



Sustainable utilization of value-added products from the catalytic and non-catalytic pyrolysis of motor car scrap tire: Suitability of produced char for energy generation and sugar mill wastewater treatment

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ABSTRACT

Clean fuel and sustainable energy utilization are essential requirements to address the impacts of global warming and climate change. In this study, the pyrolysis of motor car scrap tire was investigated in a fabricated cylindrical stainless steel reactor, operated at 450, 500, and 550 °C for 50 min with or without the addition of a catalyst. The catalytic condition yielded maximum char of 59% w/w obtained at 450 °C. The addition of the catalyst also enhanced oil yield up to 33% w/w at 500 °C while the maximum gas fraction of 44% w/w was obtained under the non-catalytic condition, at 550 °C. The TGA/DSC analysis showed that the pyrolysis char had a specific heat capacity (C_p) of 35 J/g.K, relating to its high thermal stability for applications in furnaces, reactors, and heat construction materials. The char, after chemical activation, with the XRD analysis, showed that the produced activated carbon (AC) has a good crystalline structure (with high interplanar distances). The BET analysis revealed that the AC has a high surface area of 1065 m²/g (average pore diameter of 3.36 nm) which enhanced the adsorption capacity of the AC to about 90 % efficiency for the removal of the heavy metal, cadmium, from sugar mill wastewater.

Introduction

Environmental and health hazards are associated with conventional waste tire disposal methods such as combustion processes in landfills and incinerators which often lead to the emission of hazardous products such as oxides of carbon and sulphur, and hydrocarbons [1]. These hazards are created because of the high thermal resistance to degradation of tires, caused by its highly complex structure, compositions, and the quality of the raw rubber materials used in the production process. Therefore, it is very vital to reduce these wastes from the environment and also reduce the costs of recycling the waste into new products. Viable different strategies for the conversion of scrap tires into useful end products include the thermochemical processes (pyrolysis, gasification, and direct

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liquefaction), mechanical grinding, chemical degradation, catalytic cracking, hydrogenation, and de-vulcanization [2]. Amongst these strategies, pyrolysis, which is the thermal decomposition of materials at elevated temperatures leads to the production of useful industrial raw materials such as solid carbon black, liquid hydrocarbon fuels, and gases [3]. After the pyrolytic degradation of waste tire, solid (char), liquid (oil), and gas are the primary products that can be upgraded to useful fuels and chemicals [4]. The solid (char) can be used as a solid fuel with high energy content [5], as adsorbent (after activation) [3], and for soil amendment (the high-carbon content increases soil carbon concentration) [6]. The liquid fraction (tire pyrolysis oil) can be used as hydrocarbon fuel for energy generation or as raw material for obtaining chemical products of interest [6,7]. The gas fraction is the non-condensable fraction from the pyrolysis process [8]. After pyrolysis, the gas fraction has sufficient higher heating value of about 37 MJ/m³ which makes it suitable to be used as a fuel in producing electricity or can be used directly to feed the pyrolysis process [9].

Under the influence of catalysts, challenges associated with the end products of the pyrolysis process are appreciably reduced [10, 11], in addition to further reduction in the energy input of the process and influencing the composition of the products [11]. Several studies have been reported in the literature bearing the influence of catalysts on the pyrolysis of waste tires. Reports indicated that the yields of the end products were greatly influenced by many factors such as type and form of catalysts, reactors (pyrolyser) size, operating conditions as temperature, heating rate, and residence time. Li et al. [12], using USY, ZSM-5, and ZSM-22 zeolite on scrap tire pyrolysis at 500 °C obtained more oil fractions than char. Kordoghli et al. [13] carried out comparative studies of ZSM-5, Al₂O₃, CaCO₃, and MgO on the pyrolysis of scrap tire. They reported that the pyrolytic process was delayed when the catalysts were used. However, CaCO₃ and Al₂O₃ influenced increasing gas fractions in the end-products while MgO promoted the formation of the liquid fractions [13]. Influences of other catalysts such as natural zeolite [10], NiW/HY [5], Ca(OH)₂, [14], and MgO [15] have been reported.

Industrial wastewaters are laden with many pollutants that are hazardous to the environment. Some of these pollutants can be in form of dyes [16–18], heavy metals [19], and some other related water pollutants. The presence of heavy metals as part of wastewater effluents is a potential threat to living things, because they are non-biodegradable and they bioaccumulate in the food chain [20–22]. There are numerous approaches for the removal of heavy metals from wastewater such as through membrane filtration, bioremediation, ion-exchange, chemical coagulation, chemical precipitation, electrochemical methods, and adsorption [23]. Adsorption, which is a physicochemical technique is considered as the most effective among all other methods because it is very simple to operate [19]. The adsorption process is economically viable, and the adsorbent can be regenerated [19]. Many materials have been developed as adsorbents for the removal of heavy metals from wastewaters. Kwak et al. [24] reported that biochar obtained from selected biomasses through high pyrolysis temperature (700 °C) was viable for the production of adsorbents for the removal of lead from synthetic oil sands process water. Other studies on removal of heavy metals from wastewater by adsorbents were reported by Li et al. [25] using cellulose nanofibers. Shahrokhi-Shahraki et al. [19] used pulverized waste tire while Kwon, et al. [26] used zeolite mixed with local soils.

In this study, we explored the efficiency of a laboratory fabricated fixed bed reactor for the pyrolysis of motor car scrap tire to its end products (char, oil, and gas) at varying temperatures (450, 500, and 550 °C) at constant feed and residence time, with and without the influence of calcium chloride (CaCl₂), as catalyst. The produced char was further investigated for its thermal stability, heat storage, fuel, and energy generation tendencies. In addition, through chemical activation of the char, the activated char was evaluated for its adsorptive properties for the removal of heavy metals from industrial (sugar mill) wastewater. The char and produced adsorbent were characterized by a set of analytical techniques which included thermogravimetric analyser (TGA/DSC), scanning electron microscopy equipped with energy dispersive x-ray (SEM-EDX), Fourier Transform Infra-red (FTIR), X-ray diffraction (XRD), and the Brunauer–Emmett, and Teller (BET).

Materials and methods

Raw materials sourcing and preparation

The scrap tire was sourced from a mechanic workshop in Ota Town, Western Nigeria. It was thoroughly washed with clean water to remove debris, stones, and sand. The manually chopped scrap tire pieces had the fabric thread embedded in them. The zinc chloride (ZnCl₂) catalyst used for this study was purchased from J.T. Baker, a division of Mallinckrodt Baker Inc. with a purity level of 98 %. The catalyst was used as received with no further processing.

