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Anaerobic treatment of pinkwater in a fluidized bed reactor containing GAC

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Abstract

Pinkwater is generated during the handling and demilitarization of conventional explosives. This listed hazardous waste contains dissolved trinitrotoluene (TNT) and cyclo trimethylene trinitramine (RDX), as well as some by-products. It represents the largest quantity of hazardous waste generated by the operations support command, and its treatment produces a by-product hazardous waste—spent granular activated carbon (GAC).

Anaerobic treatment in a fluidized bed reactor (FBR) containing GAC is an emerging technology for organic compounds resistant to aerobic biological treatment. Bench scale batch studies using an anaerobic consortium of bacteria fed ethanol as the sole electron donor demonstrated the transformation of TNT to triaminotoluene (TAT), which then degrades to undetectable end products. RDX is sequentially degraded to nitroso-, dinitroso-, trinitroso- and hydroxylaminodinitroso-RDX before the triazine ring is presumably cleaved, forming methanol and formaldehyde as major end products. The bacterial members of the anaerobic consortia are typically found in sludge digesters at municipal or industrial wastewater treatment plants.

The results of a pilot scale evaluation of this process that was conducted at McAlester Army Ammunition Plant (MCAAP, OK) over a 1 year period are reported in this paper. The pilot test experienced wide fluctuations in influent concentrations, representative of true field conditions. The FBR was a 20 in. (51 cm) diameter column with an overall height of 15 ft (4.9 m) and a bed of GAC occupying 11 ft (3.4 m). Water was recirculated through the column continuously at 30 gpm (114 l/min) to keep the GAC fluidized, and pinkwater for treatment was pumped into the recirculation line. Several flowrates were evaluated to determine the proper mass loading rate (mass of TNT and RDX per reactor volume per time, kg/m^3 per day) which the reactor could handle while meeting the discharge limitations. Based on the tests performed, a 1 gpm (3.785 l/min) rate in the 188 gal (710 l) volume of the fluidized GAC bed was determined to consistently meet the discharge requirements.

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This information was used to develop a cost estimate for a system capable of treating the total effluent currently produced at MCAAP. The cost of installing and operating this system was compared to the cost of GAC adsorption for MCAAP at current pinkwater generation rates. The GAC–FBR system had an annual operating cost of approximately US$ 19K, compared to US$ 71K annually for GAC adsorption. When including the amortization of the capital equipment required for the GAC–FBR, the payback period for installation of this new process was estimated at 3.7 years.

Keywords: Pinkwater; TNT; Fluidized bed reactor; Anaerobic wastewater treatment; Munitions wastewater

1. Introduction

Production and handling of high explosives produces wastewater which is contaminated with the explosives and their by-products. One such wastewater is referred to as pinkwater, due to its characteristic color. Pinkwater is primarily contaminated with trinitrotoluene (TNT) and cyclo trimethylene trinitramine (RDX). The explosive compounds enter the wastewater stream during load, assemble and pack (LAP) operations, and from the deactivation of old munitions. LAP operations generate wastewater from cleanup and washdown operations. The deactivation, often called demilitarization, is accomplished by washing out or steaming out the explosives from bombs and shells. Pinkwater is generated directly from the water used to remove the high explosives, as well as the final washdown and cleanup of the facilities.

The past practice was to let the pinkwater flow into lagoons, from which the water evaporated or seeped into the groundwater. This has resulted in contamination of groundwater at military installations, most notably the industrial production facilities. The current practice is to remove the contaminants using a combination of filtration and granular activated carbon (GAC) adsorption before discharging the wastewater to lagoons or wastewater treatment plants. This has been a safe and effective method, but it is expensive, and generates a secondary hazardous waste in the spent activated carbon.

