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Case Report

Removal of disinfection byproduct precursors by granular activated carbon: Hillsborough county water treatment facility case study

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ABSTRACT

To control disinfection by-products (DBPs) formation, removing the organic precursor before the disinfectant application is important. Granular activated carbon (GAC) is widely used in water treatment plants due to its cost-effectiveness. To assist the Hillsborough County Water Treatment Facilities (HCWTFs) to optimize the design of GAC systems, the efficiency of different GACs with different empty bed contact times (EBCTs) was assessed. This study evaluated the performance of GACs for removing organic precursor from groundwater with both batch and column tests. Coconut shell-based (CS) GAC has the highest adsorption capacity (2.83 (mg/g) $(L/mg)^{1/n}$) and the lowest adsorption rate (3.54×10^{-5} g/mg•min). Rapid small scale column tests (RSSCTs) were conducted with EBCT of 1 and 1.5 min to evaluate adsorption performance. F400 treated more water at the breakthrough effluent TOC concentration of 1 mg/L than the other two GACs. A preliminary capital cost and operating and maintenance (O&M) cost of the full-scale implementation of the GAC system were estimated and the selection of GAC and EBCT led to the trade-offs between system capital costs and O&M costs. From an economical perspective, F400 with 15 min EBCT is the best option with the lowest total annual cost. Additionally, simulated distribution system (SDS) tests were performed with F400 treated water from the pilot study which indicated a significantly lower chlorine demand (1.95 mg/L) and DBP formation (HAA is 9 μg/L and THM is 11 μg/L) at 96 hours when compared with raw groundwater.

1. Introduction

Due to the increasing awareness of health concerns for disinfection by-products (DBPs), water quality regulations for DBPs have become more stringent. The most common DBPs are trihalomethanes (THMs) and haloacetic acids (HAAs), which may potentially cause human cancer risks such as kidney, bladder, liver, and colorectal [1,2]. Hillsborough County Water Treatment Facilities (HCWTFs) use chlorination for water disinfection, which results in various chlorine byproducts due to oxidation reactions with natural organic matter (NOM) and chlorine in the water [3]. One practice for reducing THMs and HAAs formation in a water system is to reduce NOM concentration. Therefore, the removal of organic precursors prior to disinfectant application is important. This could also reduce the added disinfectant dose by reducing the oxidant demand [2].

The DBP precursor can be controlled using coagulation/flocculation [4], powdered and granular activated carbon [5], membrane filtration [6], biofiltration [7], and ion exchange [8]. Among alternatives, powdered activated carbon (PAC) and granular activated carbon (GAC) are widely used in water treatment plants due to their cost-effectiveness for NOM removal [8]. Activated carbon can be reused by reactivating the spent carbon and has a smaller environmental footprint than new activated carbon [5]. For typical water treatment, GAC has more advantages than PAC due to its lower dose and shorter contact time requirements for efficient removal of NOMs [9]. GAC is used extensively in water treatment in various roles, including removal of heavy metals [10], NOM [11], taste and odor compounds [12], and synthetic organic compounds [13]. Using GAC for the removal of NOM has increased, which is recommended by the USEPA for the control of DBPs precursors [5].

Using chloramines as a secondary disinfectant may also reduce chlorine demand thereby lowering DBP formation. The terms “chloramines” and “ammonia addition” are exchanged and used synonymously. The formation of THMs, HAAs, and most other resulting DBPs from

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chlorination are almost completely halted by this addition [14]. This makes the addition of ammonia to produce chloramines an attractive residual maintenance option for utilities [14]. Chloramines, also known as combined chlorine, are more effective in controlling microbial growth in distribution systems, have a lower odor threshold, and are generally more stable than the use of free chlorine alone; this gives utilities who employ chloramines in their distribution system an advantage against other factors as well as DBP formation [14].

To assist the HCWTFs in optimizing the design of GAC systems, the treatment efficiency of different GACs with different empty bed contact time (EBCT) was assessed using rapid small-scale column tests (RSSCT). In addition, simulated distribution system (SDS) tests were conducted to evaluate the potential formation of DBPs at the full scale HCWTF. The costs of the proposed GAC systems based on the results from RSSCTs and SDS tests were analyzed to provide the design recommendations.

