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Effect of biofiltration process on the control of THMs and HAAs in drinking water

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ABSTRACT

Natural organic matter (NOM) is the precursor of disinfection by-product (DBP) formation potential. In this study, the aim was to investigate NOM removal and chlorinated DBP reduction by the biofiltration process. Different materials (zeolite, sand, and granular activated carbon (GAC)) and contact time effects were evaluated by feeding Porsuk water (PW) from Eskisehir, Turkey. The reduction performances of trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAFP) were higher in the GAC column than in the sand and zeolite columns. The GAC biofilter column removed 64% of dissolved organic carbon (DOC), and therefore, THMFP and HAAFP were decreased by about 68 and 64% in 30 min. The zeolite and sand biofilter columns only reduced HAAFP by 27 and 21%, respectively.

Keywords: Biodegradable dissolved organic carbon (BDOC); Biofiltration; Biological activated carbon; Disinfection by-products (DBPs); Eskisehir Porsuk water (PW); Haloacetic acids (HAAs); Natural organic matter (NOM); Trihalomethanes (THMs); Water resource

1. Introduction

Natural organic matter (NOM) is a heterogeneous mixture of different organic compounds with a wide range of molecular weights in natural water resources. These organics can be divided into two main factions: humic (hydrophobic) and non-humic (hydrophilic) substances [1,2]. Humic substances, which are composed of fulvic and humic acids, are more resistant to biodegradation, while non-humic substances—including carbohydrates, lipids, and amino acids—are easily biodegradable [3,4]. The human health effects of NOM are not known in terms of drinking water. On the other hand, it is the precursor of chlorinated disinfection by-products (DBPs) (trihalomethanes (THMs), haloacetic acids (HAAs), chlorinated ketones, and haloacetonitriles) [5–7], and it causes biological growth in the distribution systems.

The control of NOM is important to ensure the safety of drinking water. The NOM-removal efficiency of conventional water treatment processes (typically involving coagulation, filtration, and disinfection) is about 30%, which is likely not enough to guarantee

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satisfactory water quality. Therefore, the present challenge is to improve NOM control to meet the DBP regulations and prevent biological growth in distribution systems by modifying existing treatment plants [8–10].

The biofiltration process can be applied to remove non-humic substances that are part of NOM and easily biodegrade organics with simple structures and hydrophilic characteristics. The principle of organic-substance removal in biofiltration is the utilization of the bacteria attached to the surface of the filter media [11]. The biofiltration process is commonly applied in water treatment after the ozonation or oxidation process to convert complex humic matter to the simple non-humic form. Microorganisms that are grown on the surface of the filter media (granular activated carbon (GAC), sand, or anthracite) can consume the simple organics or biodegradable dissolved organic carbons (BDOC) easily [6,12–14]. The filter media plays an important role in water quality improvement. Rapid filters can be operated as a biofiltration process in terms of the biologically active mode in existing treatment plants.

Biofilters can be easily retrofitted for any plant that has rapid granular filtration as part of its treatment and can have significant effects on NOM [6,8,15]. Organic materials are degraded by microbial communities within the filter [16,17]. Biofiltration has several benefits: It diminishes microbial regrowth in distribution systems and biostabilizes the water, it reduces the amount of precursors available to form DBPs and decreases chlorine demand, and it controls taste, odor, and new emergent pollutants (pharmaceutical/personal care products, etc.) [9,17–19].

The benefits of biofilters are highly attractive when there is an excess of organic matter in the source water caused by retrofitting an existing filter; for example, sand or zeolite filters are relatively inexpensive and easy to operate. The filter material selected is largely determined by the desired water quality. On the other hand, the feasibility of the filter media has to be considered. Besides the biofilter treatment performance, investments in capital construction, land requirements, and operational costs also have to be considered. In water treatment plants, sand is commonly used in rapid filtration, but natural zeolite can be a more effective biofilter than sand when compared to particles having smaller total surface areas, such as quartz sand beds [20,21]. It has been observed that GAC filters can remove dissolved organic carbon (DOC) in most natural waters even after their adsorption capacity is exhausted because of the biofilms developing on them [19]. GAC is a porous material that initially removes organic precursors through adsorption and then slightly more through biological activity. Once its adsorption capacity is exhausted and biofilm accumulates, removal is achieved solely through substrate utilization, and then, the GAC is called biologically activated carbon. Generally, adsorption and biodegradation of organics can take place simultaneously on the surface. Biodegradation can help bioregenerate some of the adsorption sites on the active carbon. However, it is difficult to separate and identify the degree of the mechanisms [22–25]. Biologically degradable organic matter has more non-humic characteristics compared to the humic bioresistant organics [26] and removes organic precursors effectively.

