



## Research Article

# Evaluation of characterization and adsorption kinetics of natural organic matter onto nitric acid modified activated carbon

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## ABSTRACT

Natural organic substances (NOM) found in drinking water are a major contributor to disinfection by-product formation and are potentially toxic to humans. Conventional water treatment techniques may not always effectively treat NOMs. Therefore, an advanced treatment method such as adsorption can be inexpensive, simple and efficient. The selected adsorbent's and the NOMs properties both affect the removal effectiveness of the adsorption method. Activated carbon (AC), which is widely used in real-scale water treatment plants, has been modified and used in recent years in order to oxidize the porous carbon surface, raise its acidic qualities, eliminate mineral components, and enhance the surface's hydrophilic qualities. In this research, AC was modified with nitric acid (M-PAC) and NOM removal was investigated. In addition, it is discussed how the modification with nitric acid changes the adsorbent structure and chemistry. A morphology with smooth and irregular voids was observed as a result of nitric acid modification of the original AC by scanning electron microscopy (SEM) analysis. The particle size increased from 387.65 nm to 502.07 nm for the M-PAC adsorbent. The fourier transform infrared spectrophotometer (FTIR) spectrum indicates that structures connected to aromatic rings get formed in the M-PAC adsorbent as a result of the modification. The highest NOM removal for the original powdered activated carbon (PAC), 47%, was observed at 36 hours of contact time. On the other hand, M-PAC adsorbent achieved 40% NOM removal at contact times of 72 hours and above. It was concluded that the pseudo-second order kinetic model better represented NOM adsorption for both adsorbents.

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## INTRODUCTION

Over the last two decades, increased natural organic matter (NOM) concentration because of global warming, soil erosion, heavy rains [1, 2] and water pollution [3], poses challenges for water treatment plants in terms of operational optimization and proper process control [4, 5]. In addition to the increase in the amount of NOM in drinking water, changes in its quality (for example UV, SUVA)

also have a substantial effect on how water treatment systems function [6]. Furthermore, the interaction of NOM with chlorine-based disinfectants leads to the formation of disinfection by-product (DBPs) in drinking water [7]. Chronic exposure to these DBPs for example, trihalo-methanes (THMs) and haloacetic acids (HAAs) in drinking water through eating, inhalation, and skin contact can result in mutagenic and carcinogenic adverse health consequences [5, 8].

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The most effective method for reducing and controlling DBPs formation is to remove precursors (such as NOM) prior to disinfection. Kristiana et al. [9] study is a good example of this situation. According to the study, adding powdered activated carbon (PAC) to the coagulation process increased NOM removal efficiency by 70% and significantly decreased the generation of DBPs (80–95%). Similarly, Álvarez-Uriarte et al. [10] observed that the addition of 50 mg/L PAC resulted in a reduction in coagulant dose and increased removal of high molecular weight fractions of NOM. This confirmed that the THM formation potential increases the removal tendency. On the other hand, Joseph et al. [11] achieved a similar NOM removal efficiency (71.2%) using only commercially activated carbon.

NOMs are commonly removed from drinking water using a variety of treatment techniques, including adsorption, electrochemical treatment, membrane filtration, oxidation, biochemical treatment, coagulation, and flocculation [12]. Owing to its advantages, including high efficiency, the absence of toxic byproducts, practicability, and affordability, the adsorption method is widely regarded as one of the most effective water treatment technologies for NOM removal [13, 14]. It is used in the appropriate dosages before, during, and after coagulation to remove NOM more effectively, particularly during the adsorption process utilizing PAC. The drawback of PAC is the potential for carbon leakage into treated water [15].

Worldwide, studies has concentrated on many methods of modification to improve the important characteristics of AC, including surface chemistry, surface area, and morphological characteristics. Particularly in modification research, the factors impacting AC's properties and the impact of modifying agents on the morphological/adsorptive properties of the adsorbent are discussed [16]. It consists of three main categories of chemical, physical, and biological AC modification procedures and is further divided into subcategories according on the methods applied to change the surfaces [17, 18]. The porous surface of the AC is modified using an acidic process to boost its acidic properties, remove rid of undesired minerals, and make it more hydrophilic [19]. Nitric and sulfuric acids are the most often employed acids for this modification. There are more acidic functional groups and structures with –N–O– linkages and various oxygen groups formed on the surface of activated carbon due to nitric acid (HNO<sub>3</sub>) modification [20].

Modification with nitric acid increases and/or decreases the pore volume and surface area and increases the amount of carbonyl, carboxyl, phenolic and lactone groups that give acid character to the surface. The modification of activated carbon with nitric acid resulted in the occurrence of functional groups with high amounts of accessible oxygen on the adsorbent surface, as observed by Gökçe and Aktaş [21] and Valentin-Reyes et al. [22]. Similar to this, Li et al. [23] observed that following modification, groups like carboxyl and lactone increase the oxygen-containing groups on the AC surface while also increasing the surface's hydrophilicity. Numerous investigations have found that nitric acid

oxidation has a positive effect on the micro and mesopore volume. Nitric acid modification, according to Su et al. [24], increased the maximum surface area by 15%, which had a substantial impact on micropore formation and enhanced the adsorption area for the required pollutant removal. Our previous studies showed that the total pore volume of powdered activated carbon modified with nitric acid increased significantly from 0.22 cm<sup>3</sup>/g to 0.76 cm<sup>3</sup>/g [25]. On the other hand, in a different study, nitric acid modification of AC resulted in a major reduction in total surface area (from 13% to 25%), a slight increase in mesopore volume, some expansion of average pore size, and a slight increase in adsorption capacity [26].

