Preparation and Characterization of Sulfonic Acid Functionalized Activated Carbon for Applications in Water and Wastewater Treatment

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Abstract - Activated carbon (AC) has been considered one of the oldest and most widely used adsorbents for the removal of organic and inorganic pollutants in water and wastewater treatment**.** The physical and chemical structure of AC can be altered by various modification methods, especially to improve the treatment performance for specific pollutants**.** The modification can be classified into three categories namely, chemical, physical and biological which are further subdivided into their related treatment techniques (such as acidic, basic, heat etc.). The aim of this study is to modification and characterization of the original powder activated carbon (PAC) with sulfonic acid. Original AC and modified AC characterization analysis were performed based on morphological properties, pore size distributions and structural properties such as scanning electron microscope (SEM), brunauer–emmett–teller (BET), fourier transform infrared spectrophotometer (FTIR) and dynamic light scattering (DLS). The sulfonic acid modification method was effective in alteration the porous structure and surface properties of PAC. As a result of the sulfonic acid modification, the BET surface area increased from 273.56 m^2/g to 868.48 m^2/g. It was observed that AC-S had lower pH_{PZC} values than the original adsorbent. In the FTIR spectrum of AC-S adsorbent, it was observed that 1993.6 cm^{-1} band was added to the structure, unlike the original AC. This peak indicates S=O groups and SO_3H group, which indicates that the AC surface is functionalized with sulfonic groups. Overall, the results showed that sulfonic acid functionalized activated carbon can be used effectively in adsorption studies depending on the properties of the targeted pollutants.

Keywords: Activated carbon, adsorption, characterization, modification, sulfonic acid.

1. Introduction

Activated carbon (AC) has been proven as a commonly used adsorbent for remove organic and inorganic pollutants in conventional treatment processes [1]. Main advantages of AC are including high adsorption capacity [2], large surface area, high porosity [3] and the presence of a wide spectrum of surface functional groups. Two types of often used activated carbon are powdered activated carbon and granular activated carbon [4]. Commercial powdered or granular activated carbon adsorption has not been feasible used in water treatment plants in practice for large molecular weight and heterogeneous mixtures such as natural organic matters. The modification is widely used to change various physicochemical properties of AC for different types of applications. Various modification methods highly effective on the adsorption properties of ACs have been developed that changes the amount and diversity of the surface functional groups [5]. The modification can be classified into three categories namely, chemical, physical and biological which are further subdivided into their related treatment techniques (such as acidic, basic, heat) [6, 5].

In the literature the most studied modification methods were treatment with acids, bases and impregnation with different materials. Particularly, acid modification is employed to oxidize the porous carbon surface, increase its acidic properties, remove mineral elements and improve the hydrophilic properties of the surface [7]. Various reagents such as nitric acid, sulfuric acid, potassium permanganate, hydrogen peroxide and ozone have been frequently used in the modification of the carbon surface to obtain a more hydrophilic surface structure associated with the greater presence of oxygen-containing groups [7, 8]. In many studies, it has been stated that acid modification is a very effective method especially because of the addition of a significant number of strong or weakly oxygenated acidic groups containing mainly carboxylic, lactone and phenolic hydroxyl groups to the carbon surface [9, 10].

Recently, it has been thought that modification with sulfonic acid instead of sulfuric acid, which is another method that could increase surface acidity, may have significant potential [11, 12]. It has been reported that chlorosulfonic acid

modification bring about an electrostatic interaction between the adsorbent and the surface, and is effective on the surface morphology [13, 14]. Before determining the adsorption capacity of AC on various pollutants, it is important to understand how the modification changes the surface properties and the factors affecting the adsorption. These features including surface area, pore diameter, surface morphology, pore size distribution and surface functional groups with different properties [15].

This study aimed to investigate modification and characterization of activated carbons by sulfonic acid for water treatment. Commercial powdered activated carbon (PAC) with different properties was preferred in this study. Original AC and modified with sulfonic (AC-S) characterization analysis, were determined morphological properties, pore size distributions and structural properties such as scanning electron microscope (SEM), brunauer–emmett–teller (BET), fourier transform infrared spectrophotometer (FTIR) and dynamic light scattering (DLS). Original and modified AC was compared in terms of physicochemical properties. The characterization results can be considered a reference for activated carbon modification with sulfonic acid especially, for studies investigating the choice of adsorbent in specific pollutant adsorption.

