

Removal of Natural Organic Matter by Using Original and Chemically Modified Adsorbents

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Abstract - The aim of this study is to investigate natural organic matter (NOM) removals in drinking water with using original and chemically modified activated carbons (ACs). ACs were modified by nitric acid and sulfonic acid. The result of modification studies revealed that both acids were effective in changing the structural and chemical properties of ACs. Kinetics and isotherm experiments were performed with various adsorbent dosages. The maximum NOM removal for original AC, nitric acid and sulfonic acid modified ACs were 66%, 48% and 80%, respectively. Although NOM removal performance decreased after nitric acid modification, it significantly enhanced for sulfonic acid modified AC compared to original AC. The maximum adsorption capacity (q_m) was obtained 221.43 mg/g for sulfonic acid modified AC. The experimental isotherm data were best described by the Freundlich isotherm model with R^2 value of 0.99.

Keywords: Activated Carbon, Adsorption, Disinfection By-products, Drinking Water Treatment, Isotherm, Modification, Natural Organic Matter.

1. Introduction

Natural organic matter (NOM) is a non-homogeneous mixture of complex organic compounds naturally present in drinking water supplies [1]. NOM consists of humic substances, hydrophilic acids, proteins, lipids, carbohydrates, carboxylic acids, amino acids, and hydrocarbons including aromatic, aliphatic, phenolic, functional groups [2, 3]. Although NOM does not have direct health effects, the presence of NOM in water is associated with many problems related to water quality and performance of treatment processes [4]. Some of NOM-related issues are i) high demand of coagulant/disinfectant; 2) shorter filter run times 3) membrane fouling 4) regulated and non-regulated disinfection by-products (DBPs) formation 5) bacterial growth and biofilm formation in drinking water distribution systems 6) carrier for hydrophobic organic (pesticides) and metals [1,2]. DBPs formation is the major problem in the presence of NOM during treatment of drinking water because they are known possible carcinogenic and mutagenic compounds [5]. Because of their potential adverse effects on human health, the United States Environmental Protection Agency (USEPA) has set thresholds for certain DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs) in drinking water [6]. The most effective approach to reduce and control for DBPs formation is to remove precursors (i.e. NOM) prior to disinfection.

NOM removal from waters is a compelling issue all around the world. The adsorption process, is generally considered as one of the best water treatment technologies because, viable and economical methods for NOM removal due to its high efficiency and no harmful by-product formation [7, 8-9]. Activated carbon (AC) adsorption, a process recommended by the EPA, is one of the most effective NOM treatment process. AC contains well developed internal pore structure and functional groups and/or atoms as chemically bonded to the structure [10]. Particularly, powdered activated carbon (PAC) is being investigated as an adsorbent on its own, to be added as needed before, during and after coagulation to remove DOM with higher performance [11]. Various modification methods highly effective on the adsorption properties of activated carbons have been developed that changes the amount and diversity of the surface functional groups [12]. Chemical modification provides important advantages such as being able to be carried out with controlled process in only one step at lower temperatures, providing higher surface area in ACs and improving micro- and meso-porosity distribution [12-13]. Therefore, there is a need to investigate the development of new and existing modification techniques to increase the removal efficiency

of AC used for NOM removal in water treatment. In this context, the main objective of this study is to investigate NOM removal performances of chemically modified ACs in drinking water.

2. Materials and Method

Figure 1 shows the experimental procedures were conducted in three phases. Commercial AC Puriss in PAC form (Sigma-Aldrich) was selected to investigate the chemical modification performance in the study. Firstly, modification studies of AC Puriss were carried out with sulfonic acid and nitric acid. All chemicals were of either analytical or reagent grade. Secondly, physicochemical characterization of ACs in terms of specific surface area, point of zero charge (pH_{PZC}) and FTIR analysis were determined. pH_{PZC} values of the adsorbents were determined through a pH equilibration method [14]. Specific surface area of samples was determined using a Micromeritics Gemini V analyzer employing nitrogen adsorption at 77 K. Brunauer–Emmett–Teller (BET) equation was used to calculate surface areas from nitrogen adsorption isotherms. FTIR analyzes were performed with Perkin Elmer 400 Ft-IR/FT-FIR spectrometer in the wavelength range of 400-4000 cm^{-1} .

