and G.E. Speitel Jr. 1997. "Performance Evaluation of Granular Activated Carbon System at Pantex: Rapid Small Scale Column Tests to Simulate Removal of High Explosives from Contaminated Groundwater." Amarillo National Resource Center for Plutonium, Report ANRCP-ENV-TWD-97-16.

12. Hutchinson, D.W. and C.W. Robinson. 1990a. "A Microbial Regeneration Process for Granular Activated Carbon – I. Process Modeling." *Water Research* 24(10):1209-1215.

13. Hutchinson, D.W. and C.W. Robinson. 1990b. "A Microbial Regeneration

Process for Granular Activated Carbon – II. Regeneration Studies." *Water Research* 24(10):1217-1223.

14. Jafvert, C.T. 1996. *Surfactants/Cosolvents.* Technology Evaluation Report TE-96-02, Ground-Water Remediation Technologies Analysis Center, Pittsburgh, PA.

15. Kile, D.E., and C.T. Chiou. 1989. "Water Solubility Enhancements of DDT and Trichlorobenzene by Some Surfactants Below and Above the Critical Micelle Concentration." *EST* 23(7):832-838.

16. Liu, J.C., and P.S. Chang. 1997. "Solubility and Adsorption Behaviors of Chlorophenols in the Presence of Surfactant." *Wat. Sci. Tech.* 35(7):123-130.

17. Murai, S., S. Imajo, Y. Takasu, K. Takahashi, and K. Hattori. 1998. "Removal of Phthalic Acid Esters from Aqueous Solution by Inclusion and Adsorption on β-Cyclodextrin." *Env. Sci. Tech.* 32:782-787.

18. Myers, D. 1988. *Surfactant Science and Technology.* VCH Publishers, New York.

19. Orshansky, F., and N. Narkis. 1997. "Characteristics of Organics Removal by PACT Simultaneous Adsorption and Biodegradation." *Water Research* 31(3):391-398.

20. Park, J.-S., Y.J. Kim, and I.S. Kim. 1998. "Modeling the Effect of Nonionic Surfactants on the Biodegradation of Polycyclic Aromatic Hydrocarbon in Soil Slurry Using the Respirometric Technique. – 1. Physicochemical Effect." *First Intl. Conf. on Remediation of Chlorinated and Recalcitrant Compounds*, ed. by G.B. Wickramanayake and R.E. Hinchee. C1-4: 39-43.

21. Randtke, S.J., and Snoeyink, V.L. 1983. "Evaluating GAC adsorptive capacity." *J. Am. Water Works Assn.* 75:406-413.

22. Roberts, B.L., J.F. Scamehorn, and J.H. Harwell. 1989. "Use of Surfactant-Enhanced Carbon Regeneration to Remove Volatile Organics from Spent Activated Carbon" in *New Directions in Sorption Technology*, ed. by G.E. Keller II and R.T. Yang. Butterworths, Boston, MA.

23. Shiau, B.-J., J.D. Rouse, D.A. Sabatini, and J.H. Harwell. 1995. "Surfactant Selection for Optimizing Surfactant-Enhanced Subsurface Remediation." *Surfactant-Enhanced Subsurface Remediation: Emerging Technologies*, ed. by D.A. Sabatini, R.C. Knox, and J.H. Harwell, pp. 65-79. ACS Symposium Series No. 594. American Chemical Society, Washington, DC.

24. Sontheimer, H., Crittenden, J.C., and Summers, R.S. 1988. *Activated Carbon for Water Treatment.* Second edition, in English. DVGW-Forschungsstelle, Karlsruhe, Germany.

25. Speitel, G.E. Jr., C.-J. Lu, M. Turakhia, and X.-J. Zhu. 1989. "Biodegradation of Trace Concentrations of Substituted Phenols in Granular Activated Carbon Columns." *Env. Sci. Tech.* 23(1):68-74.

26. Szejtli, J. 1982. *Cyclodextrins and Their Inclusion Complexes.* Akadémiai Kiadó, Budapest, Hungary.

27. Thacker, W.E., V.L. Snoeyink, and J.C. Crittenden. 1983. "Desorption of

Compounds during Operation of GAC Adsorption Systems." *J. Am. Water Works Assn.* 75(3):144-149.

28. USAMC. 1971. *Engineering Design Handbook – Explosives Series. Properties of Explosives of Military Interest.* U.S. Army Material Command, AMCP 706-177.

29. USEPA. 1994. "Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)." SW-846, Method 8330. Revision 4, September 1994.

30. Van Os, N.M., J.R. Haak, and L.A.M. Rupert. 1993. *Physico-chemical Properties of Selected Anionic, Cationic, and Nonionic Surfactants.* Elsevier Science Publishers, New York.

31. Wang, X., and M.L. Brusseau. 1993. "Solubilization of Some Low-Polarity Organic Compounds by Hydroxypropyl-β-cyclodextrin." *Env. Sci. Tech.* 27:2821-2825.

32. Wilkie, J.A. 1994. *Biological Degradation of RDX.* Master of Science Thesis, Civil Engineering, University of California at Los Angeles.

33. Wujcik, W.J., W.L. Lowe, P.J. Marks, and W.E. Sisk. 1992. "Granular Activated Carbon Pilot Treatment Studies for Explosives Removal from Contaminated Groundwater." *Env. Progress* 11(3):178-189.

34. Yeh, D.H., K.D. Pennell, and S.G. Pavlostathis. 1998. "Toxicity and Biodegradability Screening of Nonionic Surfactants using Sediment-Derived Methanogenic Consortia." *Wat. Sci. Tech.* 38(7):55-62.