2. Material and Methods

The modification process steps are shown in Figure 1. The study, commercial AC Puriss (AC) in powder activated carbon (PAC) form (Sigma-Aldrich) was selected to modification. Goswami and Phukan [14] has been implemented by modifying the method applied in his study. Modification studies of AC were carried out with sulfonic acid and all chemicals were of either analytical or reagent grade. In the modification of sulfonic acid, firstly added 900 ml of dichloromethane and mixed ultrasonically for 45 minutes. Next, has added 30 ml of chlorosulfonic acid and stirred for 180 minutes. Finally, filtered the sample, and washed it with ethanol and distilled water. After these stages, the modification process was completed. The modified activated carbon obtained is labelled as AC-S. Subsequently, physicochemical characterization of ACs in terms of specific surface area, point of zero charge (pH_{PZC}), SEM and FTIR analysis were determined. pH_{PZC} values of the adsorbents were determined through a pH equilibration method [16]. The 0,1 M NaCl solution in purified water was adjusted with 0.5 M HCl and / or 0.5 M NaOH so that the pH values were 2, 3, 4, 5, 6, 7, 8, 9, 10, 11,12. After, 20 ml samples were taken from these solutions into 25 ml amber sample bottles and 100 mg of adsorbent was added on each. Control samples without adsorbents were also prepared for each pH value. The prepared samples were mixed for 48 hours at 100 rpm and $20 \pm 5\ ^{0}C$. At the end of the mixing period, the samples were kept for 1 hour to precipitate the adsorbents and the pH values of the samples were measured. The pH_{PZC} value is the pH value that remains constant after 48 hours of contact time. For the original and modified activated carbons, the pHpzc value remaining constant after 48 hours was recorded, and the effect of modification with acid on the net surface load of the adsorbents was determined.

The surface morphology of the adsorbents was analyzed with a Zeiss Evo LS10 scanning electron microscope (SEM).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 analysis were performed with Perkin Elmer 400 Ft-IR/FT-FIR spectrometer in the wavelength range of 400-4000 cm^{-1}. DLS measurements were performed at room temperature with the Malvern NanoZS90 instrument equipped with a 633 nm laser. Data were collected with a scattering angle of 173°.
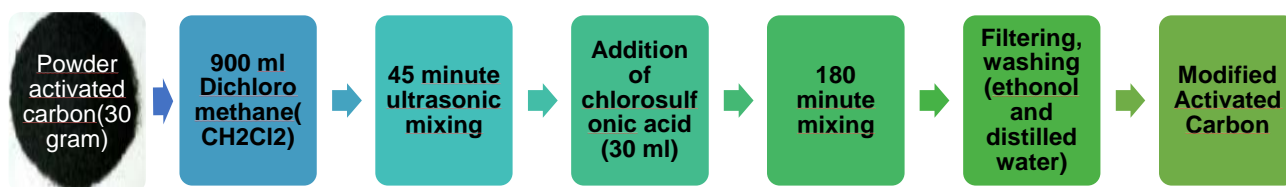

Fig.1: Sulfonic acid modification

3. Results/Discussion
Characterization of Original and Modified AC

It is very essential to know the porous structure and specific surface chemistry of any adsorbent in order to understand the absorptive capacity [17]. The physical characteristics of activated carbon are commonly described with surface area, pore size, pore volume and their distribution. N_2 adsorption desorption isotherms were used to understand the changes caused by the modification on the surface area and pore properties. The pore structure properties and pH_{pzc} values obtained by using these isotherms are given in Table 1. A significant increase in surface area was observed AC-S after modification. BET surface area increased from 273.56 m^2/g to 868.48 m^2/g after sulfonic acid modification. Saha et al. [18] stated that such an increase in surface area is due to the development of the mesopore region. Another important characterization result is that total pore volume. An increase was observed in the total pore volume of AC adsorbent from 0.22 cm^3/g to 0.88 cm^3/g in AC-S adsorbent. Pore size is a vigorous determinant for the performance of activated carbon than the total surface area and can increase the removal capacity for pollutant molecules targeting exclusively the pore size [19, 20]. AC, typically has 3 pore classes, these are classified as macropores greater than 50 nm, mesopores between 2 and 50 nm, and micropores less than 2 nm [21] In this study, the original and modified adsorbents have mesopore structures ranging from 2 to 5 nm. The pore diameter, which was 3.24 nm for the original AC adsorbent, was determined as 4.18 nm after sulfonic acid modification.

