Fenton-driven chemical regeneration of MTBE-spent granular activated carbon – A pilot study

Scott G. Huling [a,*], Eunsung Kan [b,1], Caleb Caldwell [c,2], Saehan Park [c,3]

[a] U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, P.O. Box 1198, Ada OK, 74820, United States
[b] National Research Council, Robert S. Kerr Environmental Research Center, Ada OK, 74820, United States
[c] College of Health and Sciences, East Central University, 1100 E. 14th, Ada OK, 74820, United States

ABSTRACT

Three columns containing granular activated carbon (GAC) were placed on-line at a ground water pump and treat facility, saturated with methyl tert-butyl ether (MTBE), and regenerated with hydrogen peroxide (H_2O_2) under different chemical, physical, and operational conditions for 3 adsorption/oxidation cycles. Supplemental iron was immobilized in the GAC (≈ 6 g/kg) through the amendment of a ferrous iron solution. GAC regeneration occurred under ambient thermal conditions (21–27 °C), or enhanced thermal conditions (50 °C). Semi-continuous H_2O_2 loading resulted in saw tooth-like H_2O_2 concentrations, whereas continuous H_2O_2 loading resulted in sustained H_2O_2 levels and was more time efficient. Significant removal of MTBE was measured in all three columns using $(USD) 0.6 H_2O_2/lb GAC. Elevated temperature played a significant role in oxidative treatment, given the lower MTBE removal at ambient temperature (62–80%) relative to MTBE removal measured under thermally enhanced (78–95%), and thermally enhanced, acid pre-treated (92–97%) conditions. Greater MTBE removal was attributed to increased intraparticle MTBE desorption and diffusion and higher aqueous MTBE concentrations. No loss in the MTBE sorption capacity of the GAC was measured, and the reaction byproducts, tert-butyl alcohol and acetone were also degraded.

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1. Introduction

1.1. Process description and optimization

Extensive laboratory studies have demonstrated that Fenton-driven oxidative treatment of granular activated carbon (GAC) can effectively transform organic contaminants concentrated and immobilized on the GAC, and restore the sorptive capacity of the GAC for subsequent use [1–4]. Parameters that influence oxidative treatments have been investigated in detail, and optimized, including the effects of Fe and H_2O_2 concentrations [5], temperature [6], GAC particle size [7], and iron type amended to GAC [8].

1.1.1. Fenton-driven regeneration of GAC

MTBE oxidation and GAC regeneration is achieved by amending H_2O_2 to the Fe-amended, MTBE-spent GAC. The reaction between H_2O_2 and Fe in the GAC forms hydroxyl radicals (•OH) that oxidize MTBE. The reaction rate constant between •OH and MTBE is high (1.6×10^9 L mol^{-1} s^{-1}) [9,10], indicating the vulnerability of MTBE to radical attack in Fenton systems. Tertiary butanol (TBA) and acetone, the primary reaction byproducts from MTBE oxidation [4,11], are oxidized forming a variety of carboxylic acids which also undergo oxidation. Formation of the highly reactive, non-selective •OH in proximity to high concentrations of target organics near carbon surfaces favors high transformation efficiency and enhances reaction kinetics relative to Fenton-driven oxidation in dilute aqueous systems [4].

1.1.2. GAC particle size and thermal effects

A reaction zone exists within the GAC particle where H_2O_2, Fe catalyst, and the target contaminant co-exist in sufficient concentrations for oxidative transformation and GAC regeneration to occur (Fig. 1). Development of the reaction zone during oxidative treatment relies on the successful penetration of Fe into the GAC during amendment, the diffusion of H_2O_2 into the GAC, and the intraparticle desorption and diffusion of contaminants from the

* Corresponding author. Tel.: +1 580 436 8610; fax: +1 580 436 8615.
   E-mail addresses: huling.scott@epa.gov (S.G. Huling), eunsungkan@gmail.com (E. Kan), ccaldwe3@ouhsc.edu (C. Caldwell), saebal00@hotmail.com (S. Park).
1 Current address: Center for Biofilm Engineering, Montana State University, Bozeman, MT 59715, United States. Tel.: +1 406 579 3370.
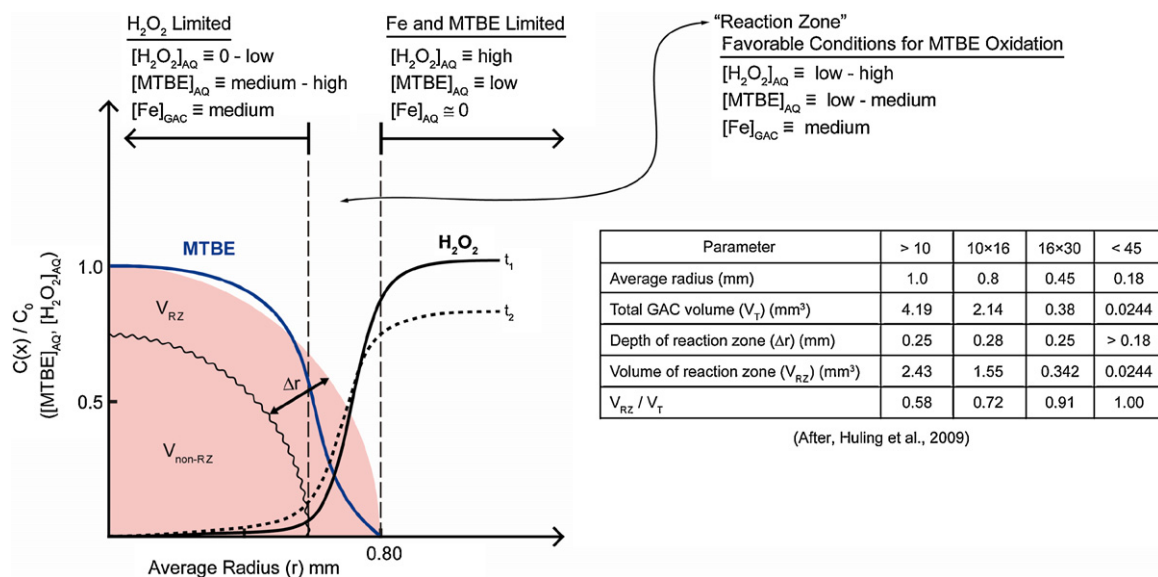2 Tel.: +1 580 272 3370.
3 Tel.: +1 520 409 4096.

