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Synthesis of activated carbon from scrap tires with petroleum kerosene as a decomposition auxiliary agent

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In this study, we report for the first time the use of kerosene, a petroleum-based product, as an auxiliary decomposition agent to produce scrap tire-based activated carbon with a high surface area. The scrap tires tread was converted to char using multi-step pyrolysis starting at 250 °C through 350 °C. We carried out the rubber decomposition with and without using kerosene in a small amount, followed by steam activation. We evaluated the chars through adsorption-desorption isotherm, electron microscopy, dye removal besides iodine number. The results revealed that the specific surface area of the kerosene treated sample was 1227 m^2/g, whereas the non-kerosene treated char was 473 m^2/gm. The electron microscopic results of the kerosene treated sample demonstrated significant changes in the char's topography surface compared to the untreated samples. In addition, the products showed exceptional ability to eliminate synthetic methylene blue dye from the aqueous solution, suggesting a great potential in the wastewater treatments of the textiles industry.

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Introduction

The vulcanization process discovery in 1839 has opened a substantial investment of rubber in the automobile tires industry; since then, the development of that material has increased. The production has expanded to overpass 1.5 billion/ year globally [1,2]. The colossal production has led to environmental issues compromised by landfills, ground, subsurface water pollution, and air pollution caused by chaos incineration and random burdening [3]. Therefore, environmental pollution and the necessity for energy urge researchers to recycle, convert, and reuse tire materials via different thermal processes like combustion, gasification, and pyrolysis; despite pyrolysis being difficult, it seems the most effective method [4,5,6]. Pyrolysis is a thermal decomposition of components that occur at high temperatures without oxygen [7]. There are three major types: first is the slow type, where the deterioration happens at a low temperature of about 400 °C and a slow heating rate. Therefore, this will take hours; the second type is the fast pyrolysis, where the decomposition happens at a higher temperature and fast heating to decrease the time and increases liquids yield; the last type is the catalytic pyrolysis, and is meant to enhance the characteristics of certain products (like aromatic liquids) by applying a specific catalyst within the process [7]. The resulted products of pyrolysis typically are chars (30-40%, primarily used as activated carbon or as rejuvenator in the industry of

rubber), liquids (40-60%, organic compounds) used as fuel, and gases (5-20%) which may use in the pyrolysis process [7,8].

Tires are a valuable source of energy fuels and carbon; they are complex materials composed of organic materials, namely styrene-butadiene and synthetic or natural polyisoprene rubbers. Other components include steel cord, carbon black, zinc oxide, sulfur, and other chemicals [8-10]. Tires are normally retreading or ground to powder or crumb for different purposes like paving or surfacing [8]. Carbon from an environmental point of view is an unimpeachable element. In addition, it is used as an adsorbent material because of its surface area, which may enhance further, either chemically or physically [11]. It has carried out studies to prepare active carbon with a surface area suitable for water treatments, especially those intended to remove water contamination with dyes, toxins, and other contaminants [12,13].

In some cases, pyrolysis has been used to prepare active carbon at 900 °C, then chemically activated it using hydrogen peroxide and phosphoric acid for comparison. The prepared active carbon was used to remove cadmium-(II) and lead-(II) ions from domestic wastewater, reaching a removing ratio of less than 90% for both metals. However, the surface area of the prepared carbons was less than 50 m^2/gm [14]. On the contrary, waste tire-based active carbon is used effectively to remove chromium-(IV) and manganese-(II) ions from aqueous solutions [15].

