



Enhancing the adsorption of disinfection by-products onto activated carbon using TiO₂ nanoparticles

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Received: 01 November 2018; Revised: 10 May 2019; Accepted: 11 May 2019

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Citation: Moustafa, R.; Hesham, A. *Int. J. Chem. Technol.* 2019, 3 (1), 67-71.

ABSTRACT

The removal of contaminants from consumable waters by the traditional water treatment techniques is highly difficult. Disinfection of water alludes to the inactivation or pulverization of unsafe living pathogenic beings, which living in the water. Occurrence of disinfection by products (DBPs) during disinfection normally demonstrates lethal impacts on human health. Granular activated carbon (GAC) has the oldest history of decreasing of organic matters, but its role is reducing by time. TiO₂ is used to accelerate the removal of the DBPs. TiO₂ nanoparticles have good adsorption phenomena on the removal of those organic compounds at various pHs and temperatures and give good results. This study proved that TiO₂ nanoparticles enhanced the efficiency of GAC to remove DBPs from water. While the elimination of trihalomethanes (THMs), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) using 0.5 g of GAC was determined as 61.7, 69.8 and 83.2% respectively, the elimination of them by 0.1 g of TiO₂ nanoparticles:GAC (1:1) was estimated as 100, 96 and 100%, respectively.

Keywords: Disinfection by-products, drinking water, nanoparticles TiO₂, THMs.

TiO₂ nanopartikülleri kullanılarak dezenfeksiyon yan ürünlerinin aktif karbon üzerine adsorpsiyonunun artırılması

ÖZ

Geleneksel su arıtma teknikleri ile kirletici maddelerin tüketilebilir suların uzaklaştırılması oldukça zordur. Suyun dezenfekte edilmesi, suda yaşayan, güvensiz yaşayan patojenik varlıkların etkisizleştirilmesine veya toz haline getirilmesine yol açar. Dezenfeksiyon sırasında dezenfeksiyon yan ürünlerin (DBP'lerin) oluşması normalde insan sağlığı üzerinde ölümcül etkiler göstermektedir. Granül aktif karbon (GAC) organik maddeleri azaltma da en eski geçmişine sahiptir, ancak onun rolü zamanla azalmaktadır. TiO₂, DBP'lerin uzaklaştırılmasını hızlandırmak için kullanılmaktadır. TiO₂ nanopartikülleri, çeşitli pH'larda ve sıcaklıklarda bu organik bileşiklerin uzaklaştırılmasında iyi adsorpsiyon olgusuna sahiptir ve iyi sonuçlar vermektedir. Bu çalışma, TiO₂ nanopartiküllerinin DBP'leri sudan uzaklaştırmak için GAC'nin etkinliğini arttırdığını ispatlamıştır. 0.5 g GAC kullanılarak trihalometanlar (THM'ler), dikloroasetik asit (DCAA) ve trikloroasetik asit (TCAA)'in eliminasyonu sırasıyla % 61.7, 69.8 ve 83.2 olarak belirlenirken, bunların 0.1 g TiO₂ nanopartikülleri:GAC (1:1) ile giderilmesi sırasıyla % 100, 96 ve % 100 olarak belirlenmiştir.

Anahtar Kelimeler: Dezenfeksiyon yan ürünler, içme suyu, nanopartiküller TiO₂, THMs.

1. INTRODUCTION

The disinfection procedure of drinking water plans to execute as well as inactivate pathogens may have the unintended outcome of framing disinfection by-products (DBPs).¹ At the point when the disinfectant free chlorine is utilized, more than 500 disinfections by-products (DBPs) have been recognized. Trihalomethanes (THMs)

and haloacetic acids (HAAs) account for a significant portion of the total DBPs formed in the reaction of free chlorine with natural organic matter (NOM) in water and are related with human health concerns.² They are directed in numerous nations according to world health organization (WHO) regulation. DBP formation can be overseen in metropolitan drinking water frameworks through antecedent expulsion and modification of disin-

