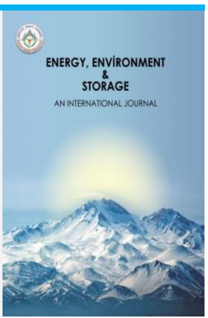
Energy, Environment and Storage (2025) 05-03: 113-127

Energy, Environment and Storage

Journal Homepage: www.enenstrg.com



Tailoring Activated Carbon Surfaces: A Comparative Study of Nitric and Chlorosulfonic Acid Modifications

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ABSTRACT. Surface modification approaches can improve the adsorbent's physicochemical characteristics, which are crucial to the adsorption process's effectiveness. In this study, the effects of chemical modification on the structural and chemical properties of four different powdered activated carbon (AC) samples were investigated. Surface modifications were performed using nitric acid and chlorosulfonic acid. The modified adsorbents were comprehensively characterized by Brunauer–Emmett–Teller (BET) surface area analysis, Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Dynamic Light Scattering (DLS). Additionally, the Boehm titration method was employed to evaluate the surface acidity and functional group composition. According to the research results, nitric acid modification led to a smoother and more uniform surface morphology, along with a more consistent pore size distribution, compared to chlorosulfonic acid treatment. Nitric acid introduced functional groups such as –OH, –COOH, and C=C=C, while chlorosulfonic acid resulted in the incorporation of sulfonic groups (S=O and SO_3 H). Among the modified samples, AC4S exhibited the highest surface area (868.48 m^2/g) and pore volume (0.88 cm^3/g). The largest average particle size (1419.44 nm) was observed in the AC1S sample. While double modification increased particle size distribution, it negatively affected surface area and pore volume. Overall, the findings indicate that both nitric acid and chlorosulfonic acid modifications are effective in tailoring the chemical and structural features of activated carbon, offering promising potential for adsorption-based applications.

Keywords: Activated carbon, adsorption, characterization, chemical modification, chlorosulfonic acid, nitric acid.

Article History: Received: 10.August 2025 Revised: 04 September 2025; Accepted: 10 September 2025; Availableonline: 10 September 2025
Doi: **https://doi.org/10.52924/SUTR5652**

1. INTRODUCTION

Restoring ecosystem balance and ensuring a more sustainable future need study on the removal of micropollutants from water at low concentrations (µg/l-ng/l), such as pesticides, drugs, and personal care products. Conventional treatment methods are not efficient enough to remove these pollutants from water [1]. Adsorption is one of the most promising advanced treatment technologies, especially for the removal of micropollutants, due to its high removal capacity, ease of application and no toxic by-products [2]. The biggest disadvantage of the adsorption process is the need for regeneration [4]. At this point, this problem can be eliminated by using commercial powdered activated carbon (PAC) in the adsorption process.

Adsorption performance is generally evaluated according to the capacity and selectivity of adsorbents and considering this situation, adsorbent selection is an important factor in pollutant removal [3]. In the interest of environmental sustainability, high-performance materials like activated carbon are now needed for the adsorption of persistent organic and inorganic chemicals from water sources. In general, activated carbon (AC) is an amorphous type of carbon that can be produced from various carbon sources employing one of the two fundamental activation techniques chemical or physical. [5-7]. The material has several uses in a variety of sectors due to its high surface area, porosity, advanced internal pore structure with micro, meso, and macro pores, and a large number of functional groups on its surface [8].

The addition of different functional groups and/or structural modifications to ACs improves their characteristics by increasing their selectivity and capacity

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for adsorption of contaminants. In particular, recent studies on modifying adsorbents to increase their capacity present an innovative adsorption approach to the literature. Numerous methods have been examined in the literature, including chemical, biological, and physical change [9-13]. It is well known that these modified ACs enhance the adsorbent structure and boost the adsorption capacity [14-16].

Differences in the modification procedure and the type of modifying agent used have a direct impact on how the AC adsorbs pollutants and how it works [17]. Therefore, choosing the right modification technique is very important on the physicochemical structure of the AC. The specific surface area of the adsorbent can be increased, surface functional groups, pore structures and particle size distributions can be changed by AC modification. In particular, chemical modification techniques that use organic acids, hydrogen peroxide, and inorganic acids (such as hydrochloric, sulfuric, and nitric acids) are successful in boosting the quantity of surface functional groups [13, 18, 19].

Modification of AC with nitric acid resulted in the formation of functional groups with a high amount of accessible oxygen on the adsorbent surface in the studies conducted by Gökçe and Aktaş [20] and Valentin-Reyes et al. [21]. Following modification, Li et al. [22] found that groups like lactone and carboxyl enhanced the number of oxygen-containing groups on the AC's surface while also making the surface more hydrophilic. Wolak and Orzechowska-Zięba [13] claimed in their study that when polar adsorbates are adsorbed, the presence of oxygen groups on the carbon surface is evident. In many studies using nitric acid as oxidizer, it was observed that the modification had a positive effect on the micropore and mesopore volume, increasing the adsorption capacity of pollutants [23-25]. Liu et al. [26] observed that the adsorption capacity of Cr (VI) increased from 7.61 mg/g to 13.74 mg/g as a result of AC modification with nitric acid. In another study, the increase in adsorption capacity from 24.86 mg/g with the original AC to 54.74 mg/g as a result of modification with nitric acid is an important result [27].

Recently, it has been thought that sulfonic acid modification, another technique that may raise surface acidity, has a lot of promise [28]. Alvear-Daza et al. [29] reported that very strong acid sites were formed as a result of the effective incorporation of SO_3H compound into the structure by chlorosulfonic acid modification. When Goswami and Phukan [30] used sulfonic acid modification to remove dyes (RhB and Orange G), they found that the adsorption capacity rose from 318.5 mg/g to 757.6 mg/g.

Characterization of the adsorbent's properties is necessary to assess the effectiveness of the adsorption process and get a better understanding of it [31].

Various methods have been developed to characterize structural and physicochemical properties such as pore volumes, surface area, thermal stability, hydrophilicity, surface chemistry, functional groups of surfaces, pH, elemental analysis, water vapor adsorption, nitrogen adsorption, moisture content [32]. Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), N_2 adsorption/desorption isotherm, Fourier transform infrared spectroscopy (FTIR), X-Ray photoelectron spectroscopy (XPS), Boehm titration, Potentiometric titration, Zero charge point are some of the commonly used characterization techniques for adsorbents [33, 34].

In this paper, commercial powdered activated carbons, which are preferred for obtaining adsorption modified adsorbents, were modified with nitric acid and chlorosulfonic acid. In the literature searches, no recent study comparing the modification of commercial powdered AC with nitric acid and sulfonic acid was found. The effect of double modification (steam+nitric acid, steam+sulfonic acid, chemical treatment+nitric acid, chemical treatment+sulfonic acid) was also investigated in this study. The effect of modification on adsorbent structures was elucidated by SEM, Brunauer, Emmet and Teller (BET), FTIR and dynamic light scattering (DLS) analysis. At the same time, the changes in surface chemistry were investigated by pH_{PZC} and surface acidic and basic groups experiments.