Table 1: Some physicochemical characterization properties of adsorbents

Adsorbents	BET Surface Area S_{BET} (m^2g^{-1})	Total Pore Volume (cm^3g^{-1})	Pore Diameter (nm)	pHpzc
Original AC	273.56	0.22	3.24	7.09
AC-S	868.48	0.88	4.18	2.95

*SBET: Surface area calculated by Brunauer-Emmett-Teller theory; Pore diameter: It represents the point of adsorption average pore diameter (BET 4V/A).

The surface chemistry of adsorbents is characterized by the neutral charge point (pH_{PZC}, pH value at which the total net surface charge is zero). Above the zero charge point, the particle is negatively charged, and below that, the particle is positively charged. This situation affects the adsorbate-adsorbent system in adsorption and thus the pollutant removal capacity [22]. It was observed that all modified carbons had lower pH_{PZC} values than the original carbon sample. As should be expected, introduction of acidic functional groups can decrease the PH_{PZC} of carbon surfaces. The pHpzc value of the original AC adsorbent showed a decreasing trend from 7.09 to 2.95 values in the AC-S adsorbent. This indicates that the acidic properties have been more dominant in the AC-S adsorbent and may contain more weakly acidic functional groups. Goswami and Phukan [14] determined pHpzc values of activated carbon and sulfonic acid modified activated carbon and pH_{PZC} values of modified and virgin activated carbons were 5.18 and 2.4, respectively, in their dye adsorption study.

Activated Carbon Morphological and Chemical Structure Characterization

SEM is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons, and is a technique used to determine the surface morphologies and surface physical properties of the materials under investigation [23]. The results of SEM analysis of original AC and sulfonic acid modified AC-S samples at 2 µm size and 500 KX magnification scale are given in Figure 2. It was observed that AC, had minimal differences in surface morphology after sulfonic modification. AC-S appears to have a cleaner and smoother structure compared to AC. The high surface area created by the modification in the structure of AC-S is consistent with the BET results. It is thought that this will increase the contact area and facilitate mass transfer during adsorption.
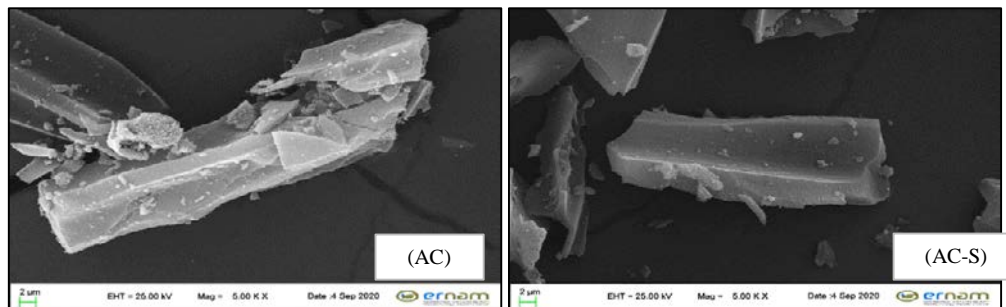
Fig. 2: SEM micrographs (2 μm mag: 500 KX) AC and AC-S

