

GRANULAR ACTIVATED CARBON REGENERATION WITH ADVANCED OXIDATION TO CONTROL VOCs

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INTRODUCTION

Air emissions are a major concern in America because of their substantial magnitude. The initial results of the EPA's 1988 Toxic Release Inventory reported that 2.43 billion pounds of toxic chemicals were released into the air annually. Granular Activated Carbon (GAC) adsorption offers a best available technology for capturing volatile organic chemicals (VOCs). The large surface area, microporous structure and highly adsorptive surface character provide a very efficient mechanism for the removal of pollutants from air emissions. However, while in service, the GAC will eventually become exhausted in its capacity to adsorb organic compounds. At this point the GAC can be either discarded and replaced or regenerated and reused. If discarded, the landfilled GAC potentially creates a hazardous waste problem and cradle-to-grave responsibility. The research herein focuses on UV/ozone regeneration of GAC which may be completed in-situ.

The Pennsylvania State University is researching an advanced oxidation (AO) system for controlling VOCs that has been commercialized by Terra-Aqua Environmental Systems (TAES) of Fontana, CA. The system includes an air-phase photolytic chamber, an air/water stripping tower, and GAC beds. This system has controlled the VOCs from 12 industries that together exhaust 0.5 million cfm air, and the systems have complied for seven years with stringent emission standards of the California South Coast District. Compliance has been accomplished while the GAC has been cyclically regenerated with AO at ambient temperatures, and the operators have never seen a need to replace the GAC. The Penn State Applied Research Laboratory role, as funded through the Strategic Environmental Research and Development Program (SERDP), is to improve this system's efficiency via fundamental research so that it can be more cost effective.

EXPERIMENTAL

Laboratory studies employed a GAC bed that was 1 1/2-inches in diameter and 6-inches high. This was initially placed in series with a 4-inch diameter by 5-foot long PVC pipe that contained three low pressure Atlantic Ultraviolet UV lamps. This UV reactor was later replaced with a 4-inch diameter by 18-inch long PVC pipe that contained one low pressure Heraeus-Amersil UV Lamp.

Methyl isobutyl ketone (MIBK) was loaded onto the GAC bed and the amount of MIBK adsorbed was determined by CS₂ extraction of the loaded GAC that was analyzed using a Hewlett-Packard 5890 Series II Gas Chromatograph. The loaded bed was then regenerated for 2 to 24 hours using ozone and associated oxidants, that were created by the UV light, and the efficiency of the oxidation and/or desorption of the MIBK that had been adsorbed was determined. The

regeneration efficiency and by-product formation was analyzed using CS₂ extraction, gas chromatography, and gas chromatography mass spectrophotometry.

The apparatus was also used to test the extent to which ozone and oxidation potential could penetrate into a GAC bed. The penetration was measured as a function of both time, from 0 to 24 hours, and depth, from 1/8-inch to 3-inches. Ozone concentration was measured via Dasibi 1008-HC Ozone Meter, while oxidation potential was measured using method 2350 E Ozone Demand/ Requirement Semi-Batch Method, Standard Methods for the Examination of Water and Wastewater.

RESULTS AND DISCUSSION

The investigation evaluated the effectiveness of a UV/ozone process in reactivating a bed of GAC that had been loaded with MIBK. Under these specific laboratory conditions, with a GAC bed that was completely saturated with MIBK, the UV/ozone regeneration, with Atlantic UV lamps, achieved its greatest effectiveness in the first 2 inches of the GAC bed (Figure 1). An 83% removal of MIBK transpired at the inlet surface, where initial contact occurred between the ozone/OH* radicals and the GAC. The 24 hour reduction of adsorbed MIBK dropped rapidly to 33% removal at 1 inch, 25% at 2 inches, and roughly 17% removal at distances greater than 2 inches.

In another round of experiments, a virgin coconut GAC experienced an air stream that was laden with 160 ppm MIBK. After 24 hours of this loading regime the adsorbed MIBK concentrations were characterized by saturated values of 230 mg/g in the first two inches of the GAC bed, and a mass transfer zone that tailed off to low values at 4 to 5 inches of bed depth (Figure 2). The 160 ppm condition represented the upper bound of industrial exhaust air conditions.

This bed was then regenerated for 24 hours using one Heraeus-Amersil UV lamp. The ozone concentration produced by the UV lamp was approximately 360 ppm when the air stream was bubbled through a water bath that caused the air to contain high humidity. Under these conditions, MIBK removal amounted to approximately 45% of the MIBK that had been loaded onto the influent face of the GAC bed. The data suggests that a significant amount of the MIBK removed from the first inch of the test bed was merely transferred further into the bed. The majority of the MIBK that was loaded onto the bed remained within the bed and was not exhausted into the atmosphere.