2. MATERIALS AND METHODS

2.1 Materials and chemicals

In the modification studies, four commercial powder ACs were used: Norit CA1 (Cat. No. 97876), Norit SX F Cat (Cat. No. 901933), AC Puriss (Cat. No. 31616), and Norit SX ULTRA (Cat. No. 53663). Chemical modification was done to Norit CA1, and steam modification was done to Norit SX ULTRA. The two additional ACs are original, untreated activated carbons that were acquired from Sigma-Aldrich. The general characteristics of the ACs are presented in Table 1. The concentrated nitric acid (specific gravity 1.43 g/m^3, 65% purity) used for modification was of high purity and was supplied by Merck. Purchased from Sigma-Aldrich were hydrochloric acid (specific gravity 1.19 g/m3, 37% purity) and chlorosulfonic acid ($ClSO_3H$), with a specific gravity of 1.48 g/m3, 99% purity.

Table 1. Properties of commercial adsorbents used in modification experiments

Adsorbents	Surface Area (m^2/g)	Pore size	Density (g/ml)
Norit CA1	1400	Macro/Meso	0.9
Norit SX ULTRA	1200	Micro/Meso	0.743
Norit SX F Cat	750	Micro/Meso	1.8 – 2.1
AC Puriss	300	Micro/Meso	1.8 –2.1

2.1.1 Nitric acid modification of activated carbons

In the nitric acid modification of PACs, the method of Guha et al. [35] was modified and applied. Prior to modification, the adsorbents were cleaned with deionized and distilled water and dried at 105 °C in an oven.

Five steps were used to modify the dried activated carbons. Summary of the five-step modification process:

1. HCl Pre-treatment: The activated carbon is treated with 2.5 M HCl at 120 °C for 18 hours to remove impurities.

2. Boiling in Water: The sample is boiled in pure water at the same temperature for 8 hours to further purify it.

3. Nitric Acid Modification: The AC is treated with 7 M HNO_3 at 120 °C for 16 hours to introduce functional groups that can enhance adsorption.

4. Washing: The modified AC is washed with distilled and deionized water until a constant pH of ~5-6 is achieved.

5. Drying: Ultimately, a vacuum oven is used to dry the AC at 60-70 °C for about 48 hours until a constant weight is reached, indicating complete drying.

The 40% weight loss during washing is significant, as it reflects the removal of soluble impurities and possibly some of the carbon structure. The resulting modified activated carbons are labeled as ACN (*Table 2*).

2.1.2 Chlorosulfonic acid modification of activated carbons

The technique used by Goswami and Phukan [30] in their study was adapted and used to modify activated carbons using sulfonic acid. It was carried out in 5 step. Each step of the method is clearly summarized below.

1. Preparation of Activated Carbon:

Washing: Water that was deionized and distilled was used to wash the activated carbons.

Drying: 105 °C in an oven to dry.

2. Dichloromethane Treatment:

Weighing: 30 grams of activated carbon were weighed.

Solution Preparation: 900 mL of dichloromethane (CH_2 Cl_2) was added.

Ultrasonic Bath: Stirred for 45 minutes.

Cooling: Cooled using ice molds.

3. Chlorosulfonic Acid Addition:

Dropwise Addition: 30 mL of chlorosulfonic acid was added dropwise over 30 minutes at room temperature.

Shaking: The mixture was agitated for an additional 3 hours to ensure complete dispersion of the acid.

4. Filtration and Washing:

Filtration: The final product was filtered.

Washing: Washed with ethanol and water.

5. Final Drying:

Drying: Dried at 80 °C until a constant weight was achieved.

Storage: The dried activated carbons were stored in a desiccator.

Final Product: The modified activated carbons were labeled as **ACS** (*Table 2*).

Table 2. Properties and codes of original and modified adsorbents

Adsorbents	Codes	Properties
Norit SX ULTRA	AC1	Original steam modification
Norit CA1	AC2	Original chemical modification
Norit SX F Cat	AC3	Original
AC Puriss	AC4	Original
Norit SX ULTRA	AC1N	Steam + Nitric acid modification
Norit CA1	AC2N	Chemical + Nitric acid modification
Norit SX ULTRA	AC1S	Steam + Sulfonic acid modification
Norit CA1	AC2S	Chemical + Sulfonic acid modification
Norit SX F Cat	AC3N	Nitric acid modification
Norit SX F Cat	AC3S	Sulfonic acid modification
AC Puriss	AC4N	Nitric acid modification
AC Puriss	AC4S	Sulfonic acid modification

2.2 Characterization techniques

2.2.1 pH_{PZC} analysis

The neutral charge point (pH_{PZC}, the pH value at which the total net surface charge is zero) and the ability to neutralize acids and bases are qualities that define the surface chemistry of adsorbents. The pH_{PZC} values of activated carbon samples were determined by pH equilibration method [36]. By adding 0.5 M HCl and/or 0.5 M NaOH, the pH values of the 0.1 M NaCI solution produced in distilled water were brought within the range of 2 and 12. From these solutions, 20 ml of samples were taken in 25 ml amber sample bottles and 100 mg of adsorbent was added to each. Adsorbent-free control samples were also made for every pH level. The prepared samples were shaken for 48 hours at 20±5 0C and 100 rpm. Following the mixing time, the samples were allowed to settle for an hour before their pH levels were determined. The pH_{PZC} value is the same pH value that does not change after 48 hours of contact. Nonetheless, in order to determine the pH_{PZC} value precisely, interpolation is typically necessary. The effect of acid modification on the adsorbent's net surface charge was ascertained by noting the pHpzc values of the original and modified activated carbons that remained consistent over a 48-hour period.

2.2.2 Total surface acidic and basic values of adsorbents

The Boehm technique (alkalimetric titration) was used, with some slight adjustments, to quantify the total surface acidic groups (NaOH adsorption) and total surface basic groups (HCl adsorption) [36]. 20 ml of 0.05 N NaOH or 0.05 N HCl solution was added to 25 ml bottles containing 200 mg of adsorbent each. Control samples without adsorbent were also prepared with the samples. For 48 hours at room temperature, the prepared samples were agitated at 100 rpm. After the specified period of time, the samples were left for an hour to allow the adsorbents to settle before being filtered. Taking into account pH variations, ten milliliters of the filtered samples were used in the titration procedure. The final stage was titrating the solution with 0.05 N HCl using 0.05 N NaOH. The total number of surface basic groups was determined by comparing the quantity of NaOH absorbed by the control sample with the sample that included the adsorbent. To find the total number of acidic groups on the surface, 0.05 N HCl was used to titrate the sample that contained 0.05 N NaOH. The amount of total surface acidic groups was calculated by using the amount of HCl consumed for the sample containing adsorbent and the control sample.