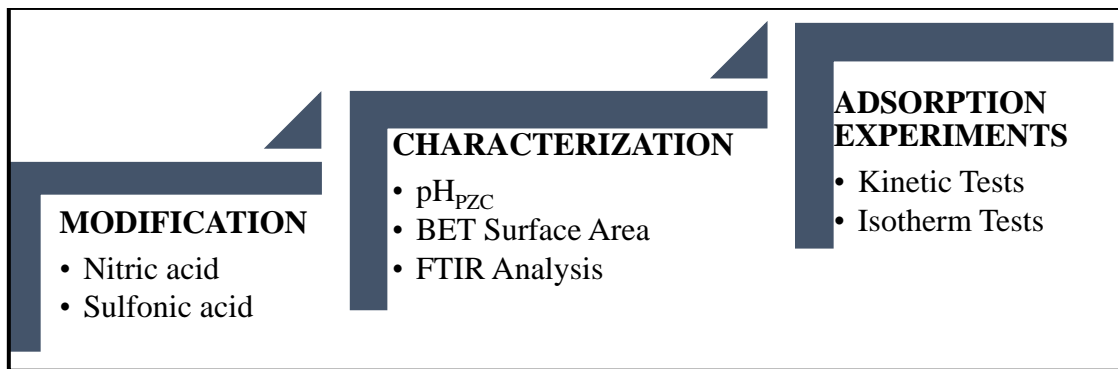


Fig. 1: Experimental Procedure Flow Chart

Finally, adsorption experiments were carried out in water samples collected from the influent of the coagulation unit in Konya Drinking Water Treatment Plant (Turkey). Original AC Puriss and acid modified AC Puriss were used in kinetic and isotherm tests. Kinetic and isotherm tests were performed employing bottle-point method in completely mixed batch reactors. In all experiments, water samples were adjusted to pH value of 7 ± 0.1 by either H_2SO_4 or NaOH solutions without any buffer. Kinetic experiments were tested for 2, 4, 8, 12, 24, 36, 48, 72, and 96 hours at constant adsorbent doses of 300 mg/L. Varied adsorbent doses of 10 mg/L - 600 mg/L at a mixing speed of 100 rpm were employed in isotherm experiments during required the contact time to reach equilibrium condition (72 hours) which was determined previously in kinetic test. After each contact period, samples were filtered using 0.45 μm PES filter paper to separate the adsorbent particles from the water phase. The filter papers were prewashed with distilled water (500 mL) before filtration to prevent possible leaching from filter paper. In order to evaluate NOM removal performance of ACs, supernatant was analyzed for DOC and UV_{254} absorbance. UV absorbance values (in triplicate) were measured at 254 nm using a UV-visible spectrophotometer (UV1700, Shimadzu). DOC content was determined in the TOC-L CPH (Shimadzu) instrument according to the high temperature combustion method (Standard Method 5310B).

3. Results/Discussion

3.1. Characterization of Original and Modified AC

In this study, removal performance of NOM by original and chemically modified AC adsorbent in drinking water source was investigated. The physicochemical characterizations of original and modified ACs were evaluated to determine the effect on structure of ACs. Table 1 shows the surface area and pH_{PZC} values of adsorbents. A significant increase in surface area was observed as a result of the original AC Puriss after modification. Especially for sulfonic acid modification, the surface area increased from 273.56 m^2/g to 868.48 m^2/g . The surface chemistry of activated carbons is characterized by their neutral charge point, acid and base neutralization capacities. Above the zero-charge point, the adsorbent is negatively charged, and below that, the adsorbent is positively charged. The charge of adsorbent

