

Research Article

Removal of Trihalomethane (THM) Precursors by Activated Carbon

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Submitted: 03 November 2018

Accepted: 27 November 2018

Published: 30 November 2018

ISSN: 2333-7079

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Abstract

The aim of this work is to study the ability of activated carbon (both powdered activated carbon: PAC and granular activated carbon: GAC) to adsorb trihalomethane (THM) precursors (mainly humic substances) in drinking water treatment. Three different types of water were studied in this work: natural water from the Úzquiza Reservoir (Burgos, Spain), synthetic water prepared using natural fulvic acids extracted from the Úzquiza Reservoir and synthetic water prepared using a commercially supplied humic acid.

The adsorption isotherms using PAC show that the adsorbability of the natural organic matter (NOM) onto activated carbon is in the following order: humic acids > fulvic acids > Reservoir natural water. PAC removes efficiently humic and fulvic acids from water, therefore, THMFP (THM formation potential) decreases but specific THMFP (THMFP/TOC) was found to increase after PAC adsorption. PAC also shifts THM speciation towards the more brominated THM, as evidenced by the increase in the bromine incorporation factor (*n*). GAC filters were also found useful to remove THM precursors, mainly via adsorption mechanism. The biodegradation mechanism (a biofilm of microorganisms grown on GAC surface) only contributes around 3% to NOM removal.

Keywords

- Trihalomethanes (THM)
- Humic substances
- Adsorption
- Activated carbon

INTRODUCTION

Chlorine has been the traditional choice of chemical treatment for the disinfection of public water supplies. Chlorination of water can lead to the formation of disinfection by-products (DBPs), which are usually measured by the surrogate parameter total organic halides (TOX). Among the organic halide precursors present in drinking waters, humic substances (humic and fulvic acids, which are the main components of natural organic matter: NOM) have been strongly implicated as the principal organic precursors for trihalomethanes (THMs) and TOX [1-4].

A strategy to control DBP formation is the use of granular-activated carbon (GAC) as a filter media in drinking water treatment plants (Figure 1). GAC shows a good adsorptive capacity for NOM as well as for many organic micropollutants. There are two key parameters that influence the activated carbon adsorption of humic substances: the organic acidity and the molecular weight of the humic macromolecules. In general terms, low molecular weight macromolecules could be more readily adsorbed onto GAC due to lesser steric hindrances to the adsorption process. On the other hand, humic macromolecules with high organic acidity (which means an increase in molecular solubility) usually show a lesser adsorption onto GAC. Therefore, some authors have suggested that the most suitable approach to

study humic substances adsorption by activated carbon would be to use a parameter which includes the two aforementioned effects, such as the total organic acidity normalized by molecular size [5]. The higher this parameter the lesser adsorption onto activated carbon.

GAC filters in drinking water treatment plants really act as biofilters (biologically active filters), consisting of porous media with high specific surface area on which a large amount of aerobic biomass grows naturally when waters containing biodegradable organics are treated. The combination of the adsorption and biodegradation mechanisms in GAC is usually called biological activated carbon (BAC), where the biodegradation is a result of the presence of microorganisms on the external surface and in micropores of the GAC [6].

MATERIALS AND METHODS

Types of water

Three different types of water have been used in this study: natural water from the Úzquiza Reservoir (Burgos, Spain), synthetic waters prepared using natural humic substances (fulvic acids extracted from the Úzquiza Reservoir) and synthetic water prepared using a commercially supplied humic acid (Aldrich Chemical Co, UK).

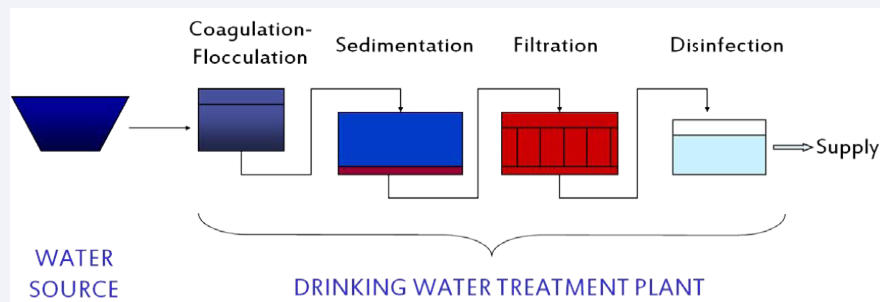


Figure 1 Scheme of a conventional drinking water treatment plant in Spain.