2.2.3 Surface area measurement (BET) analysis

The Micromeritics Gemini VII Surface Area and Porosity Surface Analyser was used to measure the adsorbents' surface areas and total pore volumes. N_2 adsorption-desorption isotherms were used to determine the surface area of adsorbents. BET analyses were carried out at Erciyes University Technology Research and Application Centre.

2.2.4 Scanning electron microscope (SEM) analysis

SEM analyses of the original and modified adsorbents were carried out at Erciyes University Nanotechnology Research Centre. Using a Zeiss Evo LS10 scanning electron microscope (SEM), the surface morphology of the adsorbents was reviewed.

2.2.5 Fourier transform infrared spectrometry (FTIR-ATR) analysis

FTIR analyses provide information at the molecular level about new functional groups added to the surface or changes on the surface as a result of surface modification processes. FTIR analyses of the original and modified adsorbents were measured in the wavelength range of 400-4000 cm^{-1} by Perkin Elmer 400 Ft-IR/FT-FIR device at Erciyes University Technology Research and Application Centre.

2.2.6 Particle size distribution analysis

The dynamic light scattering (DLS) technique was used to determine the particle size distribution of the original and modified activated carbons. A Malvern NanoZS90 device with a 633 nm laser was used to perform DLS measurements at room temperature. A scattering angle of 173° was used to acquire the data.

Dimensional analyses were performed at Erciyes University Nanotechnology Research Centre on a retainer basis.

3. RESULTS AND DISCUSSIONS

3.1 SEM Analyses

SEM analysis is a method for figuring out the physical characteristics and surface morphology of the materials being studied. The adsorbents modified by nitric acid and sulfonic acid are shown in Figure 1 as SEM images with a size of 2 µm and a magnification scale of 500 KX. Upon examining the AC1 and AC2 adsorbents prior to modification, they exhibit a very wide particle size distribution, containing very small, activated carbon granules within their structure. Post nitric acid modification, both adsorbents (AC1N, AC2N) appear more homogeneous in terms of size. During the nitric acid modification, repeated washing of activated carbon with acid and pure water results in the removal of the smaller activated carbon particles.

Consequently, as evidenced by the SEM images of AC1N and AC2N adsorbents, larger and cleaner activated carbon granules remain. This characteristic is attributed to the modification process's cleansing impact. A similar observation was reported by Ge et al. [37], who noted that the surface of the modified adsorbent was cleaner and the surrounding pores smoother. Additionally, literature reports indicate that post nitric acid modification, activated carbon forms a smoother, more uniform, and narrow-pored structure, supported by a reduction in BET surface area [25, 38, 39].The SEM images of AC1N and AC2N adsorbents also corroborate the low surface area obtained from BET analysis results. Moreover, a number of investigations in the literature have documented that the physical shape of activated carbon may be considerably impacted by nitric acid treatment [40-42].

Upon examining the SEM images of the AC3N and AC4N adsorbents, it is observed that a clean and smooth structure similar to that of other adsorbents has formed. Lu et al. [14] noted that the surface morphology of adsorbents activated with coconut exhibited a clean and eroded appearance due to the oxidation by nitric acid. Unlike the other adsorbents, the AC3 and AC4 adsorbents showed a significant increase in surface area as a result of nitric acid modification. This is attributed to the fact that AC3 and AC4 are original (untreated) adsorbents, while AC1 and AC2 are pre-treated adsorbents. It was concluded that the modification of untreated adsorbents with nitric acid positively impacts the surface area. According to Su et al. [25], mass transfer during adsorption was facilitated by the creation of new pores following nitric acid modification, which expanded the contact area.

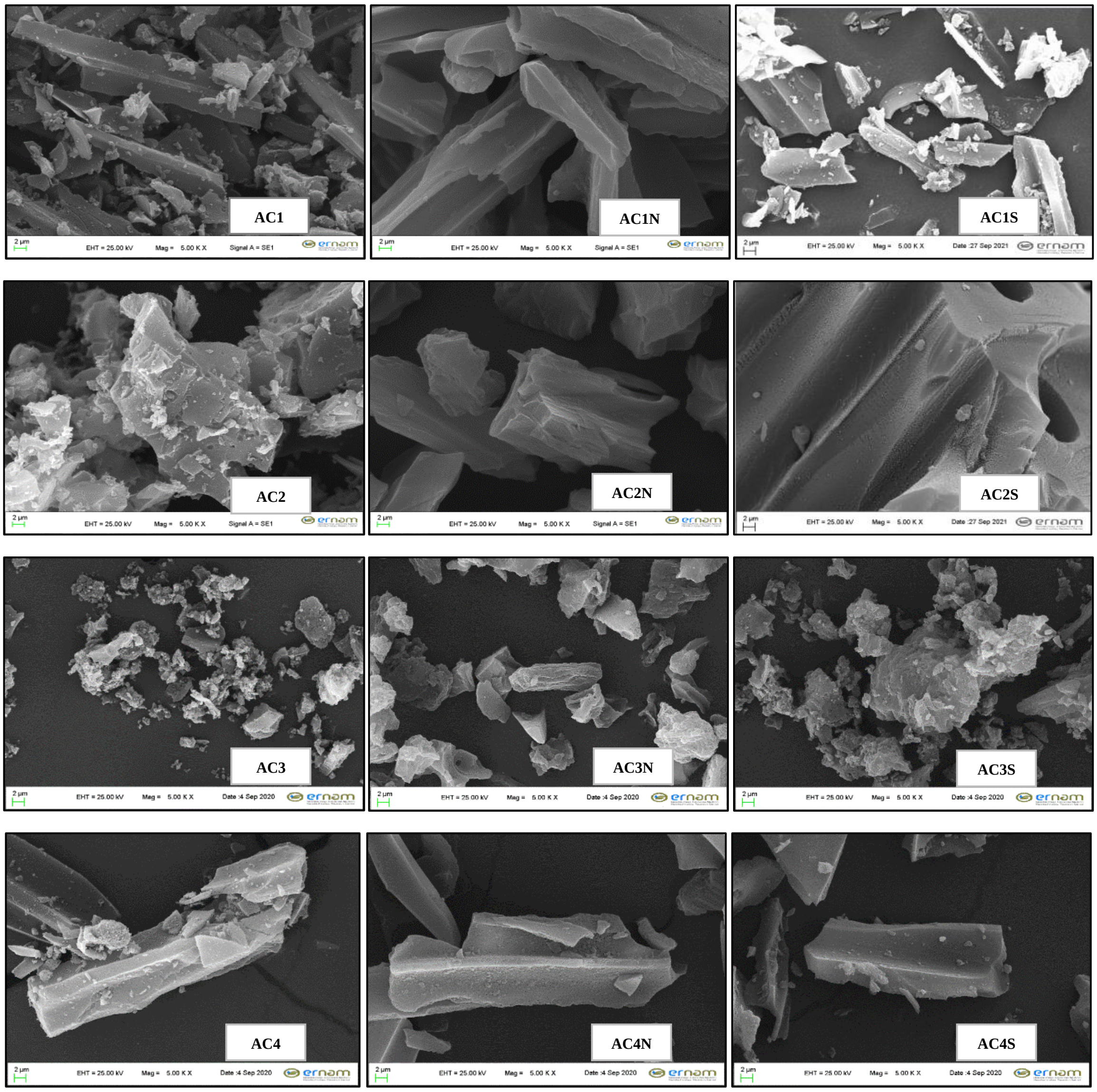

Figure 1. SEM images of original and modified ACs (2 µm mag: 500 KX)