Use of GAC in fluidized bed reactors (GAC–FBR) is an emerging technology for difficult-to-degrade organics, operated under anaerobic conditions. The GAC provides a temporary storage place, through adsorption [9], for occasions when the contaminant concentration is in excess of the bacterial capacity to transform. The contaminant then desorbs when concentrations decrease, maintaining the feed of the contaminant to the bacteria. FBR for water treatment have most often been operated aerobically [15], so existing available equipment had to be modified for the pilot scale demonstration. GAC–FBRs have also been used for treatment of coal gasification wastewaters and chlorinated solvents at the laboratory scale [5,10,11].

Initial studies of the GAC–FBR were focused on the treatment of dinitrotoluene (DNT) in propellant wastewater. A bench scale study in a university laboratory, using synthetic wastewater [4], was undertaken to evaluate this technology for use in the field. The results indicated that DNT is effectively transformed anaerobically, based on the absence of DNT in the effluent, chemical oxygen demand (COD) balances and gas production in the column. Based on the success of using a two-step (anaerobic–aerobic) process [4], a field demonstration of commercially available components followed by an aerobic pilot scale rotating biological contactor (RBC) was conducted [8]. The results of these studies showed that DNT could be cost effectively biodegraded in the two-step process.

The GAC–FBR has also been evaluated in the laboratory environment for TNT degradation. A small scale system demonstrated that TNT could also be degraded [13,14]. The system was operated with ethanol as the electron donor and at constant influent concentrations. Unlike the DNT studies cited above, the anaerobic transformation did not yield a stable reduced analog of TNT. The expected analog would be triaminotoluene (TAT), but it was not detected in the effluent of the GAC–FBR. Thus, a mass balance was used to determine the fate of the nitrogen originally associated with the TNT. Based on the mass balance, between 80 and 90% of the nitrogen originally incorporated in the TNT was recovered as nitrate and biomass in the effluent from the aerobic system [13].

Further bench scale studies of TNT and RDX degradation have been conducted at the laboratory scale using anaerobic bacteria in the absence of GAC. These studies have been conducted in shaken flasks or in fluidized beds using sand as the microbial support media. Hwang et al. [7] demonstrated that TNT could be stoichiometrically converted to the partially reduced analogs in shaken flasks under anaerobic conditions, with stepwise progression to the fully reduced compound, TAT. Following complete conversion, the TAT also degraded to unknown products while still under anaerobic conditions. RDX has also been shown to degrade under anaerobic conditions [1–3]. RDX is sequentially degraded to nitroso-, dinitroso-, trinitroso- and hydroxylaminodinitroso-RDX before the triazine ring is presumably cleaved, forming methanol and formaldehyde as major end products.

Based on the results obtained at the bench scale, a pilot test of anaerobic biodegradation of pinkwater was undertaken at McAlester Army Ammunition Plant (MCAAP). MCAAP generates pinkwater from demilitarization of out-of-date munitions. The high explosives are removed by melting them out of the shells and onto a conveyor belt. Pinkwater results from the handling and cleanup operations and contains varying quantities of TNT and RDX. Solids are removed from the pinkwater by coagulation, flocculation, settling and pressure filtration. The resulting wastewater is currently treated using GAC adsorption. The pilot demonstration was conducted on a slipstream of the wastewater, taken after pressure filtration.

This paper reports on a field operating system that was evaluated based on its ability to meet the compliance requirements placed on MCAAP. Most chemical and toxicological analyses were conducted using state of OK sanctioned procedures for compliance with the criteria of the national pollution discharge elimination system (NPDES) permit. Detailed descriptions of the chemical analytical techniques have not been included. The analysis for TNT and RDX were conducted by MCAAP personnel, using a modification of EPA method 8330 [12]. Toxicological testing was performed commercially by Huther and Associates (Carrollton, TX). TAT is not covered by NPDES permits, so there is no current standard method for it. TAT was analyzed in the author's laboratory using the method described in [7].