Others had utilized carbon dioxide instead of nitrogen atmosphere to degrade scrap tires at 800-900 °C and different times. They found that the best time was 3 h; these conditions gave an active carbon with a surface area of 414 m^2/gm [16]. Pyrolyzing crumb tires at 550 °C for 4 h followed by potassium hydroxide or carbon dioxide activation was also carried out. The surface area of the active chars was 720 and 242 m^2/gm for carbon dioxide and potassium hydroxide,

respectively [17]. The fast and catalytic pyrolysis variables seem not to affect the total area of the final active carbon, where the latter is used to remove iron ions from potable water [18]. The acid treatment of the prepared active carbon from the pyrolysis of tires at high temperatures (700 °C) plays a significant role in developing carbon structure [19]. The environmental pollution of river water and even groundwater arising from textiles, paper, tanning, and other industries besides the domestic wastewater, has increased enormously in the last decades and put pressure on the waste treatments facilities. As an adsorbent material, activated carbon is advantageous, especially in removing dyes from solutions. Carbon prepared from carbonizing Lapsi seed with phosphoric acid was used to remove methylene blue from the solution. Using the carbon without activation could still remove methylene blue from the prepared solution [20]. Another study found that active carbon prepared from Pea shells effectively removed methylene blue from water and can employ it for the dye removal step in the water treatment process [21].

Recently, the adsorption of methylene blue on activated carbon has been enhanced using surfactants. It was observed that using anionic surfactants like sodium lauryl sulfate significantly improved the adsorption of methylene blue on activated carbon, unlike the cationic surfactants like hexadecyl trimethyl ammonium bromide, which showed a drastic reduction in the activated carbon ability for adsorption of the dye [22]. Yet, another recent interest is using nanoparticles like ferrous oxide nanoparticles to prepare active magnetic carbon. The magnetic carbon has high efficiency in adsorbing reactive blue 19, and it can be adopted in the adsorption process after future examination for accurate scale utilization [23].

The present research study aimed at using a petroleum-based liquid, namely kerosene, to speed up the rubber tire thermal decomposition and to improve the structure of

the tire-derived carbon and use the resulting carbon after activation to remove methylene blue from the aqueous solution and potentially utilize the product for the real-scale application.

Materials and methods

Chemicals

1- Methylene blue (the absorbate) provided from Sigma-Aldrich (chemical formula $C_{16}H_{18}ClN_3S.3H_2O$, molecular weight 373.90) was used. Known weight (0.02 g) of cationic methylene blue dye was dissolved in 1 L of distilled water to prepare 20 ppm solution of the dye. The solution was kept in a dried container for later measurements.
2- Iodine solution (concentrated) supplied by BDH. was used to determine the iodine number3- Waste tire-rubber (salon cars bought from local retail shops) was washed to remove dirt and left to dry for 3 days before use; after that, we shredded it to a size of about 2 cm^3 and kept it in a dry container.
4- Petroleum kerosene was provided from a local petrol station and was used without any pretreatment.

Activated carbon fabrication

Waste tires-rubber and kerosene in a ratio of 10:1 was placed in a semi-closed utilized pyrolysis apparatus and subjected to a ramp heat from ambient until 350 °C within 25 min, then maintained at 350 °C for about 1 h; after that, the device was shuttered down and left to cool naturally. We optimized the conditions of the experiment from several experiments. The as-obtained chars were grounded and then activated using steam activation for 1 h at 500 °C. The product was left to cool and sealed in a dry and clean vial.

Testing

Thermal analysis

Thermal gravimetric analysis (TGA) was conducted via Thermo-gravimetric Analyzer Perkin-Elmer TGA 4000. Nitrogen gas was at a flow of 20 cm^3 min^{-1} and the heating rate of 20 °C min^{-1}.

Methylene blue adsorption

0.1 g of activated carbon was placed in 1 L conical flask; 100 mL of 20 ppm methylene blue was added, and the mixture was shaken using an electrical shaker (with suitable speed) until the dye vanished before another 100 mL was added until the dye remains i.e. reaching the equilibrium. The shaker was stopped, the clear solution was taken out and placed in a cell for spectrophotometric measurement with its absorptivity at 665 nm.

