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Ozone regeneration of granular activated carbon for trihalomethane control

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HIGHLIGHTS

- Thermally regenerated GAC showed the best recovery in DOC adsorption.
- F400, TiO_2- and Ag-GAC exhibited preferential adsorption for hydrophobic Br-THMs.
- Greater adsorption recovery was observed for Br-THMs than Cl-THMs.
- Free chlorine were completely decomposed before and after all GAC regeneration.
- Ag-GAC showed a strong anti-microbial activity recovery after ozone regeneration.

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ABSTRACT

Spatial and temporal variations of trihalomethanes (THMs) in distribution systems have challenged water treatment facilities to comply with disinfection byproduct rules. In this study, granular activated carbon (GAC) and modified GAC (*i.e.*, Ag-GAC and TiO_2-GAC) were used to treat chlorinated tap water containing $CHCl_3$ (15–21 μg/L), $CHBrCl_2$ (13–16 μg/L), $CHBr_2Cl$ (13–14 μg/L), and $CHBr_3$ (3 μg/L). Following breakthrough of dissolved organic carbon (DOC), GAC were regenerated using conventional and novel methods. GAC regeneration efficiency was assessed by measuring adsorptive (DOC, UV absorbance at 254 nm, and THMs) and physical (surface area and pore volume) properties. Thermal regeneration resulted in a brief period of additional DOC adsorption (bed volume, BV, ~6000), while ozone regeneration was ineffective regardless of the GAC type. THM adsorption was restored by either method (*e.g.*, BV for ≥80% breakthrough, $CHBr_3$ ~44,000 > $CHBr_2Cl$ ~35,000 > $CHBrCl_2$ ~31,000 > $CHCl_3$ ~7000). Cellular and attached adenosine triphosphate measurements illustrated the antimicrobial effects of Ag-GAC, which may have allowed for the extended THM adsorption compared to the other GAC types. The results illustrate that ozone regeneration may be a viable *in-situ* alternative for the adsorption of THMs during localized treatment in drinking water distribution systems.

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1. Introduction

Microbial control within a drinking water distribution system can be managed by maintaining a chlorine residual. However, reactions between chlorine and organic matter form halogenated disinfection byproducts (DBPs). Regulated and unregulated DBPs are a primary concern for water utilities, due to their potential genotoxic and carcinogenic impacts on human health [1]. Trihalomethanes (THMs) are an important group of DBPs regulated by the United States Environmental Protection Agency [2]. The Stage 1 Disinfectants and Disinfection Byproducts Rule (DBPR) requires the running annual average (RAA) for total THMs (TTHM) for all sampling locations in the entire distribution system to be below 80 μg/L. According to the Stage 2 DBPR promulgated in 2006, utilities must comply with a locational running annual average (LRAA) of TTHM <80 μg/L at each of its sampling locations [2]. In addition, the Stage 2 DBPR requires an Initial Distribution System Evaluation (IDSE) to identify the sites with elevated DBP concentrations [2,3]. The new DBPR makes the regulatory compliance much more challenging for water utilities which emphasizes the requirement for improved THM control [4]. Even though treatment processes can be adjusted and optimized, changes in the hydrological, biological, chemical and physical environment of a distribution system make

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the centralized control of THMs a difficult task. In fact, many studies have demonstrated the strong spatial and temporal variations of THMs [5–9], which has prompted the need for localized THM treatment technologies in drinking water distribution systems.

Air stripping has shown potential for the localized control of THMs. By blowing air into water, volatile organic compounds are transferred into the atmosphere. This process has been proven to be effective in removing chloroform [10]. However, brominated THMs (Br-THMs) are more difficult to remove via air stripping, which is consistent with their respective lower air-water partitions as shown by Henry's law volatility constants (K_H^{pc}, Table 1), *i.e.*, 2.12×10^{-3} atm. m^3 mol^{-1} for bromodichloromethane ($CHBrCl_2$), 7.83×10^{-4} atm. m^3 mol^{-1} for dibromochloromethane ($CHBr_2Cl$), and 5.32×10^{-4} atm. m^3 mol^{-1} for bromoform ($CHBr_3$), as compared to 3.39×10^{-3} atm. m^3 mol^{-1} for chloroform ($CHCl_3$) [11–13]. Contrary to air stripping, granular activated carbon (GAC) adsorption is more effective for the removal of Br-THMs than for $CHCl_3$. In fact, Br-THMs have shown higher hydrophobicity, as demonstrated by their higher *n*-octanol to water partition coefficients, *i.e.*, a log *Kow* value of 2.10, 2.24, and 2.38 for $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$, respectively, *versus* 1.97 for $CHCl_3$ (Table 1) [14], contributing to the greater affinity of Br-THMs toward activated carbon (AC) when the surface hydrophobicity of AC is one of the dominant factors controlling the degrees of adsorption [12,14–16]. GAC has been applied in many water treatment plants, generally for a physical adsorptive removal of water contaminants and DBP precursors, but it can also be used as a substrate for microbial growth during biofiltration, *i.e.*, in the form of biological AC, aiming to transform the contaminants biologically [15,17,18]. Therefore, it is beneficial to evaluate the potential of GAC for a localized control of THMs.