Extraction of humic substances

The extraction of humic substances from the reservoir water is based on the resin adsorption procedure described by Thurman and Malcolm [7]. In this procedure Amberlite XAD-7 resin is used to isolate the humic substances, pumping initially the natural water through the column at pH 2.0; humic substances adsorbed on the resin are eluted with 0.1N NaOH. Fulvic and humic acids are then separated by precipitation at pH 1.0; after precipitation for 24h, the sample is centrifuged (8000 rpm-20 min): humic acids precipitate whereas fulvic acids remain in solution.

TOC analysis

TOC (Total Organic Carbon) was measured with a carbon analyzer (Shimadzu TOC-5050, Kyoto, Japan), based on the combustion-infrared method.

THMFP tests

Trihalomethane formation potential (THMFP) is a simulated chlorination test, useful to evaluate the THM precursors. Samples were placed in 125mL glass bottles with PTFE-lined septa and buffered (phosphate buffer) at pH 7.0. Chlorine was added as sodium hypochlorite (NaClO) diluted from a 5% hypochlorite solution to give 10 mg/L of free chlorine; bottles were then capped free of headspace. After incubation for 3 days at 25°C, sodium thiosulfate was added to quench the THM formation reaction. The quenched samples were stored for no more than 48 h under refrigeration, after which they were analyzed. THM analyses were performed with a gas chromatograph (Hewlett Packard 5890, Palo Alto, CA, USA) equipped with a mass selective detector (Hewlett Packard 5971 A) and a HP-624 column (30m x 0.25mm x 1.4µm film thickness), specially designed for the analysis of volatile organic compounds; samples were introduced through a purge and trap concentrator, which made it possible to achieve quantitation limits around 0.1µg/L for all the compounds. Triplicate series were run on each of the samples to determine the experimental error associated with THM measurement. In most cases, the CV (coefficient of variation) was lower than 8%.

Adsorption tests

Adsorbents: Powdered activated carbon (PAC) was selected for this study. PAC was purified prior to use by the following sequence: agitation in 0.01M NaOH, rinse with milli-Q water, agitation in 0.01M HCl, rinse with milli-Q water until a constant conductivity of the milli-Q water filtrate was obtained, and oven

drying at 105°C for 24h. The dried PAC was stored in air-tight, screw cap glass bottles in a desiccator until use.

Adsorption experiments: The adsorption experiments used in this study are based on the procedure described by Lambert [8]. Adsorption tests were conducted by adding an accurately weighed dose of PAC (range of adsorbent masses: 0.01-0.4g) to a series of 125mL bottles containing 125mL of solution (humic or fulvic acids, at an initial concentration of 10mg/L TOC). A phosphate buffer was added to the solutions to maintain a constant pH of 7.0. The bottles were sealed with Teflon-faced-screw-caps, protected from the light and agitated by moderate stirring (150 rpm); a small head space in the bottles aided solution mixing during agitation. The experiments were conducted at room temperature (20 ± 2°C). The bottles were agitated for an equilibrium period of 3 days (previously determined), after which time the solutions were separated from the adsorbents by filtration through prewashed 0.45µm cellulose nitrate membranes and analyzed for TOC.

Adsorption isotherms: A modified form of the Freundlich equation was used to model the results of the adsorption experiments

$$q_e = K_f (C_e/D)^n$$

where: q_e (adsorptive capacity) is the amount of solute adsorbed per gram of adsorbent (mg TOC/g PAC); C_e is the equilibrium solution phase solute concentration (mg TOC/L); D is the initial PAC dose (g/L); K_f is the Freundlich affinity parameter for a heterodisperse system, which is related to the capacity of PAC for the solute; and n is the exponential Freundlich coefficient, which is related to the magnitude of the adsorption driving force and to the distribution of the energy sites on the adsorbent. The results of the adsorption trials, expressed as q_e and (C_e/D) , were plotted as logarithms on opposing axes. This modification of the Freundlich equation relates q_e to $(C_e/D)^n$ rather than C_e^n (the equilibrium concentration is normalized by the adsorbent dose). The modified Freundlich equation was originally developed to model the sorption of heterodisperse polymers by nonporous adsorbents; subsequent applications of the equation have been reported for describing sorption from heterogeneous mixtures of humic substances and other natural NOMs by activated carbon [9].