Experimental procedure for the pyrolysis of scrap tire

The main unit of the pyrolysis process is the pyrolysis reactor, providing the core performance of the entire set-up [27,28]. A stainless steel cylindrical reactor was fabricated as the pyrolysis unit, having an outer diameter of 22.5 cm and a depth of 30.5 cm. The simplified schematic representation of the pyrolysis set-up is provided in the supplementary file (Fig. S1). Each batch of experiments was carried out by loading 235 g of the shredded tyre (average size of 13 mm) into the reactor followed by purging through route 3 (Fig. S1) with nitrogen, for its inert characteristics, for 5 min. After the purging, external heating was performed through an electrical furnace having a temperature controller. The scrap tire pyrolysis occurred at a fixed heating rate (10 °C/min) for a constant set-point time of 50 min at varying temperatures of 450, 500, and 550 °C with 50 g zinc chloride addition in case of catalytic pyrolysis, and then without catalyst addition (non-catalytic or thermal pyrolysis). The gas supply channel from the externally heated pyrolysis unit had a control valve (point 4) which ensured enough pressure built up in the reactor before the release of the vapour through the channel to the condenser. Reaction temperatures were monitored using a K-type thermocouple. The reactor was externally insulated with glass

wool to minimize heat loss. The vapour (laden with both condensable and non-condensable gases) that was released from the reactor was passed through a gas supply channel (point 7 in Fig. S1) to the condenser (having five internal cooling channels) for the condensation of the condensable gases into liquid, as the tyre pyrolysis oil. The cooling was performed using tap water at ambient temperature (19 ± 2 °C). The pyrolysis oil was collected in a receiving flask. The residue left in the reactor was the solid char, viewed as carbon black. The pyrolytic products from scrap tyre pyrolysis at the different temperatures (450, 500, 550 °C) and conditions (non-catalytic and catalytic) are labelled in this study as raw scrap tyre (RS), non-catalytic pyrolysis of scrap tyre at 450 °C (S450), catalytic pyrolysis of scrap tyre at 450 °C (SC450), non-catalytic pyrolysis of scrap tyre at 500 °C (S500), catalytic pyrolysis of scrap tyre at 500 °C (SC500), non-catalytic pyrolysis of scrap tyre at 550 °C (S550), catalytic pyrolysis of scrap tyre at 550 °C (SC550).

Characterization of the raw scrap tyre and solid (char) pyrolysis products

Pyrolysis products have a very complex mixture of organic compounds. Therefore, efficient and reliable analytical methods are required for their characterization [5]. The raw scrap tyre and the pyrolysis solid products (char) quality and potential for chemicals, fuel, and clean energy generation were investigated through adequate analytical procedures. The proximate analysis was evaluated using the thermogravimetric analyser (TGA/DTG)(Universal V4.5A TA instrument.) using the ASTM D7582–15 procedure [29]. A bomb calorimeter (Model 6100, Parr Instruments, USA) following the ASTM D2382–88 protocol [30] was used to determine the higher heating value (HHV) of the solid samples. In the TGA/DTG, samples were heated from 26 °C ambient temperature to 900 °C at a rate of 10 °C/min under nitrogen as purge gas and oxygen for oxidation. A Q2000 V24.11 Build 124 model of the differential scanning calorimetry (DSC) was used to establish the thermal transition (heat absorbed (endothermic) or released (exothermic) temperatures of the raw tyre and char materials obtained after the pyrolysis step. Samples of 6 mg were placed in Tzero alumina pans, and empty pans were used as references. All samples were first equilibrated at -65 °C for 1 min after which there was ramping at 10 °C to a temperature of 290 °C and kept at this temperature for 1 min. Following, the samples were cooled to -65 °C, then ramped again at 10 °C/min to 290 °C isothermally for 1 min. After each test, the crystallization region was analysed to determine the crystallization temperature (T_c) as well as the specific heat capacity of the char product.

The morphological and qualitative analyses of the solid samples (chars) were performed using a scanning electron microscope (SEM) equipped with energy-dispersive X-ray analysis (EDX). The samples were mounted on aluminum stubs using double-sided carbon tape and the surfaces were coated with iridium at 5 nm to make them conductive before SEM studies. A TESCAN equipped with Oxford instrument X-Max was used for the SEM/EDX analyses at an acceleration voltage of 15 kV. The EDX spectra were obtained by scanning through the surfaces of the samples to determine the elements in the sample.

The functional groups present in the raw tyre (RS) and the char products were evaluated by the Fourier-transformed infrared (FTIR) spectroscopy in transmission mode. The spectra of each sample were characterized by a Perkin Elmer Spectrum 100 spectrometer. The FTIR spectra of samples were obtained in the range of 550–4000 cm^{-1} using the KBr. 32 scans were co-added and averaged to achieve an acceptable signal-to-noise ratio. In all cases, spectra resolution was maintained at 16 cm^{-1} .

In establishing the suitability of the produced char as a potential adsorbent, the surface area of the pores of the raw tyre and char was characterized by using the Brunauer–Emmet, and Teller (BET) technique with a bath temperature of -195.75 °C and sample mass of 0.05 g. The pores size distributions were evaluated with the Barrett–Joyner–Halenda (BJH) method [31].

Production of activated carbon from the char and treatment of sugarcane mill wastewater

Produced char from the optimized pyrolysis experiment was chosen for the production of activated carbon (AC) and for investigating the removal of heavy metals in wastewater from a sugarcane mill. Before the activation process, the obtained char from the pyrolysis process was oven-dried at 105 °C for 4 h. The dried sample was crushed and sieved to an average size of 0.45 mm [32]. The physicochemical activation was carried out by the initial impregnation of 5 g of the char with 10 ml of 85 % phosphoric acid, a chemical activating agent for one hour [32,33]. The activated samples were washed with distilled water to a pH of 7 and further carbonized at 700 °C for 15 min in a muffle furnace.

The wastewater (from sugar mill) treatment occurred by adding dosages of 60, 80, and 100 mg of the activated carbon into 100 ml of the wastewater in a beaker. With the aid of a magnetic stirrer, thorough mixing of the samples in the beaker (wastewater and the adsorbent) occurred at temperatures of 40, 50, and 60 °C, with time periods of 15, 30, 45, and 60 min. The presence of heavy metals in the raw and treated sugar mill wastewater was investigated with the PerkinElmer atomic absorption spectrometer (AAS) using the flame technique. Standards of heavy metals (copper, nickel, lead, chromium, cadmium, and zinc) were used to generate the calibration curves.