Fig. 1. Conceptual model of the volume of the reaction zone within GAC particles of different sieve sizes (>10, 10×16, 16×30, <45) where H_2O_2, iron, and the target contaminant (i.e., MTBE) co-exist.

GAC. Due to rapid H_2O_2 reaction, H_2O_2 diffusion transport limitations, and limited penetration of Fe into the GAC, the reaction zone may predominantly exist on the periphery of the GAC particle. The penetration depth of H_2O_2 into GAC particles was estimated using reactive transport modeling [7]. In small GAC particles, the relative volume of the reaction zone represents a larger fraction of the GAC particle, indicating greater treatment potential (Fig. 1).

1.1.3. Fe amendment to GAC

The pH point of zero charge (pH_{PZC}) of GAC is the pH where the net surface charge of solid surfaces is neutral and the number of positive charges is approximately equal to the negative charges [12]. Often, Fe amendment to GAC has been accomplished using strongly acidic Fe solutions [2,4,13], where the pH of the Fe solution is less than the pH_{PZC} of the GAC. Under this condition, repulsive forces between the positive charged GAC surface and iron cations in solution may impede intraparticle transport of Fe into the GAC. Acidic treatment of GAC will oxidize the carbon surfaces through the addition of acidic surface oxide functional groups [14], resulting in a reduction of the pH_{PZC} [15]. When the iron solution $pH > pH_{PZC}$, the carbon surface is covered by deprotonated carboxyl groups (i.e., acidic surface oxide functional groups); the negative charges attract and adsorb cations from the solution, serve as anchoring sites for Fe, and favor higher dispersion of metal catalysts [16]. Previously, Fe was amended under these conditions where the GAC was pre-treated with acid which lowered the pH_{PZC} from 5.1 to 4.2–4.5, and was followed by the amendment of a Fe(II) solution where the $pH \geq pH_{PZC}$ [6,7]. This procedure resulted in more uniform distribution of Fe in the GAC and greater MTBE oxidation through Fenton-driven regeneration.

1.2. Pilot study

A slip stream of MTBE-contaminated ground water from an extraction well was passed through three pilot-scale columns containing GAC. The ground water was predominantly contaminated with MTBE, and concentrations of petroleum compounds (i.e., benzene, toluene, xylenes) were negligible. Once the GAC was fully saturated with MTBE, the GAC was chemically regenerated with H_2O_2 under different chemical, physical, and operational conditions. The GAC underwent 3 adsorption/oxidation cycles where the

columns were intermittently placed on-line at the ground water pump and treat facility, saturated with MTBE, and regenerated with H_2O_2. The objectives of this study were to investigate operational parameters that influence chemical oxidation efficiency, to quantify treatment performance, and to assess the general feasibility of Fenton-driven regeneration of MTBE-spent GAC at a field site where MTBE-contaminated ground water was being pumped and treated.

2. Methods, materials, and analytical procedures

2.1. GAC

The GAC (URV) used in this study was supplied by Calgon Carbon Corp. (Pittsburgh, PA). URV is a bituminous-coal based, 8×30 mesh carbon. The as-received GAC was liberally rinsed with deionized (DI) water, dried (105 °C) and stored in a desiccator until it was used. The three GAC columns used in this study were prepared and/or operated under different chemical and physical conditions (Table 1, Fig. 2). The GAC used in columns A and B was amended with iron using the bulk loading method (described below) and regenerated under ambient (21–27 °C), and elevated temperatures (50 °C), respectively. Due to the exothermic H_2O_2 reaction, the temperature of the recirculation solution in column A increased during each oxidation event, from room temperature (21 °C) to $\approx$27 °C. The GAC in column C was iron-amended using the acid pre-treatment method (described below), and was regenerated at an elevated temperature (50 °C).

2.2. Iron loading

Previously, the optimal Fe concentration in GAC was determined to be ~6710 mg/kg (1020 mg/kg background; 5690 mg/kg amended) [5] and was used as a design guideline. In the bulk Fe loading method, the GAC (1.65 kg) was placed in a large glass container (20 L), saturated with DI water (>24 h), and amended with a solution of ferrous sulfate (4.96 L, 2 g/L as Fe^{2+}). The vessel was vigorously mixed by hand (1 h) and periodically mixed (3–4 times per day) for 3 days. The post-Fe amendment aqueous solution was sampled (5×), filtered (0.2 μm), analyzed for total Fe, and decanted. In the acid pre-treatment method, the GAC (1.76 kg) was placed in a large glass container (20 L) and amended with hydrochloric

Table 1
Pilot-scale oxidant re-circulation operational parameters for chemical regeneration of MTBE-spent GAC.