Rapid and slow sand filters are commonly employed after sedimentation to eliminate or transform inorganic species and remaining particles. In the meantime, bacterial growth can develop, serve as biofiltration, and improve the water quality.

The objective of this study was to evaluate the role of the materials (GAC, sand, and zeolite) used in biofilter columns for NOM removal and the reduction of chlorination DBPs (THMs and HAAs) in circumstances in which no oxidation process (e.g. ozonation in natural water resources) was used in Porsuk water (PW) from Eskisehir, Turkey.

2. Materials and methods

2.1. Source water

The experiments were carried out with PW, which is the main source of public water for Eskisehir municipality (Fig. 1). There are several upstream discharges from farmland and industrial and domestic origins.

Based on total P and chlorophyll-a, PW is considered a eutrophicated water resource with respect to Turkish surface water quality management law [27]. Table 1 presents the typical characteristics of raw PW. Samples were collected during August 2006 to September 2008 from the Porsuk River which was quite close to the inlet of Eskisehir water treatment plant.

The Eskişehir public water treatment plant consists of mainly screening, pre-chlorination, coagulation, sedimentation, filtration, and disinfection steps with chlorine, and it has a capacity of 80,000 m^3/d [28]. Water pollution and subsequent eutrophication problems complicate the water treatment process, which must be overhauled.

2.2. Materials

GAC with a particle size range of 0.5–2.5 mm and a BET surface area of 900–1,000 m^2/g (Lurgi-Hydroffin

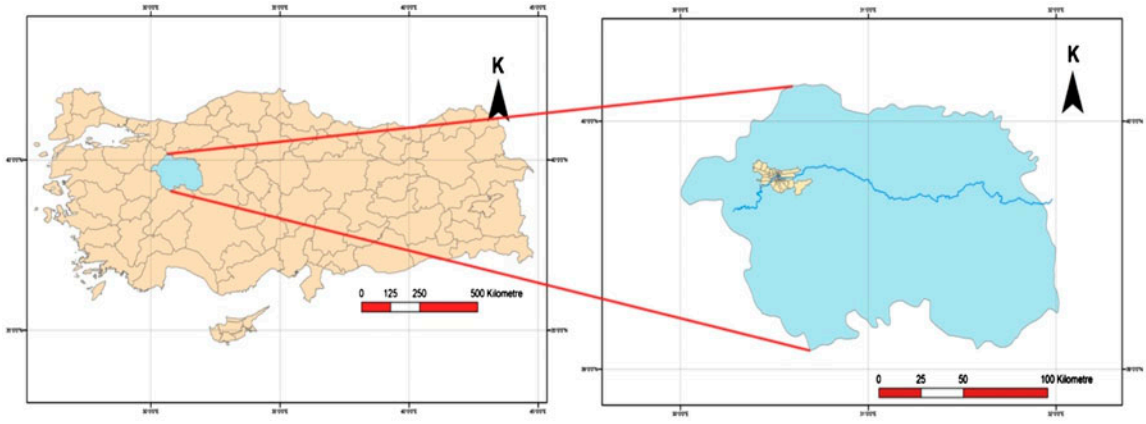

Fig. 1. Study area.

Table 1
Typical characteristics of raw PW

Parameter	Number of sample	Avr. value	Range	Std. dev.
pH	77	7.92	7.8–8.02	0.05
TOC (mg/L)	77	4.338	2.886–6.015	0.608
DOC (mg/L)	77	4.013	2.781–5.048	0.502
UV_{254} (1/cm)	77	0.076	0.047–0.106	0.016
Vis_{400} (1/cm)	77	0.009	0.001–0.019	0.005
Total alkalinity (mg/L)	36	258.86	179–300	21.69
Total P (mg/L)	21	0.980	0.580–1.50	0.260
Ortho-phosphate-P (mg/L)	36	0.76	0.17–1.5	0.37
Chlorophyll-a (mg/m^3)	20	7.820	3.37–18.98	4.150
Suspended solids (mg/L)	36	16.29	1–49	8.30
Turbidity (NTU)	36	13.460	5–45	7.98

30), Bigadic zeolite with a particle size range of 1.0–2.0 mm and a surface area of 22–28.40 m^2/g, and quartz with a particle size range of 1.0–2.0 mm and a surface area of 0.22 m^2/g were used.