2. Process description

The pilot GAC–FBR consists of a fluidized bed of activated carbon granules in a cylindrical reactor. The FBR is a 20 in. (51 cm) diameter column with an overall height of 15 ft

Table 1
Trace nutrients and minerals

Component	Source
Magnesium	$MgCO_3 \cdot 6H_2O$
Manganese	$MnSO_4$
Potassium	KCl
Calcium	$CaCl_2 \cdot 2H_2O$
Iron	$FeCl_3 \cdot 6H_2O$
Cobalt	$CoCl_2 \cdot 6H_2O$
Nickel	$NiCl_2 \cdot 6H_2O$
Boron	H_3BO_3
Copper	$CuCl_2$
Molybdenum	$NaMoO_4 \cdot 2H_2O$
Sulfur	$MnSO_4$

(4.9 m) and a bed of GAC occupying 1 ft (3.4 m). Water is recirculated through the column continuously at 30 gpm (114 l/min) to keep the GAC fluidized, and pinkwater for treatment was pumped into the recirculation line. Nutrients and co-substrate (electron donor) are also fed into the recirculation line. The nutrient solution consists of nitrogen, phosphorus and several trace nutrients and minerals. The trace nutrients and minerals are listed in Table 1. The nutrient solutions are fed from two reservoirs, with the bulk of the materials in one reservoir and the calcium and manganese salts in a second reservoir. Separation into the two reservoirs was necessary to avoid precipitation of compounds that formed when all nutrients were mixed together.

In addition to the nutrients and co-substrate, sodium hydroxide was injected into the feed solution as needed to control the pH. The pH was controlled using a probe in the recirculation line connected to a programmable logic controller (PLC). The system was designed to operate with a pH set point of 6.8–7, and when the pH in the reactor dropped below that range, a solution of sodium hydroxide (20%) was injected into the system until the pH reached the top of the range. Controlling pH is critical to maintaining favorable conditions for the anaerobic bacteria and has presented a problem in small scale reactors used at laboratory scale. The use of the automated control system has eliminated this as a problem in pilot and full scale systems.

The influent water was heated prior to injection in the recirculation line. The system was designed to be operated at 90 °F, to provide favorable conditions for the anaerobic bacteria. The recirculation pumps also add heat to the system. Maintaining the temperature proved to be difficult during parts of this year long study, as the temperature of the influent water varied greatly over the full year and the heater had not been designed to accommodate the maximum heat input needed during one period. This contributed to less than optimal results during this portion of the test, as described further.

The GAC–FBR process has two removal mechanisms that are operative. Biological degradation is the principal mechanism of contaminant removal. The GAC acts primarily as a support media for the attachment and growth of bacteria that from biofilms. However, the adsorptive capacity of the GAC provides a second benefit in that it can cut-off peaks of

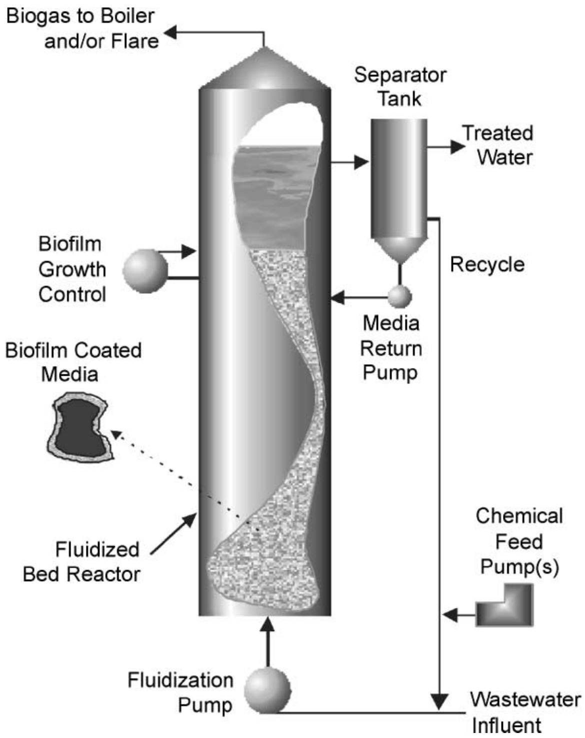

Fig. 1. Conceptual drawing of anaerobic granular activated carbon—fluidized bed reactor.

influent concentration through adsorption, and later desorb the contaminants when the bacteria have reduced the aqueous phase concentration. This allows the bacteria to work at a relatively steady state mass removal, and the GAC functions to buffer the aqueous phase concentration. This is particularly important in industrial operations, because the influent concentrations tend to vary widely.