The removal ratio of the dye from the solution and the adsorption amount of methylene blue at the time was calculated as follows

$$Removal\ ratio = \frac{Co-Ct}{Co} x\ 100\ \text{--------------------(I)}$$

$$Qt = \frac{(Co-Ct)V}{m}\ \text{------------------------(II)}$$

Where:

Qt: The quantity of dye (mg. g^{-1}).

Co and Ct: Initial and equilibrium concentrations, respectively.

V: Volume of Methylene blue (Liter).

m: Weight of adsorbent (gm).

Iodine number

We measured iodine number according to the American Water Works Association (AWWA) standards [24].

Results and discussion

Thermal stability

Thermal stability was measured through TGA for the original and activated chars with and without kerosene addition. Figure 1 and Figure 2 represent the TGA graph of them. The original char (C) shows two transition regions; the first zone ranges from 30-512 °C with a weight loss of about 3% which, is attributed to the water evaporation [25-27]. In the same context, the activated carbon (AC) shows the same transitions zone with a temperature zone from 33-482 °C and weight loss of 4%,

which can be attributed to the evaporation of water. Thus, the weight loss was 80% for both samples. On the other hand, in the second region from 480-580 °C for kerosene treated char (C-K), a drastic loss was observed at about 76%; this relates to the organic remnant's decomposition. However, unlike the kerosene treated char (C-K), the activated carbon with kerosene addition (AC-K) showed excellent thermal stability where two transitions zones are also observed; the first one from 33-540 °C with weight loss of about 0.9% while the amorphous decomposition in the second zone reached 32%; this means that the (AC-K) is a material of good thermal resistivity as well as it reflects an enhancement in the topography of its surface, as recorded using scanning electron microscopy (SEM), shown in Figure 3.
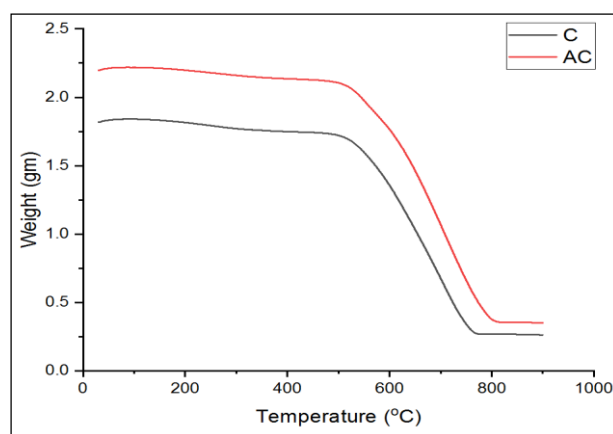

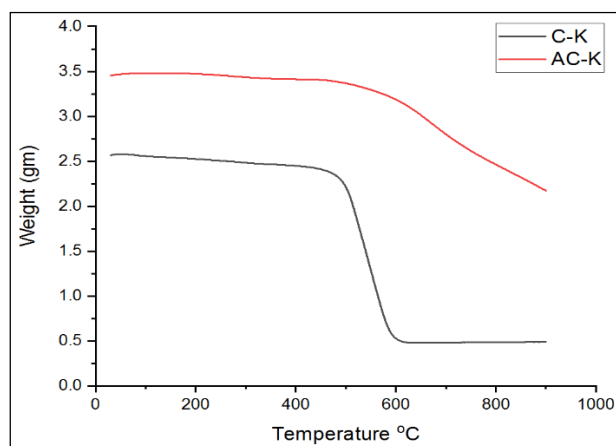**FIGURE 1** Thermal stability of the activated and non-activated carbons (Kerosene = 0%)

FIGURE 2 Thermal stability of the activated and non-activated carbons (Kerosene = 10%)