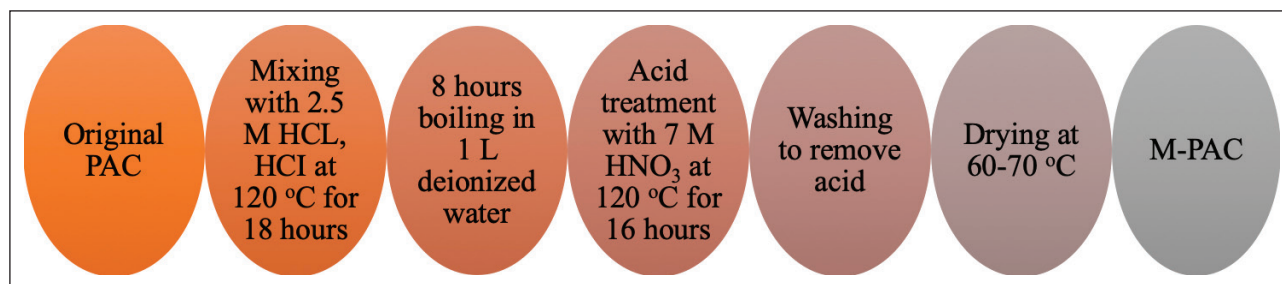
The modification method using acids like nitric acid and sulfuric acid had favorable impacts by enhancing the adsorption capacity in the adsorption of organic pollutants like NOM. Yang and Fox [27] as a consequence of modification with nitric acid, isotherm data showed that the adsorption capacity of humic acid increased from 30 mg/g to 45 mg/g compared to unmodified PAC. It was also stated that the acid-modified carbon adsorption fits the pseudo-second-order model. However, only a small number of studies have taken into account the adsorption of organic matter and its compounds using AC modified with nitric acid. The use of nitric acid modified AC is frequently encountered in metal adsorption research [20, 24, 28–31].

The performance of powdered activated carbon treated with nitric acid during the removal of NOMs from water has been the subject of numerous investigations [5, 27, 32], but the information is still insufficient. There are no investigations in the literature on the modification and characterization of the Purolite AC20 powder activated carbon chosen for this investigation using nitric acid. On the other hand, the research differs from other studies in that it was carried out using drinking water that actually contained NOM.

The objective of this study i) to investigate the effect of surface modification with nitric acid on the characterization of powder activated carbon, ii) to evaluate the adsorptive removal performance of original and nitric acid-modified PAC, iii) to determine the adsorption kinetic model of original and modified adsorbents. In the scope of the study, Purolite AC20 activated carbon was selected and modified with nitric acid. Additionally, NOM adsorption capacity was estimated using kinetic models (pseudo-first-order and pseudo-second-order) in water samples collected from the coagulation unit inlet for evaluation.

## MATERIALS AND METHODS

Purolite AC20 is a commercially activated black spherical bead-like carbon obtained from the bituminous coal mineral. The adsorbent has a size range of 0.4–1.4 mm, a BET surface area of 900–1000 m<sup>2</sup>/g, and a maximum moisture content of 2%. Purolite AC20 activated carbon was supplied in granular form and was used in experimental studies after grinding and sieving under laboratory con-



**Figure 1.** Nitric acid modification steps of original PAC.

ditions. High purity concentrated nitric acid from Merck (specific gravity 1.43 g/m<sup>3</sup>, 65% purity) was provided for modification. On the other hand, hydrochloric acid with a specific gravity of 1.19 g/m<sup>3</sup> and 37% purity was bought from Sigma Aldrich.

**Preparation of Modified Activated Carbon**

Guha et al. [33] method with a few minimal changes was applied for the nitric acid modification procedure of the original PAC. Before AC modification, it was washed with distilled and deionized water and dried in an oven at 105 °C. Modification of AC was carried out in 5 stages as seen in Figure 1. In the initial stage of the modification, a flask containing 15 g of the adsorbent sample was slowly stirred in 500 ml of a 2.5 M HCl solution for 18 hours at 120 °C. After pre-treatment, in the second step, the samples were boiled in 1 L of distilled water at 120 °C for 8 hours. Nitric acid was used for the alteration process after pretreatment. The adsorbents added to 1 L of 7 M HNO<sub>3</sub> were shaken quietly for 16 hours at 120 °C using a magnetic stirrer in a flask. Following acid treatment, the adsorbent and acid phase were separated by precipitation in a flask.

Step 4 involved washing the samples with distilled and deionized water until they acquired a consistent pH of between 5 and 6. Following the washing procedure, the samples were dried in a vacuum oven at 60 °C to 70 °C. The drying process was continued for approximately 48 hours. In order to understand that the activated carbons are dry, weightings were made at certain intervals until they reach the constant weight, and after reaching the constant weight, the dry activated carbons are kept in the desiccator. In the samples weighed after drying, a loss of approximately 40% was observed due to the washing processes compared to the pre-modification. The resulting adsorbent was labeled as M-PAC.