The adsorptive capacity of the GAC is very large compared to the influent variations. As a result, bench scale studies have not shown any build-up of munitions on the activated carbon. In one case [8], a stable by-product (diaminotoluene) did build up on the GAC surface and could be recovered by desorption in acetonitrile, however, similar studies were unable to recover TNT and RDX from the carbon surface. As a result, there is no direct information on what the upper limit for the GACs capacity to buffer influent concentrations, only that it has not been reached in any studies to date. The one exception, described below, occurred when the temperature declined to 67 °F.

As the bacteria develop into a biofilm on the GAC, the net density of the biofilm coated GAC decreases. The particles with the greatest biofilm buildup migrate to the top of the fluidized bed. Fig. 1 shows a conceptual drawing of the GAC–FBR. A biofilm growth control is used to gently shear the excess biomass off of the GAC particles at the top of the bed. The particle then becomes more dense and migrates back lower into the bed. This is shown on the left side of Fig. 1. If the control fails to capture all of the particles, they then pass out into the separator tank, where they settle out. This provides a second opportunity to gently shear the biofilm off of the particle, and the GAC and residual attached biofilm are sent back to the column by a media control pump, shown on the right side of Fig. 1.

Gas produced as a by-product of anaerobic degradation is collected at the top of the column, and sent to a flare to burn off the methane. It can also be vented to the atmosphere. For work inside an Army Ammunition Plant, venting is the preferred method because of a prohibition on open flames.

3. Results and discussion

The GAC–FBR was operated for 1 year from June 1998 to May 1999. Start-up activities for the GAC–FBR include washout of fines associated with the virgin GAC, and inoculation of the reactor with anaerobic bacteria. The carbon washout is conducted until the effluent appears clear of fines to the human eye. Inoculation is accomplished using anaerobic sludge from a local wastewater treatment plant. No specialized bacteria are used in the inoculum as the ability of anaerobic bacteria to reduce nitro substituent groups is widespread in nature [6], and during the course of development of this process for munitions wastewaters, anaerobic sludge has been used from Radford, VA [8], Urbana, IL [7], and McAlester (current study), all with similar results. After inoculation, the system is operated without influent for 2 weeks, to build up the population of microorganisms in the GAC–FBR, by adding co-substrate and nutrients while the system is in recycle mode (i.e. no effluent).

Several flowrates were evaluated to determine the proper mass loading rate (mass of TNT and RDX per reactor volume per time, kg/m^3 per day) which the reactor could handle while meeting the discharge limitations. The approach taken during the demonstration was to acclimate the GAC–FBR to a certain flowrate, and then run a 2-week period of “campaign testing”, during which sampling intensified. In the acclimation periods in between, less data was collected, but influent and effluent analyses for TNT and RDX were always performed. Table 2 is a summary of conditions tested during the six campaign periods used throughout the year.