fection parameters.³ Disinfection parameters that may affect DBP formation include concentration and type of disinfectant, pH, temperature and contact time. DBP precursors, especially those of THMs and HAAs, include humics (hydrophobic) and other compounds with UV254 absorbance.⁴ Upgraded coagulation is the best available technique that is economically for removal of DBP precursors (hydrophobic NOM), where coagulation parameters are acclimated to accomplish greatest DBP precursor removal.⁵ Advanced oxidation processes combining ozone, H₂O₂, and/or UV light are also emerging as effective ways to degrade contaminants in water including DBP precursors.⁶ TiO₂ nanomaterial is promising with its high potential and outstanding performance in photocatalytic environmental applications TiO₂ photo catalysis has been shown to reduce THM and HAA formation by degrading DBP precursors and also by providing disinfection capability.⁵ TiO₂ absorbs light and dissipates it through the excitation of an electron to its conduction band, creating what is termed an electron/hole pair.⁷ The electrons and holes can then directly degrade NOM in the water or can create reactive oxygen species (ROS) such as the hydroxyl and superoxide radicals that can then degrade NOM.⁸ TiO₂ requires low chemical and energy inputs; needing only UV light and the TiO₂ catalyst. Elimination of NOM and DBPs from drinking water using photo catalytically regenerable nanoscale adsorbents has been developed by Stephanie and others during 2019.⁹

2. EXPERIMENTAL

2.1. Materials

Pentane 99 % – sodium thiosulfate anhydrous 99% assay–sulfuric acid 99%. Methyl tert-butyl ether (MTBE) 99%-Ultra pure water. All chemicals, reagents and reference materials of THM, HAAs, and inorganic chemicals used were of high purity grade. They were obtained from Acustander Co., Riedel Co, Sigma Aldrich Co. and Fluka Co. GAC purchased from Calgon Carbon Corporation, particle sizes of 1.18–2.36 mm – Mexico, TiO₂ nano particles purchased from Reinste Co. -India, 99+%, 20 nm. Activated carbon loaded by TiO₂ nanoparticles were prepared by direct mixing in (1:1) ratio.

2.2. Methods

2.2.1. Determination of Trihalomethane (THM)

The THM species (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) were measured according to EPA method 551^{10,11}, sample was collected in 40 ml brown glass bottle with screw cap, and then 15 ml was discarded from each sample bottle. A micro extraction technique was

used, for each bottle, 4 ml pentane were added, then the Sample bottle was shaken for 1 minute, and left for 10 minutes. About 1 ml from the organic upper layer was transfer into autosampler vial for injection using gas chromatography Gas chromatography Varian CP- 3800, split/spitless injector, Electron Captures Detector, CP-8400 Autosampler, and Galaxie Chromatography Data System for acquisition and data analysis have Primary column - CP SIL 5 CB 30 m X 0.32 mm, 0.25µm film thickness.¹² While the carrier gas was He of 99.999 % purity. Gas chromatography was performed under the following condition: - Inlet condition: split mode, initial temperature 250°C, pressure 33 psi, split ratio 20:100. The instrument was calibrated by using THM standards at 8, 16, 32, 48 and 64 µg l⁻¹ to construct calibration curve.

2.2.2. Determination of Haloacetic Acids (HAAs)

A micro extraction technique with methyl tert-butyl ether (MTBE) as the extraction solvent, the HAAs species (Dichloroacetic acid, Trichloroacetic acid) were measured according to EPA method 552.2, and GC chromatography was performed under the following condition: - Inlet condition: split mode, initial temperature 35°C, pressure 33 psi, split ratio 100:20 and Carrier gas type Helium.^{13,14} The instrument was calibrated by using HAA standards at 8, 16, 32, 48 and 64 µg l⁻¹ to construct calibration curve.

3. RESULTS AND DISCUSSION

Standard THM have been prepared equal concentration from all (Chloroform, bromodichloromethane, dibromochloromethane, bromoform), taken suitable volume as (100 ml) treated with granular activated carbon (GAC), shacking 20 min as duration at pH 6.9 and temperature 25°C, filtrated by micro filter have pore size 0.47 µm, extraction and injection on the system which determine DBPs, the removal of DBPs from treated water by using activated carbon in bench scale experiment found that an increase of GAC dosage have a significant in DBPs removal.

GAC has been used to adsorb the DBPs from water using 0.025, 0.05, 0.1 and 0.5 g. as different dose of adsorbent. The removal of THMs was 18.4, 26.3, 36.5 and 61.7% respectively while the removal of DCAA was 25.3, 31.7, 50.5 and 69.8% respectively and the removal of TCAA was 27.8, 43.6, 58.9 and 83.2% as shown in Table 1, Figures 1, 2 and 3 respectively.