The crystal structures of the char, the activated char, and the spent materials after the treatment of the sugar mill wastewater were determined with the Rigaku D/Max-IIIC X-ray diffractometer (XRD)(Rigaku Int. Corp. Tokyo, Japan). Powdered samples were pelletized and sieved to 0.074 mm. Each sample was taken through the X-ray diffractometer and set to produce diffractions at a scanning rate of 2 °/min in the 2 to 50 °C range at room temperature with a Cu-K α radiation set at 40 kV and 20 mA. The diffraction data (d value and relative intensity) obtained were compared to that of the standard data of minerals from the mineral powder diffraction file, International Centre for Diffraction Data (ICDD), which contained and included the standard data of more than 3000 minerals. The d-spacing (diameter of the crystallite) was obtained using Bragg's law ($2d\sin\theta = n\lambda$).

The surface area of the char product at 500 °C catalytic pyrolysis, the activated carbon obtained from the char, and spent materials after the wastewater treatment were characterized using the Brunauer–Emmet, and Teller (BET) with bath temperature of -195.75 °C and sample mass of 0.05 g. The pores size distributions were evaluated with the Barrett–Joyner–Halenda (BJH) method [31].

All experimental runs in this study were replicated twice and obtained data represent the mean values.

Results and discussions

Characteristic estimations of the raw tire sample

The proximate analysis (volatile matter, fixed carbon, ash, moisture contents), and the higher heating value, HHV (caloric value) are efficient parameters in confirming the quality of materials for energy generation and other useful applications [30]. Precursors for the production of fuels, chemicals, and for energy generation must possess adequate short-chain, long-chain, and aromatic hydrocarbons in the volatile matters [33]. The volatile matter inherent in the raw tire was 65.50wt%, the fixed carbon content of 22.50wt%, the ash content was 11.20wt%, while the moisture content was 0.8wt%. The HHV of the scrap tire was obtained to be 35.90 MJ/kg, which is closer to the values reported in the literature [34]. The higher heating value of the raw tire can be compared to that of crude oil and coal, presenting their high energy recovery potentials [15]. The HHV relates to the high volatile matter content, which indicates that the scrap tire is a suitable material for fuel, chemical, and energy generation.

Effect of non-catalytic (thermal) and catalytic pyrolysis on the tire for products yields

In optimizing the pyrolytic process, the effects of the experimental conditions on product recovery (char, oil, and gas) were investigated. The process reaction temperature variations (450, 500, and 550 °C) for thermal (non-catalytic) and catalytic conditions affected the distributions of the yields of the char, oil, and gas in different proportions. Looking closely at Fig. 1, the solid products (chars) that were obtained decreased with increasing temperatures for both thermal and catalytic processes. Maximum char production (58.7% w/w) was obtained at a much lower temperature of 450 °C with catalyst addition for SC450 (oil yield was 27% w/w and 14.30% w/w of the gas fraction was produced). Subsequent increments in temperature (500 °C and 550 °C), even with the addition of the catalyst, brought about a reduction in char production; SC500: 52.10% w/w, SC550: 52.30% w/w. The char fractions increased at lower temperature which may be due to lower loss of volatile matters caused by partial pyrolysis burning. Lower yields of char at elevated temperature involved both dehydration and thermal degradation of the tire into lower molecular weight compounds and gases [35–37]. Pradhan and Singh [37] observed the effect of temperature on tire pyrolysis having the same trend with maximum char yield of about 60% w/w obtained at 450 °C. Ayidin and İlkilic [14] reported about 62% w/w of char yield at 450 °C compared to 47.12% w/w at a higher temperature of 550 °C. Following the same trend with much lower yields, the thermal process (non-catalytic) showed decreasing char production. Thermal pyrolysis at S450 was 43.70% w/w followed by S500 producing 38.00% w/w, and 33.50% w/w char production at 550 °C.

Liquid product (for both thermal and catalytic processes) increased between 450 °C and 500 °C, and then decreased beyond this at 550 °C. For the thermal process, at S450 oil yield was 17.50% w/w increasing to 22.40% w/w for S500 and then decreasing to 22.10%

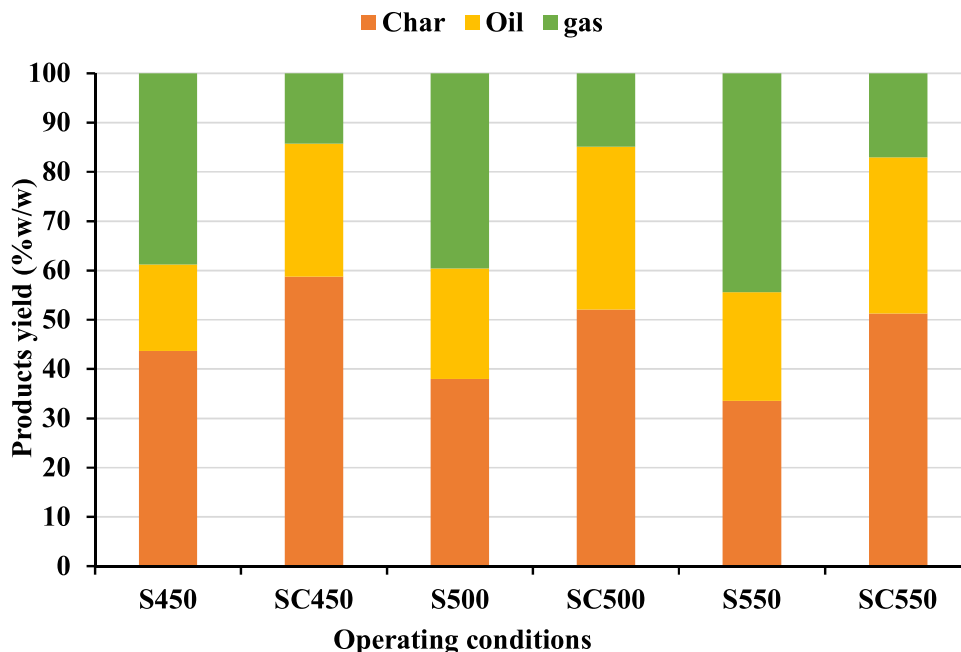


Fig. 1. Product yields for the catalytic, non-catalytic pyrolysis, and co-pyrolysis of the scrap tyre.