Sulfuric acid (95–97%) (7664-93-9), sodium hydroxide (1310-73-2), hydrochloric acid (HCl) (7647-01-0), anhydrous Na_2SO_4 (7757-82-6), *n*-pentane (109–66-0), methyl tert-butyl ether (MTBE) (1634-04-4), and sodium bicarbonate (144-55-8) were procured from Merck; methanol (99%) (67-56-1) was obtained from Riedel de Haen; and sodium hypochlorite (7681-52-9) was obtained from Sigma-Aldrich.

2.3. Experimental setup

In this research, the three biofiltration columns were filled with three different materials: sand, zeolite, and GAC, respectively. The diameter and height of each column were 2.5 and 25.0 cm, respectively. Bench scale columns had 15 cm of filter media, and they were operated at 15- and 30-min empty bed contact time (EBCT) by connecting two columns in series (Fig. 2). The hydraulic loading rate of the columns was 0.6 m^3/m^2 h, and they were operated in up-flow mode using a peristaltic pump in parallel feeding (Heidolph Pumpdrive 5201).

Microorganisms grew on the surface of the filter media of the biofilter columns. The growth was established on the filter materials through the process of seeding with Eskisehir tap water by feeding over a period of 8 months. During that time, the materials were exposed to the microbial community present in the water, which contributed to a rapid initial colonization. After this period, columns were fed for 2 months with raw PW before the experimental study to acclimatize and establish biological activity. After these stages, samples were taken to see the DOC-removal results. All experiments were carried on at 20–22 ℃ (i.e. room temperature).

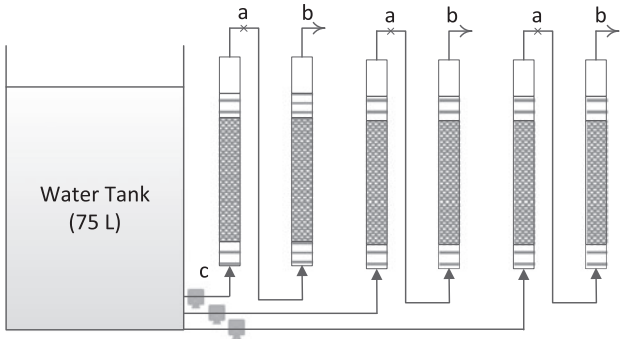

Fig. 2. Experimental schematic of laboratory-scale biofiltration system. (a) Sampling port (EBCT = 15 min), (b) sampling port (EBCT = 30 min), and (c) peristaltic pump.

2.4. Analytical procedures

Samples taken from the influent and effluent of the biofiltration columns were analyzed according to procedures described in Standard and EPA Methods.

In DOC analysis, samples were filtered through a 0.45-μm membrane filter, and the measurements were performed by the high-temperature combustion method in accordance with 5310 B [29] using a TOC-5000 analyzer (Shimadzu, Corp., Japan), which utilizes high-purity dry air as the carrier gas and is equipped with an auto sampler. The inorganic carbon was removed by acidifying the sample to pH values between 2 and 3 with 1.0 N HCl followed by sparging with CO_2-free air. pH measurements were taken with a WTW-pH meter, and pH arrangements were done by H_2SO_4 and NaOH. Thus, the measured dissolved carbon was equal to the DOC.

UV_{254} absorbance measurements were performed in accordance with Standard Method 5910 B [30] using a Hach-Lange Dr 5000 UV/Vis spectrophotometer at a wavelength of 254 nm with a 1-cm quartz cell. The samples were first filtered through a pre-washed 0.45-μm membrane filter to remove turbidity, which can interfere with this measurement.