Then 1:1 mixture of GAC and TiO₂ nanoparticles has been used to adsorb the DBPs from water using 0.02, 0.04, 0.06 and 0.1 g. as different dose of adsorbent, the results were as shown in Table 2. The removal of THMs was 34.8, 50.5, 83.3 and 100% respectively as shown in Figure 4, while the removal of DCAA was 27.8, 40.2, 63 and 96% respectively as shown in Figure 5, and the

Table 1. Removal % of DBPs using GAC

GAC (g)	THMs µg l ⁻¹	DCAA µg l ⁻¹	TCAA µg l ⁻¹	THMs Removal %	DCAA Removal %	TCAA Removal %
0	63	28.1	28	0.0	0.0	0.0
0.025	51.4	21	20.22	18.4	25.3	27.8
0.05	46.4	19.2	15.8	26.3	31.7	43.6
0.1	40	13.9	11.5	36.5	50.5	58.9
0.5	24.1	8.5	4.7	61.7	69.8	83.2

Table 2. Removal % of DBPs using GAC with TiO₂ nanoparticles

(1:1) GAC + TiO ₂ g.	THMs µg l ⁻¹	DCAA µg l ⁻¹	TCAA µg l ⁻¹	THMs Removal %	DCAA Removal %	TCAA Removal %
0	63	28.1	27.8	0.0	0.0	0.0
0.02	41.1	20.3	18.9	34.8	27.8	32.0
0.04	31.2	16.8	14.16	50.5	40.2	49.1
0.06	10.5	10.4	8.45	83.3	63.0	69.6
0.1	0	1.11	0	100.0	96.0	100.0

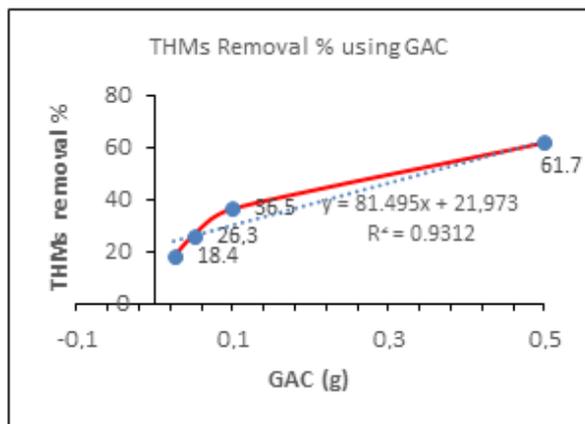


Figure 1. Removal % of THMs using GAC.

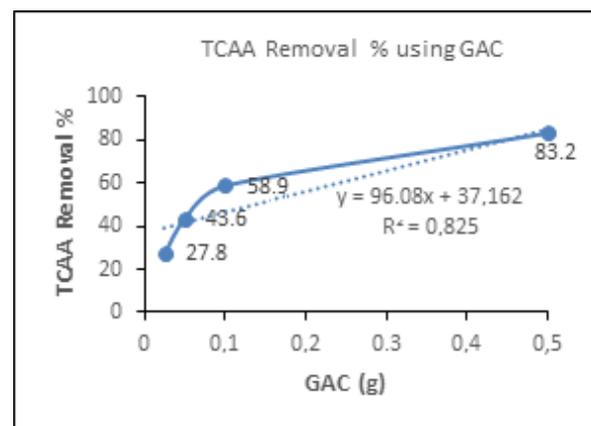


Figure 3. Removal % of TCAA using GAC.

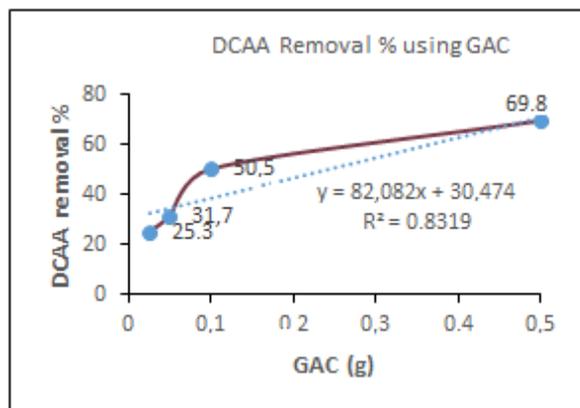


Figure 2. Removal % of DCAA using GAC.