SC = pyrolysis with catalyst addition; S = pyrolysis without catalyst. 450, 500, and 550 are the operating pyrolysis temperatures in °C. All experiments were carried out under constant feedstock loading of 235 g and operating temperature of 50 min.

w/w at higher temperature of 550 °C. Pyrolysis oil yield (33% w/w) was maximum at 500 °C under the catalytic condition. Similar trends were reported by Pradhan and Singh [37] as well as Ayidin and İlkilic [14], with improved oil yields under increasing temperatures (450 °C to 700 °C), and then attaining optimum yield at 600 °C beyond which the yields decreased. More gas fractions were obtained during the thermal pyrolysis at increasing temperatures (from 38.80% w/w at 450 °C to the highest of 44.40 % at 550 °C) compared to the catalytic processes under the same conditions. The production of 38.80% w/w gas fraction at the low temperature of 450 °C reflected the high volatile matter (65.5% w/w) present in the raw material, which included the plasticizers and other additives that can easily volatilize at low temperatures [38]. Gas fractions for the catalytic process showed that at SC450, 14.30% w/w was obtained, 14.9% w/w was produced at SC500, and 17% w/w for SC550. The increasing gas yields at elevated temperatures than oil production may be due to the formation of more gases caused by secondary reactions during the process [37].

Generally, results showed that more of the oil and gas fractions were obtained at higher temperatures (500 and 550 °C), and the maximum value of char was produced at a reduced temperature (450 °C) which also supports the findings of Li et al. 2016 ([12]). More of the oil and gas fractions were obtained at elevated temperatures due to enhanced cracking of the waste tire. A similar finding was reported by Aziz et al. [39] which indicated increased production of the gas fraction leading to maximum production of oil at an elevated peak temperature before the gradual reduction in the weight fractions as the temperatures increased. Therefore, it may be inferred that scrap tires were not completely degraded during thermal (non-catalytic) pyrolysis at a temperature much below 500 °C. The styrene butadiene rubber (SBR) and butadiene rubber (BR) components of tires have a degradation temperature of close to 480 °C [40]. The addition of a catalyst showed enhanced product yields. The presence of a catalyst not only increased the yield of the oil but there was a corresponding increase in the yield of the char compared to that obtained in the non-catalytic pyrolysis (52.10% w/w solid and 33% w/w gas fractions were produced from SC500). The increases in oil and char yields may be attributed to the activity of zinc chloride. Zinc chloride is known for its medium acidity (acts as a moderately strong Lewis acid serving as a useful catalyst) and reveals the relatively high activity and selectivity [41]. The increased production in the solid char can be explained by the increase in the strength of the Lewis acid [42]. The electronegative value of zinc which increases its bond formation tendencies could attest to the increase in the oil yield when compared to non-catalytic pyrolysis.

Thermal stability and weight loss of solid (char) products with temperature changes

The differential scanning calorimetry (DSC) scans were used to evaluate whether the degradation reaction nature of the tire was either exothermic or endothermic. This was to provide insights into understanding the heat flow of the samples as a function of pyrolysis temperature. This allowed the determination of temperature dependence on the specific heat capacity of the substances [2]. From the DSC scans, exothermic peaks were observed from the thermal responses of all the char products (the heat flow values with the corresponding crystallization temperatures, T_c , are provided in Table 1). The exothermic peaks indicate points where a molten amorphous material changes to crystalline material (through ionic bond formation) upon cooling, to give highly ordered structures [2] leading to the formation of crystals and a definite melting point. The specific heat capacity which is the ability of the material to store heat at the different operating conditions provided insights into the suitability of the char products in chemical processes, as materials in furnaces, and in reactor or heating construction. The SC500 (catalytic pyrolysis at 500 °C) conditions had the highest specific heat capacity of 35 J/g.K followed by SC550 (19.36 J/g.K). The best heat storage ability provided by the SC500 char may have been caused by the excellent cracking of the raw tire during pyrolysis at the elevated temperature as well as the quickened reaction mechanism caused by the catalytic condition.

The catalytic experimental conditions (500 °C and 550 °C) therefore provided a greater environment for the formation of char products usable in chemical and heat-related processes, as a result of the high specific heat capacity of obtained chars at the temperature ranges. High operating temperatures lead to complex degradation reactions caused by the relatively unstable polar compounds present in the materials, leading to exothermic peaks [2].

At lower operating temperature conditions (S450 and SC450), the specific heat capacity values were much lower. High specific heat capacity (heat storage ability) of any material leads to better thermal stability. Therefore, the char products showed thermal stability at the corresponding crystallization temperatures, though with varying degrees (Table 2) [18].

Thermogravimetric analysis (TGA/DTG) was used to detect the temperature effects involved in weight changes during the pyrolysis process. The percent weight loss with temperature (Fig. 2) shows that the moisture removal rate increased with the produced chars

Table 1

Crystallization temperature and the corresponding specific heat capacity (C_p) of the char products at the different operating conditions.

Sample	Temperature ^a (K)	Heat flow (W/g)	Heat capacity ^b (J/K)	C_p ^c (J/g.K)
RS	374.89	-0.44	0.10	18.55
S450	375.33	-0.25	0.05	7.81
SC450	362.66	-0.25	0.05	8.33
S500	390.61	-0.25	0.05	8.07
SC500	358.01	-0.98	0.21	35.00
S550	408.86	-0.52	0.11	17.74
SC550	348.62	-0.55	0.12	19.36

^a Crystallization temperature, T_c .

^b The ratio of the heat flow (W/g) and the pyrolysis heating rate (10 °C/min).

^c Specific heat capacity, which is the ratio of the heat capacity in J/K, and the tire or char sample mass in g.