Chlorination was accomplished in headspace-free 111-mL amber vials with Teflon-lined screw caps. Before chlorination, water samples' pH values were regulated by the addition of HCl or NaOH solution up to pH 7.0. A phosphate buffer solution was used to maintain a constant pH of 7.0. Preliminary chlorination experiments with varying Cl_2:DOC ratios were performed for all samples to provide the above range of chlorine residuals after 7 d of contact time. This was necessary because natural waters have different chlorine demands [31]. The appropriate chlorine dosage was determined for Cl_2:DOC ratios to be 3. A concentrated sodium hypochlorite dosing solution (5 mg mL^{-1}) was added to PW to obtain the free residual chlorine dose of 2 mg L^{-1}. The chlorinated samples were then incubated in a dark room for 7 d at 25°C. The free chlorine residuals of samples were measured by Standard Method 4500-Cl.C with a spectrophotometer (DR 5000, Hach-Lange), and residual chlorine was removed in the sample bottle using a sodium sulfite solution [32]. Then, THM and HAA species were analyzed.

THM concentrations were reported as total THMs (TTHMs) in μg/L. THM formation potential (THMFP) and its four fraction measurements (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) were determined in accordance with liquid–liquid extraction according to EPA Method 551.1 [33]. Calibration standards were prepared using the standard mixture procured from AccuStandard, USA. Firstly, the sample was poured into a glass vial with a polypropylene screw cap and TFE-faced septum. Then, *n*-pentane was added, and liquid–liquid extraction was performed.

Haloacetic acid formation potential (HAAFP) concentrations were determined using liquid–liquid extraction according to EPA Method 552 [34]. The sum of the mass concentration for the five HAA species (monochloro-, dichloro-, trichloro-, monobromo-, and dibromo-acetic acid) was reported as total HAAs (THAAs) in μg L^{-1}. Calibration standards were prepared using the standard mixture obtained from AccuStandard, USA. The procedure of acidic methanol etherification was used for HAA analysis in order to avoid the use of the toxic diazomethane.

THM and HAA samples were measured by a gas chromatograph (Agilent-6890 Series) with a micro electron capture detector and auto sampler. The capillary column (J&W Scientific DB-5.625, 30 m × 0.25 mm I.D. × 0.25 μm film thicknesses) was used in splitless injection mode. The system was supported by Agilent ChemStation software. Ultra-high-purity helium as the carrier gas and nitrogen as the make-up gas were used for the gas chromatography. The detection limits for the THM and HAA species were about 0.5–1.5 μg/L.

To determine the limit of detection (LOD) and limit of quantification (LOQ) values of each DBP, the standard solution at targeted level was injected into the chromatographic system, and the LOD and LOQ values were predicted from the signal to noise (S/N) ratio data. LOD (LOQ) values were 0.1864 (0.6214) μg/L, 0.0528 (0.1762) μg/L, 0.0558 (0.1860) μg/L, and 0.1427 (0.4756) μg/L for the 16 μg/L concentration of chloroform, bromodichloromethane, dibromochloromethane, bromoform, respectively. LOD (LOQ) values were 0.0138 (0.0459) μg/L for the 7.5 μg/L, 0.0152 (0.0508) μg/L for the 5 μg/L, 0.0102 (0.0341) μg/L for the 7.5 μg/L,

0.0190 (0.0.0635) μg/L for the 2.5 μg/L, and 0.0264 (0.0881) μg/L for the 2.5 μg/L concentration of monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid, respectively.

3. Results

The successful NOM elimination of the biofilter columns was observed by measurements of the influent and effluent DOC concentrations. Fig. 3(a)–(c) shows DOC-removal efficiencies at 15 and 30-min EBCT of biofilter columns filled with GAC, sand, and zeolite materials, respectively. Because the DOC concentrations in the effluent of the biofilter columns were always lower than those in the influent and almost constant, apparent steady-state DOC removal was approached after 1100 Bed Volume operation.

Biologically activated GAC could reduce the average influent DOC concentration from 4.01 mg/L to an effluent DOC concentration of 1.43 mg/L. The percent removals of DOC were about 50 and 65% for 15- and 30-min in GAC columns, respectively. Thus, by increasing the contact time from 15 to 30 min, the DOC-removal rate could be increased by about 15%.

Fig. 3(b) and (c) shows the DOC-removal efficiencies from the sand and zeolite filter columns at different contact times. When the sand and zeolite filter column contact time was increased from 15 to 30 min, there was no effect on DOC removal. Biological activity on the sand and zeolite material may have interfered with DOC-removal values, and it was almost the same as 25%. Even though EBCT was increased from 15 to 30 min, there was no increase in DOC removal. In the first of the two columns with a 15-min EBCT, colonized organisms easily consumed biodegradable organics or rapid BDOC, but the second column with a 30-min EBCT did not have enough rapid BDOC, and therefore, no extra removal was observed for raw PW.