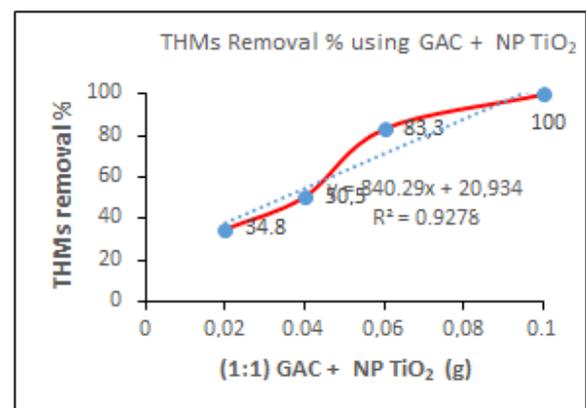


Figure 4. Removal % of THMs using (1:1) GAC + NP TiO₂.

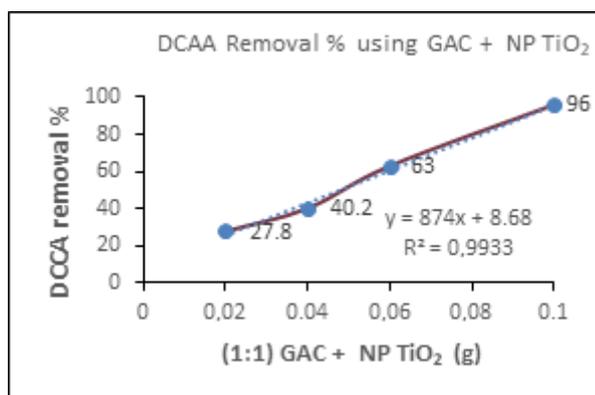


Figure 5. Removal % of DCAA using (1:1) GAC + NP TiO₂.

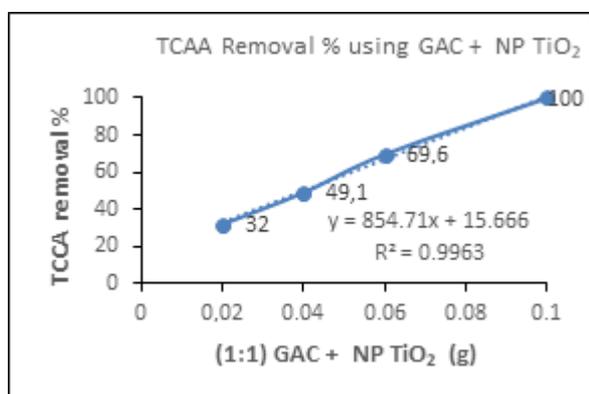


Figure 6. Removal % of TCAA using (1:1) GAC + NP TiO₂.

removal of TCAA was 32, 49.1, 69.6 and 100% respectively as shown in Figure 6. It is very clear that TiO₂ nanoparticles improved the efficacy of GAC in DBPs adsorption, this enhancement of the GAC activity will reduce the required QTY of GAC to adsorb the pollutants from the water.

4. CONCLUSIONS

The study proved that addition of TiO₂ nanoparticles improved the efficiency of the GAC to remove DBPs from water. The maximum removal of THMs, DCAA and TCAA was 61.7, 69.8 and 83.2% respectively using 0.5 g of GAC. The full removal of THMs and THAA was achieved using 0.1 g. (1:1) of GAC:TiO₂ nanoparticles, while the same QTY was achieved 96% removal of DCAA. This due to the properties of TiO₂ and its Photocatalysis / surface phenomenon, which consider a critical step in intervening in the effectiveness of photodegradation and adsorption of pollutants on the photocatalyst surface. Even the results of DBPs removal using 0.1 g. (1:1) of GAC:TiO₂ nanoparticles was very

promising we recommend further investigation about TiO₂ nanoparticles residues and its toxicity, also risk assessment for overall process for large scale applications.

Conflict of interests

Authors declare that there is no a conflict of interest with any person, institute, company, etc.

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