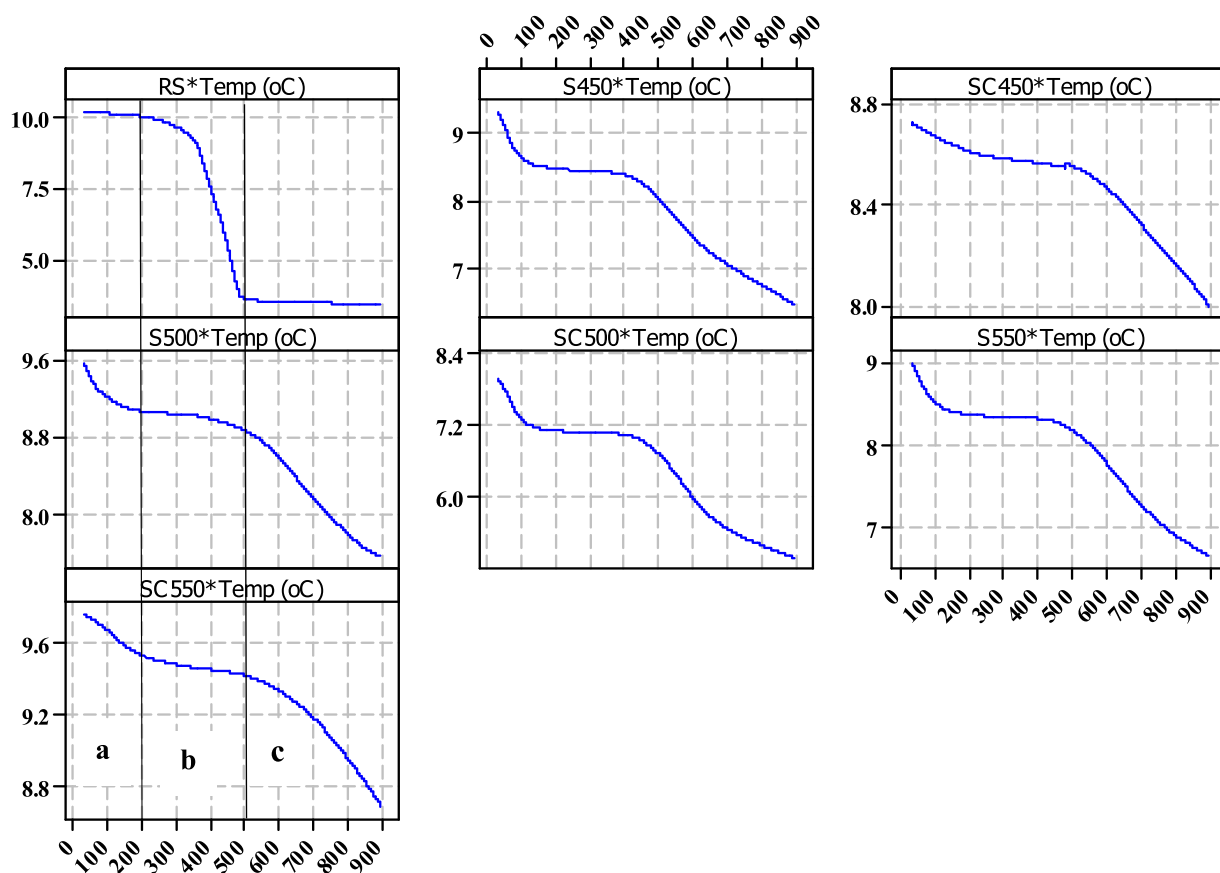
Table 2

The EDX analysis of the raw tire, catalytic, and non-catalytic pyrolysis operating conditions showing the elemental compositions.

	RS	S450	SC450	S500	SC500	S550	SC550
Elemental Composition							
C	85.59	84.71	42.84	85.41	56.59	85.02	60.03
O	10.15	7.11	3.10	5.68	4.62	5.45	4.02
Al	0.75	0.10	2.77	0.59	0.81	1.26	1.19
Si	0.70	2.10	0.10	2.74	0.73	3.63	0.41
S	1.15	2.10	0.46	2.12	1.38	1.87	2.80
Cl	0.09	0.20	9.04	0.17	15.01	0.11	4.84
Ca	0.68	0.97	0.73	1.20	0.99	0.73	1.09
Fe	0.85	–	–	–	0.20	–	1.16
Zn	0.79	2.26	40.98	2.13	16.71	2.54	25.33

RS = raw scrap tire. S = scrap tire. SC = scrap tire + catalyst. 450, 500, and 550 are the operating temperatures in °C.

(due to moisture gathering after the thermochemical conversion processes) at the different operating conditions unlike the raw scrap tire (RS). In all the experimental conditions, primary and secondary devolatilization began at roughly 200 °C and ended around 500 °C, supporting the temperature decomposition ranges of waste tires [43,44]. Furthermore, the primary devolatilization (b) decreased considerably with the pyrolyzed scrap tires because the volatile matters have been expelled due to high heating [45]. More of the chars in all the experimental conditions were made of fixed carbon and ash, as indicated by the secondary volatilization step (c). From the raw scrap tire (RS) having an initial volatile matter of about 66% w/w, it was degraded to less than 0.50% w/w (SC550) in all the pyrolysis steps, leading to the production of pyrolysis oil and gas fractions. The volatile matter degradation during the thermochemical conversion processes was related to the amount of oil and gas produced. SC500 with the volatile matter reduction to 2 % produced about 33% w/w oil and 14.90% w/w gas fractions (Fig. 1).

**Fig. 2.** Thermogravimetric analysis (TGA) curves for the raw sample (RS) and the different pyrolysis experimental conditions (S450, SC450, S500, SC500, S550, SC550). a is drying (moisture removal), b is the primary devolatilization step, and c is the secondary devolatilization step.