affects the adsorbate equilibrium between water and adsorbent phases and pollutant adsorption capacity of adsorbent [15]. The pH_{PZC} values of AC Puriss were determined as 7.09, 2.92 and 2.95 for original, nitric acid and sulfonic acid modifications, respectively. The decrease in pH_{PZC} values is attributed to the decrease in weak functional groups on the surface of activated carbons, the increase in oxygen-containing functional groups and surface acidic groups [16, 17]. FTIR analysis showed that the 3793 cm^{-1} band in the original AC Puriss disappeared and the 3564 cm^{-1} band peaked as a result of modification with nitric acid. The result of the modification of sulfonic acid, 1993.6 cm^{-1} band was formed different from the original AC Puriss.

Table 1: Some physicochemical characterization properties of adsorbents

Adsorbents	Surface Area S_{BET}^{\dagger} (m^2/g)	pH_{PZC}^*
Original AC	273.56	7.09
Nitric acid modification	822.48	2.92
Sulfonic acid modification	868.48	2.95

$^{\dagger}S_{\text{BET}}$: Surface area calculated by Brunauer-Emmett-Teller theory * pH_{PZC} : point of zero charge.

3.2. NOM Adsorption with Original and Modified AC

The results of kinetic experiments of original, nitric and sulfonic acid modified ACs are given in Figure 2. DOC removal efficiencies (%) as a result of the determined contact times are given in Figure 2. As it is shown in the figure, kinetic experiments results indicated that no more statistically significant adsorption of NOM (as measured by DOC) occurs after 48 h of reaction. Kinetics data for the removal of NOM were obtained and were best fitted by the pseudo-second-order model. The highest capacity is observed as 8 mg/g for sulfonic acid modified AC regarding to kinetic experimental results.