2. Materials and methods

2.1. Sample collection and characterization of GACs

The HCWTF is operated by Hillsborough County Water Resources Department, Tampa, Florida. The raw groundwater (from well 21-8) was obtained from the Lake Park Water Treatment Plant (LPWTP). Three commercially available GACs were examined for NOM removal. These included one coconut shell-based carbon (CS) and two bituminous coal-based carbons: Filtrasorb 300 (F300) and Filtrasorb 400 (F400). The GACs used in this study and their general properties are listed in the Supplementary material (Table S1).

2.2. Precursor adsorption tests

All kinetic and isotherm experiments were performed based on the bottle-point methods described by USEPA [15] using Amerex Instruments GYROMAX 818 shaker at 50 rpm. Experiments were conducted in duplicate trials in ambient laboratory temperature of 23 °C. Batch kinetic tests were performed using the raw water with the same GAC dose to evaluate the time required to reach equilibrium. 0.8 g GAC were added into the 200 mL raw water, shaking for 1 day, 2 days, 3 days, 4 days, 5 days, 6 days and 7 days. To evaluate the equilibrium adsorption capacities of GACs for NOM, seven ample bottles were filled with varying masses of GACs (GAC dosage from 0.5 to 5.0 g/L) using the same raw water. The concentration of NOM was measured using UV_{254} and total organic carbon (TOC). Pseudo-first-order (PFO) and pseudo-second-order (PSO) models have been used to determine the rate of adsorption in liquid-solid interactions given in the Supplementary material (Table S2). Freundlich and Langmuir isotherm models were used to fit the experimental data and quantify the adsorption capacity (Table S2).

In this study, the proportional diffusivity (PD)-RSSCT design was used to determine the appropriate RSSCT parameters based on the information of the pilot-scale operation conditions. The constructed RSSCT including reservoir, peristaltic pump, pulse damper, and column, were shown in the Supplementary material (Fig. S2).

2.3. DBP formation tests

DBP formation was assessed using the SDS tests to predict the amount of DBPs that would form in a distribution system. Chlorine dosage, incubation temperature and incubation holding time were the parameters employed to simulate the conditions of the HCWTFs and its distribution system. The SDS tests were performed with influent and effluent samples from the pilot scale GAC column in the HCWTFs.

Each test consisted of a 2 L raw or treated water to be dosed at time zero, with chlorine using sodium hypochlorite (5.8%), followed by holding the containers in room temperature (23 °C) and on magnetic stir plate running with ~800 rpm for 96 hours. Duplicate containers in 2 L were employed for each experiment and samples in 40 mL and 250 mL were taken to measure chlorine residual, THMs, and HAAs after 15 min, 30 min, 24 hours, 48 hours, and 96 hours of dosing.

2.4. Analytical methods

TOC, THMs, and HAAs were measured externally by the Hillsborough County Lab. TOC was measured using Shimadzu TOC analyzer, while THMs and HAAs were measured following EPA Method 524.2 and 524.3, respectively. The other parameters such as pH, UV_{254}, free and total chlorine were measured in Environmental Engineering laboratory at the University of South Florida (USF) using HQ411D Laboratory Starter pH Meter (Hach) with PHC201 General Purposes pH Electrode, Genysis UV/visible spectrophotometer, and Pocket colorimeter II (PC II, Hach), respectively.

2.5. Preliminary cost analysis of full-scale GAC system

A preliminary cost analysis was conducted to estimate total capital cost, operating and maintenance (O&M) cost, and annualized cost of the full-scale implementation of the GAC system with different GAC types and EBCTs at LPWTP using work breakdown structure (WBS) model. In addition, the average useful life for the system along with a discount rate, was used to annualize total capital cost [16]. The sum of annual O&M cost and the annualized capital cost was estimated as the total annual cost in dollars per year.