Operational parameter	Column		
	A	B	C
Fe amendment method	Bulk	Bulk	Acid pre-treated
Temperature (°C)	21–27	50	50
H$_2$O$_2$ loading[a]			
Oxidation event 1	Semi-continuous	Semi-continuous	Semi-continuous
Oxidation event 2	Semi-continuous	Semi-continuous	Semi-continuous
Oxidation event 3	Continuous	Continuous	Continuous

[a] The semi-continuous H$_2$O$_2$ loading method involved the addition of H$_2$O$_2$ (1.9 L; 30%) in 10 applications of 190 mL, where 20–30 mL aliquots were added every 5–7 min; the continuous H$_2$O$_2$ loading method involved the addition of H$_2$O$_2$ (1.95 L; 30%) to the mixing reservoir (5 mL/min).

acid (HCl 40 mL) to lower both the pH of the GAC slurry and the pH$_{PZC}$ of the GAC. Previously, using the pH drift method to measure the pH point of zero charge (pH$_{PZC}$) [12], acidic treatment of the GAC reduced the pH$_{PZC}$ of the GAC from 5.1 to 4.2–4.5 [6]. Acidic pre-treatment of the GAC and reduction in the pH$_{PZC}$ reduced repulsive forces between positive surface charges on the GAC and positive charged iron ions (Fe^{+2}, Fe^{+3}) in the solution [7]. Subsequently, a solution of ferrous chloride (pH 3.9; 5 L; 2140 mg/L as Fe^{2+}) was amended using similar procedures as described in the bulk Fe loading method above. In both methods, DI water was added and decanted (×3) to remove sulfate or chloride residuals. The final pH was measured after 7 days of contact time.

2.3. MTBE adsorption

The columns (15.25 cm diameter; 38.1 cm height) were placed on-line at the ground water pump and treat system. MTBE-contaminated ground water (190–820 μg/L) was diverted through the columns in down-flow direction (flow = 0.5–0.7 L/min) over a period of ten days to assure MTBE saturation of the GAC. The flow rate through the columns was high to enhance mass transfer and to specifically achieve rapid MTBE saturation of the GAC.

2.4. Oxidation of MTBE-spent GAC

The H$_2$O$_2$ solution was re-circulated through the columns in the upflow mode (Fig. 2). The mixing reservoir was a 2 L Ehrlenmeyer glass side-arm flask, and was used to add H$_2$O$_2$ (30% by wt.) and reagents, and to collect aqueous samples. A Masterflex I/P model 77600-62 peristaltic pump was used with Masteflex PharMed BPT tubing between the mixing tank and the influent to the column. Pipe (Teflon) was used between the column effluent and the influent to the mixing reservoir. Details regarding column dimensions, MTBE adsorption, H$_2$O$_2$ recirculation, and other design parameters are included in the Supporting Information section (Table SI-1).

2.5. pH

The pH of the ground water and the post-sorption (i.e., pre-oxidation) solution was 7.4. Unless specified differently, before oxidative treatment, the pH was lowered to 4 using HCl. During oxidation, if the pH of the recirculation solution fell below 3.0, the pH was adjusted using tap water containing 330 mg/L alkalinity (as CaCO$_3$) that was added to the recirculation system.

2.6. Temperature

Column A was operated at room temperature (21 °C); however, due to exothermic reactions of H$_2$O$_2$, the temperature rose to approximately 27 °C during oxidation. The mixing reservoirs used with columns B and C were placed on stir/hot plates and the solution temperature was maintained at 50 °C during oxidative treatment.

2.7. Aqueous and GAC sampling

After the MTBE adsorption and each oxidation event, five aqueous samples (40 mL) were collected from the mixing reservoir, filtered (0.2 μm filter), and analyzed for MTBE, TBA, and acetone. Wet GAC samples (3 g) were collected near the top of the column, 2–3 in. below the top of the GAC bed, and analyzed for MTBE.

2.8. H$_2$O$_2$

The semi-continuous H$_2$O$_2$ loading method involved the addition of H$_2$O$_2$ (30 wt.%, 1.9 L) in 10 applications of 190 mL, where 20–30 mL was added every 5–7 min. The continuous H$_2$O$_2$ loading method involved the addition of H$_2$O$_2$ (1.9 L) to the mixing reservoir (5 mL/min). The H$_2$O$_2$ concentrations in the mixing reservoir and column effluent were routinely measured to assess the reaction rate of H$_2$O$_2$.
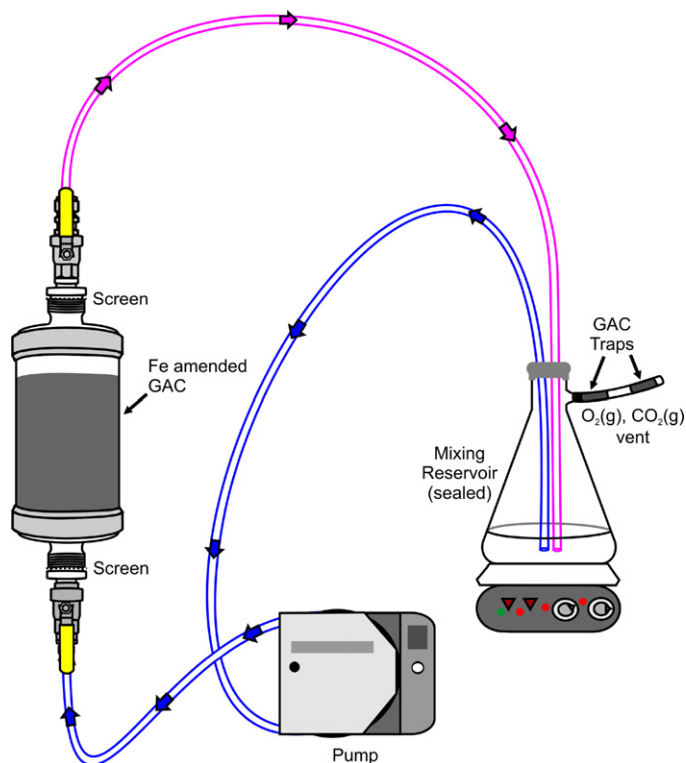

Fig. 2. Pilot-scale oxidant re-circulation (up-flow) hydraulic configuration for chemical regeneration of MTBE-spent GAC.