The percent removals of the GAC, sand, and zeolite biofilter columns in terms of DOC at 30 min are compared in Fig. 4.

Results of the columns showed that the GAC column had more effective DOC removal than the sand and zeolite columns. Sand and zeolite have

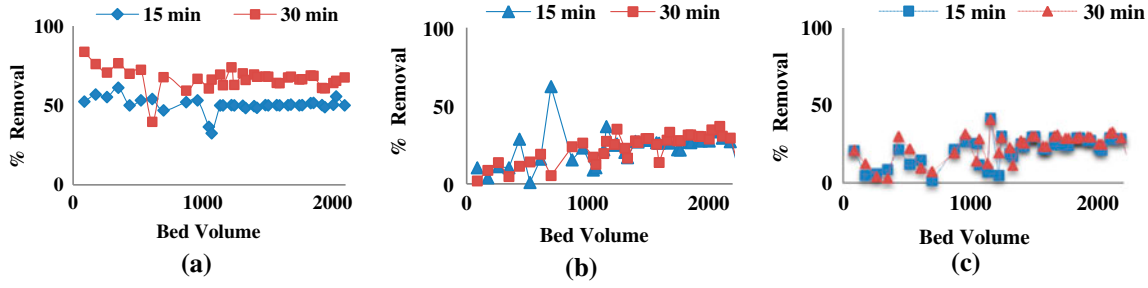

Fig. 3. DOC-removal efficiencies at 15- and 30-min EBCT. (a) GAC, (b) sand, and (c) zeolite.

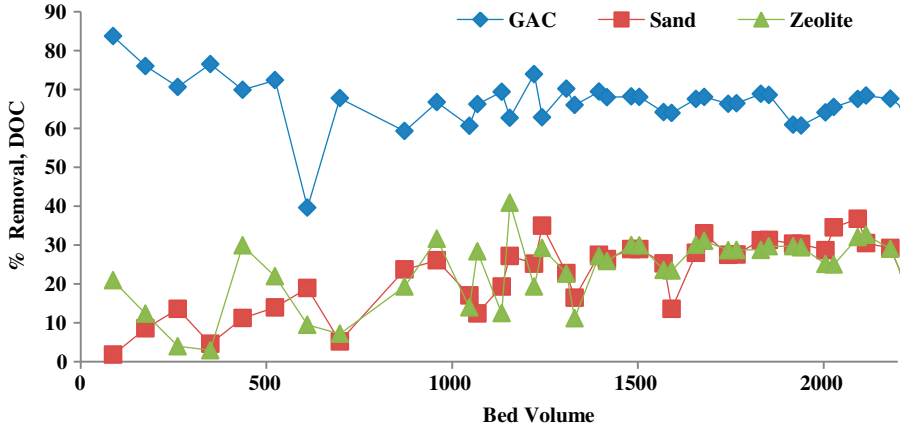

Fig. 4. DOC-removal efficiencies of GAC, sand, and natural zeolite column effluents at 30-min EBCT.

lower surface area and porosity when compared with GAC, and they do not have organic adsorption capacity. Some parts of organics, such as those that are not easily biodegradable, can be adsorbed on the bioregenerated GAC surface site, and then organisms use them later. Persson et al. [35] used GAC, expanded clay as filter material for water treatment and GAC had a greater microbial biomass densities and higher DOC removal. On the other study, direct comparison among GAC, sand and anthracite showed that the GAC biofilter gave best performance for DOC removal [36]. Higher biomass concentrations accumulate on GAC media, which may be a result of GAC's rough surface. The rough surface and macrospores provide suitable sites on the GAC to protect bacteria from shear forces during filter operation and backwashing, which causes denser colonization of bacteria to develop to provide more organic matter utilization [24,25].

Another parameter that is used for quantifying NOM removal in biofiltration processes is UV absorbance at 254 nm. UV absorbance provides information about the composition of NOM and is correlated with the aromaticity content of dissolved organic matter according to Weishaar et al. [37]. As a result, monitoring of the UV absorbance of NOM surrogates in filter effluents during biofiltration processes shows changes in NOM characteristics. Since the UV absorbance of a water sample is proportionally correlated with its NOM amount, UV absorbance can be correlated with the formation of DBPs when water is chlorinated [38]. The percent removals of the effluent results of UV_{254} absorbance of GAC, sand, and zeolite filters at 30-min EBCT in this experimental study are shown in Fig. 5.