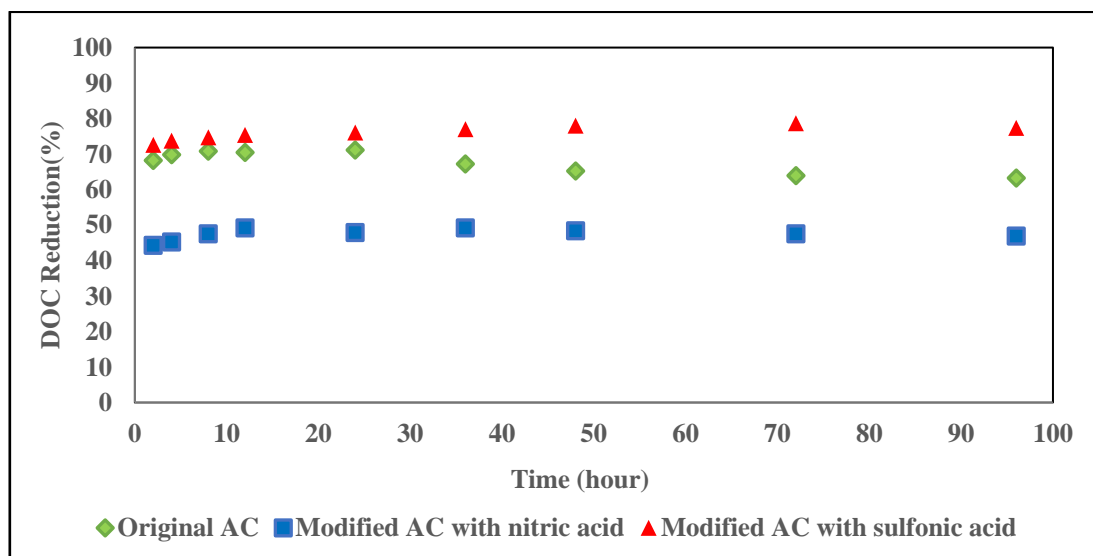


Fig. 2: Adsorption kinetics of NOM with original and modified ACs

Although the adsorbents reached equilibrium around 48 hours in kinetic experiments, 72 hours was chosen in isotherm experiments in order not to limit the contact time of adsorbents to reach equilibrium and also to compare with the studies in the literature. Figure 3 shows the original and modified AC Puriss UV_{254} absorbance reduction (A) and DOC removal efficiencies (B) in the water samples after 72 hours of contact time. UV_{254} absorbance removal performances revealed that the original AC and sulfonic acid modified ACs showed similar trends. In general, UV_{254} absorbance removal performance of nitric acid modified AC was observed to be lower than original and sulfonic acid modified ACs. The maximum NOM removal for original AC, nitric acid and sulfonic acid modified ACs was 66%, 48% and 80% after 72 hours of contact time,

respectively. NOM removals were observed with a decrease in nitric acid modified AC compared with original AC to NOM removal, but significantly in sulfonic acid modified AC.