MCAAP currently discharges their GAC treated pinkwater to a wastewater treatment plant, and has a 1 mg/l discharge limit for their current treatment process. Campaign test

Table 2
Summary of campaign testing conditions[a]

Period	Days	Flow (gpm)	Temperature (°F)	HRT (min)	TNT influent (mg/l)	TNT effluent (mg/l)	TNT LR (kg/m^3 per day)	COD/TNT (mg/mg)
1	1–44	0.5	106.5	375	31.7	<0.03	0.12	42
2	45–87	1.0	90	188	43.4	<0.03	0.31	26.3
3	87–127	1.5	90	125	29.2	<0.03	0.34	27.8
4	127–177	1.0	67	188	56.2	2.8	0.43	24.4
5	249–289	1.0	90	188	15.1	0.6	0.12	8.6
6	290–353	1.0	90	188	3.5	<0.03	0.03	283

[a] gpm: gallons per minute; HRT: hydraulic residence time in minutes; TNT LR: TNT loading rate; kg/m^3 per day: kg of TNT applied per volume of reactor per day.

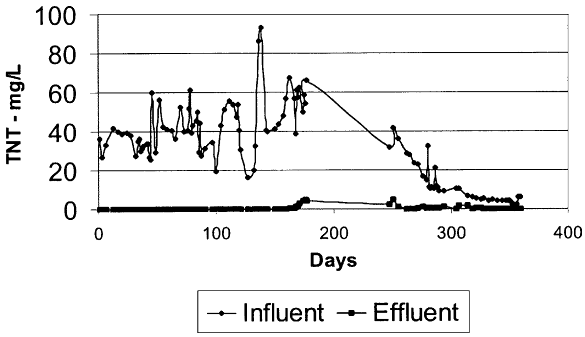

Fig. 2. Influent and effluent TNT concentrations.

4 was the only period when effluent from the system exceeded the pretreatment discharge level of 1 mg/l. This effluent was recycled back through the system for further treatment. During campaign test 4, problems were experienced with maintaining the temperature, and the overall reactor temperature dropped to 67 °F. At the same time, the TNT concentration increased sharply, from 29.2 to 56.2 mg/l. This lower temperature significantly affected the anaerobic biomass, and the TNT began to break through the treatment process. During this period, the buffer provided by the GAC became exhausted.

The influent and effluent profiles for TNT and RDX are shown in Figs. 2 and 3, respectively. These figures show the wide variability in contaminant concentration encountered in an industrial setting. There is also a long break between mid-November and mid-January corresponding to days 180–250 on the figures. This break occurred due to a number of factors, including a holiday shutdown period for MCAAP, renovations at the pressure filter plant and replacement of the heater used for the influent water on the GAC–FBR. Campaign test 4 ended in mid-November, and campaign test 5 started in late January. During this period of time, the GAC–FBR was shut down completely. This provided a test of the ability of the system to recover after periods of inactivity.

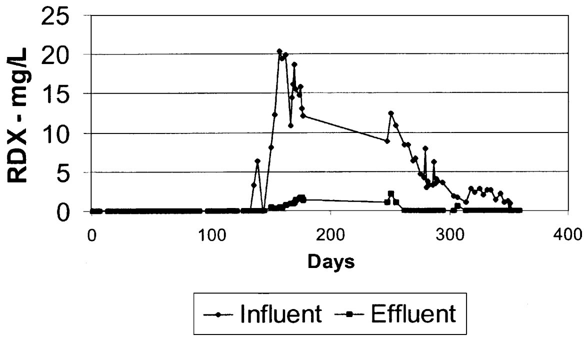

Fig. 3. Influent and effluent RDX concentrations.

The system was restarted with a new heater after 60 days of inactivity, and recovered very smoothly. Although, the influent TNT concentration had decreased dramatically (from 56.2 to 15.1 mg/l), it was still well above the breakthrough effluent concentration observed in the middle of November (2.8 mg/l). If the GAC were exhausted and the biomass was ineffective, the effluent TNT concentration should have continued to rise even when the influent concentration declined. The effluent concentration of TNT declined, indicating the bacteria were able to degrade the influent TNT as well as degrade the TNT adsorbed on the carbon once the temperature was increased. If the biomass had not, the TNT concentration should rise and possibly even exceed the influent concentration, as adsorptive equilibrium is re-established at a lower aqueous phase concentration and the TNT on the carbon surface desorbs.