UV_{254} absorbance values were higher in sand and zeolite filter column effluents than in GAC filter column effluents. GAC outperformed sand in removing NOM and consequently decreasing UV_{254} absorbance. The average UV_{254} removal efficiencies were 54% in the GAC column and about 4.5% in the sand and zeolite columns.

The specific UV absorbance (SUVA) at 254 nm also provides an evaluation of the reactivity of NOM. The value is calculated by dividing UV_{254} absorbance (1/m) by DOC concentration (mg/L), and it helps to make inferences about the reactivity of NOM in natural water. If a water source has a high SUVA value (>4 L/mg m), it implies that the organic matter is largely composed of hydrophobic dissolved organic materials with a higher aromatic structure. On the contrary, a low SUVA value (<2 L/mg m) indicates that water contains mainly organic compounds that are hydrophilic with lower aromaticity [39]. The SUVA value of raw PW is about 1.85 L/mg m (<2 L/mg m), which implies that NOM has hydrophilic characteristics [36]. Water treatment plants normally enhance coagulation, the most economical and conventional NOM-removal technique, which mostly removes hydrophobic NOM fractions. However, hydrophilic compounds promote the formation of DBPs, especially in natural water with low SUVA values.

Thus, water treatment should be optimized in order to remove both hydrophobic and hydrophilic organic compounds that can mitigate the formation of DBPs. Due to water quality problems and stricter regulations for drinking water treatment, there is a need for more efficient yet economical methods for the removal of NOM.

It was expected that the formation potentials of TTHM and THAA values would be lower effluents of the GAC columns. The formation potential concentrations of TTHM were measured using the effluent water of biofilter columns after 30-min contact time. TTHM percentage reductions of GAC, sand, and zeolite filters are compared in Fig. 6.

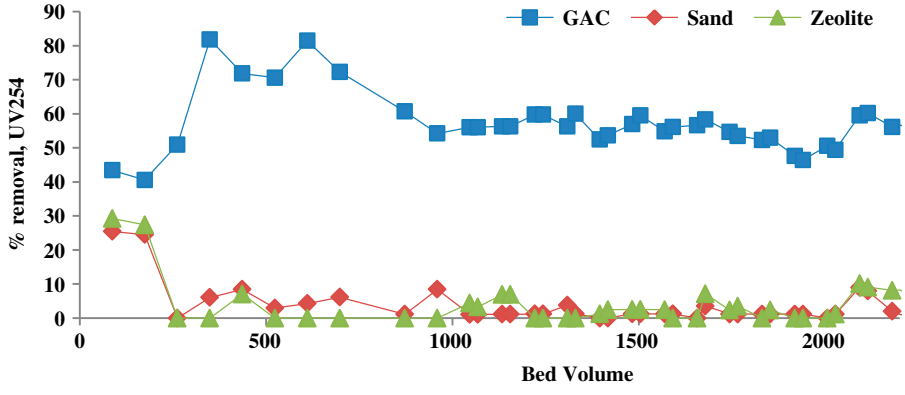

Fig. 5. UV_{254} removal efficiencies of GAC, sand, and natural zeolite column effluents at 30-min EBCT.

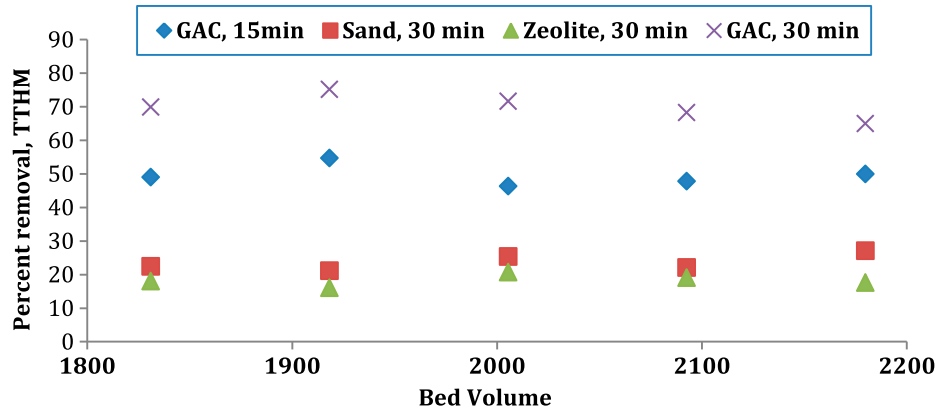

Fig. 6. Formation potential removal of TTHMs of GAC, natural zeolite, and sand biofilter columns.