Filtration column tests

Filtration tests were performed on GAC column filters using

two different operating conditions: sterile filters (using $HgCl_2$ to avoid microorganism growth on the filter) and biologically active filters (seeded with natural water from the reservoir). The columns (4-cm-diameter and 1-m-height glass cylinders) were fixed bed operated in up-flow mode and the operating parameters were the following: the depths of filter media (GAC) were 50 cm, the empty bed contact time (EBCT) in the columns was 17 min and influent flow rate was 1.2m/h. According to some reports, biofilters usually reach steady state (the biofilter has developed a mature biofilm) after 40-50 days from the start-up process, corresponding to roughly 3800 bed volumes of operation; in this study, the biofilters were operated for 45 days (3800 bed volumes) before data collection for the experiments.

RESULTS AND DISCUSSION

Figure 2 shows the adsorptive capacity of powdered activated carbon (PAC) for the three types of NOM studied in this work: natural water from the Úzquiza Reservoir (Burgos, Spain), a synthetic solution of fulvic acids extracted from the aforementioned Reservoir and a synthetic solution of commercial humic acids. For a quick comparison of the results, isotherms towards the upper left corner of the plots indicate higher adsorbent loadings achieved by equivalent masses of adsorbent in solution.

It can be seen in Figure 2 that, in general, PAC shows the greater adsorptive capacity for the humic acids followed by the fulvic acids, being the natural water from the Reservoir the one with the lesser adsorption onto PAC. The Úzquiza Reservoir water is composed of humic substances (52%, being fulvic acids the bulk of them) and the rest of NOM are hydrophilic compounds of lower molecular weight than humic substances (low-molecular-weight hydrophilic acids, hydrophilic bases and neutral hydrophilic compounds) [10]. These low-molecular-weight hydrophilic compounds are little adsorbable onto activated carbon and are responsible for the lesser adsorption of the Reservoir NOM onto PAC. Humic substances, nevertheless, are high-molecular-weight hydrophobic compounds, which explains their greater adsorption onto PAC. Humic acids are more aromatic, larger molecular

weight organic compounds than fulvic acids. Table 1 summarizes the main characteristics of the two humic substances used in this study [5], where it can be seen that the humic acids show higher values for the molecular weight, SUVA (aromatic character) and color parameters whereas the fulvic acids show higher values for organic acidity (carboxylic, phenolic and total acidity). The fulvic acids show the highest value for the combined parameter total acidity/molecular weight, which explains their lesser adsorption capacity onto activated carbon in comparison with humic acids.

Table 2 shows the main results of the adsorption experiments of humic substances onto PAC. As shown by the adsorption isotherms, PAC removes more efficiently humic acids (35.1% TOC removal) than fulvic acids (26.9% TOC removal). Humic acids also show a greater THMFP (trihalomethane formation potential) than fulvic acids for similar TOC concentrations. In order to compare the THMFP of different substances, such as humic and fulvic acids, it is more suitable to use a normalized parameter: the specific THMFP (THMFP/TOC). It can be seen that humic acids have a higher specific THMFP than fulvic acids, therefore, their capacity to form THM is greater.

Following PAC treatment THMFP decreases for both humic substances, obviously due to the decrease in TOC, but specific THMFP (THMFP/TOC) increases. That means that the remaining NOM in solution after PAC treatment has a greater capacity to form THM than the original NOM before the treatment. PAC has preferentially adsorbed compounds with lesser ability to form THM within the humic substances.

An important variable to be considered when studying the effect of chlorine on THMFP is the presence of bromide ion in the water: chlorine oxidizes bromide ion (Br^-) to hypobromous acid-hypobromite ion ($HOBr - OBr^-$) and $HOBr$ can react with humic substances in the water to form brominated THMs.