3.2 FTIR Analyses

Figure 2 shows the FTIR spectra of the original and modified AC1 and AC2 adsorbents. In the FTIR spectrum of the AC1 adsorbent, bands observed at 2987.3 cm^{-1} and 2899.6 cm^{-1} are attributed to the aliphatic υ(C-H) stretching in the –CH– bond found in the aromatic methoxyl group and the side chains of methyl and methylene groups [43]. Both symmetric and asymmetric C-H vibrations are linked to bands seen roughly between 2950 and 2800 cm^{-1}, suggesting the existence of aliphatic compounds [44]. The band in the range of 1800-1300 cm^{-1} is characteristic of highly conjugated C=O stretching and C-O structures [45]. The peak at 1407.2 cm^{-1} is attributed to the C=O stretching vibration of carboxylic acid or ketone. The presence of peaks at 1080 and 1300 cm^{-1} in the AC1 spectrum can be associated with the C-O stretching vibrations of carboxylic acids, phenols, alcohols, or esters [30]. The FTIR spectra for AC1 reveal that the modification with HNO3 resulted in significant chemical changes in the structure of AC1N, with the disappearance of many bands. There are just two large peaks in the modified AC1N spectrum, and these may be linked to the allen (C=C=C) group. Another band around 2100 cm^{-1}, which is relatively broad, is also attributed to the allen (C=C=C) group [46-47].

In the FTIR spectrum of the AC2 carbon, the peaks at 2986.9 cm^{-1} and 1987.6 cm^{-1} disappeared after nitric acid modification. The 2099.2 cm^{-1} band in the AC2 sample slightly increased after modification, forming the 2111.5 cm^{-1} band. This relatively broad peak around 2100 cm^{-1} is attributed to the allen (C=C=C) group [46-47]. The presence of carboxyl groups produced by nitric acid is shown by the signal in the AC2N sample at 1707 cm^{-1} [8]. Similarly, Schepetkin et al. [48] observed a strong absorbance in the 1650-1720 cm^{-1} band, which they attributed to –COOH group vibrations. Another study associated the peak at 1729 cm^{-1} with the specific peak of the C=O bond stretching vibrations in the carboxylic acid functional group [49]. Shim et al. [50] reported an increase in adsorption bands in the 1750-1400 cm^{-1} range for carboxylic acid and quinone groups when comparing the spectra of activated carbon fibers modified with HNO3 to general spectra.

The bands observed between 1500-1600 cm^{-1} in both spectra of AC2N and AC2S originate from C=C stretching vibrations in the aromatic rings of quinone and keto-enol [51]. According to the FTIR data, oxidation with HNO_3 produces a number of surface functional groups, including quinone, carboxyl, and carbonyl. Following activated carbon activation, certain functional groups persisted while others were destroyed or new functional groups were created, according to an analysis of the FTIR spectrum. This observation aligns with the literature, confirming the presence of observed functional groups for AC2N in our experiments [52]. New peaks appeared at 3791 cm^{-1} and 3483 cm^{-1} in AC1S carbon, and at 3289.8 cm^{-1} in AC2S carbon. These peaks around 3300 cm^{-1} correspond to the –OH group [53]. New peaks observed at 611.24 cm^{-1} and 530.62 cm^{-1} in AC2S adsorbent are attributed to S-O stretching vibrations [30].

Figure 3 presents the FTIR spectra of original and modified AC3 and AC4 activated carbons. The original AC3 carbon structure includes bands at 2314, 2103, 2000, and 585.44 cm^{-1}. Nitric acid modification caused the bands at 2103 and 2314 cm^{-1} to widen, and peaks at 2355 and 2116 cm^{-1} to emerge. The 585.4 cm^{-1} band decreased after nitric acid modification, with a peak observed at 576.8 cm^{-1}. Upon examining the FTIR spectrum of AC4 and nitric acid-modified AC4N carbon, it was observed that the band at 3793 cm^{-1} disappeared after nitric acid modification, replaced by a peak at 3564 cm^{-1}. Peaks in the range of approximately 3700-3500 cm^{-1} are attributed to –OH groups [30].

The broad and strong band observed between 3655-3000 cm^{-1} after both modifications is attributed to the stretching vibration of ν(O-H) from adsorbed water or functional groups on the surface [43]. The sulfonic acid modification of the original AC3 carbon resulted in a peak at 1058.4 cm^{-1} corresponding to the S=O structure in AC3S carbon. Similarly, Huang et al. [54] associated peaks between 1030-1100 cm^{-1} with sulfonic structures. Following sulfonic acid modification, the band at 3793 cm^{-1} in the spectra of AC4 carbon vanished, and this was replaced by a band at 3560.3 cm^{-1} in the spectrum of AC4S carbon. Additionally, a new band at 1993.6 cm^{-1} was observed in AC4S, indicating functionalization of the adsorbent surface with S=O and SO3H groups. In a similar vein Kamari et al. [55] associated peaks with the S=O groups and SO3H group OH stretching absorption roughly between 1649 and 2900 cm^{-1}. Double-bonded C=O groups are responsible for the peaks in the AC4S carbon spectrum that are seen between 2100 and 2400 cm^{-1} [41]. At some point the findings show that, depending on the properties of the targeted contaminants, activated carbon functionalized with sulfonic acid can be employed in adsorption investigations with good results.