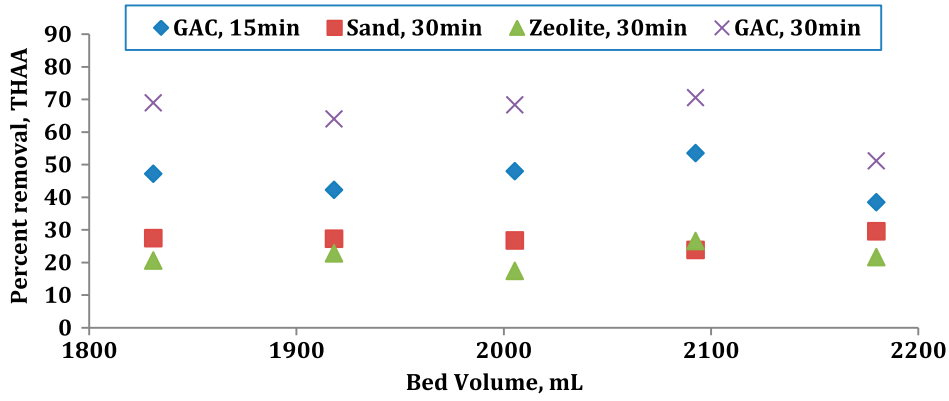

Fig. 7. Formation potential removal of THAAs of GAC, natural zeolite, and sand biofilter columns.

GAC filters exhibited higher TTHM-removal performance than sand and zeolite filters comparing average removal efficiencies (69, 24, and 18%, respectively). The GAC biofilter reduced the TTHM value to 58.55 μg/L, and the sand biofilter reduced the TTHM value to 113.91 from 153.65 μg/L. GAC has higher porosity, providing a better living surface for microorganisms than sand, and another issue is its adsorption capacity for organic materials. Microorganisms might be effective in terms of bioregeneration on GAC surfaces, so this also increases the efficiency of GAC. Therefore, GAC acts as a better media for TTHM-precursor removal than sand and zeolite for both biological and adsorption mechanisms.

Reductions in the HAAFP values of biofilter columns' effluent waters are compared in Fig. 7 as percentages at 30-min contact time. The average formation potential of THAA reduction was obtained using GAC at 65%, and it was a more effective material than sand and zeolite (27 and 21% at the same EBCT). GAC filters provide better media for organic precursors to be removed through either adsorption or biological processes, as similar results were found for the formation potential of THAA (Kim and Kang [11]). The GAC biofilter reduced the THAA value to 116 μg/L, the sand biofilter reduced the HAAFP value to 242 μg/L, and the zeolite biofilter reduced the value to 281 from 341 μg/L.

4. Conclusions

A significant amount of DOC in the form of hydrophilic fractions (precursors of DBPs (THM and HAA)) was well removed through biofiltration from raw PW from Turkey. As expected, the formation potentials of TTHM and THAA concentrations were lower in GAC biofilter column effluents than in sand and natural zeolite biofilter column effluents. As an important result of this study, formation potentials of TTHM were reduced by 48 and 68% by only the GAC

biofiltration column at 15- and 30-min EBCT, respectively. In addition, the removal efficiencies of THAA formation were 46 and 64% by only the GAC biofiltration column at 15 and 30 min, respectively.

Biofiltration can be an attractive unit process, because the reduction of biodegradable DOC in water resources can provide positive results. These include decreasing chlorine requirements and thus chlorinated DBP formation, reducing taste and odor problems, preventing biofilm growth in water distribution systems, and ensuring better water quality.

Because regulations for drinking water treatment are being improved and applied to increase water quality and protect public health, more efficient yet economical methods for the removal of NOM are needed. To meet this need, biologically active filter processes using both hydrophobic and hydrophilic organic compounds should be established after classic treatment (coagulation/sedimentation) processes.

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