FTIR spectra is an important method used in the qualitative analysis of the distributions of functional groups on the surface [24]. IR spectra, the x-axis represents the wave number of the ray in cm^{-1}, and the y-axis represents the %T (% transmittance) value related to the intensity of the transmitted ray. FTIR spectra AC and AC-S are shown in Figure 3. The 3793 cm^{-1} band of AC adsorbent in the IR spectrum disappeared in AC-S adsorbent as a result of modification with sulfonic acid. The spectrum of AC-S revealed the peak at 3560.3 cm^{-1} corresponding to the bonded -OH group. Another newly formed peak has a wavelength of 1993.6 cm-1. Similarly, Kamari et al. [25] associated the peaks between about 1649-2900 cm^{-1} with relate to S=O groups and OH stretching absorption of the SO_3H group, respectively. The peaks at 2100-2400 cm^{-1}, which are also included in the spectra of the AC-S carbon, are attributed to the double bonded C=O groups [9].
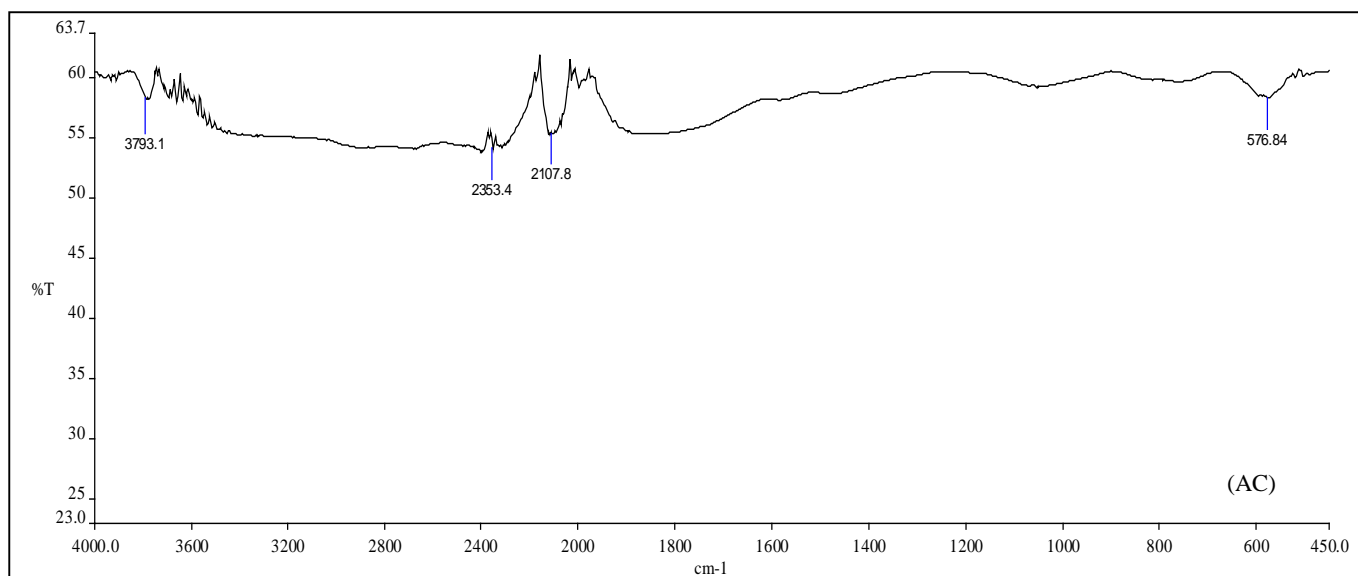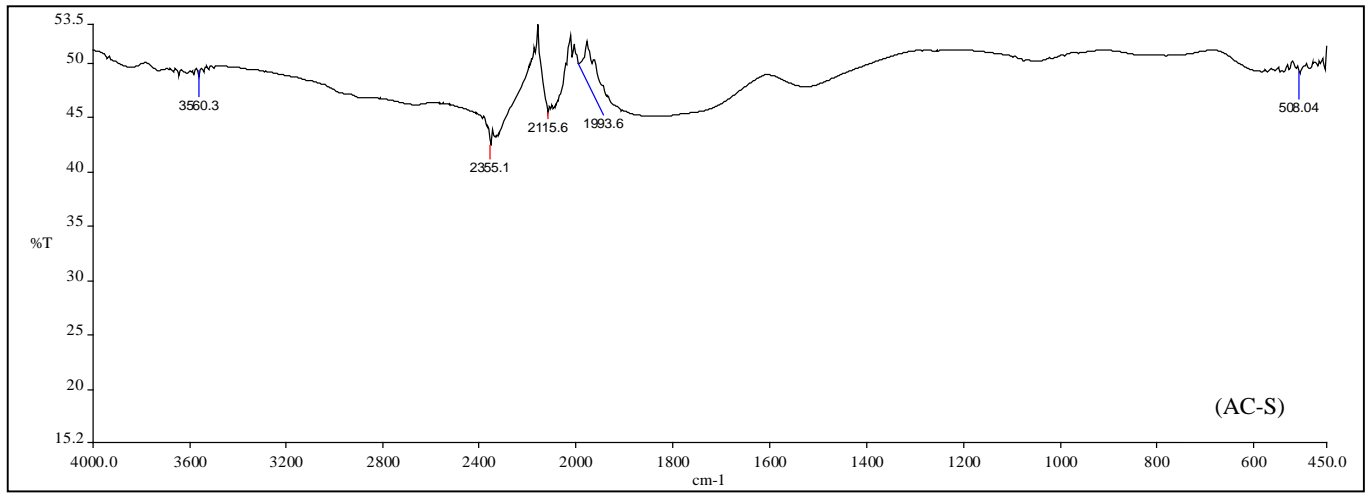
Fig. 3: FTIR spectra AC and AC-S