In waters with a high bromide ion content the contribution of the brominated species to the whole of THM is important. A useful parameter to evaluate the formation of brominated THMs is the "bromine incorporation factor: n " [4]. This factor is defined as:

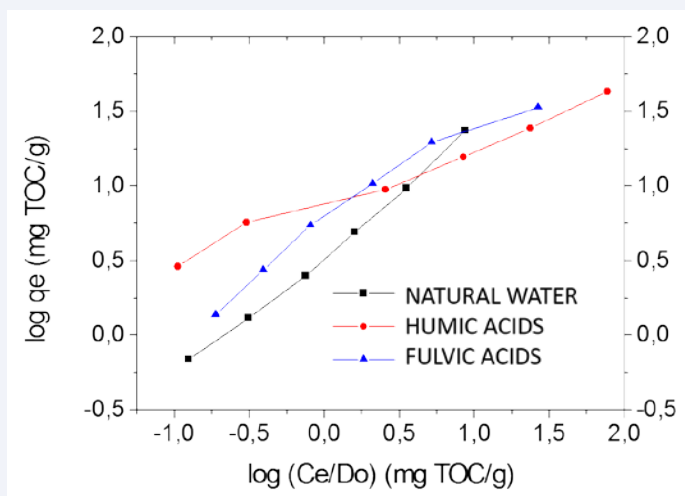


Figure 2 Adsorption isotherms on powdered activated carbon (PAC).

Table 1: Main characteristics of the humic substances used in this study.

	HUMIC ACIDS ^a	FULVIC ACIDS ^b
Average Molecular Weight (Da)	4500	1000
SUVA (UV ₂₅₄ /TOC) (L/mg-m)	5.0	2.9
Colour/TOC (Pt-Co U/mg C)	35,53	5,87
Carboxylic acidity (mEq/g C)	7,4	9,1
Phenolic acidity (mEq/g C)	3,1	4,5
Total acidity (mEq/g C)	10,5	13,6
Total acidity/Molec. Weight (mEq/g C Da)	2,3 10 ⁻³	13,6 10 ⁻³

^aCommercial humic acids: Aldrich Co, UK. ^bNatural fulvic acids: (extracted from the Úzquiza Reservoir, Burgos, Spain). Samples buffered at pH = 7.2

Table 2: Main results of the adsorption experiments on powdered activated carbón.

	FULVIC ACIDS SOLUTION				HUMIC ACIDS SOLUTION			
	TOC (mg/L)	THMFP (µg/L)	THMFP:TOC (µg/mg)	n	TOC (mg/L)	THMFP (µg/L)	THMFP:TOC (µg/mg)	n
Raw Water	5.39	385.4	71.5	1.14	5.14	551.9	107.4	0.98
After Pac Treatment	3.94	335.1	85.0	1.38	3.34	409.4	122.6	1.25

Br⁻ concentration: 0.8mg/L. PAC dosage: 0.05g PAC/L. TOC: Total Organic Carbon THMFP: Trihalomethane Formation Potential. PAC: powdered activated carbon

$$n = \frac{\text{TTHM-Br}}{\text{TTHM}} \text{ (}\mu\text{mol}/\mu\text{mol)}$$

3 where TTHM-Br is defined as: $\text{TTHM-Br} = \sum i \times \text{CHCl}_{3-i}\text{Br}_i$ (units: $\mu\text{mol}/\text{l}$)

$$i=0$$

Table 2 shows the values of “n” obtained for both humic substances (Br⁻ concentration in solution around 0.8mg/L in both cases). It can be seen that fulvic acids have a higher capacity to form brominated THM (higher value of “n”) than humic acids for a similar concentration of bromide ion in both cases. Another interesting fact is that “n” increases following PAC adsorption due to a higher Br⁻: TOC ratio remaining in solution after the adsorption treatment (Br⁻ hardly adsorbs onto PAC and therefore, Br⁻ concentration does not practically change).

Figure 3 shows the results of the filtration tests for both types of GAC filters studied using two operating conditions: sterile and bioacclimated media (biologically active filters); the water used in these tests was the solution of commercial humic acids. Sterile GAC filters only remove NOM from water via adsorption whereas in biologically active filters (BAC) adsorption and biodegradation occur together; the difference between them represents the TOC removed via biodegradation [6]. It can be observed in Figure 3 that sterile GAC filters removed NOM with a great efficiency (percentages of TOC removal around 82%) and biologically active filters (BAC) even achieved a slightly higher TOC removal than sterile filters (the contribution of the biodegradation mechanism to NOM removal was around 3%). This result is in agreement with some studies from the literature [11,12], reporting between 2-5% of biological removal of DOC.