**Characterization Methods**

Surface characteristics, pore size distributions, and structural characteristics of modified and unmodified activated carbons were determined by characterization analysis using scanning electron microscopy (SEM), Brunauer, Emmet, and Teller (BET) analysis, fourier transform infrared spectrophotometer (FTIR), and dynamic light scattering (DLS). The surface morphology of the adsorbents was determined by Zeiss Evo LS10 scanning electron microscope (SEM) at Erciyes University TAUM center. In the 400–4000 cm<sup>-1</sup>

**Table 1.** The characteristics of the water used in adsorption experiments

Parameters	Unit	Value
pH	–	7.84
UV <sub>254</sub>	(cm <sup>-1</sup> )	0.044
TOC	(mg/L)	3.05
SUVA <sub>254</sub>	(L/(mgTOC.m))	1.73
Alkalinity	(mgCaCO <sub>3</sub> /L)	210
Total hardness	(mgCaCO <sub>3</sub> /L)	225
Electrical conductivity	(µS/cm)	400

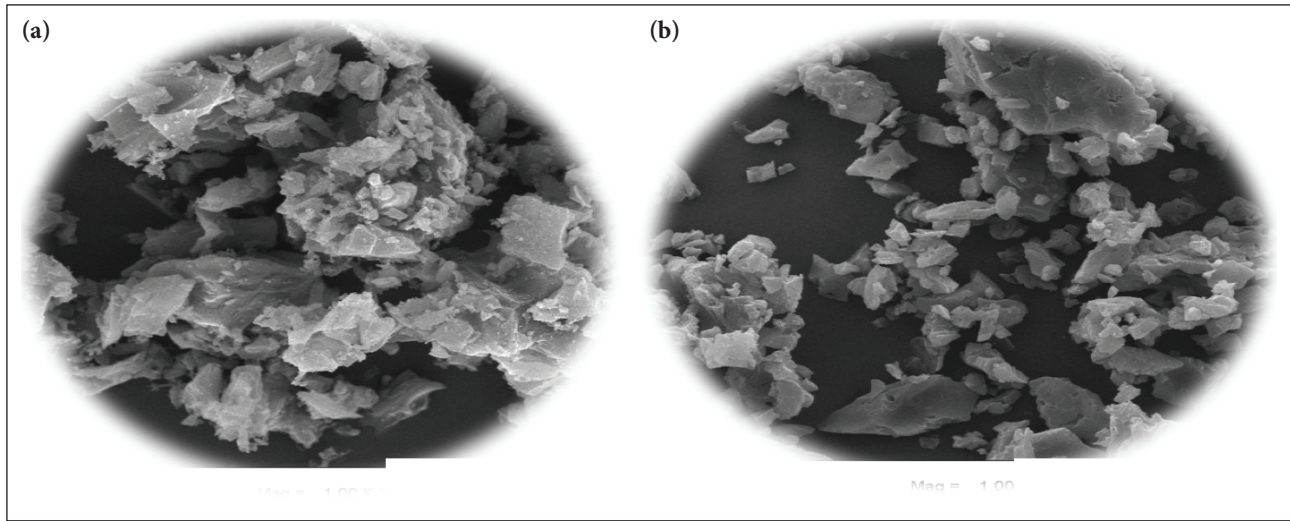
wavelength range, FTIRanalyses were carried out using a Perkin Elmer 400 Ft-IR/FT-FIR spectrometer at Erciyes University Technology Research and Application Center. The surface areas and total pore volumes of the adsorbents were determined with the micromeritics gemini VII surface area and porosity surface analyzer device. The surface area of the adsorbents was determined using N<sub>2</sub> adsorption-desorption isotherms. At the Technology Research and Application Center of Erciyes University, BET analyses were conducted through service procurement. The point of zero charge (pH<sub>PZC</sub>) and pH equilibrium methods were employed for evaluating the surface chemistry of the adsorbents. Total surface acidic groups (NaOH adsorption) and total surface basic groups (HCl adsorption) were measured using the Boehm method (alkalimetric titration) with minor modifications [34].

**Water Characterization**

Water samples collected from the coagulation process's input at Konya Drink Water Treatment Plant (KOSKİ) Plant were used in the kinetic testing for the adsorption experiments. The characteristics of the coagulation process inlet water are given in Table 1. The removal efficiencies of UV<sub>254</sub> and NOM from filtrate were computed as a result of kinetic testing, and models were developed.

**Adsorption and Kinetic Analysis**

Adsorption kinetic tests were conducted for the original and nitric acid modified activated carbon. In the kinetic tests, the contact time required for the adsorbent to reach equilibrium was determined. The kinetic tests were carried out in 125 ml (solution volume 100 ml) polytetrafluoroethylene (PTFE) capped, dark (amber) glass bottles, on



**Figure 2.** SEM images original PAC (a) and nitric acid modified M-PAC (b) (1  $\mu\text{m}$  mag: 5.00 KX).

the samples taken from the coagulation inlet unit of the KOSKÍ Drinking Water Treatment Plant. The pH value of natural waters is required to be between 6.5 and 9.5 for human consumption purposes. Considering this situation, the pH value of the samples was adjusted to be between  $7 \pm 0.1$  with  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$ . The original PAC changed the pH value of the water between 7.63 and 7.74 during the contact times determined after adsorption. It was observed that the M-PAC adsorbent changed the pH of the water in the range of 7.2–7.34 after adsorption. During the predetermined contact times, shaking was carried out in the shaker horizontally at a speed of 100 rpm. Adsorption periods of 2, 4, 8, 12, 24, 36, 48, 72 and 96 hours were examined for kinetic tests at a fixed adsorbent dosage of 300 mg/L. The sample was filtered with 0.45  $\mu\text{m}$  PES filter paper after each contact period to separate the adsorbent particles from the aqueous phase.