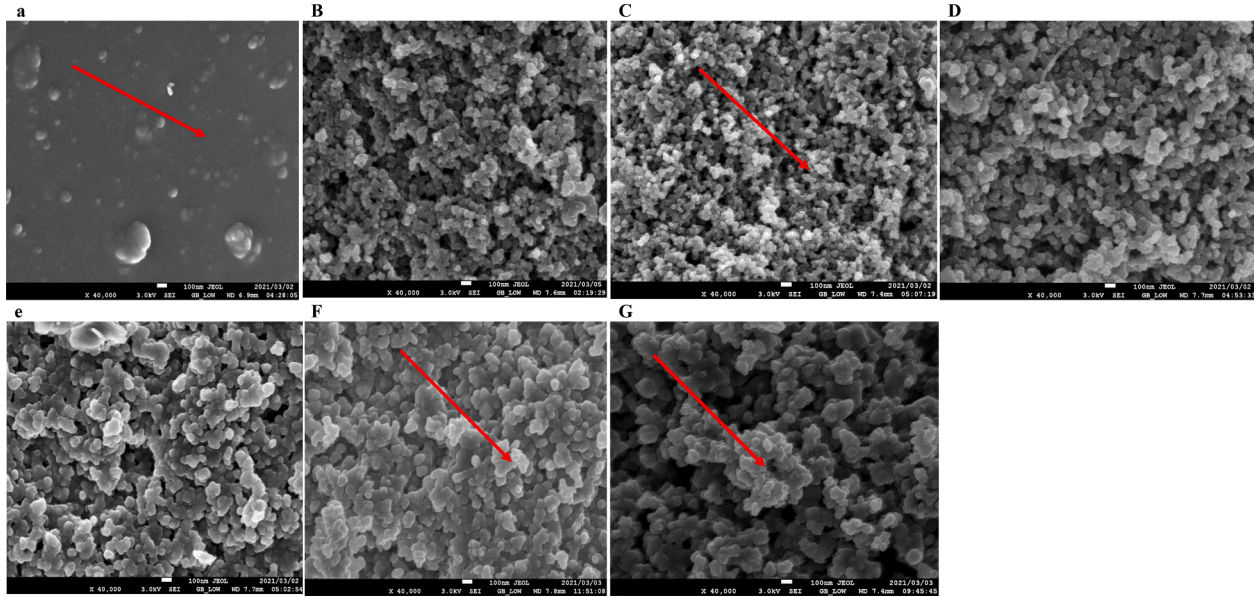


Fig. 3. The SEM images of the raw scrap tire (a) and the produced chars at the different thermochemical conversion operating conditions; S450 (b), SC450 (c), S500 (d), SC500 (e), S550 (f), and SC550 (g), all operated at constant time of 50 min and feedstock loading of 235 g. The arrow in (a) shows a well-ordered scrap tire surface while (c), (d), (e), (f), and (g), show the spherical-shaped carbon black particles occasioned by the high heating. The EDX analysis in the scrap tire and the produced chars showed the presence of carbon, oxygen, aluminum, silicon, sulphur, chlorine, calcium, iron, and zinc (Table 2). The major elemental composition of the scrap tire and the produced char is carbon (with a high presence in rubber matter as well as carbon black, which are normally used during tire production), followed by oxygen and zinc. The remaining elements were in trace amounts. Elemental carbon in the raw sample, closely 86% w/w, was reduced to about 43% w/w during SC450 operation (about 50 % reduction) (Fig. S3 (a)). Generally, elemental carbon reduction was greater during the catalytic pyrolysis than in the non-catalytic condition (Fig. S3), confirming that more of the cracking occurred during the catalytic process leading to increased oil production [42].

SEM – EDX analysis of the raw and solid product (char)

At increasing pyrolysis temperatures (500 °C (d, e, h) and 550 °C (f, g)), as provided in Fig. 3, the grain sizes became bigger, indicating that there were modifications to the structural arrangements. The grain sizes were relatively more orderly arranged at a lower temperature, 450 °C, (b and c), than at higher temperatures (indicating appreciable degradation of the tire sample at elevated temperatures). The SEM images for the produced chars revealed the spherical shapes (Fig. 3, (b) to (g)) of the carbon black particles forming different aggregates [46], compared to the well-arranged surface (no visible pores) of the raw sample (Fig. 3(a)). In general, thermal treatments showed gradual volatilization of the inherent matters leaving behind depressed channels with pores appearing more with increasing pyrolysis temperature (Fig. 3(g)).

The EDX spectral of the pyrolysis process are provided in Fig. S2 The compositions of the different elements present in the chars showed different degrees of increase (Fig. S3). Zinc and chlorine depositions increased due to the addition of zinc chloride during the catalytic conditions (SC450, SC500, and SC550 (Fig. S3(e)). For zinc, SC450 had the highest increase of 98 %, followed by SC500 (about 95 %), and SC550 (about 97 %) compared to its composition in the scrap tire (0.79% w/w). Correspondingly, chlorine increased in SC450 to 99 %, SC500 to 99 %, and SC550 to 98 % (Fig. S3 (d)). Consequently, the empirical formulas for the raw and produced solid samples were determined through the EDX elemental compositions by dividing the weight percent of the elements by their atomic weights. Obtained empirical formulas (Table 3) were estimated based on one carbon atom. Increased molecular weights were observed for the catalyzed pyrolysis conditions as a result of the introduction of aluminum, silicon, chlorine, sulphur, and zinc (in addition to carbon and oxygen), compared to the non-catalyzed conditions made up of only carbon, oxygen, and silicon.

FTIR characterization of the scrap tire and char products

The FTIR analysis was used to understand the chemistry of the functional groups in the raw scrap tire and the produced chars at different process conditions. Different intensities and their corresponding peaks were identified for the produced chars (Fig. 4). The different bonds such as O—H, C—H, C—C, C=O, C—H, C=C were obtained at different wavelengths [47–49] (Table S1). The pyrolysis operating conditions of S450, SC500, S550 were identified for compounds such as alcohols, phenols, and carboxylic acid between the wavelengths of 3216–3364 cm^{-1} which is the region of O—H stretching [3,47]. Other prominent peaks for S450, SC450, S500, SC500, S550, and SC550 were identified at 1476–1818 cm^{-1} and 750–982 cm^{-1} (for alkenes), 2970–3084 cm^{-1} and 2790–2936 cm^{-1} (for alkanes) representing C=C and C—H stretching respectively.

The C—H bending, also classified for the alkanes [48] occurred at the wavelength 1302–1394 cm^{-1} for S450, SC450, S500, SC500, S550, and SC550 pyrolysis conditions. The aromatic compounds along with the aldehydes or the ketones were identified with C—H stretching (2970–3084 cm^{-1}), C=C and C—C stretching (1476–1818 cm^{-1}) [49] for the pyrolysis conditions of S450, SC450, S500, SC500, S550, SC550. All the functional groups identified clearly indicated these materials for diverse industrial applications.

The potential of the produced char as an adsorbent for industrial wastewater treatment

Considering the high thermal stability (specific heat capacity of 35 J/g.K), and high crystallization tendencies of the char obtained from the catalytic pyrolysis condition at 500 °C (SC500)(Table 2), the solid product, after chemical activation, was used as an adsorbent in the removal of pollutants from sugar mill wastewater. Generally, activation of tire chars provides high surface area and porosity as well as rich surface functional groups, making them excellent adsorbents for the removal of pollutants [50], whether inorganics or organics from water and wastewaters.