One limitation of GAC treatment is the depletion of adsorption pore sites leading to a necessity for material replacement or regeneration [15]. Various methods have been developed for the regeneration of GAC, including ultrasound, plasma, microwave, thermal, biological, chemical, and electrochemical approaches [19–24]. The most common method is thermal regeneration by incinerating the material to volatize and/or char the adsorbed organic compounds [15]. Since the mechanism comprises a release of CO_2 or CO through the decomposition of surface oxygen groups, this process generates a considerable volume of exhausted gas creating potential air pollution [15]. Physical removal of GAC, transportation costs, energy costs, and losses in the adsorption capacity and the mass of carbon material are reasons to search for alternative regeneration techniques [15,25–27]. Ozone has been used alone or in combination with GAC for water decontamination [28–31]. Ozone itself can selectively destroy organic compounds by reacting with electron rich compounds (*e.g.*, amines and aromatics), and generate non-selective hydroxyl radicals (•OH) [29,30]. It also reacts with GAC, known as a catalytic carboxone process [32], to yield a larger amount of reactive oxygen species leading to prolonged GAC adsorption as well as hydroxyl radical oxidation and mineralization [28].

In this study, the performance of different GAC materials with ozone regeneration was investigated as a potential *in-situ* process to extend the GAC adsorption capacity of DOC, UV absorbance at 254 nm ($UV_{254\,nm}$), and THMs. Silver-impregnated GAC (Ag-GAC) was evaluated due to its unique anti-microbial characteristics [29,33–35]. The limited growth of microorganisms may allow more adsorption sites within the Ag-GAC to remain accessible. Considering the catalytic role of titanium dioxide (TiO_2) nanoparticles in producing •OH in the presence of ozone [36], GAC modified with TiO_2 (TiO_2-GAC) was also assessed to enhance •OH exposure either on the GAC surface or within the GAC pores, improving the destruction of the adsorbed organic compounds during the regeneration process. The proficiency of a conventional thermal regeneration method in restoring DOC, $UV_{254\,nm}$, and THM adsorption capacity was also examined and compared to ozone regeneration. Overall, the study provides a direct comparison between ozone regeneration and conventional thermal regeneration to recover adsorption capacity for DOC, $UV_{254\,nm}$, and especially THMs.

2. Materials and methods

2.1. Materials

Conventional bituminous GAC (Filtrasorb® 400 (F400), Calgon Carbon Corporation, Pittsburgh, PA USA) and silver-impregnated coconut shell GAC (Ag-GAC, CE12 × 30, Calgon Carbon Corporation, Pittsburgh, PA USA) were obtained for the bench-scale study. TiO_2-GAC was synthesized following a previously reported sol-gel method [37]. Briefly, a molar ratio of 1:2:1:1 for TBT:EtOH:HNO_3:H_2O (TBT, Titanium (IV) butoxide; EtOH, ethanol; and H_2O, Milli-Q water) was used. TBT was initially dissolved in EtOH, and stirred vigorously for 2 h at room temperature before a H_2O/HNO_3/EtOH mixture was added. Hydrolysis of the resulting alkoxide solution occurred during the next stagnant 2 h. The formed TiO_2-sol was then mixed with an appropriate amount of F400 GAC, oven-dried overnight at 105 °C, and calcined subsequently at 600 °C in nitrogen (N_2) for 2 h, forming rutile TiO_2, which is more stable and reactive for catalytic ozonation than anatase [38–40]. The scanning electron microscope-energy dispersive x-ray spectroscopy (SEM-EDX) imaging in Fig. S1 (Supplementary information, SI) provides evidence of TiO_2 and Ag deposited on the GAC surface.

2.2. Column experiments

A sketch of the experimental setup and material type in each column (15 × 600 mm chromatography column, Ace Glass) is shown in Fig. 1. A detailed experimental procedure can be found in Text S1. The empty bed contact time (EBCT) for each column was calculated and is shown in Table 2. The pH of influent tap water was relatively steady during the whole experimental period (Table 3); while GAC effluent showed comparable pH levels (Table 2). There was no significant difference in water temperatures between the 1st and 2nd run, averaging 20.3 ± 0.6 °C and 20.1 ± 0.5 °C, respectively. Other major water quality parameters of the influent tap water are shown in Table 3.

2.3. Regeneration

Thermal regeneration was performed using a GSL-1100 high temperature vacuum tube furnace (MTI Corporation, Richmond, CA USA). The GAC media were heated starting at a temperature of 25 °C, which increased by 20 °C/min for 49 min in N_2 [41]. The temperature was programmed to 983 °C for the next 135 min in steam. Afterwards, the reactor was cooled down naturally in N_2.

Ozone regeneration was performed by placing the spent GAC into a gas washing bottle with 100 mL deionized (DI) water. An ozone generator (CFS-1A, Ozonia North America, Elmwood Park, NJ USA) supplied the gaseous ozone (>12% wt, with <0.1 m^3_{STP}/h gas flow rate) into a gas washing bottle where ozone was transferred from gas phase into aqueous phase at room temperature (20 °C). The GAC media was continuously stirred inside the gas washing bottle to promote homogenous mixing and ozone exposure. The GAC was treated with ozone for either 30 or 60 min for the different materials, as shown in Table 2. The dissolved ozone residual in the GAC suspension was not measured due to the rapid decomposition of O_3 in the presence of GAC.