The particle size distribution of the original and modified activated carbons was determined by DLS analysis. DLS measurements were performed at room temperature with the Malvern NanoZS90 instrument equipped with a 633 nm laser. DLS is the most suitable technique for the estimation of nanoparticle sizes dispersed or dissolved in solvents and can be applied to a wide variety of particle sizes ranging from a few nanometers to micrometers [26]. DLS histograms of AC and AC-S are shown in Figure 4. The particle size distribution of the AC adsorbent was calculated as 313.32 nm as a result of the weighted average calculation method. The particle size distribution value of AC-S adsorbent compared to the original AC increased by 34% and was calculated as 417.64 nm.
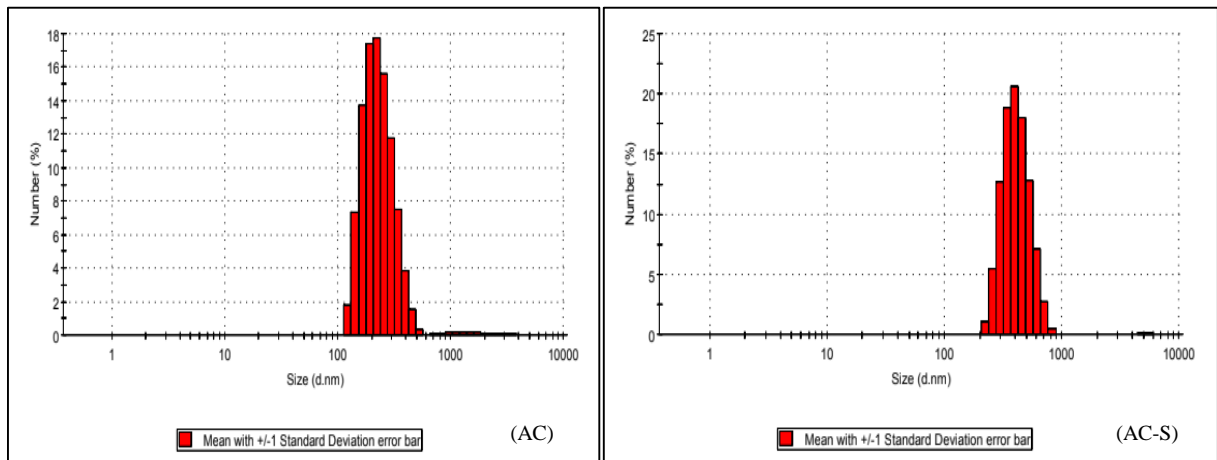

Fig. 4: DLS histograms of AC and AC-S

4. Conclusion

The performance of the adsorption process largely depends on the properties of the adsorbent used, and the adsorption performance can be increased by changing the properties of the adsorbent with surface modification methods. In addition, it is very important to interpret the effect of modification on adsorbent characterization in organic and inorganic pollutant adsorption. In this study, it was investigated how the modification of the original activated carbon with sulfonic acid changed the adsorbent characterization. The results showed that the sulfonic modification method was effective in changing the physical and chemical properties of AC surfaces.