Surface characteristics

The SEM images in Figure 3 show a change in the surface topography of the activated carbons (AC and AC-K) relative to the non-activated carbons (C and C-K. The non-activated carbon (Micrograph C) surface appears as deformed materials with bulk and condensed agglomerates, unlike that treated with kerosene (Micrograph C-K) which occurs with some assembled amorphous domains. On the other hand, the activated carbon (Micrograph AC) looks like the materials have melted and fused, losing their previous shapes (the agglomerates). In contrast, the activated carbon treated with kerosene (AC-K) looks to assemble undeveloped domains with large voids, giving a shred of firm evidence for heterogeneous and bizarre porosity of the mesoporous structure [19]. Our suggestion is that activation of the carbon will expand the pores, which reconstructs the surface because of multiple effects of heat and steam simultaneously, leading to the change in the shape from macro to mesoporous.
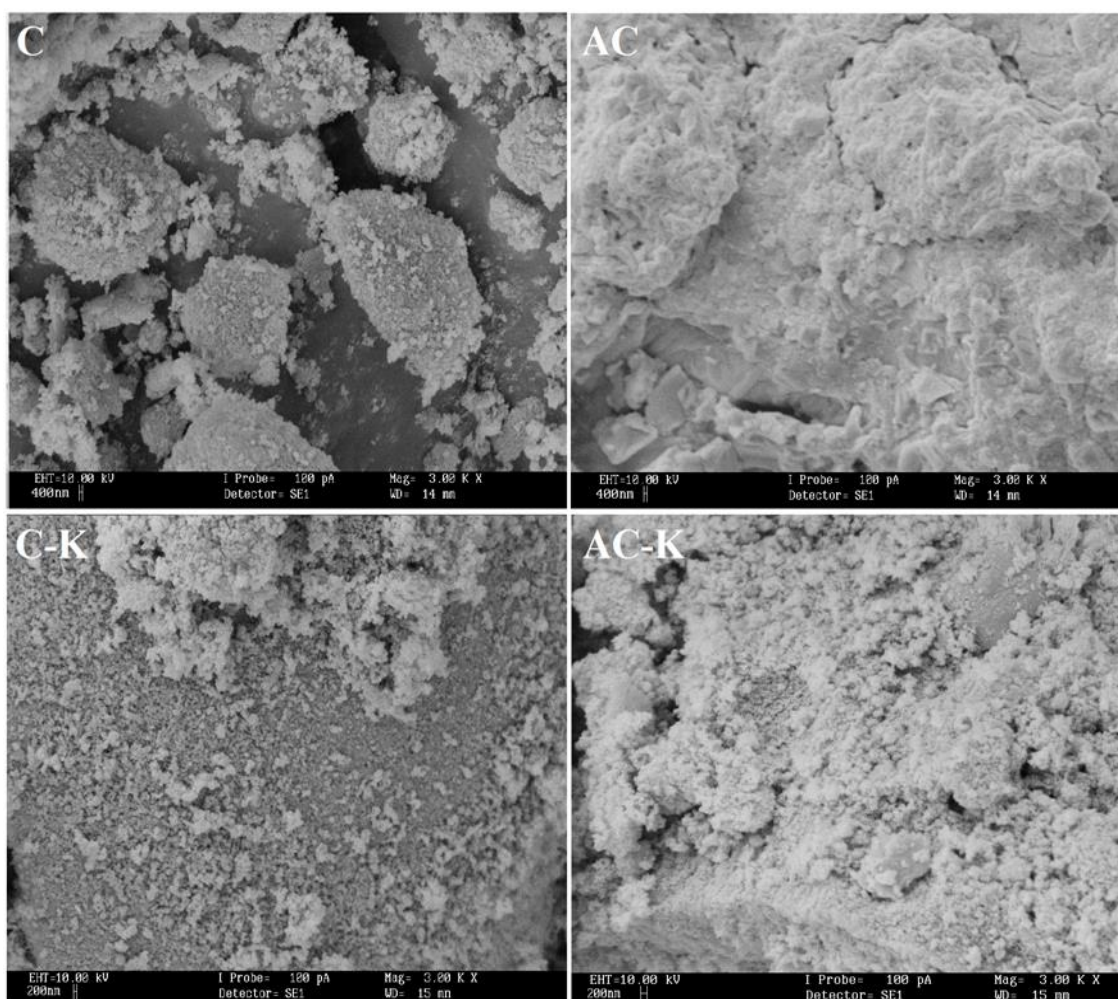