2.9. Analytical methods

A detailed description of the analytical procedures used in this study is provided in the Supporting Information (Section I. Analytical Methods and Materials) and has been provided in previous studies [4,5,8,9]. These same methods and materials were used in this study to analyze H_2O_2, iron, and pH, and the MTBE and metals in the aqueous phase and in the GAC.

3. Results

3.1. Fe amendment

The average Fe concentration (90 mg/L) after Fe amendment in the GAC suspension used in columns A–C indicated 96% immobilization of the initial iron concentration. The background average Fe concentration in the GAC (1020 mg/kg) was previously measured [5], and was supplemented (5740 mg/kg) through the addition of a ferrous solution. Post-oxidation sampling and analysis of the GAC indicated that the concentration of iron in the GAC ($[Fe]_{GAC}$) in columns A and B was 7950 mg/kg (6020–9880 mg/kg 95% confidence interval (CI); $n = 4$; coefficient of variation = 0.21) and 6120 mg/kg (5010–7230 mg/kg 95% CI; $n = 4$; coefficient of variation = 0.16), respectively. Although these concentrations were in the design concentration range, i.e., 6000–8000 mg/kg, intra-batch variability of Fe concentration in the GAC limited accurate measurements of Fe concentration in the GAC.

The average effluent concentration ($n = 10$) of aqueous iron leaching from the iron-amended GAC during MTBE adsorption in columns A and B was 0.028 and 0.047 mg/L, respectively. Ferrous sulfate and ferrous chloride were used to amend Fe to GAC in columns A and B, respectively. Sulfate is retained on GAC, whereas Cl^- remains in solution and readily elutes from the GAC. Residual sulfur immobilized in the GAC may have formed Fe–S complexes and anchor Fe in the GAC in column A, relative to column B.

Given the flow rate through the GAC during adsorption, these values indicate that the loss of iron during MTBE adsorption was approximately 2–4% of the initial iron mass loaded on the GAC.

3.2. MTBE concentrations in GAC and ground water

Over the course of the study, MTBE concentrations in ground water extracted from the subsurface declined exponentially from 820 μg/L to 190 μg/L (Fig. 3). Consequently, the influent MTBE concentration in the ground water applied to the GAC decreased with each successive application.

Significant MTBE removal was achieved through oxidative treatment in all three columns (Table 2). The concentration of MTBE in the recirculation reservoir declined exponentially in response to the oxidative treatment (Fig. 4). Higher temperatures played a significant role in oxidative treatment given that the lower removal in column A (62–80%), operated at 21–27 °C, relative to the MTBE removal measured in columns B (78–95%) and C (92–97%), operated at 50 °C. MTBE removal measured in column C was consistently high and suggests that the improved Fe distribution played a significant role. In the 2nd and 3rd regeneration cycles, MTBE removal remained consistently high when regenerated at elevated temperatures, indicating iron and H_2O_2 loading methods played a limited role.

Up-flow recirculation of the H_2O_2 solution resulted in 20–30% bed expansion and caused the upward vertical transport of GAC through the central region of the column, and the downward transport of GAC along the periphery. Bed expansion and GAC migration in this manner was enhanced by the buoyancy effect of O_2(g) bubbles which formed as a result of the H_2O_2 reaction. The transport
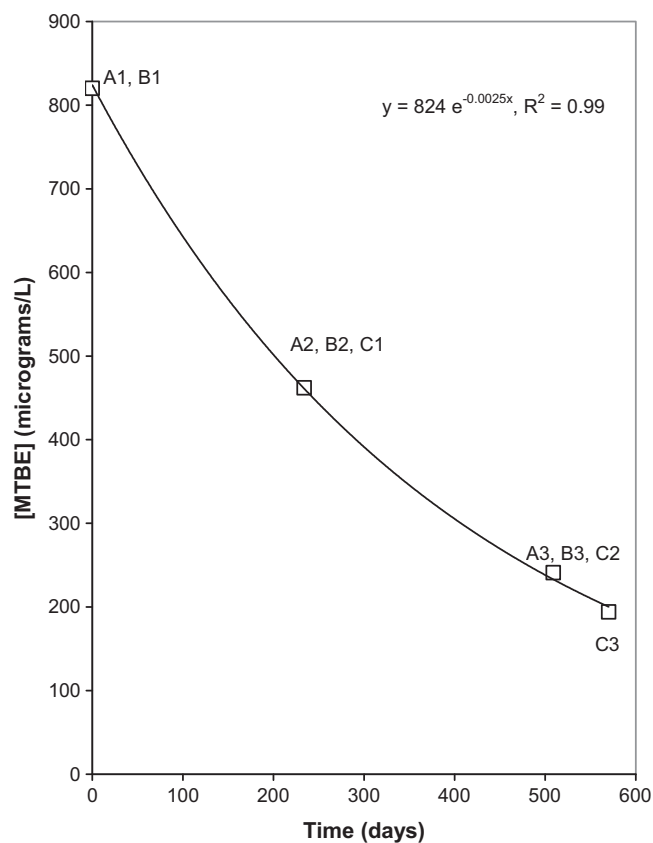
Fig. 3. The MTBE concentrations in the extraction well (well 23 M) decreased exponentially over the course of the pilot study, and consequently, the influent MTBE concentrations to the GAC columns declined with each cycle. Three adsorption/oxidation cycles (i.e., A1–A3, B1–B3, C1–C3) were carried out for each column A, B, and C.

and mixing of the GAC in the column resulted in more uniform contact between H_2O_2 and GAC, and more uniform distribution of the GAC particles. No overlap in 95% confidence intervals of the MTBE concentration in GAC ($[MTBE]_{GAC}$) between oxidation events for all three columns indicated that MTBE removal was statistically significant (Supporting Information, Table SI-2).