However, an analysis of the products formed during the regeneration indicate that roughly 10-15% of the MIBK is actually degraded by the advanced oxidation process. This degradation produces molecules that generally contain fewer carbon atoms and more oxygen functional groups than MIBK. Initial analysis of the end products from the reactions indicate

that a number of different organic fragments are formed during the process. The smallest molecules which have been identified are acetone and acetic acid. Other possible products of the MIBK degradation include 2-methyl-propanoic acid, valeric acid, 4-methyl-3-penten-2-one, and 2,4-dimethyl-3-pentanol. A number of other products may be produced during the oxidation of MIBK. These products show that the MIBK is being broken down into molecules smaller than the parent compound. It is hypothesized that these product compounds could be degraded even further, potentially to CO₂ and H₂O, during subsequent regenerations, since the regeneration effluent is recycled back to the head of the system, in the full-scale process. These results suggest that the full scale system could degrade the VOCs by an iterative manner, with additional degradation taking place in the second and subsequent cycles through the system.

The regeneration experiments provided evidence that the ozone and oxidation potential did not penetrate more than an inch or two into the GAC test bed. This penetration into the GAC bed is a critical parameter in the UV/Ozone regeneration system design optimization. This depth will define the maximum regeneration area and the reaction zone of the system.

In order to test the depth to which oxidants had the opportunity to react with VOCs, further experiments were conducted to better delineate the maximum ozone and oxidation potential penetration. Ozone penetration through a bed of virgin GAC appeared to rapidly increase in the first 30 minutes of the experimental run and then reach a slower penetration rate which continues for at least 48 hours. After 24 hours the ozone reached 26% of its inlet concentration at 1/8-inch (Figure 3). The percent penetration decreased slightly to 20% at 1/4-inch, then more rapidly to 9% at 1/2-inch and ~2% at 3-inches. This data indicates that advanced oxidants interact with GAC at both (a) reactive or immediately available sites and (b) less reactive or less available sites. The number of reactive or immediately available sites is limited, and their capacity becomes exhausted within a half an hour of exposure to advanced oxidants. Following this initial time, oxidants react with the remaining less active or less available sites in a somewhat steady-state manner at which time the advanced oxidants can penetrate further into the GAC bed.

Oxidation Potential penetrates the bed at a smaller percentage of the initial concentration than the ozone (Figure 3). However, this smaller percentage is a significantly higher absolute concentration ~2,000 ppm vs ~50 ppm, at 1/8-inch into the GAC bed. This indicates that there is a significant oxidation potential created in the system and that the oxidation potential is more reactive than ozone.

CONCLUSIONS

Ozone/oxidation potential generated by UV light has been used to regenerate GAC containing MIBK. This process effectively regenerates the first 2 inches of a GAC bed to remove 45 to 85% of the VOC contained in the bed. The regeneration process may be controlled by the ability of ozone/oxidation potential to penetrate into the GAC bed.

These compounds are readily consumed by the GAC and decrease from 26% of the inlet concentration at 1/8-inch into the bed to 2% at three-inches into the bed.

FIGURE 1 UV/OZONE REGENERATION ZONE IN GAC TEST BED

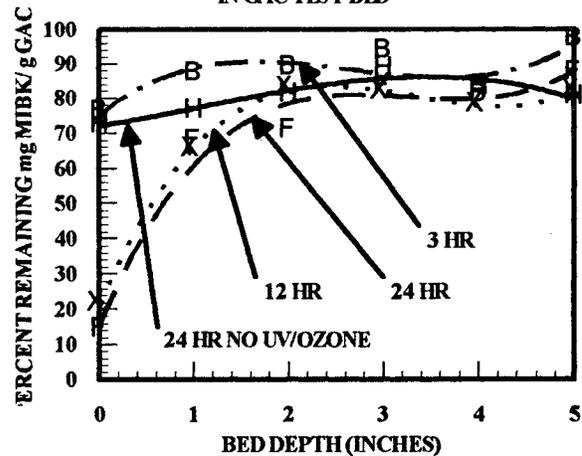


FIGURE 2 24 HOUR UV/OZONE REGENERATION OF GAC TEST BED LOADED AT 160 PPM FOR 24 HOURS

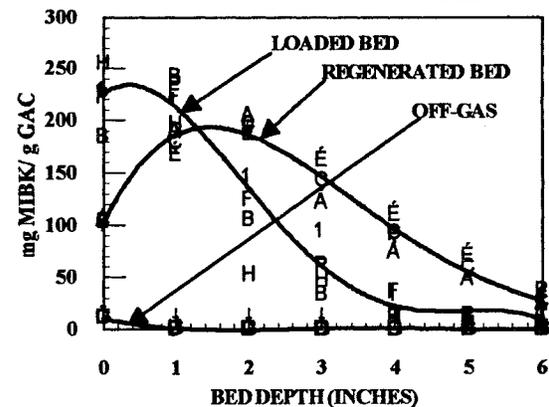


FIGURE 3 OXIDATION POTENTIAL/OZONE PENETRATION VERSUS TIME INTO GAC TEST BED