FIGURE 3 SEM of the original char (C), activated carbon (AC), kerosene treated char (C-K), and kerosene treated activated carbon (AC-K)

Adsorption behavior

Elemental composition

Elemental components of the chars produced by this study are presented in Table 1. Data were obtained from the elemental analyzer for the samples before and after activation. Carbon is the abundant component for all instances. In addition, there was a slight increase in the carbon contents, which relates

to the volatiles released [28,29]. There was also an increase in the carbon content for the kerosene treated char; We attribute this to the existence of kerosene as an auxiliary decomposition agent during charring since the kerosene is a petroleum fraction, a hydrocarbon, whereby carbon is the principal component. The kerosene will act as a rejuvenating agent and enrich the rubber tire matrix with extra carbon. Therefore, we recommend using it in the production process, since the used amount is small and can be considered a catalyst.

TABLE 1 Elemental components of the produced chars

Sample	Carbon (wt%)	Hydrogen (wt%)	Nitrogen (wt%)	Sulfur (wt%)
C	81.28	1.43	1.18	3.74
AC	82.83	1.35	1.18	2.18
C-K	83.47	1.52	1.17	3.86
AC-K	86.39	1.21	1.15	1.91

Adsorption isotherms

The nitrogen adsorption-desorption isotherms for the chars before and after activation were examined. As shown in Table 2, the Brunauer–Emmett–Teller (BET) surface area of the non-treated carbon (C) increases from 396 to 473 m^2/g when activated (AC), and the micropore volume has increased twice. For the kerosene treated samples (C-K and AC-K), the BET surface area has increased about three times from 459 to 1227 m^2/g. The micropore volume has also increased; however, not like that for non-treated kerosene samples. The average pore diameters for the non-treated sample (C) and its corresponding activated carbon (AC) and the kerosene treated waste tires sample (C-K) were more prominent while, the activated char-based kerosene treated (AC-K) was decreased drastically, indicating that the size of the pores has become predominantly micro and mesoporous [30]. Figure 4 reveals the adsorption-desorption graphs for all prepared samples. According to the IUPAC classification, the isotherms for all samples are of type I [29,30], which can be distinguished from the increase of the relative pressure at low data and reaching the plateau at higher relative pressures.

(AC-K) isotherm is an ideal type (I) showing dense micropores and reflecting that the prepared sample is rich in micropores and contains a certain amount of mesopore structures [31,32]. It is noteworthy that using kerosene in the charring process has enhanced the surface area and the porosity of the produced chars giving the high potential for this process to be applied in the industry, as it will be a very effective method for the fast production of activated carbon from waste materials. In the same context, the iodine value may be used to approximate the surface area and porosity of the activated carbon with precision. The higher the iodine number, the higher is the degree of activation [33]. As for the (AC-K) sample, the iodine value is as high as its BET surface area, differing from the rest of the samples whose iodine values are contrasting, giving supportive evidence of the higher adsorptive activity of the product.

TABLE 2 Characteristics of the carbon-derived waste rubber tire before and after activation

Sample	Kerosene %	Surface area (m²/g)	Average pore diameter (nm)	Micropore volume (cm³/g)	Iodine number (mg/g)	Methylene blue number (mg/g)
C	0.0	396	3.17	0.130	287	71.7
AC	0.0	473	2.66	0.274	371	123.6
C-K	10	459	2.89	0.320	310	101.2
AC-K	10	1227	1.91	0.469	968	283.1

