

Manuscript Title: Iron Optimization for Fenton-Driven Oxidation of MTBE-Spent Granular Activated Carbon (ES06 2666k)

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Supplemental Information

Supplemental information is provided below on the analytical methods and materials used to analyze the aqueous suspension of granular activated carbon (GAC) and the GAC including GAC metals, GAC surface area and pore volume, aqueous phase and GAC MTBE, imaging and microanalysis of GAC particles (Scanning Electron Microscopy (SEM)/Energy Dispersive X-ray Spectrometry (EDS)), H₂O₂, iron, and pH.

GAC Metals Analysis Representative samples (0.4 g) of the GAC taken from the batch reactors after oxidation were digested using 40 mL of 10% nitric acid for 40 minutes in a microwave oven at 150 °C and 1000 kPa. Extracts were analyzed for metals by an inductively coupled plasma - optical emission spectrometer (Perkin Elmer, Model Optima 3300 DV, Norwalk, CT).

GAC Surface Area and Pore Volume N₂ BET surface area analysis of the GAC was conducted by nitrogen adsorption using a surface area analyzer (Beckman Coulter Surface Area and Pore Size Analyzer, Model SA-3100, Fullerton, CA). Samples were outgassed (200 °C, 120 minutes), capped, and analyzed. A 10-point BET regression method was used to estimate surface area, assuming a molecular parking area of 0.162 nm² for N₂ at 77 °K. The micropore volume was determined from an N₂ thickness plot using the Harkins and Jura equation and the mesopore + macropore volume was determined using the Barrett, Joyner, and Halenda pore size distribution method (1).

Aqueous MTBE Liquid-phase MTBE analyses were performed by purge and trap gas chromatography (GC) (Hewlett-Packard, Model 5890 series II). Analytes were desorbed from a Supelco BTEXTRAP trap then transferred to the GC equipped with a Restek column (RTX 624) and flame ionization detector (FID). The standard curve was 1-1000 $\mu\text{g/L}$ ($r^2 > 0.99$) with a 0.1 $\mu\text{g/L}$ detection limit.

GAC MTBE Solid-phase MTBE analyses were performed by extracting approximately 1 g GAC sample with 20 mL of methanol for > 3 days with periodic shaking each day. Subsequently, the GAC-methanol slurry was sonicated for 3 minutes and 250 μL of the methanol extract and 10 μL of an internal standard (D6-Acetone and Fluoroobenzene) were added to 2.5 mL of deionized (DI) water containing 0.6 g Na_2SO_4 . The methanol extract was analyzed using an automated headspace gas chromatograph/mass spectrometer (GC/MS) method. The GC was a Varian (Model 3400, Varian Instruments, Sugarland, TX) with a J&W column and the MS was a Varian (Saturn II Ion trap detector, Varian Instruments, Sugarland, TX). The percent recovery for MTBE, TBA, and acetone extracted from the GAC was 96% (S.D. 3.6%), 111% (S.D. 7.4%), and 68% (S.D. 8.7%), respectively (n=9). The method detection limit for MTBE, TBA, and acetone were 0.24, 0.28, and 0.34 $\mu\text{g/L}$, respectively.

Scanning Electron Microscopy (SEM)/Energy Dispersive X-ray Spectrometry (EDS)

Imaging and microanalysis of GAC particles were conducted using scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS). GAC particles were examined with a JEOL scanning electron microscope (Model JSM-6360, Montgomery, TX) with a beam current

of 10 nA. The microscope is equipped with an Oxford Instruments energy dispersive x-ray spectrometer (Model 6587) with high resolution germanium detectors. GAC particles were coated with gold for SEM and EDS analysis. Three particles were selected from test reactors and three sites were randomly selected on each particle (n=9). For surface elemental composition analyses, the acceleration voltage was 20 keV and the surface area interrogated by EDS (47,000 μm^2 per site) represented approximately 0.3-4.2% of the external surface area of 8 \times 30 GAC particles (i.e., assuming spherical GAC particles). The beam electron-specimen interactions are used to derive information on the nature of the specimen (2). The acceleration voltage was varied (5-30 keV) to assess depth dependent elemental composition of GAC particles.

H₂O₂, Iron, and pH Filtered samples (0.2 μm) were measured for H₂O₂ (n=3) using a modified peroxytitanic acid colorimetric procedure (3) with a detection limit of 0.1 mg/L. TiSO₄ reagent was from Pfaltz and Bauer Inc., and H₂O₂ (30% wt. solution in water, reagent grade) was from Aldrich. Iron was measured in the GAC slurry solution using the Phenanthroline Method (Method No. 3500-Fe D) (4). The slurry pH was measured using an Orion Sure-Flow ROSS Combination pH probe.

References

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