An MTBE sorption isotherm was prepared utilizing post-sorption measurements of MTBE in aqueous and GAC samples (Fig. 5) from all adsorption/oxidation cycles (i.e., A1–A3, B1–B3, C1–C3) and columns. The isotherm data represent the initial aqueous and GAC MTBE concentrations ($n = 5$) in equilibrium after the GAC was saturated in columns A, B, and C. Data points A1, B1, and C1 represent the initial aqueous and GAC MTBE concentration associated with the virgin GAC ($n = 5$), and data points A2–A3, C2–C3 represent concentrations in the regenerated GAC after MTBE saturation, but prior to the respective oxidation treatment. The sorption data for regenerated GAC in columns A and B (i.e., A2, B2) are consistent with the sorption data for virgin GAC in column C (i.e., C1) indicating no loss in sorption capacity from aggressive oxidative treatment.

3.3. MTBE mass transfer and mass transport

Columns A and B were saturated with MTBE simultaneously during all three adsorption events. During regeneration, the average aqueous concentration ($n = 20$) of MTBE in the recirculation reservoir in column B (50 °C) was 1.7 times greater than in column A (21–27 °C). This was attributed to thermally enhanced intraparticle MTBE desorption and diffusion from the GAC particle at elevated

Table 2
Cumulative MTBE removal (%) in GAC resulting from Fenton-driven oxidation treatments. Three adsorption/oxidation regeneration cycles.

Adsorption/oxidation regeneration cycle[a]	Oxidation event[b]	Cumulative MTBE removal (%)		
		Column A[c] Ambient temperature Bulk Fe loaded	Column B 50 °C Bulk Fe loaded	Column C 50 °C Acid pre-treatment
1	1	16	22	66
	2	42	58	91
	3	62	78	97
2	4	55	61	28
	5	67	82	81
	6	80	95	94
3	7	32	77	67
	8	46	91	86
	9	62	95	92

[a] Semi-continuous H_2O_2 loading in cycles 1–2; Continuous H_2O_2 loading in cycle 3; 1.65 kg GAC in columns A and B, 1.76 kg GAC in column C.
[b] Three adsorption/oxidation regeneration cycles; three oxidation events per regeneration cycle; GAC columns sampled and analyzed after each oxidation event ($n = 5$); H_2O_2 applied (1.9 L) in each oxidation event (30%; 1.18 g/mL).
[c] Ambient temperature increased from room temperature (22 °C) to ≈27 °C during oxidation.

temperatures and is consistent with previous results where these mechanisms were correlated with temperature [6]. Higher MTBE concentrations measured at the elevated temperature indicated the potential for greater MTBE reaction rates and GAC regeneration.

During one of the semi-continuous H_2O_2 loading episodes, the MTBE concentration in the mixing reservoir was repeatedly measured ($n = 10$) over a 6–7 min period prior to the re-application of H_2O_2. The MTBE concentration declined approximately 20% in column A (21–27 °C), and approximately 14% in column B (50 °C). The decline in MTBE concentration is an indicator of destruction, but sustained MTBE concentrations suggest steady-state conditions

and that intraparticle MTBE desorption and diffusion did not limit MTBE transformation. Therefore, GAC regeneration was not MTBE mass transfer or transport limited. Fenton-driven MTBE oxidation in this system was specifically dependent on the reaction zone where the reactants co-existed (Fig. 1). Under this set of conditions, the depth of the reaction zone in the GAC particle is functionally dependent on the penetration depth of H_2O_2 into the GAC particle,
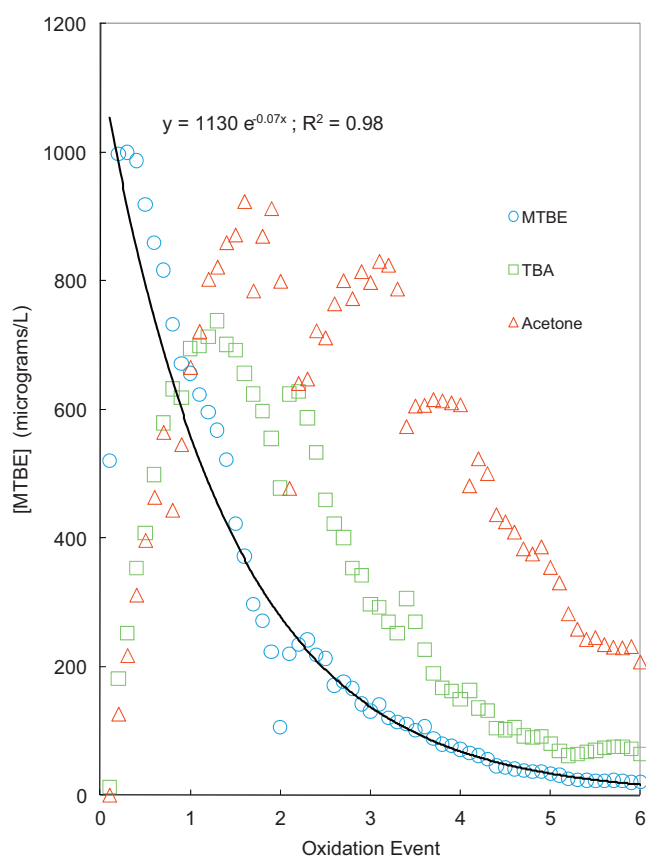