Dye removal capacity

Methylene blue is a heterocyclic aromatic dye that can be absorbed on a high surface material like active carbon. Nowadays, it is a nominated measurement for activated carbon mesoporosity. In another context, it can adsorb bulky or oversized molecules. The results of the methylene blue absorptivity in Table 2. show an increase in the char's capacity of base tire treated with kerosene (C-K) and its subsequent activated carbon sample (AC-K) in comparison with the not treated ones (C and AC). Figure 5 presents the

methylene blue removal versus contact time for the prepared chars. The removal ratio was about 50 - 99% of the methylene blue dye from the solution. Regardless of the activation process, there is a real contrast in the required time for reducing methylene blue to the minimum level. (AC-K) shows the highest rate and maximum level of dye removal within about two hours, whereas the AC took about five hours to reach about 80% of removal and never reached the highest level of that for (AC-K). This finding agrees with the results of the BET surface area and iodine value and the literature [34].
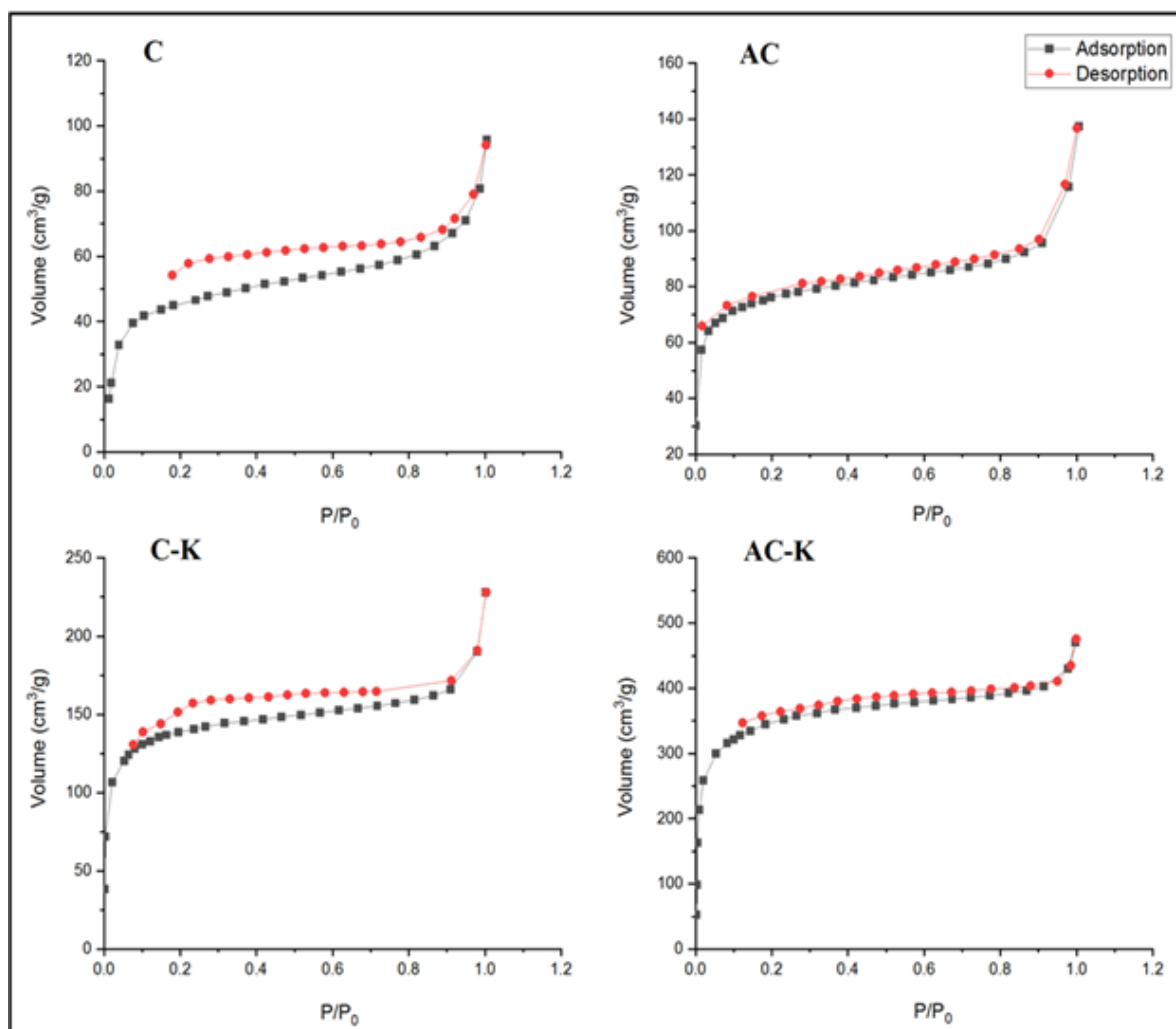