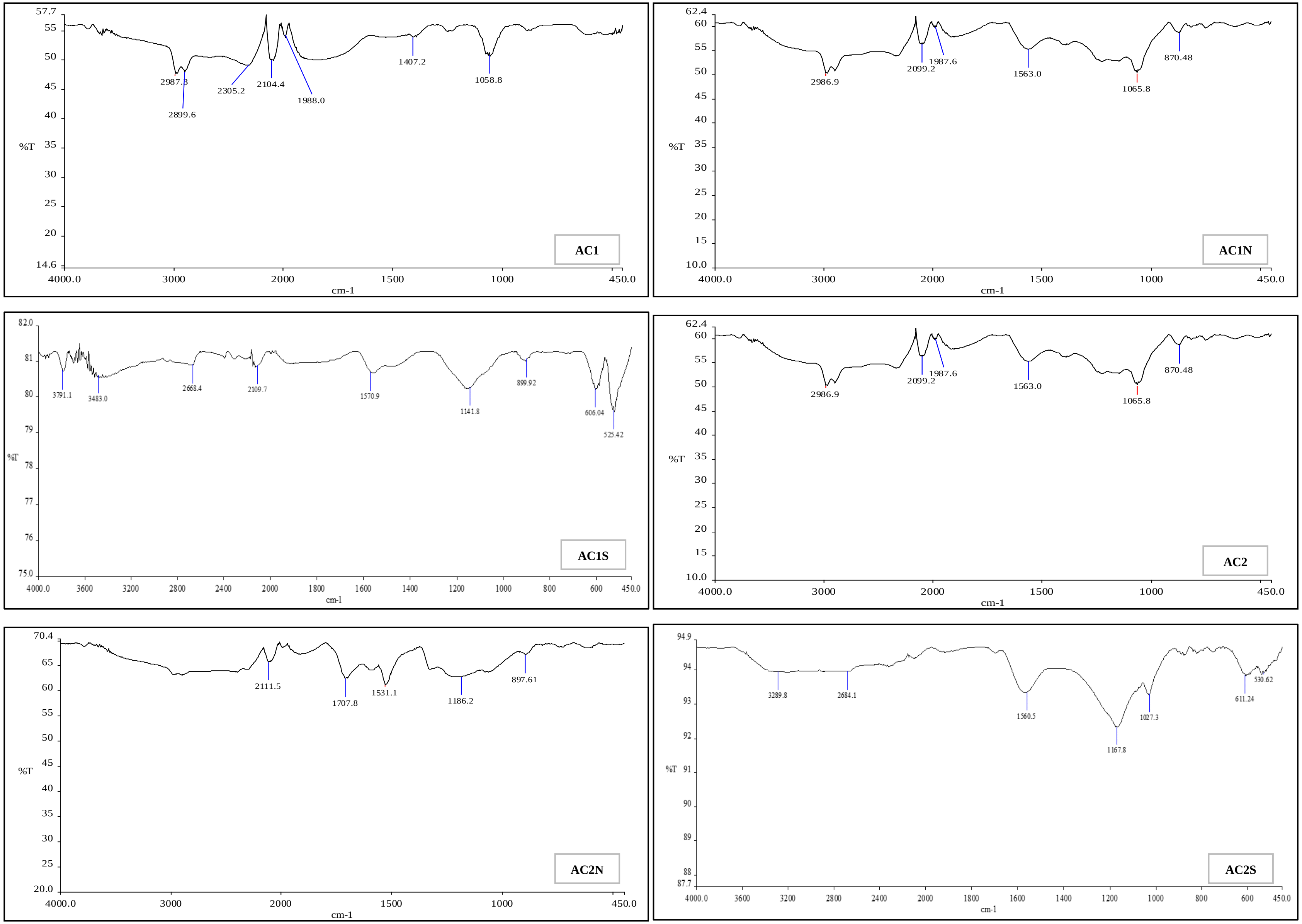

Figure 2. FTIR spectra of original and modified AC1 and AC2 activated carbons

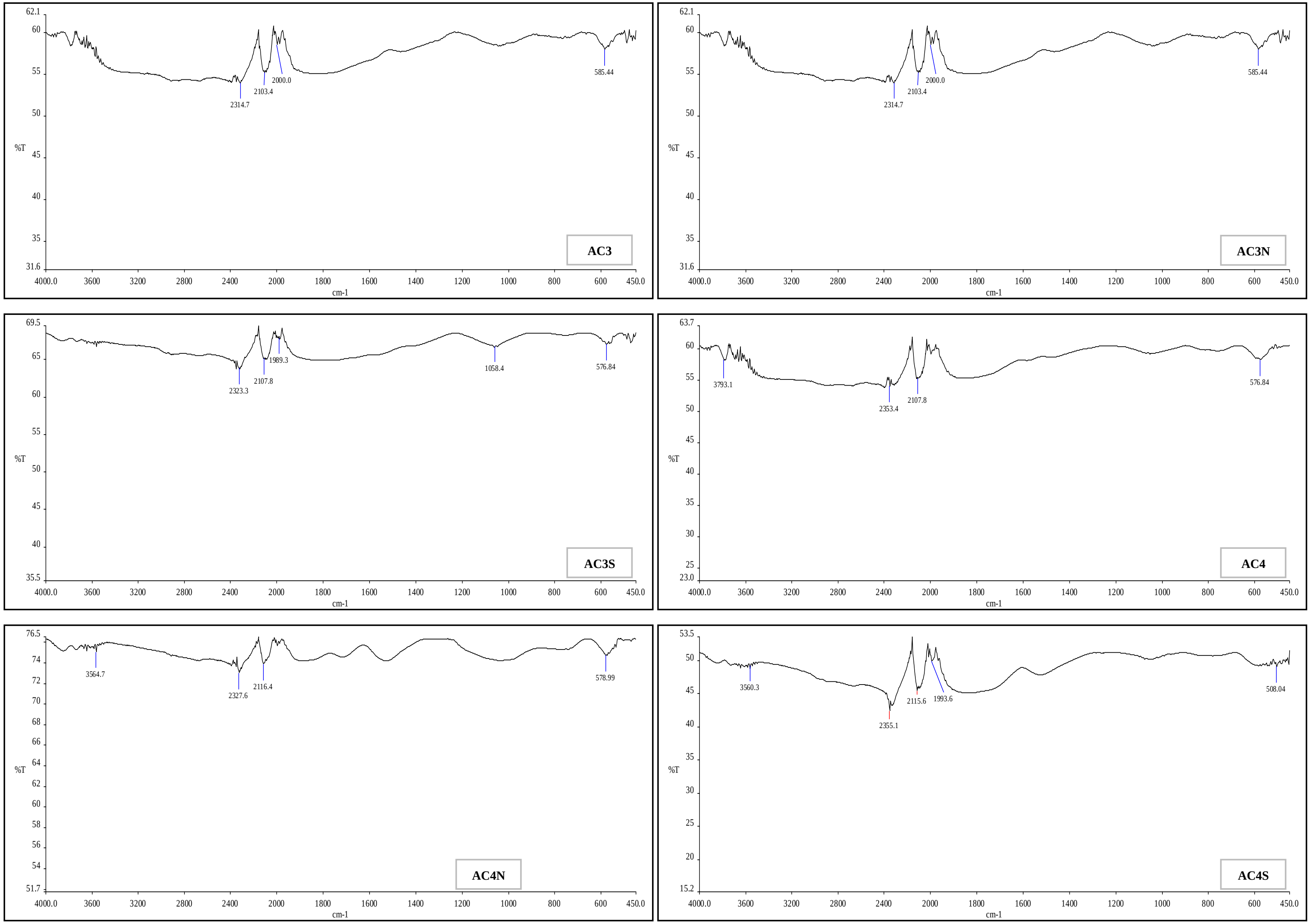

Figure 3. FTIR spectra of original and modified AC3 and AC4 activated carbons

3.3 BET Surface Area, Pore Volume, and Pore Size Analysis Results

N_2 adsorption-desorption isotherms were used to explain how modifications affected surface area and pore characteristics. The pore structure properties obtained from these isotherms are provided in Table 3. Table 2 makes it abundantly obvious how the structural properties of the activated carbon samples were affected by nitric acid and sulfonic acid modifications. Each modification agent can cause significant and distinct changes in the adsorbent structure, underscoring the importance of understanding the behavior of each agent (nitric and sulfonic acid). BET analysis based on nitrogen gas adsorption at 77 K revealed changes in surface area and porosity measurements as a result of both modifications. Nitric acid modification caused to a decrease of 39% and 76% in surface areas of AC1 and AC2 adsorbents, respectively. There are two potential implications that many researchers attribute to this observation: The first is the partial breakdown of microporous walls [10, 56, 57], and the second is the obstruction of pore entrances as a result of the development of oxygen functional groups [58]. Conversely, other studies interpret the increase in surface area after nitric acid treatment as dissolution of ash and opening of some blocked pores in activated carbon ShamsiJazeyi and Kaghazchi [49], which was observed as a 30% increase only in AC3N adsorbent. In contrast, after sulfonic acid modification, AC3 showed a slight decrease in surface area, whereas AC4 exhibited a significant increase from 273.56 m²/g to 868.48 m²/g.

Table 3. Pore structure characterization of original and modified activated carbon samples

Adsorbent	**BET Surface Area** (m^2g^{-1})	**Total Pore volume (cm^3g^{-1})**	**Pore Diameter (nm)**
AC1	1200	0.95	3.16
AC2	1161	1.12	3.85
AC3	656.6	0.78	4.74
AC4	274	0.22	3.24
AC1N	732	0.52	2.85
AC2N	273.56	0.22	3.24
AC3N	855.05	0.85	3.98
AC4N	822,48	0.76	3.71
AC1S	929.93	0.61	2.62
AC2S	500.59	0.48	3.81
AC3S	635.61	0.78	4.91
AC4S	868.48	0.88	4.18

SBET: Surface area calculated using the Brunauer-Emmett-Teller (BET) theory, Pore diameter: adsorption average pore width (BET 4V/A)

Total pore volume is another significant characterization outcome. Nitric acid modification resulted in a trend of pore loss in all adsorbents except AC3N and AC4N. The decrease in pore volume, similar to the decrease in surface area, has been attributed to the blocking of pores by oxygen functional groups due to chemical modification [59]. Yu et al. [60] investigated changes in carbon structure after oxidation with HNO3 at different temperatures. They reported significant destruction of pore structure in commercially modified activated carbon samples compared to other AC samples, which they associated with the strong oxidative power of concentrated HNO_3 at 120°C. In our study, the modification with HNO_3 was also conducted at 120°C, aligning our results with findings in the