Fig. 4. MTBE ($C_5H_{12}O$), TBA ($C_4H_{10}O$) and acetone (C_3H_6O) concentrations in the mixing reservoir of column C. Pre-oxidation aqueous samples were collected at the elevated temperature (50–55 °C) prior to H_2O_2 amendments to the mixing reservoir.
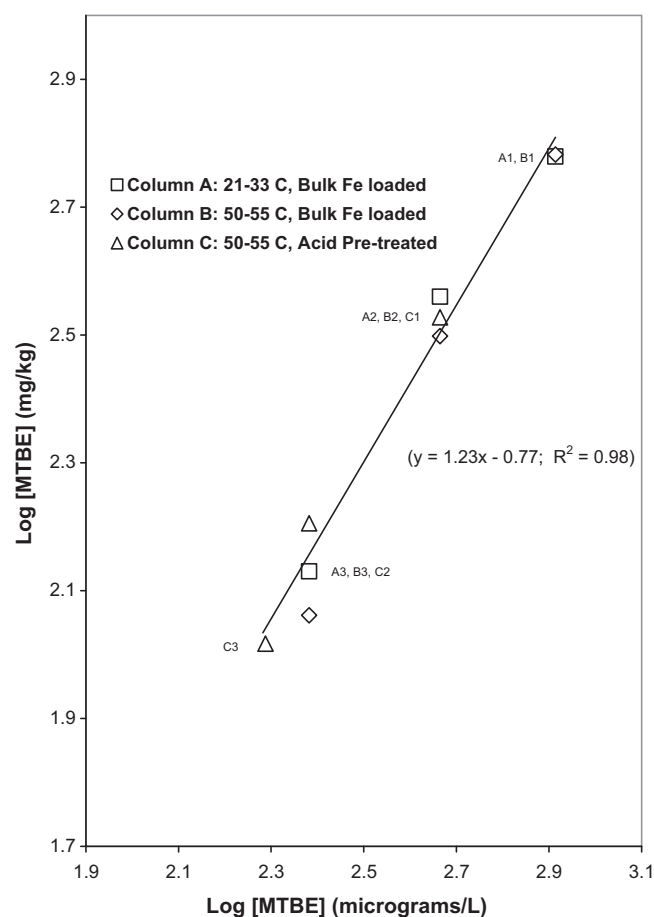

Fig. 5. The MTBE isotherm in GAC represents the initial aqueous MTBE concentrations ($n = 5$) in equilibrium with the GAC, and the initial MTBE concentration in the saturated GAC ($n = 5$) after saturation and prior to the respective oxidation cycle. Specifically, A1, B1, and C1 data represent the virgin GAC in columns A, B, and C, and A2–A3, B2–B3, and C2–C3 represent the regenerated GAC.

the H_2O_2 concentration, and the distribution of Fe within the GAC particle. Given the sieve size range of the GAC in this study (8×30), and assuming full penetration of Fe in the GAC in column C, it is estimated that the H_2O_2 penetrated approximately 60–90% of the volume of the GAC particles.

3.4. H_2O_2

Due to the periodic application of H_2O_2 into the mixing reservoir during the semi-continuous loading, H_2O_2 concentrations exhibited a saw tooth-like trend in the mixing reservoir and columns (data not included). An aliquot of H_2O_2 was added every 5–7 min and the H_2O_2 concentrations measured in the mixing reservoirs ranged from 0.1 to 3.5 g/L. This sequence of steps was performed 10 times (1.9 L total) which represent one oxidation event, and 6 oxidation events were completed for each adsorption/oxidation cycle. In contrast, the continuous H_2O_2 loading method involved the addition of H_2O_2 (30%) into the mixing reservoir at a constant flow rate (5 mL/min; 1.9 L total), and in similar quantities of H_2O_2 as the semi-continuous H_2O_2 loading method. The H_2O_2 concentration in the mixing reservoir in column A was sustained at high levels ranging between approximately 0.8 and 2 g/L, while the effluent ranged between 0.4 and 1.5 g/L. The H_2O_2 influent concentrations in columns B and C were also sustained, but at lower levels ranging between approximately 0.7 and 0.85 g/L, while the effluent ranged between 0.04 and 0.2 g/L. H_2O_2 concentrations measured in columns B and C were lower than in column A due to the elevated temperatures and greater H_2O_2 reaction rates. Nevertheless, greater MTBE removal was measured in these columns and was predominantly attributed to thermally enhanced MTBE desorption and diffusion in the GAC.

The sustained, elevated range in H_2O_2 concentration measured during continuous loading indicates greater intraparticle H_2O_2 gradients and therefore greater H_2O_2 penetration within the GAC particles. This indicates the reaction zone may have extended deeper into the GAC particle, but over a more limited time frame, relative to the semi-continuous loading method. A reduction in the overall removal of MTBE in column A was measured as a result of continuous H_2O_2 loading, compared to semi-continuous H_2O_2 loading. Given the lower aqueous MTBE concentrations under ambient temperature in column A, lower MTBE removal may have been attributed to a shorter time frame (6.5 h) of oxidative treatment with continuous loading, compared to the longer time frame (60 h) associated with semi-continuous H_2O_2 loading. However, MTBE removal in columns B and C was approximately equal using either semi-continuous or continuous H_2O_2 loading methods. Further, the limited time, energy, and effort required to carry out continuous H_2O_2 loading under elevated temperature conditions, relative to semi-continuous loading suggests that it can be successfully used to rapidly regenerate GAC.