Analyses of total organic carbon (TOC) and  $\text{UV}_{254}$  were performed on the sample obtained from the supernatant portion.  $\text{UV}_{254}$  analyses included measurements at 254 nm using a UV-1700 Shimadzu UV-visible spectrophotometer. Each sample was measured 3 times and averaged. Before starting the analysis, the spectrophotometer was reset with distilled water.

The difference between the starting and final adsorbate concentrations provided in Equation 1 was used for obtaining the adsorption capacity (adsorbed NOM onto PACs).

$$q = \frac{(C_0 - C)V}{M} \quad (1)$$

Where,  $C_0$  and  $C$  are initial and equilibrium concentrations of substance in water samples (mg/L), respectively. Adsorption capacity (mg/g), sample volume (L) and mass of PACs (g) are indicated by  $q$ ,  $V$  and  $M$ , respectively.

The TOC removal capabilities of the adsorbents were calculated and suitable kinetic models were found while taking into account the kinetic times. The formula in Equation 2 is used to calculate the adsorption process' rate constant in the pseudo-first order model.

$$\ln(q_e - qt) = (\ln q_e) - K_1 * t \quad (2)$$

The pseudo-second order velocity kinetics were calculated using the formula found in Equation 3 below.

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} * t \quad (3)$$

$K_1$ : Pseudo 1<sup>st</sup> order, adsorption rate constant (1/min)

$K_2$ : Pseudo 2<sup>nd</sup> order adsorption rate constant (g/mg.min)

$q_e$ : Amount of substance adsorbed on unit adsorbent (mg/g)

$q_t$ : Amount of pollutant adsorbed in  $t$  time (mg/g)

$t$ : Adsorption contact time (min).

## RESULTS AND DISCUSSION

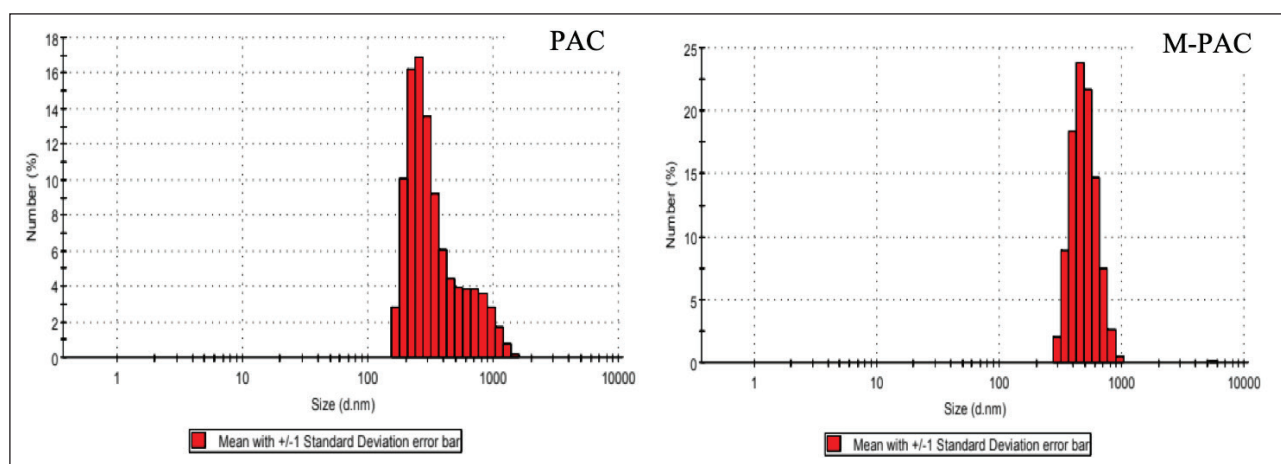
### Characterization of PAC and M-PAC

#### Morphological characterization of PAC and M-PAC

The outcomes of SEM analysis on both raw PAC and M-PAC are presented in Figure 2. There are obvious distinctions between PAC and M-PAC when the morphological images are compared. SEM images demonstrate that the original PAC adsorbent features a distinguishing surface feature and pore structure. There were numerous new irregular holes on the M-PAC surface as well as a smooth structure made of nitric acid.

The M-PAC surface area has been slightly reduced. Similarly, there are studies in the literature stating that activated carbon forms a smoother, narrower porous structure after modification with  $\text{HNO}_3$ , and this is supported by the decrease in BET surface area [30, 31, 33–35].

The reason for the absence of porosity for M-PAC in SEM analysis may be related to pore clogging and pore destruction by nitric acid. Researchers have reported that this situation can be attributed to two possible effects of nitric acid, i) partial destruction of microporous walls [36, 39] and ii) oxygen functional. They attributed it to the formation of groups and the blockage of the pore entrance [40].