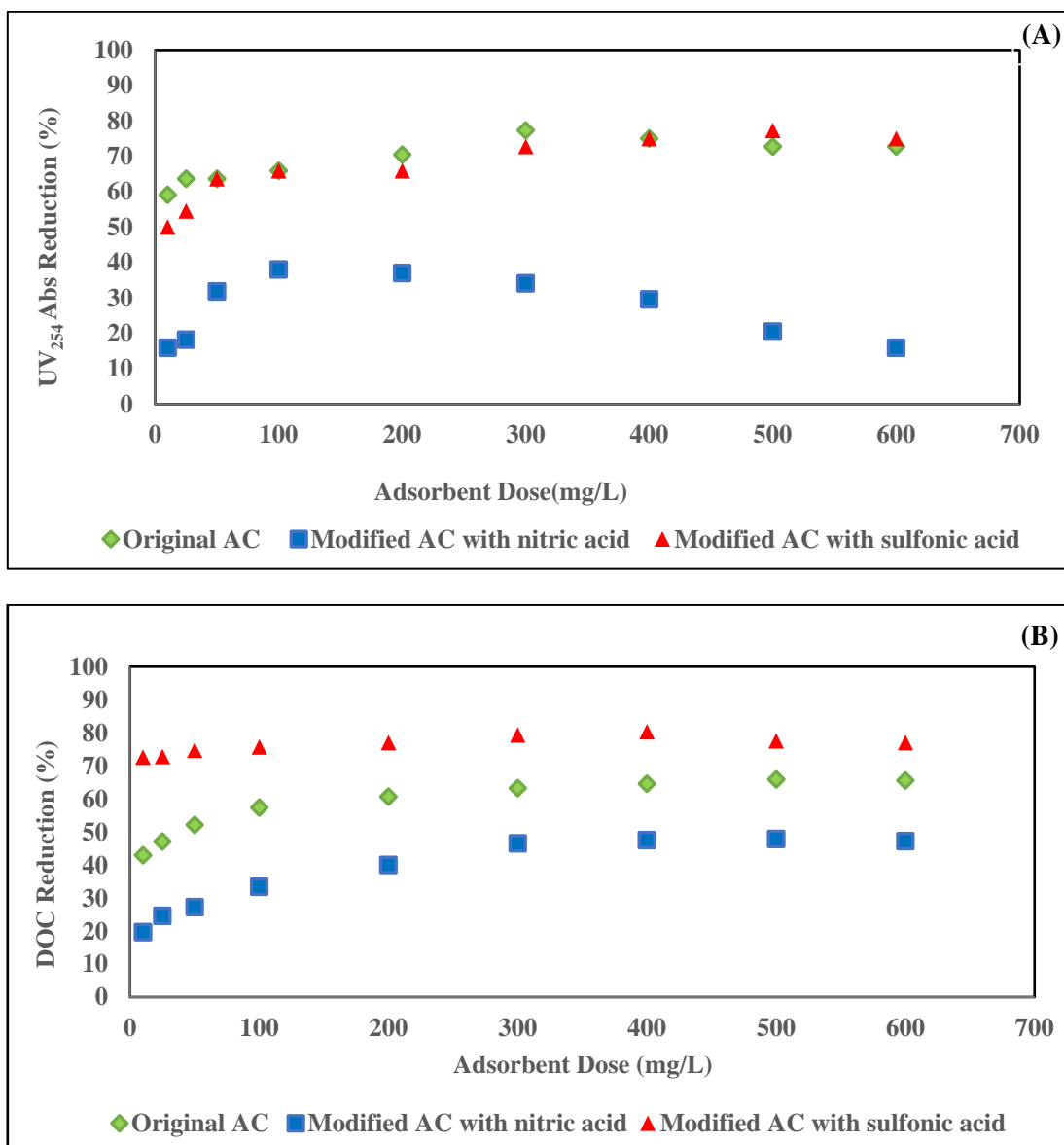


Fig. 3: Adsorption of NOM by original and modified ACs on UV₂₅₄ absorbance reductions (A) and DOC reductions (B)

The modified Freundlich model (normalized to adsorbent dose) (1) was employed to analyze the adsorption isotherm data:

$$q_e = K_F \cdot (C_e/D)^n \quad (1)$$

where, q_e is the amount adsorbed at equilibrium (normalized to adsorbent mass) C_e is the equilibrium solution phase concentration, K_F is the Freundlich parameter for a hetero disperse system, and the exponential term, n , is related to the magnitude of the adsorption driving force and to the distribution of the energy sites on the adsorbent [18].

The dose-normalized K_F , n , R^2 and q_e values of the original and modified activated carbons are shown in Table 2. The experimental isotherm data were best described by the Freundlich isotherm model as is evident from the high R^2 value of 0.99. Freundlich logarithmic term (n); while it increased as a result of modification with nitric acid, it decreased as a result of modification with sulfonic acid. This decrease is indicative of a more heterogeneous adsorbent surface formation in terms of energy. Freundlich capacity parameter (K_F) (based on adsorbent mass) is 3.71(mg DOC/g carbon) $1-n$ and it is highest in sulfonic acid modified AC adsorbent. Freundlich logarithmic term (n) values for original AC, modified ACs with nitric acid and sulfonic acid were calculated as 1.27, 1.46 and 1.09, respectively. The adsorption capacity (q_m) obtained was 3.92–221.43 mg/g for AC modified with sulfonic acid.

Table 2: Freundlich isotherm parameters of original and modified AC Puriss adsorbents.

Adsorbents	q_e	K_F	n	R^2
Original AC	3.33-133	2.24	1.27	0.99
Modified AC with nitric acid	2.40-60	1.33	1.46	0.99
Modified AC with sulfonic acid	3.92-221.43	3.71	1.09	0.99

4. Conclusion

DBPs resulting from the reaction of disinfectant and DOM are a concern because of their potential carcinogenic effects on human health. Therefore, removal of NOM from drinking water sources is an important issue for treatment plants. This work focused on the removal of DOM using original AC, nitric acid and sulfonic acid modified ACs. Within the scope of the study, the original AC Puriss carbon was chemically modified with nitric acid and sulfonic acid. As a result of the modifications, both modification methods were effective in changing the structural and chemical properties of AC. After both modification methods, the surface area of the AC samples was increased and the pH_{PZC} values decreased. Although modification with nitric acid decreased the adsorbent capacity, it increased the capacity of adsorbents modified with sulfonic acid almost 1.7 times. UV_{254} absorbance removal performances are similar to original AC and sulfonic modified ACs, but lower for nitric acid modified AC. The highest DOC removal efficiency (80%) was obtained in sulfonic acid modified AC at 400 mg/L adsorbent dose. It was found that the adsorption equilibrium was explained by the Freundlich Model with a high correlation coefficient (0.99). The K_F and n values of AC modified with sulfonic acid (3.71 mg DOC/g carbon) were found to be $1-n$ and 1.09. These values indicate that sulfonic acid modified AC is a good option for NOM removal.

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