literature. The decreasing trend in nitric acid modification was followed by an increasing trend in sulfonic acid modification. The overall pore volume of AC4 in the AC4S sample rose significantly, from 0.22 cm³/g to 0.88 cm³/g. Due to sulfonic acid modification, the adsorbents AC1S and AC2S saw a reduction in total pore volume. Specifically, the reduction from 1.12 cm³/g to 0.48 cm³/g in AC2S is notable, indicating that repeated sulfonic acid modification may lead to structural degradation, resulting in a decrease in surface area and pore volume.

Pore diameters can improve the removal capacity for pollutants that notably target pore sizes, and they are a greater driver of activated carbon performance than total surface area alone [61]. Typically, activated carbons have three pore classifications: macropores larger than 50 nm, mesopores ranging from 2 to 50 nm, and micropores smaller than 2 nm. Both original and modified adsorbents in this study exhibit mesoporous structures ranging from 2 to 5 nm. Following nitric acid modification, the pore sizes in all samples decreased. During nitric acid modification, some mesopores were blocked, leading to a reduction in mesopore volume as shown in Table 3. Numerous research investigations have documented that the addition of HNO_3 to activated carbon decreases its BET surface area, pore volume, and pore [20, 43, 62]. In contrast, sulfonic acid modification increased pore sizes. For instance, the original AC4 adsorbent had a pore width of 3.24 nm, which increased to 4.18 nm after modification. These results indicate that nitric acid and sulfonic acid modifications alter the surface properties of activated carbons, affecting pore sizes in particular.

3.4 pH_{PZC}, Surface Acidity and Basicity

Surface acidity or basicity is an important criterion defining the surface chemistry of activated carbon adsorbents. Carboxyl, lactone, phenolic hydroxyl, quinone, and carboxylic anhydride groups are common oxygen-containing functional groups found on the surface. It has been noted that the higher the oxygen content, the more acidic the surface [20]. Surface basicity, on the other hand, is associated with oxygen-free Lewis sites at the edges of carbon layers, carbonyls, pyrone, and chromene-type structures [37]. The pHPZC findings and Boehm titration total acidic-basic groups are displayed in Table 4. Titration results indicate an increase in the total acidity of the activated carbon surface after nitric acid and sulfonic acid modifications. Particularly, an increase in total acid groups (meq/g) was observed for AC2 and AC4 adsorbents after nitric acid modification.

Gokce and Aktas [20] noted that higher initial concentrations of HNO_3 lead to increased formation of carboxylic groups on the surface, promoting the likelihood of carboxylic and phenolic groups co-locating and supporting lactonic group formation. However, at high concentrations, some basic surface functional groups can be removed from the structure. These changes are typical outcomes of oxidative modifications observed frequently in previous studies [50, 63], where oxidative effects of HNO3 during modification result in reductions of basic surface functional groups as well.