**Figure 3.** Particle size distribution graph of the original PAC and M-PAC adsorbents.

**Table 2.** Pore structure and surface chemical characterization of original PAC and M-PAC adsorbents

Adsorbent	BET surface area $S_{BET}$ ( $m^2 g^{-1}$ )	Total pore volume ( $cm^3 g^{-1}$ )	Pore diameter (nm)	$pH_{pzc}$	Total acidic groups		Total basic groups	
					(meq/g)	(meq/m <sup>2</sup> )	(meq/g)	(meq/m <sup>2</sup> )
PAC	768	0,47	2,45	9.21	3.5	0.005	3.08	0.004
M-PAC	727	0,44	2,44	2.03	4.6	0.006	2.78	0.004

\* $S_{BET}$ : Surface area calculated by Brunauer-Emmett-Teller theory; Pore width: It represents the point of adsorption average pore width (BET 4V/A).

It is also seen that the modification with  $HNO_3$  causes the formation of smaller particles on the M-PAC. Activated carbon modified with  $HNO_3$  produces corrosive and particle-eroding properties, according to El-Hendawy et al. [26]. Chingombe et al. [41] observed that the modification of F400 activated carbon with  $HNO_3$  made little difference to the surface morphology other than a significant pore enlargement. In another study, when he examined the SEM image of bamboo charcoal after treatment with  $HNO_3$ , it was observed that the surface became smoother and the cell walls became thicker, and the surface was non-porous [42].

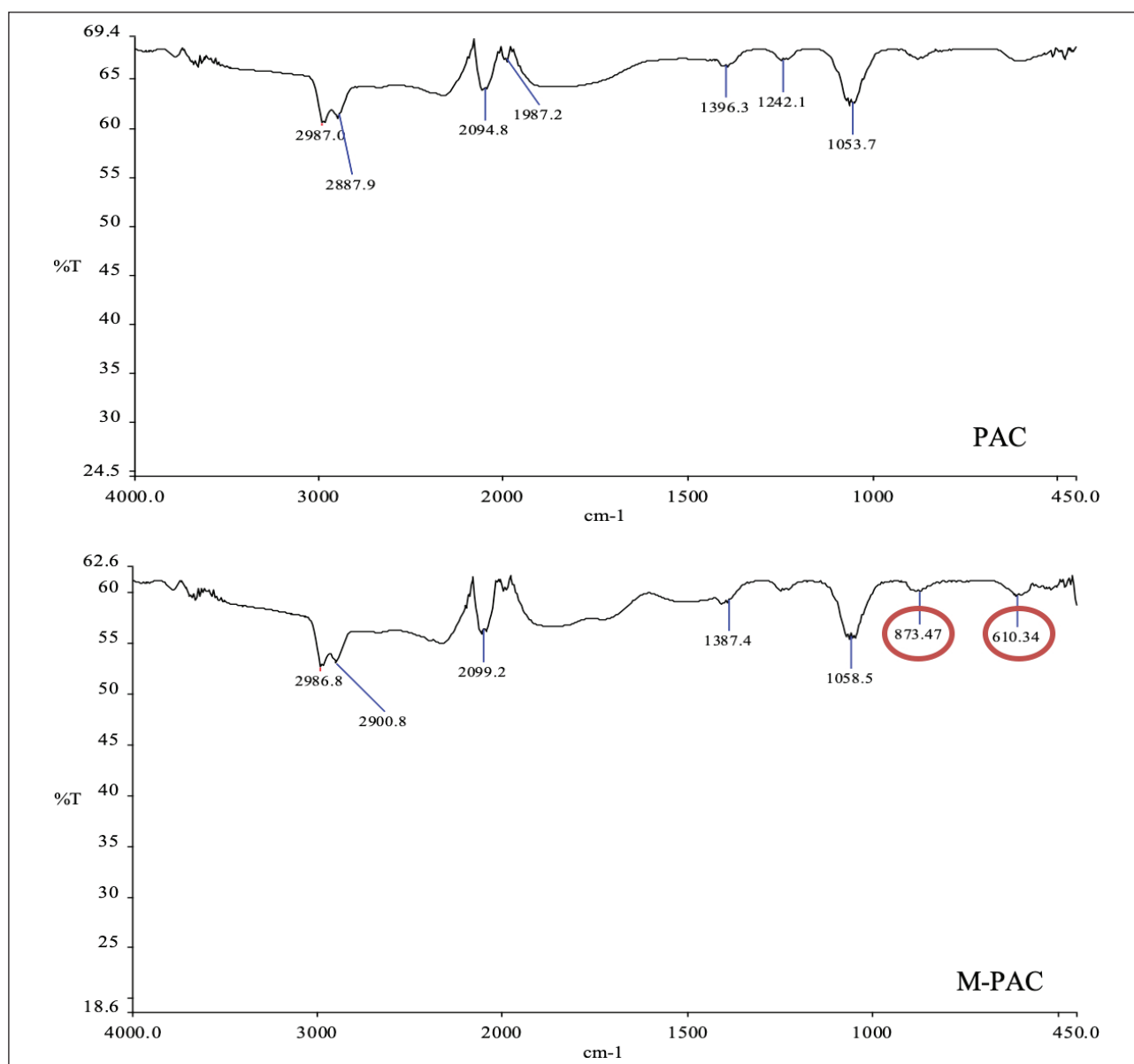
DLS analysis was used to determine the particle size distribution of the unmodified and nitric acid-modified carbon. DLS measurements were carried out using the Malvern NanoZS90 instrument, which has a 633 nm laser, at room temperature. The DLS histogram in Figure 3 indicates the particle size analysis of the PAC and M-PAC adsorbents. The graphs show the particle size diameter in nm on the x-axis and the particle size as a percentage on the y-axis. The histogram plot demonstrates the original PAC's broad particle distribution, which spans the wavelength range of 164.2 nm to 1484 nm.