3. Results and discussion

3.1. Precursor adsorption tests

3.1.1. Batch adsorption

Fig. 1 shows the adsorbent phase concentration of NOM (measure by UV_{254} and TOC) over time calculated based on the NOM concentration in aqueous phase. PFO and PSO kinetic models were applied to investigate the adsorption rate of NOM onto GACs. As shown in Fig. 1, the PSO model was a better fit to the experimental data for three GAC based on the R^2 value, which suggests the surface adsorption involving chemisorption as the rate-limiting step for the removal of NOM [17]. The adsorption behavior may involve valency forces through the sharing or exchange of electrons between NOM and the GAC. The corresponding PSO rate constant k_2 shown in Table 1 for CS is 3.54×10^{-5}, which is lower than F300 and F400. The slower adsorption of NOM onto CS can be explained by its smaller pore volume (see Table S1).

NOM can be efficiently removed by GACs, and the removal efficiency increased with the increasing GAC dosage. Under the given experimental conditions, the removal efficiencies of NOM by the CS measured by UV_{254} and TOC were 98.8% and 93.6%, respectively, which were higher than F300 and F400. This might be because coconut shell is dense and produces more micropores during activation rather than the mesopores seen in bituminous coal-based carbon, leading to higher BET surface area [18]. The equilibrium experimental results were analyzed using Langmuir and Freundlich models in order to obtain the best fit isotherm as shown in Fig. 2. The isotherm parameters obtained by linear regression analysis were provided in Table 2. Comparing of R^2 values indicates that Freundlich isotherm fits better to the experimental results than Langmuir isotherm. This indicated that multilayer adsorption occurred on CS, F300 and, F400, with the nonuniform distribution of adsorption over a heterogeneous surface [19]. According to the values of q_m (Langmuir isotherm) and K_F (Freundlich isotherm) listed in Table 2, it is concluded that the GAC adsorption capacity follows the order of CS > F400 > F300. Similarly, Golea et al. [20] showed CS GAC has a high equilibrium capacity for removing NOM due to pore characteristics.

3.1.2. RSSCT results

As shown in Fig. 3, the breakthrough of CS was very fast, with little

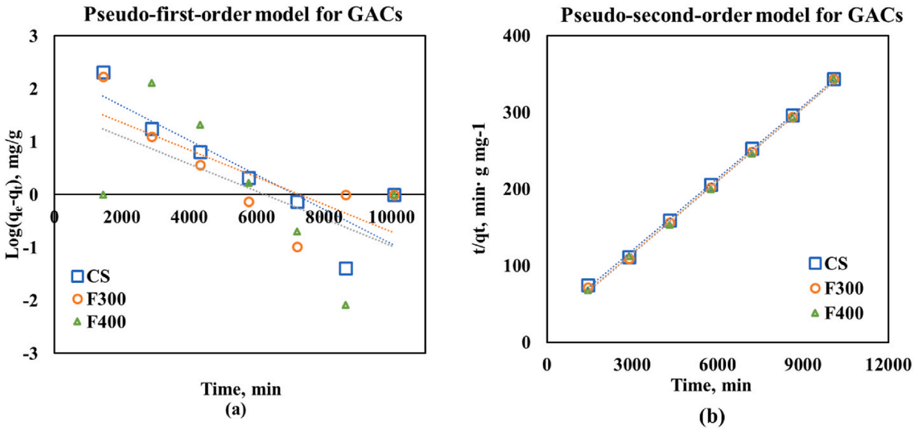


Fig. 1. Pseudo-first-order (PFO) (a) and pseudo-second-order (PSO) (b) kinetics for natural organic matter (NOM) adsorption on granular activated carbon (GACs). Where q_e is the amount adsorbed at equilibrium, mg/g; q_t is the adsorbent phase concentration at time t, mg/g; t is the time, min.

Table 1

Kinetics parameters for the adsorption of natural organic matter (NOM) onto granular activated carbon (GACs). q_e is the amount adsorbed at equilibrium; k_1 is the pseudo-first-order rate constant; k_2 is the pseudo-second-order rate constant.