The important results can be listed as follows: after sulfonic acid modification, BET surface area, pore diameter and total pore volume increase were observed in the adsorbent structure. The pH$_{PZC}$ value of the adsorbent modified with acid was lower than that of the original adsorbent. In the FTIR spectrum of AC-S adsorbent, it was observed that 1993.6 1 band was added to the structure, unlike the original AC. The presence of 3560.3 cm-1 peak, which is associated with OH stretching vibration, in AC-S adsorbent proved the effect of sulfonic acid modification. DLS analysis results was positive effect of sulfonic acid modification on the particle size distribution. The results of this research suggest that the sulfonic acid surface modification method can be used effectively in adsorption studies depending on the properties of the targeted pollutants. The adsorbent characterization results and sulfonic acid modification will contribute to the literature.

Acknowledgements

References
[1] Z. Heidarinejad, M-H. Dehghani, M. Heidari, G. Javedan, I. Ali and M. Sillanpaa, "Methods for preparation and activation of activated carbon: a review," Environmental Chemistry Letters, vol. 18, pp. 393-415, 2020.

[2] E-D. Ligneris, L-F. Dumee and L. Kong, "Nanofiber-based materials for persistent organic pollutants in water remediation by adsorption," Appl. Sci., vo. 8, no. 2, pp. 166, 2018.

[3] F-A. Abraham, R. Thenmozhi, M. Sivakumar, K. Sivakumar, G. Sasikumar and S. Thamaraimuthuayyanraj, "Wastewater treatment unit using activated charcoal," Int. Res. J. Eng. Technol., vol. 5, no. 3, pp. 312-315, 2018.

[4] Z. Fallah, E. Nazarzadeh Zare, M. Ghomi, F. Ahmadijokani, M. Amini, M. Tajbakhsh, M. Arjmand, G. Sharma, H. Ali Ali, A. Ahmad, P. Makvandi, E. Lichtfouse, M. Sillanpää and R-S. Varma, "Toxicity and remediation of pharmaceuticals and pesticides using metal oxides and carbon nanomaterials," Chemosphere, vol. 275, pp. 130055, 2021.

[5] A. Bhatnagar, W. Hogland, M. Marques and M. Sillanpää, "An overview of the modification methods of activated carbon for its water treatment applications," Chemical Engineering Journal, vol. 219, pp. 499–511, 2013.

[6] C-Y. Yin, M-K. Aroua, W-M. Ashri and W. Daud, "Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions," Separation and Purification Technology, vol. 52, pp. 403–415, 2007.

[7] W. Shen, Z. Li and Y. Liu, "Surface Chemical Functional Groups Modification of Porous Carbon," Recent Patents on Chemical Engineering, vol. 1, no. 1, pp. 27-40, 2008.

[8] Y. Huang, M. Yao, Y. Cheng, L. Wang and X. Li, "Biosynthesis of ruthenium nanoparticles supported on nitric acid modified activated carbon for liquid-phase hydrogenation of 2,2,4,4-tetramethylcyclobutane-1,3-dione," Catalysis Communication, vol. 72, pp. 20-23, 2015.

[9] J-P. Chen and S. Wu, "Acid/base-treated activated carbons: Characterization of functional groups and metal adsorptive properties," Langmuir, vol. 20, pp. 2233-2242, 2004.

[10] M-S. Shafeeyan, W-M. Ashri,W. Daud, A. Houshmand and A. Shamiri, "A review on surface modification of activated carbon for carbon dioxide adsorption," Journal of Analytical and Applied Pyrolysis, vol. 89, pp. 143-151, 2010.