The initial concentrations of heavy metals available in the wastewater from the sugar mill industry were monitored with the atomic absorption spectrometer (AAS) to be; lead = 0.22 mg/l, Nickel = 0.08 mg/l, zinc = 0.14 mg/l, cadmium = 0.02 mg/l, chromium = 1.04 mg/l, copper = 0.22 mg/l, arsenic = 0.002 mg/l, manganese = 0.002 mg/l, and iron = 0.04 mg/l. With the assistance of the World Health Organization (WHO) manual for the allowable limit of heavy metals in water/wastewater, cadmium (with the highest percent difference, 85 %, from WHO allowable limit concentration compared to the other heavy metals present in the wastewater) was chosen for consideration. WHO recommends a safe limit of cadmium in wastewater and soils for agriculture to be 0.003 mg/l [51]. In evaluating the effect of the produced activated carbon on the removal of heavy metals from the sugar mill wastewater, different experimental loadings were used for the removal of cadmium from the wastewater at different operating temperatures and times. The removal efficiency (%RE) (Fig. 4) was calculated based on the percent reduction of cadmium after the treatment of the sugar mill

Table 3
Resultant empirical formulas of the raw scrap tire and the char products calculated from the elemental compositions of the EDX analysis.

Pyrolysis condition	Derived empirical formula
RS	$\text{CO}_{0.089}$
S450	$\text{CO}_{0.063}$
SC450	$\text{CO}_{0.054}\text{Al}_{0.029}\text{Cl}_{0.071}\text{Zn}_{0.176}$
S500	$\text{CO}_{0.049}\text{Si}_{0.014}$
SC500	$\text{CO}_{0.061}\text{Cl}_{0.089}\text{Zn}_{0.054}$
S550	$\text{CO}_{0.048}\text{Si}_{0.018}$
SC550	$\text{CO}_{0.050}\text{S}_{0.017}\text{Cl}_{0.027}\text{Zn}_{0.078}$

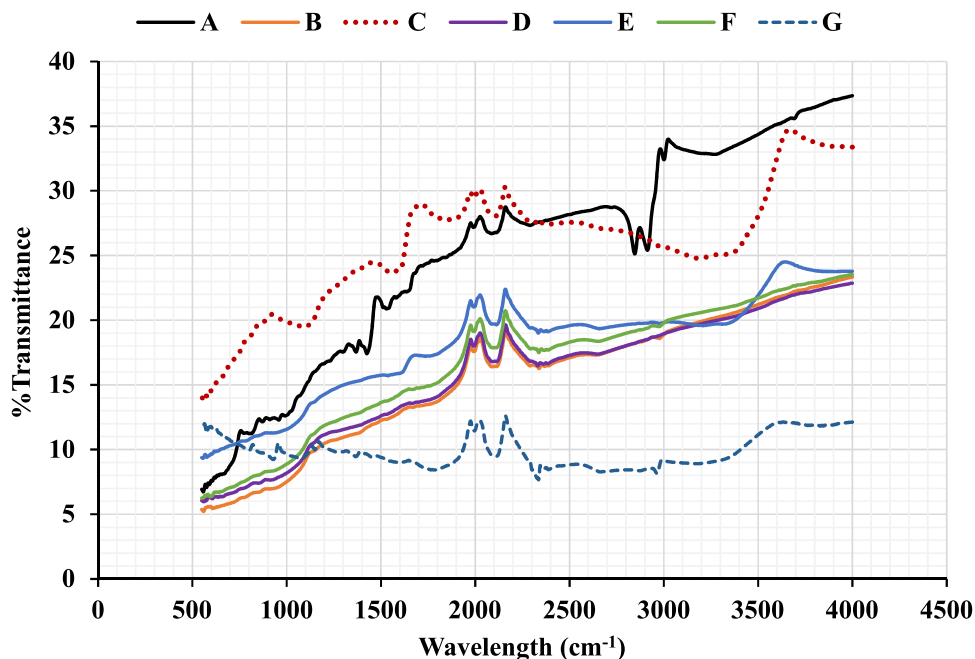


Fig. 4. FTIR spectra for the raw tire and the char products. A: Raw tire sample (RS), B: S450, C: SC450, D: S500, E: SC500, F: S550, and G: SC550.

wastewater at the different conditions of adsorbent loadings (60, 80, and 100 mg), temperatures (30, 40, 50, and 60), and treatment time (15, 30, 45, 60 min).

The removal efficiency (80 %) of cadmium was obtained for the maximum adsorbent loading of 100 mg at a mild temperature of 50 °C and 60 min (Fig. 5 (c)). However, the highest removal efficiency of 90 % was achieved for 80 mg adsorbent loading at 50 °C and 60 min treatment conditions. This follows that a greater amount of the heavy metal was adsorbed at higher temperature conditions for the same operating time. The higher %RE of cadmium at 50 °C may have been made possible because the metal releasing rate tends to increase with increasing temperature [52], which led to the increased adsorbing capacity of the activated carbon.

XRD, BET, and SEM-EDX studies of the pyro-char, AC, and spent AC

Activated carbon is more loosed and has active adsorption capacity than general carbon. During the activation process of the produced char, adsorption pores (which are the smallest pores within the particles which consist of gaps of graphite plates) were created with sufficient adsorption forces to adsorb impurities. The XRD technique was used to give information about the atomic distribution, the crystalline (planar) distances, and to detect peak relative intensities (Fig. S5).

After the activation process with phosphoric acid at the elevated temperature, new peaks (Fig. S5 (b)) were created at 101, 200, and 311 representing new graphite planes [53] from the initial peaks at (002) and (100), noticed in the produced char (Fig. S5 (a) and Table 4).

From Table 4, the planar distance (interplanar spacing within the crystal structure, d) at 002 increased in the activated char to the raw char to about 63 %. New peaks were formed because of the force (stress) that was applied during the activation process, causing deformation of the crystal structure. In this case, heating at an elevated temperature was the stress applied which caused the interplanar distance to change, resulting in the shifts of the XRD peaks. A smaller d -value means a smaller planar distance leading to a reduction in adsorption capacity. From Table 4, the d -values generally increased for the activated carbon formed, which enhanced the adsorption capacity of the AC for the high removal efficiency of cadmium from the sugar mill wastewater.

Through the activation of carbon, pore structures were created and the visible surface area and pore volume of the carbon increased [54], forming a crystalline form of carbon (e.g. graphite) from the carbon black in tyre. Also, the surface area and porosity of the materials increase by transforming mesopores or macropores to micropores [55].