	PFO			PSO		
	k_1, 1/min	q_e, mg/g	R^2	k_2, g/mg•min	q_e, mg/g	R^2
CS	6.09×10^{-4}	216.27	0.75	3.54×10^{-5}	32.25	0.99
F300	6.09×10^{-4}	76.36	0.61	3.98×10^{-5}	32.22	0.99
F400	6.09×10^{-4}	14.48	0.35	4.36×10^{-5}	32.91	0.99

improvement when increasing the EBCT, indicating coconut shell-based GAC has worse performance than bituminous-based GAC. This result showed CS has a lower mass transfer coefficient than the F400 and F300, consistent with kinetics results. As a result, the breakthrough curve became sharper and the mass transfer zone was smaller. This might be because the CS is denser and has a smaller pore volume than the F400 and F300. Compared with F300, F400 treated more water at the breakthrough point of the effluent TOC concentration of 1 mg/L, indicating F400 as the best performing carbon for NOM removal from groundwater. This result is consistent with the literature, which has demonstrated that CS GAC performs poorly for TOC removal based on breakthrough results because it is more microporous [21].

3.1.3. The trade-off between capital cost and O&M cost

The capital costs were subdivided into the following subcategories: direct capital cost (e.g., GAC contactors, tanks, piping, valves, and pumps), add-on cost (e.g., permits, pilot study, and land acquisition costs), and indirect cost (e.g., yard piping, miscellaneous allowance, and tax). The capital costs were mainly dependent on EBCT without significant difference between different GAC types. The GAC systems with an EBCT of 15 min has a capital cost around $9 M while the cost is around $6 M for the GAC systems with an EBCT of 10 min (see Fig. 4). This is because a longer EBCT requires a larger size of the carbon contactor and a higher volume of GAC in a contractor. O&M costs included labor, materials, makeup GAC, energy, and residual discharge. The O&M costs were dependent on both EBCT and GAC type. And the O&M cost can be significantly reduced by regenerating spent GAC instead of replacing it with virgin GAC. Typically, a system with a shorter EBCT or a GAC having a lower adsorption rate results in a shorter operation cycle and

Table 2

Isotherm parameters for the adsorption of natural organic matter (NOM) onto granular activated carbon (GACs) measured by total organic carbon (TOC). q_m is the saturated maximum monolayer adsorption capacity; k_L is a Langmuir constant related to the binding energy of adsorption; k_F is a Freundlich constant (an indicator of adsorption capacity); 1/n is the adsorption intensity.

GAC	Langmuir model			Freundlich model		
	q_m, mg/g	K_L, L/mg	R^2	1/n	K_F, (mg/g) $(L/mg)^{1/n}$	R^2
CS	80.00	0.0037	0.87	0.98	2.83	0.99
F300	27.47	0.067	0.98	0.94	1.72	0.99
F400	58.82	0.036	0.98	0.96	2.07	0.99