Some authors have reported that GAC filters present a higher efficiency than non-adsorbing filters (sand), not only due to the contribution of the adsorption mechanism to NOM removal but also due to an increase in biodegradation rates for GAC filters relative to sand filters. According to some authors, this behavior may be due to a better utilization of sorbed substrate (the ability

of GAC to better adsorb and retain organic matter would increase the chance of biodegradation), a more favorable acclimation environment and/or a higher surface area of GAC relative to sand, which means that GAC filters can support a larger bacterial population [6], for instance, Magic-Knezev et al. [13], reported $0.1\text{-}4 \times 10^{10}$ cells/cm³ GAC for GAC filters whereas only 3×10^7 - 2×10^8 cells/cm³ sand for slow sand filters and 3×10^7 - 2×10^9 cells/cm³ sand for rapid sand filters).

CONCLUSIONS

The adsorptive capacity of activated carbon (powdered activated carbon: PAC and granular activated carbon: GAC) for aquatic natural organic matter (NOM) has been studied in this work using three types of NOM: a natural water from the Úzquiza Reservoir (Burgos, Spain), a synthetic water prepared using natural fulvic acids extracted from the Úzquiza Reservoir and a synthetic water prepared using a commercial humic acid.

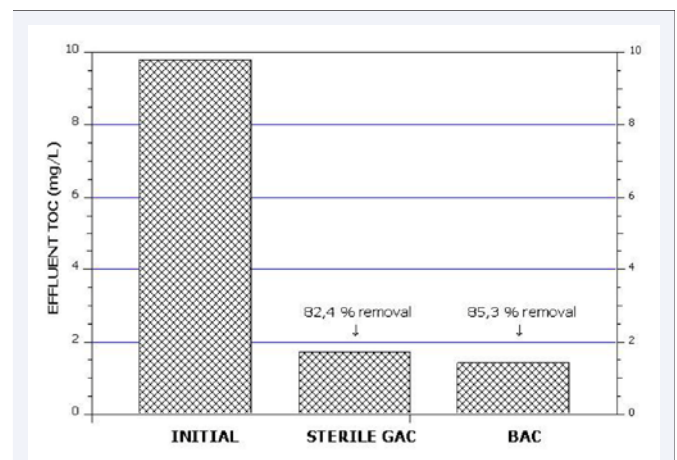


Figure 3 Adsorption of humic acids on granular activated carbon (GAC) filters.

Based on the results of the adsorption isotherms, the natural water from the Reservoir shows the lesser adsorbability onto PAC since a half of its components are low-molecular-weight hydrophilic compounds (little adsorbables onto activated carbon). Concerning humic substances, the humic acids show the greater adsorbability onto PAC, since they have a lower value of the combined parameter acidity/molecular weight than the fulvic acids.

PAC removes efficiently trihalomethane (THM) precursors (humic and fulvic acids) from water, therefore, THMFP (THM formation potential) decreases but specific THMFP (THMFP/TOC) was found to increase after PAC adsorption. That means that the remaining NOM in solution after PAC treatment has a greater capacity to form THM than the original NOM before the treatment. PAC has preferentially adsorbed compounds with lesser ability to form THM within the humic substances.

PAC also shifts THM speciation towards the more brominated THM, as evidenced by the increase in the bromine incorporation factor (n) for the remaining NOM after PAC treatment.

GAC filters operating in a drinking water treatment plant are really biologically active filters (BAC filters), since a biofilm of microorganisms grows on GAC surface. BAC filters can remove THM precursors from water via two mechanisms: adsorption and biodegradation. The results of our study using humic acids indicate that the bulk of NOM is removed via adsorption whereas the biodegradation mechanism only contributes around 3% to NOM removal.

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Cite this article

Rodríguez FJ (2018) Removal of Trihalomethane (THM) Precursors by Activated Carbon. *J Pharmacol Clin Toxicol* 6(6):1128.