The weighted average calculation method obtained an average particle size of 387.65 nm for the original PAC adsorbent. This value increased in the M-PAC adsorbent as a result of the nitric acid alteration, and it was determined to be 502.07 nm. Additionally, the M-PAC adsorbent's particle size distribution accumulated in the 387 nm region by 78%. An indicator of a sample's size-based heterogeneity is the polydispersity index (PDI). If the PDI is less than 0.3, it indicates monodispersity; if it is larger than 0.5, it indicates

that the particle is very heterogeneous. The PDI is near to 0, indicating a homogenous particle size [43]. Particle size distribution range ranging from 80 to 1100 nm with PDI 0.237 is given. PDI refers to the size of 85–850 nm with 0.246 [44]. Considering the particle size distributions calculated in our study (387.65 for original PAC; 502.07 for M-PAC), PDI corresponds to a value of 0.246. This situation indicates monodispersity.

FTIR studies were carried out with Perkin Elmer 400 Ft-IR/FT-FIR spectrometer in the wavelength range of 400–4000  $cm^{-1}$ . An important technique for analyzing the distributions of functional groups on surfaces qualitatively is the use of FTIR spectra. FTIR spectra of original PAC and M-PAC are shown in Figure 4. It was observed that the 2900  $cm^{-1}$  and 2094  $cm^{-1}$  bands, which characterize the C-H group in the original PAC, FTIR spectra, remained almost the same in the M-PAC spectrum. These bands result from symmetrical and asymmetrical C – H stretching vibrations [45]. The PAC adsorbent was modified with  $HNO_3$  and the 1987  $cm^{-1}$  band indicating the C N group eliminated as a result [46]. C-O stretching vibrations can be seen in the original PAC's 1242  $cm^{-1}$  band [47, 48]. This demonstrates that acid modification lead to the C-O stretching vibrations disappear in the M-PAC adsorbent.

The M-PAC adsorbent's 1000–1100  $cm^{-1}$  bands are the alcohol C–O stretching vibration structures, and the 1387.4  $cm^{-1}$  band is the COOH group [49]. While other vibrations at 888  $cm^{-1}$  and 749  $cm^{-1}$  are linked to the C-H deformation vibration of the benzene ring, bands emerging at approximately 1400  $cm$  in the literature are related to the O-C-O symmetrical vibration of the carboxylic acid group



**Figure 4.** FTIR spectra of original PAC and M-PAC.

[50]. According to Aguiar et al. [51] and Wang et al. [52] bands obtained between 795 and 881  $\text{cm}^{-1}$  are indicative of the existence of heteroaromatic chemicals and aromatic rings. As a result of the original PAC nitric acid modification, two new functional groups (873.47 and 610.34  $\text{cm}^{-1}$ ) that we can associate with the presence of aromatic rings were added to the M-PAC structure. The 873.47  $\text{cm}^{-1}$  band can be associated with the presence of aromatic rings and heteroaromatic compounds. In some studies, bonds between 600–900  $\text{cm}^{-1}$  have been associated with the out-of-plane bending mode of the C-H or O-H group [53]. The 610.34  $\text{cm}^{-1}$  band in the FTIR spectrum of the M-PAC adsorbent is attributed to the C-H or O-H group.

The average BET area, total pore volume, pore diameter,  $\text{pH}_{\text{pzc}}$ , total acidic and basic groups of adsorbents were given in Table 2. The changes brought about by the modification on the surface area and pore properties were comprehended using  $\text{N}_2$  adsorption-desorption isotherms.

The surface area of the M-PAC adsorbent was reduced by 5% as a result of the nitric acid modification. Researchers have linked the decrease in surface area caused by acid modification to two possible outcomes: (1) partial destruction of microporous walls [37, 39] and (2) formation of oxygen functional groups due to blockage of the pore entrance [40]. Additionally, the M-PAC adsorbent's total pore volume exhibited a slight decrease from 0.47  $\text{cm}^3/\text{g}$  to 0.44  $\text{cm}^3/\text{g}$ . Similar to this, other researchers have found that pore blockage and pore destruction caused by nitric acid modification lead to a decrease in pore volume and surface area [54].

Measurements of  $\text{pH}_{\text{pzc}}$  are made at the zero charge point, where carbon is neutrally charged, to calculate the pH of the solution [55, 56]. At pH below  $\text{pH}_{\text{pzc}}$ , the adsorbent surface will be positively charged, and at a pH above  $\text{pH}_{\text{pzc}}$ , the surface will be negatively charged. According to Dabrowski et al. [57] that event has an impact on the