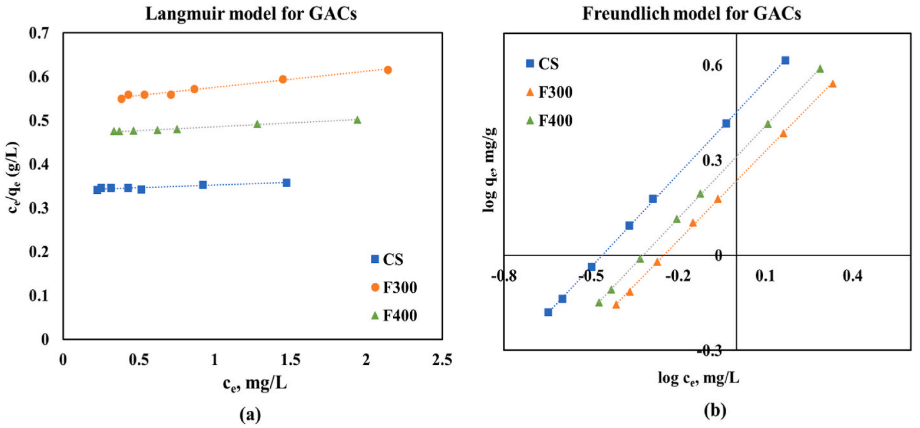
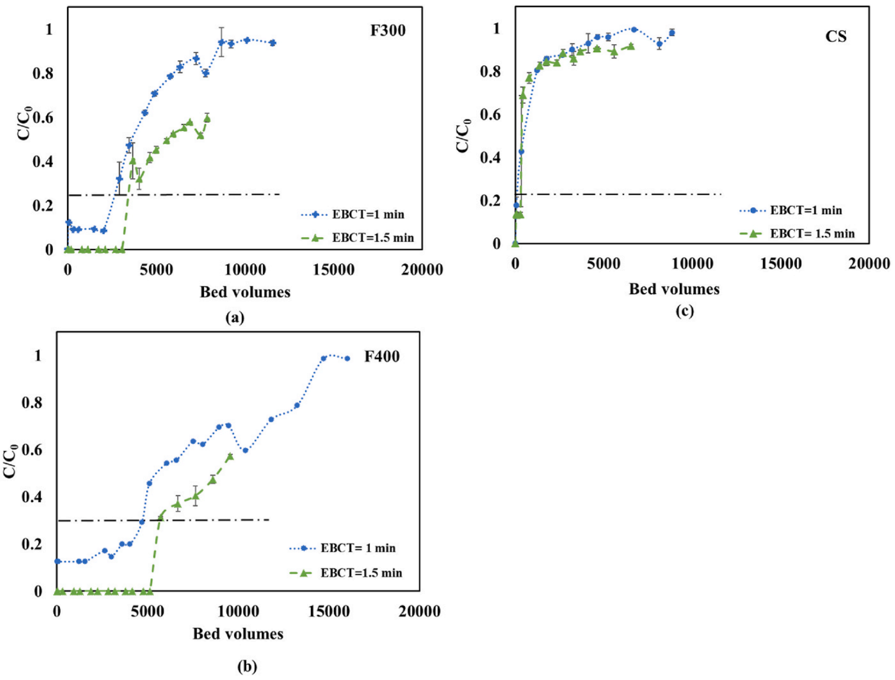


Fig. 2. Langmuir (a) and Freundlich (b) isotherms for natural organic matter (NOM) adsorption on granular activated carbon (GACs) measured by total organic carbon (TOC). Where c_e is the equilibrium concentration, mg/L; q_e is the amount adsorbed at equilibrium, mg/g.



(a)

(c)

(b)

Fig. 3. The breakthrough curves for total organic carbon (TOC) adsorption from groundwater on F300 (a), F400 (b), and CS (c) granular activated carbon (GAC) at varied empty bed contact times (EBCTs). The black dash dot line corresponds to the effluent TOC concentration of 1 mg/L.