FIGURE 4 Nitrogen adsorption-desorption isotherm plots of a charred sample and their corresponding activated carbon

The removal rate of (AC-K) and the short time to reach the equilibrium reflect the

efficiency of the sample. The attribution of the surface area and adsorption capacity to the

kerosene presence during the charring is the versatile element in explaining such change, especially the exact change noticed in the activated sample. Our suggestion for this is that the activation works on widening the pores that existed in active carbon through releasing the volatiles and since the kerosene is a liquid that can be absorbed by the rubber before the charring and introduced into the rubber matrix, which upon the pyrolysis will help to relegate the hydrocarbon chains significantly as noted from the result of the activated char-based kerosene treated (AC-K) after the activation.
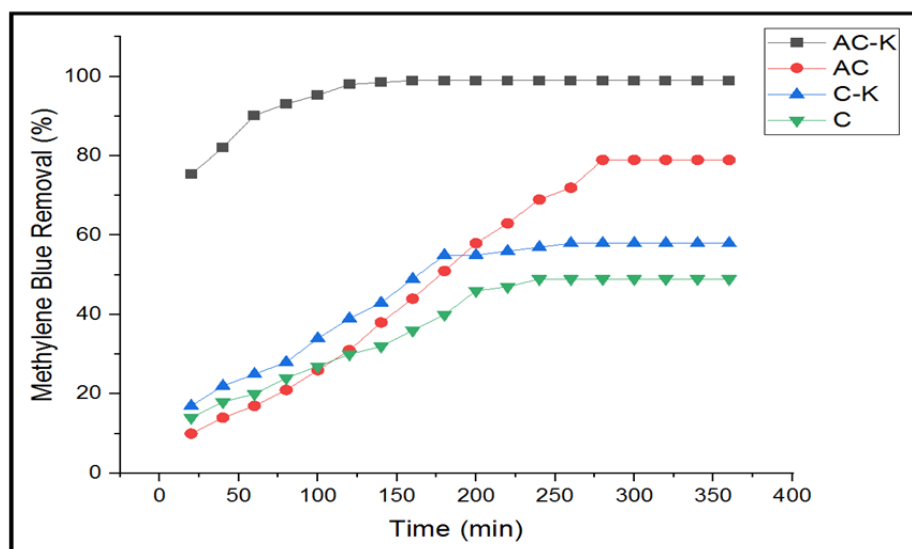
FIGURE 5 Methylene blue removal and contact time

Conclusion

Activated carbon has been produced from waste tire treads using kerosene as an auxiliary agent for the decomposition of rubber tires. The BET surface area (1227 m^2/g) and the iodine value (968 mg/g), and the methylene blue removal (283 mg/g) of the produced activated carbon showed an extreme enhancement in the surface area in both the porosity and capacity and also the ability of to remove bulk dye has also been improved. The sample pores were microporous with a certain amount of mesoporous. The thermal stability of the produced sample has been developed, and the morphology of the sample surface revealed a change in the topography of the sample. Kerosene plays a crucial role in developing and enhancing the active carbon characteristics. As of this study, an economically active carbon can be produced from waste tires treated with kerosene for effective adsorbents to remove industrial dyes from wastewater.

Conflicts of Interests

The authors declare that they have no conflict of interest.

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