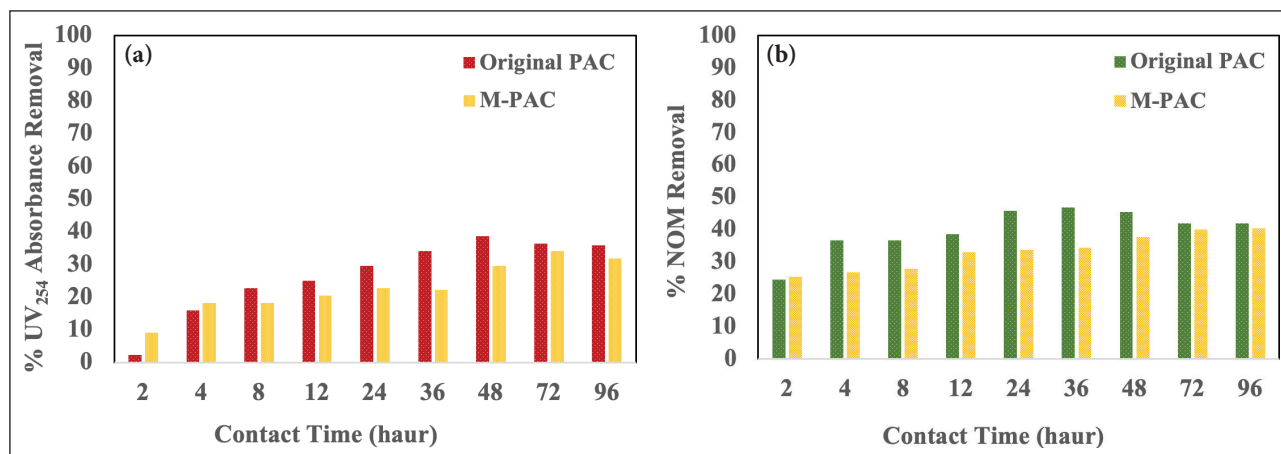


Figure 5. UV<sub>254</sub> (a) and NOM (b) removal efficiencies (%) for original PAC and M-PAC adsorbents.

adsorbate-adsorbent system's ability to remove pollutants during adsorption. Nitric acid modification caused the pH<sub>pzc</sub> value of the original PAC adsorbent decrease substantially, from 9.21 to 2.03. This indicates that the acidic properties are more dominant at these carbons and are the result of a greater number of weakly acidic functional groups than others. Total surface acidic and basic group amounts were defined by the Boehm method. An increase was observed in the total acid groups (meq/g) of M-PAC adsorbent after nitric acid modification. The total amount of acidic group for the original PAC increased from 3.5 meq/g to 4.6 meq/g for the M-PAC adsorbent. When the results reported in the literature for acid functional groups were examined, it was concluded that the use of HNO<sub>3</sub> had a dominant effect on carboxylic group formation.

### Adsorption Kinetic Analysis

#### Effect of Contact Time

Adsorption periods of 2, 4, 8, 12, 24, 36, 48, 72 hours and 96 hours were tried at a fixed adsorbent dose of 300 mg/L in order to allow the adsorbents to approach equilibrium. The NOM removal efficiencies were calculated taking into consideration the TOC parameter. Figure 5 shows the UV<sub>254</sub> (a) and NOM (b) removal efficiencies, which depend on the adsorbents contact time.

The contact time of 48 hours was found to be adequate after taking into account the removal efficiencies as a result of the kinetic testing. The maximum removal effectiveness was found to be 39% in the 48 hour contact time in the findings of the kinetic investigation, which observed at the removals of UV<sub>254</sub> absorbance in the original PAC adsorbent. On the other hand, for M-PAC, contact period of 72 hours resulted in the maximum UV<sub>254</sub> absorbance removal of 34%. The NOM removal efficiency in the coagulation unit inlet water changed from 25 to 47 percent at the determined adsorbent contact times with original PAC. This situation has been supported by studies in the literature stating that AC alone without coagulation is as effective as 0–76% in the removal of NOM [58]. The highest NOM removal, 47%, was observed in the original PAC at 36 hours of contact time. In contrast,

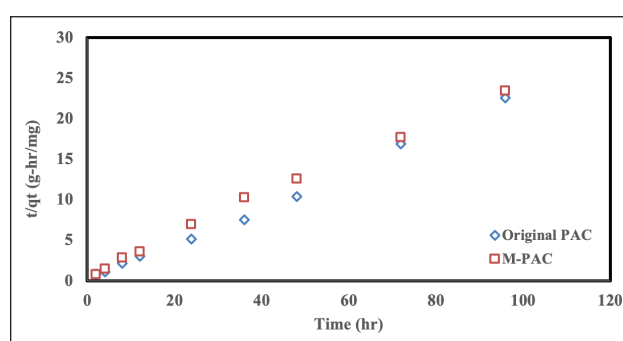


Figure 6. Pseudo-second-order kinetic for NOM adsorption by adsorbents.

M-PAC achieved 40% removal efficiency during contact times of 72 and 96 hours. This revealed that the Purolite AC20 adsorbent modified with nitric acid was not a very efficient adsorbent in UV<sub>254</sub> absorbance and NOM removal.

Pseudo-kinetic models simulating the total adsorption rate are a widely used method to model the kinetics of adsorption systems, as they accurately reflect real data [59]. The Pseudo-second order (PSO) graph plotting t versus t/qt to determine the organic matter adsorption kinetic rate is shown in Figure 6. The linearity of the t/qt versus t plot confirms the fit of the process to the pseudo-second-order kinetic model. A contact time of 48 hours was chosen to keep the results of the kinetic tests within confidence intervals and to allow comparison with literature searches. In some previous studies on the adsorption of organic substances, it was stated that the time for adsorbents to reach equilibrium ranged from 30 minutes to 72 hours [15, 60, 61].