At the end of the planned six campaign periods, a series of short tests were conducted to attempt to overload the system and force breakthrough of TNT while the temperature was maintained at 90 °F. The previous breakthrough had occurred during low temperature operation of the system. Due to the very low influent concentrations at that time, the flow rate had to be increased significantly to increase the TNT loading rate on the GAC–FBR. Table 3 shows the results of the high flow rate tests.

These tests were of short duration. Test period A lasted for 72 h and tests B and C lasted for 24 h each. The results indicate that the GAC–FBR maintained its capacity to handle peaks in mass loading. If the carbon's surface was exhausted for removal of TNT, the contaminant should have broken through the GAC–FBR. The lack of breakthrough indicates that the bioactivity had maintained the GAC capacity.

Toxicity tests were also conducted on the effluent from the GAC–FBR. Four tests were conducted on 13 effluent samples. The four tests were *Pimephales promales* survival, *Pimephales promales* reproduction, *Ceriodaphnia dubia* survival and *Ceriodaphnia dubia* reproduction, using EPA methods 1002 and 1000. Tests were performed at 91, 68, 51, 38 and 29% effluent, where 91% refers to 91% effluent mixed with 9% control water. All tests indicated a no observable effect concentration (NOEC) of 91% effluent. The Oklahoma Department of Environmental Quality requires effluent exhibit a NOEC at 68% effluent for discharge, thus all tests would have been suitable for discharge.

Transformation by-products were analyzed on a regular basis, except for TAT. Method 8330 [12] used for TNT and RDX will not detect TAT. A separate method [7] was used for TAT. In general, samples tested by 8330 did not show any transformation products. However, when the GAC–FBR was not functioning properly in terms of temperature control (period 4), and TNT was breaking through the reactor, samples were taken from the column effluent, and from the effluent storage tank. Effluent holding tanks had been included in this

Table 3
High flow rate test data

Period	Flow (gpm)	HRT (min)	TNT influent (mg/l)	TNT effluent (mg/l)	TNT LR (kg/m^3 per day)	COD/TNT (mg/mg)
A	2	94	6.15	<0.03	0.1	83.1
B	5	37.5	5.87	<0.03	0.22	35.4
C	10	18.8	6.52	<0.03	0.51	15.6

Table 4
Transformation product analysis[a]

Compound	TNT	2A46DNT	4A26DNT	24DA6NT	26DA4NT	TAT
Influent (mg/l)	50	NA	NA	NA	NA	NA
Column effluent (mg/l)	1.3	0.3	0.8	1.1	0.3	Trace
Tank effluent (mg/l)	ND	ND	ND	ND	0.3	2.6

[a] 2A46DNT: 2-amino-4,6-dinitrotoluene; 4A26DNT: 4-amino-2,6-dinitrotoluene; 24DA6NT: 2,4-diamino-6-nitrotoluene; 26DA4NT: 2,6-diamino-4-nitrotoluene; NA: not analyzed; ND: not detected.

study so that all samples could be analyzed prior to discharge to the aerobic wastewater treatment plant. This 5000 gal tank provided a hydraulic retention time varying from 2.3 (at 1.5 gpm) to 7 days (at 0.5 gpm), but was usually emptied before full.

Table 4 shows the transformation products found in the column effluent and the holding tank effluent, while TNT was breaking through the GAC–FBR. The data show that transformation products can be found when TNT breaks through the GAC–FBR, but that the transformation continued in the effluent holding tank. This behavior was observed previously in laboratory tests, in which the sequential transformation products were identified in the absence of GAC [7]. The emergence of these by-products in the pilot system when the temperature dropped, underscores the importance of maintaining temperature in the GAC–FBR.

For the purposes of this pilot study, all effluent was initially collected in a holding tank. This water would then be tested prior to discharge to the existing wastewater treatment plant. Using this method, no effluent was discharged until it was certain that the requirements of the existing NPDES permit were met. This resulted in additional time for biotransformation of the contaminants in the munitions wastewater. Table 4 shows those results, where partially transformed compounds are found in the column effluent, but not in the holding tank effluent (shown as “tank effluent”).