Aqueous subsamples removed from the mixing reservoir were analyzed repeatedly for H_2O_2. The change in H_2O_2 concentrations in these subsamples represents the reaction between H_2O_2 and soluble reactants and/or suspended colloidal GAC particles contained in the re-circulation solution. Whereas, changes in the H_2O_2 concentration measured in the mixing reservoir, represent the overall reaction of H_2O_2 with dissolved and solid phase GAC reactants. Results indicate that the H_2O_2 in contact with the GAC bed reacted significantly faster (i.e., >400 times faster) than in the subsamples removed from the treatment system (i.e., re-circulated solution outside of the GAC bed) (Supporting Information, Fig. SI-3). Overall, soluble concentrations of H_2O_2 reactants are negligible and when the solution exits the top of the GAC bed, the H_2O_2 in solution is not in contact with the GAC and H_2O_2 reaction ceases until it is re-introduced at the bottom of the column and contacts the GAC.

3.5. Oxygen gas ($O_2(g)$)

$O_2(g)$, a byproduct of the H_2O_2 reaction in the column reactors, was vented from the system through the GAC traps mounted on the mixing reservoir (Fig. 2). Balancing the Fenton-like reactions [7], one mole of O_2 is produced per 2 moles H_2O_2 reacted. Two segmented (2.5 g) GAC traps in series were designed to capture and quantify volatile emissions of MTBE. The post-oxidation average concentrations of MTBE ($n = 2$) in the GAC traps from columns A and B were 165 and 0 mg/kg, and 876 and 1.2 mg/kg, respectively. Negligible concentration of MTBE in the second segmented GAC trap in series indicated that MTBE was fully captured in the first trap. The total mass of MTBE in the traps in columns A and B was 0.04 and 0.2% of the total initial MTBE mass, respectively. Even lower MTBE mass was captured during the second adsorption/oxidation cycle (data not shown) indicating that volatile losses of MTBE were minimal and that the predominant fate mechanism was oxidative transformation.

Formation of $O_2(g)$ in the column resulted in the displacement of water from the column and an increase in the water level in the mixing reservoir. Approximately 0.5–0.8 L of water was displaced during semi-continuous H_2O_2 loading. Given the total volume of liquid in the column (Supporting Information, Table SI-1), the volume of displaced water was approximately 5–13% of the total volume of water in the column. Assuming full-scale deployment of this technology, storage for displaced water during GAC regeneration may be required. Given the differences between pilot- and full-scale operational conditions and reactor dimensions, it is unclear to what extent gas displacement will occur at full-scale; this will require further study.

3.6. pH

During Fenton-like reactions, a decline in pH is attributed to H^+ release from the reaction of H_2O_2 and the transformation of MTBE, and from the formation of acidic compounds such as carboxylic acids. The pre-oxidation pH in the mixing reservoir was 7.2 in reactors A and B, and the average post-oxidation pH after the first oxidation event was 6.8 and 6.2, respectively. Under these pH conditions, removal of MTBE was 16% and 22% in columns A and B, respectively (Table 2). Optimal pH for the Fenton reaction and production of the hydroxyl radical is attributed to Fe(III) speciation and occurs between pH 3 and 4 [17]. Given the limited removal of MTBE during the first oxidation event, the recirculation solution was subsequently adjusted to pH 4 and maintained between pH 3 and 4 to enhance MTBE removal in subsequent oxidation events in the regeneration cycles 1–3 (Table 2). The pH in Column C was maintained between 3 and 4 for all oxidation events. When the pH dropped to 3.0, tap water (330 mg/L total alkalinity as $CaCO_3$) was added to the mixing reservoir to adjust the pH into the optimal range (pH 3–4).

3.7. Reaction byproducts

TBA and acetone were reaction byproducts from MTBE oxidation and also underwent oxidative transformation as indicated by the declining concentrations in the recirculation reservoir (Fig. 4). Similar reaction byproducts have occurred in other dark-Fenton systems [4,18]. The reaction byproduct, *tert*-butyl formate (TBF), was also formed and subsequently transformed using activated persulfate in another study [19], but was not detected here. Greater acetone accumulation was anticipated, relative to TBA, because it is a byproduct from the oxidation of both TBA and other MTBE transformation intermediates [11] and has a lower reaction rate constant with $\cdot$OH (1.1×10^8 L/mol s) than TBA (6×10^8 L/mol s) [9]. Other
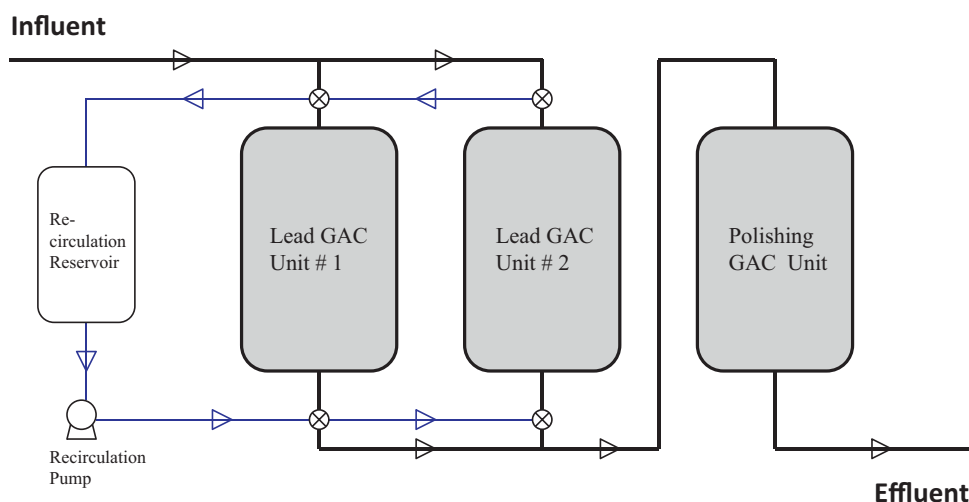
Influent

Fig. 6. Simplified three-vessel GAC treatment system where two lead units alternate between stand-by and on-line. Conceptually, this configuration involves the downflow of contaminated water through two units in series consisting of a lead GAC unit (i.e., #1 or #2), followed by the polishing GAC unit (black lines). Periodically, the spent-GAC in the lead unit is taken off-line, replaced by the standby lead GAC unit, and subsequently regenerated by re-circulating the H_2O_2 solution (blue lines) in upflow mode through the spent-GAC.

byproducts of MTBE oxidation include a variety of carboxylic acids [11,20] and, ultimately, CO_2.