#### Adsorption Kinetic Models

Adsorption kinetics were described using pseudo-first order and pseudo-second order models. Table 3 presents the kinetic parameters obtained from pseudo-first order and pseudo-second order models. According to the correlation coefficient of these two models, the pseudo-second order model displayed better fitting than the pseudo-first order model regarding experimental data. Furthermore, compared to the pseudo-first order kinetic model, the calculated

**Table 3.** Adsorption kinetic model parameters for NOM adsorbed on original PAC and M-PAC

Adsorbents	Pseudo-first order (PFO)				Pseudo-second order (PSO)		
	$q_{e_{exp}}$ (mg/g)	$q_{e_{cal}}$ (mg/g)	$k_1$ (1/h)	$R^2$	$q_{e_{cal}}$ (mg/g)	$k_2$ (g/mg-h)	$R^2$
Original PAC	4.27	1.56	0.012	0.09	4.35	132.37	0.99
M-PAC	4.07	2.12	0.01	0.76	4.20	0.066	0.99

equilibrium capacity ( $q_{e_{cal}}$ ) by pseudo-second order kinetic model better predicted the observed equilibrium capacity ( $q_{e_{exp}}$ ). When the results were examined, it was determined that the  $R^2$  values were high, and considering the correlation between the experimental  $q_e$  and the calculated  $q_e$ , the adsorption kinetics was in accordance with the Pseudo second order kinetic model. Tafvizi et al. [5] calculated that their kinetic results were the most appropriate kinetic model among all three ACs in the study of pseudo-second-order velocity kinetics. Similarly, Yang and Fox [27] observed that the adsorption of acid modified activated carbon conforms to the pseudo second-order model. Yilmaz et al. [62] found that in the adsorption of the original powdered activated carbon with 2 different properties over the TOC parameter, the contact time of 72 hours was sufficient to reach equilibrium and fit the second-order kinetic model.

Chemisorption or the valence force are the driving forces in the pseudo-second order model. The pseudo-second-order model provides the best fit in this situation because of the interplay between valence force and negatively charged organic matter at the surface functional group. Moreover, pseudo-second-order kinetics have been widely reported to explain organic compound sorption on activated carbon, suggesting that functional group interaction is important in the rate control step [27, 63].

The original PAC and M-PAC,  $q_{e_{exp}}$  values were 4.27 mg/g and 4.07 mg/g, respectively. The  $R^2$  values of both adsorbents are very close to each other. Pseudo-second order kinetic model  $q_e$  (calculated) values were calculated as 4.35 mg/g for the original PAC adsorbent and 4.20 for M-PAC. According to the first-order and second-order models for M-PAC,  $k_1$  and  $k_2$  values were calculated as 0.01 1/h and 0.066 g/mg-h, respectively. The fact that the  $k_2$  value frequently varies based on operational conditions including pH, temperature, and shaking strength explains why the  $k_2$  values of the different adsorbents varied from one another. Zhao et al. [15] reported that the adsorption of NOM by GAC was well described by the pseudo-second-order velocity model and the velocity kinetic parameters  $k_2$ ,  $q_e$  and  $R^2$  values were calculated as 0.24 g/mg.hr, 2.02 mg/g and 0.99, respectively.

## CONCLUSION

The performance of nitric acid modified powdered activated carbon during the removal of NOMs from water is still under investigation. In this study, characterization studies were conducted after the original Purolite AC20 activated carbon was modified using nitric acid. Additionally, the NOM adsorption of nitric acid modified AC (M-PAC) in

the water samples taken from the water entering the coagulation unit was estimated using kinetic models, and the NOM adsorption capacity was assessed.

The surface area of the M-PAC adsorbent was reduced by 5% as a result of the nitric acid modification. The original PAC adsorbent's  $PH_{pzc}$  value decreased significantly after nitric acid modification, from 9.21 to 2.03. It also indicates that there are more weakly acidic functional groups than other functional groups at these carbons, which is why the acidic features are more prominent there.

It was shown in the SEM pictures that the M-PAC surface had developed several new, irregular holes as well as a smooth structure. As a result of the original PAC nitric acid modification, two new functional groups were added to the M-PAC structure, which we can associate with the presence of aromatic rings. At 48 hours of contact time, it was found that the original PAC's  $UV_{254}$  absorbance removal reached a maximum of 39%. For M-PAC, a maximum  $UV_{254}$  absorbance removal of 34% was observed at contact time of 72 hours. The highest NOM removal, 47%, was observed in the original PAC at 36 hours of contact time. In contrast, M-PAC achieved 40% removal efficiency during contact times of 72 and 96 hours. The original PAC and M-PAC,  $q_{e_{exp}}$  values were 4.27 mg/g and 4.07 mg/g, respectively. As a result of the calculations, it was concluded that the pseudo-second order kinetic model better describes the NOM adsorption of the original PAC and M-PAC. This study will provide preliminary data especially in the evaluation of NOM removal with modified AC adsorbent in real natural water resources.

M-PAC adsorbent was expected to increase NOM adsorption. There are many reasons why removal efficiency does not increase. For example, the properties of water, the appropriate amount of adsorbent and the concentration of nitric acid used for modification are some of these. Modification studies can be carried out with different and lower nitric acid concentrations to increase removal efficiency. Additionally, different mixing times and different acid modifications can be tried. In our study, water source has a low SUVA value. Considering this situation, NOM removal of activated carbon modified with nitric acid from a high SUVA water source can be investigated.

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## DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

## CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

## USE OF AI FOR WRITING ASSISTANCE

Not declared.

## ETHICS

There are no ethical issues with the publication of this manuscript.

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