Based on the tests performed, a 1 gpm (3.785 l/min) rate in the 188 gal (710 l) volume of the fluidized GAC bed was determined to consistently meet the discharge requirements. The primary design parameter, TNT loading rate, was set at approximately 0.33 kg/m^3 per day, based on campaign test periods 2 and 3. A 50% safety factor was applied to this value reducing the design applied loading rate to 0.22 kg/m^3 per day. For design purposes a system sized at this loading rate was then used to develop a cost comparison between the GAC–FBR and the existing GAC adsorption treatment.

4. Cost comparison

A cost estimate was developed to compare the existing treatment process, adsorption on GAC, to biological treatment using the anaerobic GAC–FBR. For the purposes of the cost comparison, only purchase and disposal costs associated with GAC are included. This represents the operational cost of GAC, but none of the capital costs. Capital costs for the GAC system were omitted because the system is already in place. Costs for the anaerobic GAC–FBR included both amortized capital costs and operational costs.

Table 5
Operational costs for the anaerobic GAC–FBR

Item	Annual Cost (US$)
Ethanol (US$ 4.18 per gal)	11000
Temperature control	2400
Nutrients	600
pH control	1690
Power	3400
Total	19090

The baseline cost for GAC adsorption was estimated from the average quantity of GAC used during the 4 years leading up to 1999. The average quantity was then multiplied by the 1999 purchase and disposal cost. This resulted in a baseline annual cost for the existing system of US$ 71,000 per year.

The cost for the anaerobic GAC–FBR was developed using the average flowrate of pinkwater, its average concentration, and the design loading rate of 0.22 kg/m^3 per day. The design flow rate for MCAAP was 7.5 gpm, which results in a reactor size of 4.5 ft in diameter, with an overall height of 22 ft. The operational costs are shown in Table 5.

This cost estimate is based on prices encountered during the pilot demonstration. The largest cost is for ethanol, and the locally available source at MCAAP for ethanol was much higher than elsewhere, when purchasing fuel grade ethanol. The local cost of US$ 4.18 per gal may be reduced by as much as 75% if fuel grade ethanol can be purchased in bulk, lowering the overall operational costs for the GAC–FBR.

The total estimated operating costs are approximately US$ 19,090 per year. No estimate has been made for manpower costs, because the operation of the existing plant requires approximately the same level of effort as the GAC–FBR, and the sampling and analysis efforts would be the same for either system. The capital cost for the GAC–FBR was estimated to be US$ 195,000. The amortized capital cost (6%, 20 years) for the GAC–FBR is US$ 17,000 per year. Thus, the total yearly cost for the GAC–FBR is approximately US$ 36,090, or approximately half of the current cost of the GAC adsorption system.

5. Summary

A pilot scale anaerobic FBR containing GAC (GAC–FBR) as a microbial support media was tested at MCAAP. The results show that TNT and RDX can be effectively treated by anaerobic bacteria under field operating conditions, where the contaminant concentration varied widely. The test also shows the importance of temperature control to maintaining the activity of the biomass. When the reactor temperature dropped from its set point at 90–67 °F, the GAC–FBR was unable to meet the discharge criteria. However, when the temperature control brought the reactor back to 90 °F, the system recovered fully.

A cost comparison was made between the GAC–FBR and the existing granular activated carbon treatment system, using the design loading rate determined in this pilot demonstration. The GAC–FBR is estimated to cost about half as much as the existing system on a yearly basis, including the amortized capital costs for the new equipment. In addition to the cost savings, the GAC–FBR has the added advantage of eliminating the generation of hazardous waste. The current system generates spent granular activated carbon as a by-product hazardous waste, whereas there is no by-product hazardous waste in the GAC–FBR.

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