Neither acetone nor TBA is listed in the US EPA National Primary Drinking Water Regulations and a maximum concentration level (MCL) for these organic compounds has not been established [21]. Health-based screening levels (HBSL) represent the benchmark concentration of contaminants in water that may be of potential concern for human health, if exceeded. For non-carcinogens, the HBSL represents the contaminant concentration in drinking water that is not expected to cause any adverse effects over a lifetime of exposure. A concentration of 6000 ppb in drinking water has been established for acetone [22], suggesting that effluent concentrations of acetone do not represent a health risk at the levels found in the effluent.

4. Discussion

4.1. H_2O_2 cost

In this analysis, large totes of H_2O_2 (50%; 1.18 g/mL) were assumed and the cost was $(USD) 0.34/L. A lower concentration of H_2O_2 (30%; dens. 1.11 g/mL) was used and H_2O_2 equivalency was based on 50% H_2O_2. Given the weight of GAC in the columns (1.65 kg; 3.63 lbs), and an assumed H_2O_2 cost of $(USD) 0.44/kg GAC ($(USD) 0.2/lb GAC), the volume of 30% H_2O_2 applied to the columns was determined. Given these assumptions and the cost of H_2O_2, the amount of H_2O_2 applied during each oxidation cycle was approximately $(USD) 1.32/kg GAC ($(USD) 0.6/lb of GAC). The overall cost for chemical regeneration of GAC will require a detailed analysis involving additional site specific factors.

4.2. Optimal GAC regeneration

In H_2O_2-driven oxidative treatment systems, higher H_2O_2 concentrations increase the rate and extent of contaminant oxidation in GAC and soil and is attributed to the source term for $^\bullet OH$ (i.e., $k_1[Fe(II)][H_2O_2]$) [23]. Oxidation efficiency decreases with increasing H_2O_2 concentration; however, and is attributed to $^\bullet OH$ scavenging by H_2O_2 [5]. Therefore, the optimal H_2O_2 concentration in GAC regeneration may be functionally dependent on the treatment objective. For example, assuming the treatment objective is

to minimize the time of regeneration, and/or to maximize the rate or extent of regeneration, high H_2O_2 concentration is appropriate. Assuming the objective is to minimize the cost of regeneration, more frequent applications using lower H_2O_2 concentration would be more economical.

The strength and number of oxidative treatments required to accomplish an acceptable level of regeneration must be optimally balanced with the anticipated effects of declining oxidation efficiency at lower contaminant concentration, and the possible impact of oxidation on the sorptive characteristics of the activated carbon. Incomplete oxidation of MTBE limits the mass of MTBE that can be re-adsorbed on the GAC, but this strategy avoids both the increasing incremental cost required to eliminate the diminishing MTBE residual under increasingly inefficient oxidative conditions, and the potential for deterioration of GAC sorptive characteristics [4]. This optimal balance could be designed into a treatment system where the lead column, in a series of two or more GAC columns (i.e., lead and polish columns), could be periodically taken off-line and chemically regenerated (Fig. 6). Through this process, large quantities of contaminant mass could be efficiently eliminated from the treatment system, and downstream polishing column(s) could be used to achieve high quality effluent.

5. Conclusions

H_2O_2-driven chemical regeneration of the MTBE-spent GAC was carried out under different chemical, physical, and operational conditions. Background iron concentration in the GAC was supplemented through iron amendment (5740 mg/kg) by the addition of a ferrous solution to the GAC. Elevated temperature played a significant role in oxidative treatment given the lower removal in column A (62–80%) operated at 21–27 °C relative to the levels of MTBE removal measured in columns B (78–95%) and C (92–97%) operated at 50 °C. During regeneration at elevated temperature (50 °C), the average aqueous concentration of MTBE was 1.7 times greater than at ambient temperature (21–27 °C). Enhanced removal was attributed to increased MTBE desorption, diffusion, and aqueous concentrations in the solution. MTBE removal measured in column C was consistently high indicating that enhanced iron penetration into the GAC resulting from acid pre-treatment played a role in MTBE oxidation. However, during continuous H_2O_2 loading, this

method of iron loading played a limited role since MTBE removal was approximately the same as the bulk iron loading method. No loss in the MTBE sorption capacity of the GAC was measured.

Semi-continuous H_2O_2 loading resulted in saw tooth-like H_2O_2 concentrations over a wide range whereas continuous H_2O_2 loading resulted in sustained, lower H_2O_2 levels. Lower H_2O_2 concentration was measured in the columns operated at elevated temperature ($50\,^\circ$C) and was due to greater H_2O_2 reaction. H_2O_2 reaction was due to contact with the GAC, and the H_2O_2 reaction was negligible with soluble reactants or suspended colloidal GAC particles in the recirculation solution exiting the GAC bed. The cost of H_2O_2 applied during each oxidation cycle was approximately \$(USD) 1.32/kg GAC (\$(USD) 0.6/lb of GAC). The predominant reaction byproducts, TBA and acetone, also underwent significant oxidative transformation and were not present at levels that represented a health risk.

Disclosure

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.12.003.

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