Table 4. Data obtained from the Boehm method and zero point of charge

Adsorbent	pH_{PZC}	Total Acidic Groups		Total Basic Groups	
		(meq/g)	(meq/m^2)	(meq/g)	(meq/m^2)
AC1	8.11	3.6	0.003	3.33	0.003
AC2	2.53	4.0	0.003	3.03	0.003
AC3	7.8	3.5	0.005	3.80	0.006
AC4	7.09	3.8	0.014	3.90	0.014
AC1N	2.08	4.1	0.006	3.00	0.004
AC2N	2.01	4.9	0.018	2.90	0.011
AC3N	2.88	3.950	0.005	3.725	0.004
AC4N	2.92	4.775	0.006	3.675	0.004
AC1S	4.98	3.05	0.0033	4.50	0.0048
AC2S	2.90	3.35	0.0067	4.30	0.0085
AC3S	2.9	3.950	0.006	3.650	0.006
AC4S	2.95	3.900	0.004	3.725	0.004

The number of basic sites generally decreases as a result of HNO3 modification. This can be attributed to nitric acid's ability to neutralize or even eliminate basic sites [64]. In the case of sulfonic acid modification, as observed in Table 4, there is a slight increase in total acid groups while a decrease in basic groups occurs. The most notable decrease was measured in AC4 adsorbent, where it decreased from 0.014 meq/m² to 0.004 meq/m² in AC4S adsorbent. The adsorption capacity of contaminants in aqueous solutions is influenced by the pH at which the surface of the adsorbent becomes positively or negatively charged, as shown by measurements of pH_{PZC} [65]. The pH equilibrium technique was used to determine the adsorbents' pH_{PZC} values [36]. All modified carbons were observed to have lower PZC values compared to the original carbon samples. This indicates that acidic properties are dominant as a result of the modification process and that there are more weak acidic functional groups compared to others.

The adsorbent with the least change in pHPZC value is AC2, which decreased from 2.53 to 2.01 after modification to AC2N. On the other hand, despite a slight decrease in pHpzc value after modification for AC2, a significant increase in total acidic groups was observed. This phenomenon is associated with the strong oxidative effect of nitric acid modification. For AC3, AC4, and AC1 samples modified with sulfonic acid, a decreasing trend in pHpzc values was observed. However, for AC2, sulfonic acid modification resulted in a small increase in pHpzc value from 2.53 to 2.90. Similarly, in a dye adsorption study by Goswami and Phukan [30], the pHpzc values were reported as 5.18 for activated carbon (MTLAC) and 2.4 for sulfonic acid-modified activated carbon (MTLAC-SA).

3.5 DLS Analyses

Based on the DLS histograms, the changes in particle size distributions of original and modified adsorbents were determined using the weight average calculation method. Particle size analysis graphs of original and modified AC1 and AC2 adsorbents are presented in Figure 4. The x-axis in the graphs represents the particle size diameter in nm, and the y-axis indicates the percentage of particles by number. Upon examining the DLS histogram of AC1 sample, it is observed to have a wide particle distribution ranging from 190.1 nm to 1718 nm. According to the weight average calculation method, the majority of AC1 carbon is sized at 377.52 nm. After nitric acid modification, the particle size distribution of AC1N adsorbent reduced, with an average size of 241.23 nm. The AC1S sample has an average particle size distribution calculated as 1419.44 nm. This suggests that the modification significantly increased particle size for AC1S carbon. Similarly, the average size distribution of AC2 adsorbent is 685.37 nm, whereas after nitric acid modification, AC2N adsorbent showed a significant decrease with an average size distribution of 259.66 nm. However, as compared to AC1S, the average particle size distribution of the AC2S adsorbent decreased after sulfonic acid alteration, measuring 428.42 nm.

Particle size analysis graphs of original and modified AC3 and AC4 adsorbents are presented in Figure 5. The average particle size distributions of AC3 and AC4 adsorbents are calculated as 939.94 nm and 313.32 nm, respectively. These results demonstrate that nitric acid modification led to a reduction in the average particle size distribution of both adsorbents. The values for AC3N and AC4N were found to be 279.04 and 252.81 nm, respectively. The originally calculated particle size distribution for AC3 at 939.94 nm increased to 992.81 nm in AC3S sample due to the effect of sulfonic acid modification. Additionally, approximately 70% of AC3S particle sizes fall within the range of 825-1106 nm. AC4S sample also showed a similar increase of 34%, calculated as 417.64 nm. Sulfonic acid modification had a positive influence on particle size distribution, whereas nitric acid modification often had a negative effect.

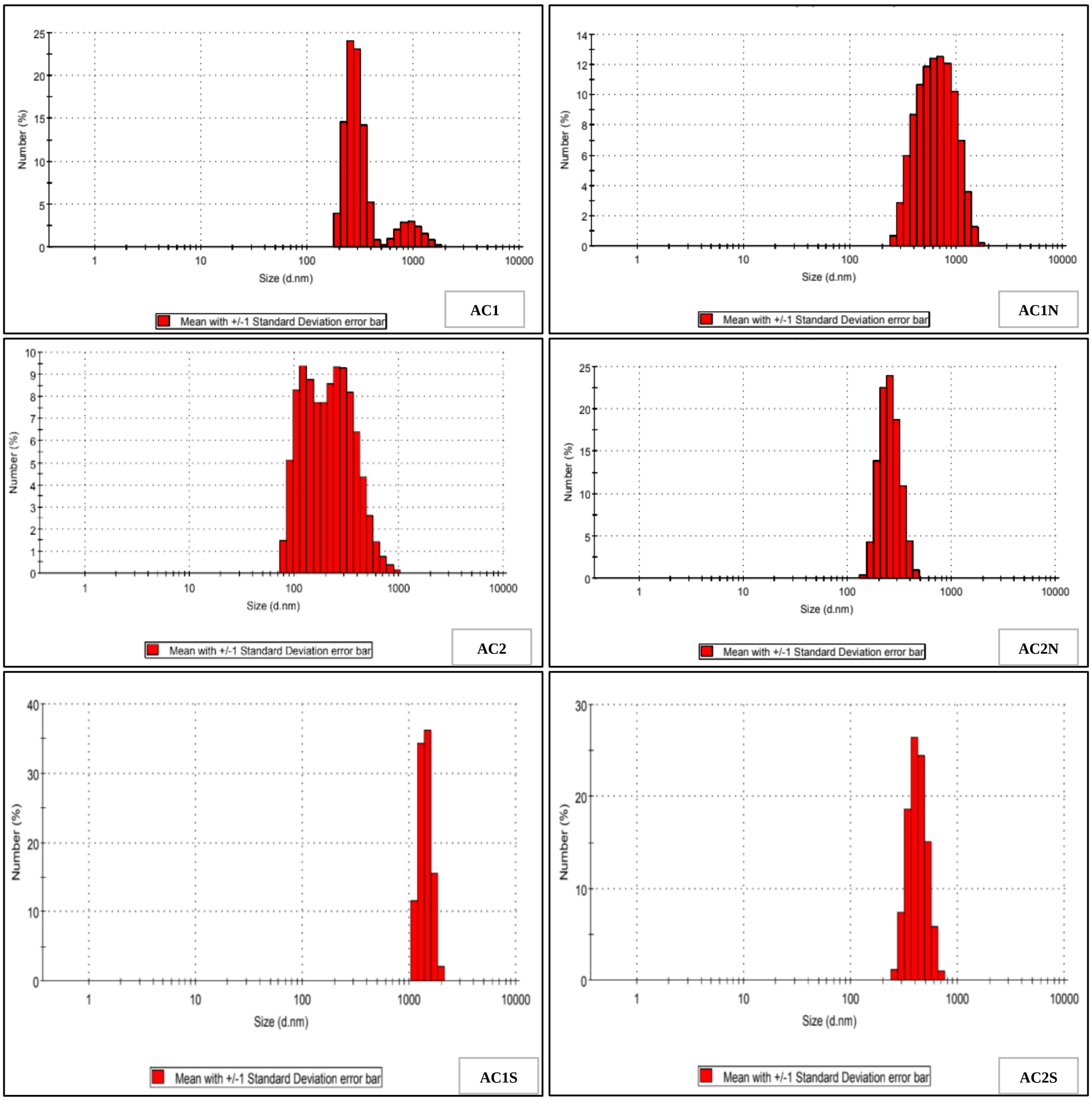

Figure 4. Particle Size Analysis Graphs of Original and Modified AC1 and AC2 Activated Carbons