[11] X. Liang, M. Zeng and C. Qi, "One-step synthesis of carbon functionalized with sulfonic acid groups using hydrothermal carbonization," Carbon, vol. 48, pp. 1844-1848, 2010.

[12] W. Mateo, H. Lei, E. Villota, M. Qian, Y. Zhao, E. Huo, Q. Zhang, X. Lina, C. Wang and Z. Huang, "Synthesis and characterization of sulfonated activated carbon as a catalyst for bio-jet fuel production from biomass and waste plastics," Bioresource Technology, vol. 297, pp. 122411, 2020.

[13] O. Rodríguez-Uicab, F. Avilés, P.I Gonzalez-Chia, G. Canché-Escamilla, S. Duarte-Aranda, M. Yazdani-Pedram, P. Toro, F. Gambo, M.A. Mazo, A. Nistal and J. Rubio, "Deposition of carbon nanotubes onto aramid fibers using as received and chemically modified fibers," Applied Surface Science, vol. 385, pp. 379-390, 2016.

[14] M. Goswami and P. Phukan, "Enhanced adsorption of cationic dyes using sulfonic acid modified activated carbon," Journal of Environmental Chemical Engineering, vol. 5, pp. 3508-3517, 2017.

[15] J. Rivera-Utrilla, M. Sánchez-Polo, V. Gómez-Serrano, P.M. Álvarez, M.C.M. Alvim-Ferraz and J.M. Dias, "Activated carbon modifications to enhance its water treatment applications. An overview," Journal of Hazardous Materials, vol. 187, pp. 1-23, 2011.

[16] T. Karanfil, "Oxygen sensitivity of natural and synthetic organic macromolecule sorption by activated carbon," The University of Michigan, Ph.D. Thesis, Ann Arbor, MI. 1995

[17] C. Yu, X. Fan, L. Yu, T-J. Bandosz, Z. Zhao and J, Qiu, "Adsorptive removal of thiophenic compounds from oils by activated carbon modified with concentrated nitric acid," Energy & Fuels, vol. 27, pp. 1499-1505, 2013.

[18] B. Saha, M. H. Tai and M. Streat, "Study of activated carbon after oxidation and subsequent treatment characterization," Trans IChemE., vol. 79, 2001.

[19] L. Li, P-A, Quinlivan and Detlef R.U. Knappe, "Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution," Carbon, vol. 40, pp. 2085-2100, 2002.

[20] E. Partlan, "Superfine powdered activated carbon (S-PAC) coupled with microfiltration for the removal of trace organics in drinking water treatment," Clemson University, Environmental Engineering, 8-2017.

[21] U. Demir and S. Elbinsoy, "Aktif karbon üretiminde yüksek kükürtlü kömürlerin kullanılabilirliğinin araştırılması," Academic Platform Journal of Engineering and Science, vol. 7, no. 1, pp. 45-51, 2019.

[22] A. Dabrowski, P. Podkoscielny, Z. Hubicki and M. Barczak, "Adsorption of phenolic compounds by activated carbon—a critical review," Chemosphere, vol. 58, pp. 1049-1070, 2005.

[23] S. Farajı, "Activated Carbon Nano-Fiber from Polymers," Istanbul Technical University, Graduate School Of Science Engineering And Technology, M.Sc. Thesıs, pp. 109, 2014.

[24] H. Sayğili, "Yeni bir hammaddeden üretilmiş karbonlu malzemenin yapısal, morfolojik ve gözenek özellikleri üzerine çalışmalar," Dicle Üniversitesi, Mühendislik Fakültesi, Mühendislik Dergisi, cilt.8, sayı. 1, ss. 245-252, 2017.

[25] M. Kamari, S. Shafiee, F. Salimi and C. Karami, "Comparison of modified boehmite nanoplatelets and nanowires for dye removal from aqueous solution," Desalination and Water Treatment, vol. 161, pp. 304-314, 2019.

[26] P. Linkov, M. Artemyev, A-E. Efimov and I. Nabiev, "Comparative advantages and limitations of the basic metrology methods applied to the characterization of nanomaterials," Nanoscale, vol. 8, pp. 8781-8798, 2013.