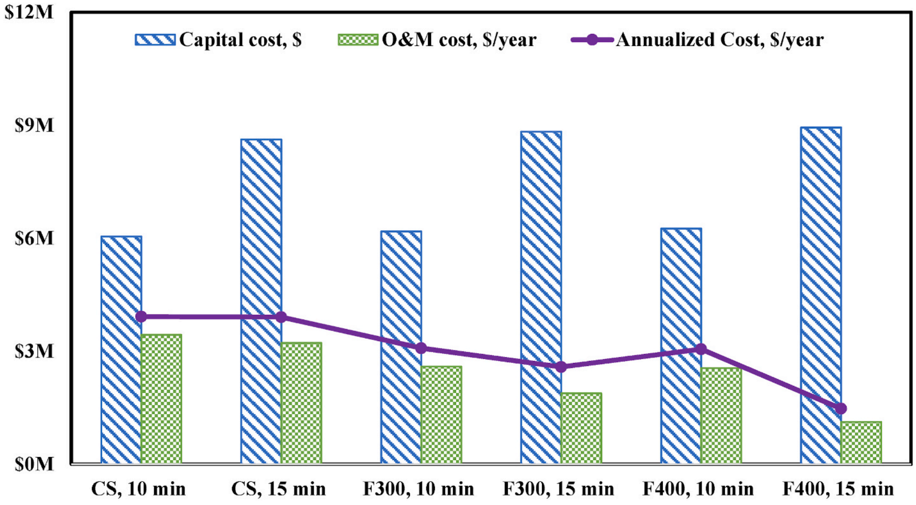


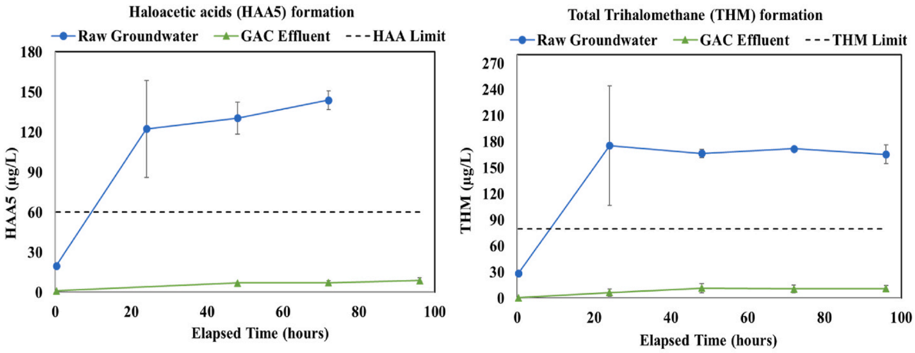
Fig. 4. Comparison of capital cost, operation and maintenance (O&M) cost, and annualized cost for full-scale granular activated carbon (GAC) systems with different GACs at varied empty bed contact times (EBCT).

more frequent reactivation of GAC in a contactor. The GAC system of the F400 with 15 min EBCT has the highest capital cost but the lowest O&M cost among all options, indicating a trade-off between the capital cost and the O&M cost. Considering both capital and O&M costs, F400 with 15 min EBCT has the lowest total annual cost and is considered the best option from an economic perspective.

3.2. SDS results and discussion

The TOC concentration of the raw groundwater from the HCWTF was measured as 3.9 mg/L. The free and total chlorine decrease from the estimated initial chlorine dose of 10 mg/L to 0.5 mg/L over the 96-h experiment for the raw groundwater (see Fig. S4). The chlorine residual was 6.1 mg/L and 0.4 mg/L after the first 15 minutes of the experiment and after 96 hours, indicating a high chlorine demand of 9.6 mg/L at 96 hours for raw groundwater. Fig. 5 compares the DBP results from the raw groundwater and shows THMs and HAAs. The value of HAA at 72 hours is 144 μg/L for raw groundwater (96-hr data point failed in the lab). The THM at 96 hours is 172 μg/L. Both HAA and THM are above their regulated level, showing the need for removing organic matter. A higher TOC concentration suggests more NOM in the water causing an increase in chlorine consumption, and therefore, potentially leading to increased DBP formation.

The TOC concentration for GAC treated water was 0.94 mg/L demonstrating the GAC pilot system at the HCWTF Lake Park Plant is effective in removing organic matter from the raw groundwater. With an initial chlorine dose of 3 mg/L, free chlorine at 96 hours was measured as 1.15 mg/L and total chlorine was 1.20 mg/L (see Fig. S5). The chlorine demand at 96 hours for GAC treated water was significantly reduced to 1.95 mg/L when compared with the raw groundwater.



(a) (b)

Fig. 5. HAA (a) and THM (b) results for raw groundwater and granular activated carbon treated trials over a 96-h period.

Finally, as shown in Fig. 5 for the GAC treated water the measured HAA concentration at 96 hours is 9 µg/L and THM concentration is 11 µg/L. The HAA and THM concentrations for the GAC treated water are significantly lower than their regulated limit, showing the effectiveness of controlling DBP formation through the GAC system as reported by Akcay et al. [22] and Babi et al. [23] and other researchers.

4. Conclusion

To assist HCWTFs in the consideration and evaluation of potential operation for GAC systems, recommendations have been made based on batch and column tests and preliminary cost analysis. A GAC column packed with F400 would have a longer service life, than the other two GACs evaluated in this work, in removing TOC from groundwater water. In addition, RSSCTs indicated that the service life of the GAC increased with increasing EBCT for both F400 and F300. The GAC system with the F400 and 15 min EBCT led to the best performance among all alternatives. The SDS experiments revealed the importance of reducing organics (TOC) prior to disinfection and effectiveness of the GAC treatment. The trade-off between capital cost and O&M cost must be considered. For the full-scale GAC system, even though F400 has a higher initial cost than F300, the O&M cost of F400 is lower than that of F300 at the same operating conditions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cscee.2022.100254.

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