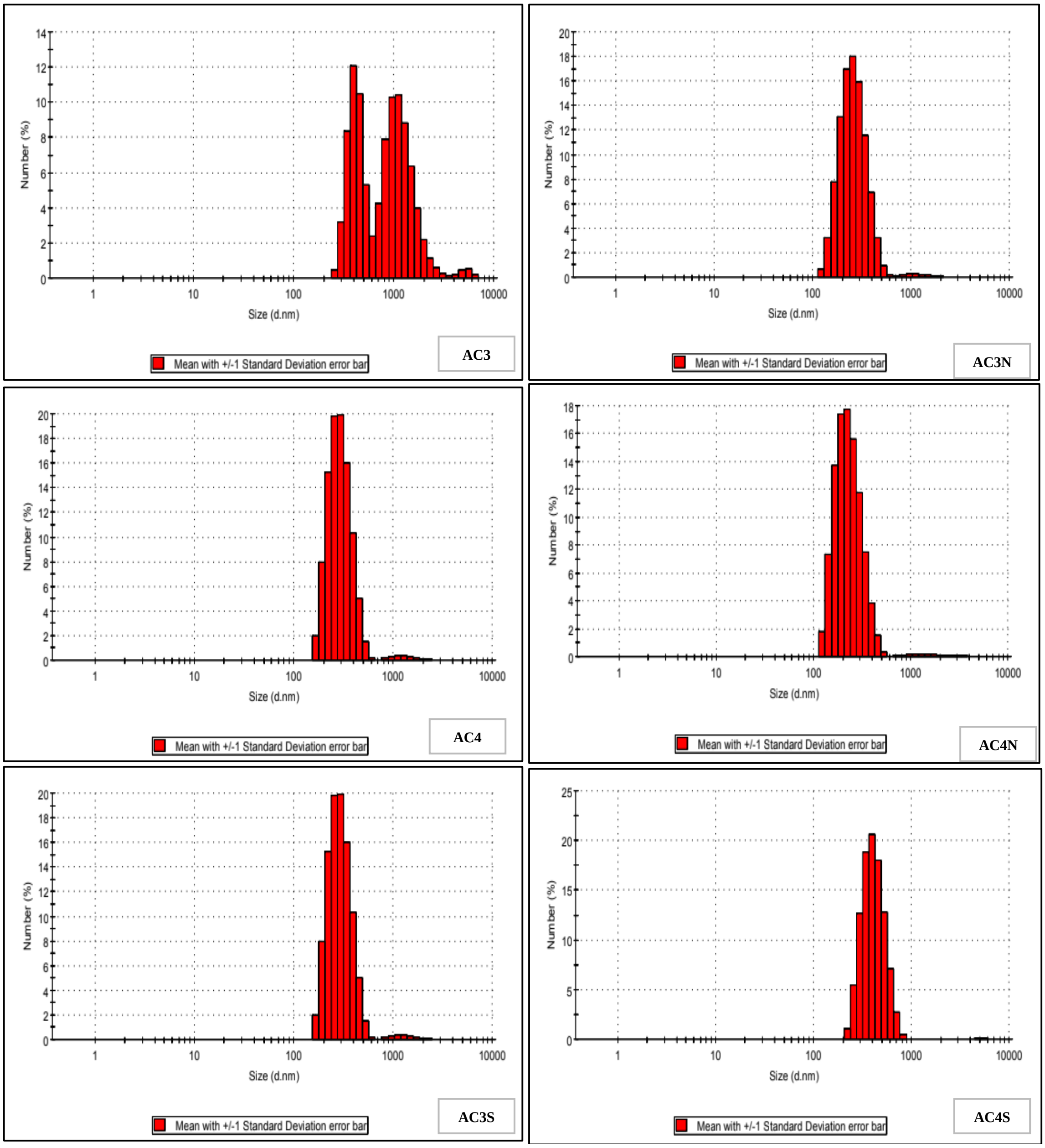

Figure 5. Particle Size Analysis Graphs of Original and Modified AC3 and AC4 Activated Carbons

4. CONCLUSIONS

In the Altinapa Dam Watershed, Activated carbons specific surface area and active sites, two crucial characteristics that significantly impact its adsorption capacity, may be adjusted through the use of chemical modification techniques. The current investigation evaluated and conducted characterization assessments on commercial powdered AC, nitric acid, chlorosulfonic acid, and double chemical modification. The key points are summarized below:

- Scanning Electron Microscopy (SEM) analysis demonstrated that nitric acid modification resulted in a smoother, cleaner, and more uniform surface morphology, whereas chlorosulfonic acid treatment did not induce significant morphological alterations.
- Fourier-transform infrared spectroscopy (FTIR) revealed the formation of oxygen-containing functional groups such as carboxyl, carbonyl, and quinone upon nitric acid modification. A new peak at 1993.6 cm^{-1} observed in the AC4S sample confirmed the presence of sulfonic groups (S=O and SO_3H), indicating successful sulfonation via chlorosulfonic acid.
- A substantial increase in surface area was achieved with nitric acid treatment, with the highest enhancement (200%) observed in AC4N. A comparable increase was also noted in AC4S, indicating the effectiveness of both acid treatments in enhancing porosity.
- Double acid modification had a detrimental effect on the porous structure, causing surface area reductions of 39% and 76% in AC1 and AC2, respectively. This decrease is attributed to micropore wall degradation or pore blockage due to the formation of surface oxygenated groups.
- All acid-modified samples exhibited a decrease in pH_{PZC} values, reflecting an increase in surface acidity. Surface acid group concentrations increased up to 0.97 meq/g following nitric acid treatment.
- Chlorosulfonic acid modification significantly broadened the particle size distribution, potentially affecting the adsorptive behavior.
- Overall, the findings suggest that nitric acid and chlorosulfonic acid surface modifications are effective techniques for enhancing the physicochemical properties of activated carbon. When choosing a modification method for adsorption applications, the unique properties of the target pollutants should be taken into consideration.

Acknowledgments

This study was supported by the Scientific and Technological Research Council of Turkey (Project No: 118Y402).

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