The BET analysis of the produced char showed increased surface area compared to the raw tire (Table 5). This also corresponded to increasing pore diameter which was directly related to the improved pore morphologies and porosity as shown in the SEM images (Fig. 3(g)) compared to the ordered arrangement in the raw scarp tire, Fig. 3(a). This led to the adsorption of the heavy metal (cadmium) present in the sugar mill wastewater. The surface area of the char increased to about 44 %. During the pyrolysis process, pore structures were created which increased the surface area and the pore volume thereby transforming the mesopores or macropores to micropores [52]. The activation process using the phosphoric acid increased the surface area of the activated char to about 56 % (Table 5), compared to the surface area of the raw char, using inference from the BET estimation, which resulted in 90 % removal (80 mg adsorbent was used) of cadmium from the sugar mill wastewater (Fig. 4 (b)).

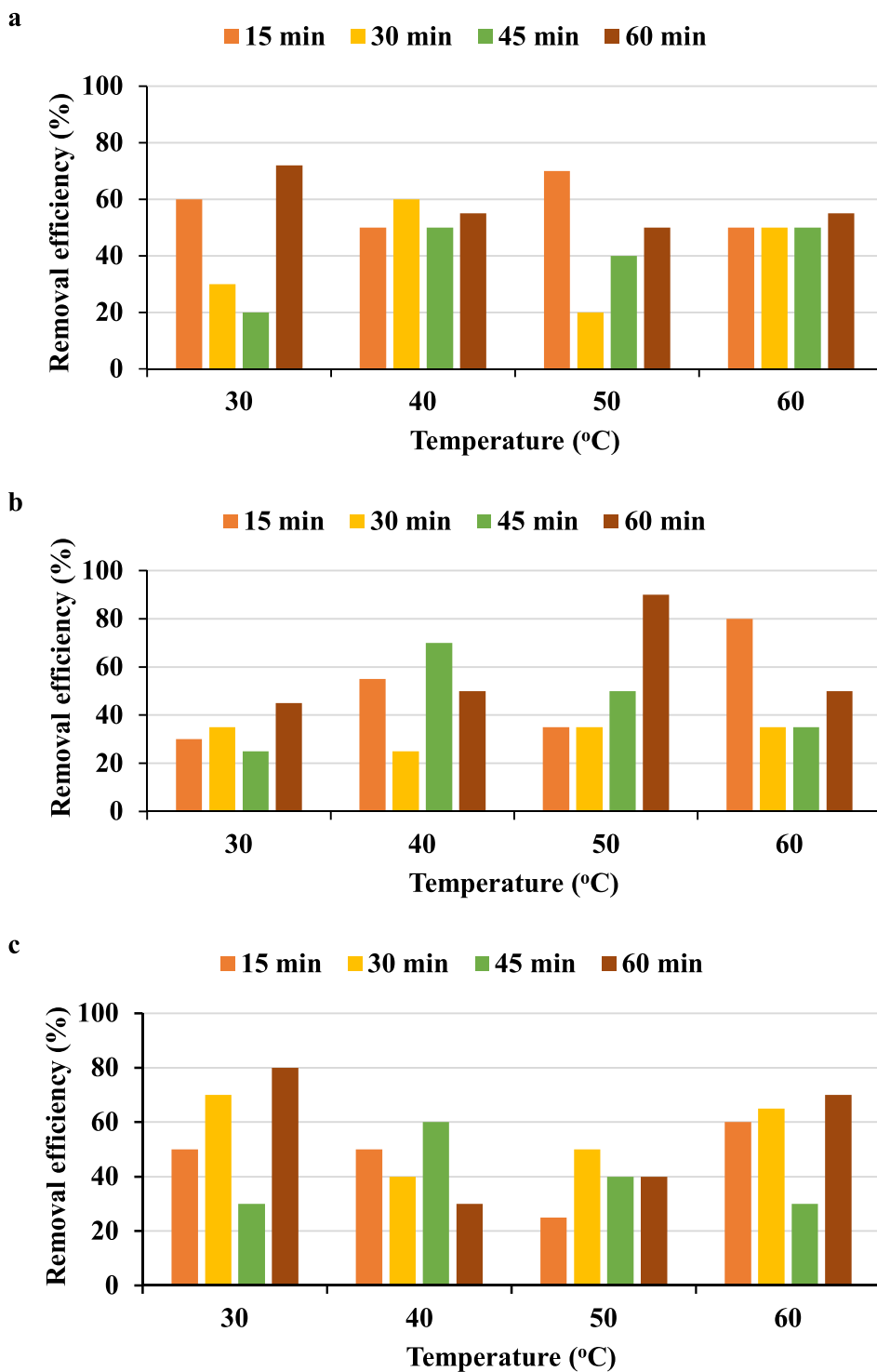


Fig. 5. Removal efficiency of cadmium after the treatment the sugar mill wastewater for different operating conditions of adsorbent loadings 60 mg (a), 80 mg (b), and 100 mg (c), temperatures, 30, 40, 50, 60 °C, and time 15, 30, 45, and 60 min.

The XRD and BET results show that the spent AC may be recycled for other sets of wastewater treatments, after undergoing required washing and pretreatments.

The EDX results (Fig. 6) of both the activated and spent char indicated that the crystalline carbon was still intact (the percent weight

Table 4

Interplanar spacing (d in Å), obtained through the XRD analysis for the char, activated carbon, and spent activated carbon after wastewater treatment.

	Char	AC ^a	Used-AC
Appearance	Black	Grey	Grey
pH	6.10	6.80	6.50
XRD peaks		Planar distance, d	
002	3.49	9.30	6.55
100	2.08	4.55	4.48
101 @ 28.5°	–	3.13	3.78
101 @ 53.5° ^b	–	1.71	–
200 @ 37.5°	–	2.40	1.86
200 @ 49.5° ^c	–	1.84	–
220	–	–	1.39
300	–	–	1.22
311	–	1.54	–

^a Activated carbon.

^{b,c} Point coordinates at different peaks. d was calculated using Bragg's law ($2d\sin\theta = n\lambda$), θ is the diffraction angle and λ is the wavelength = 0.154 nm.

Table 5

BET values for the raw tire, char sample (obtained at catalytic pyrolysis condition of 500 °C), activated carbon (AC), and spent AC.

	Raw sample	Char	AC	Spent AC
Surface area (m ² /g)	265.50	470.65	1065.44	940.65
Total pore volume (cm ³ /g)	0.45	0.63	0.63	0.60
Average pore diameter (Angstrom unit, (Å) ^a)	32.54	28.22	33.55	32.54

^a Å = Angstrom unit (= 0.1 nm).

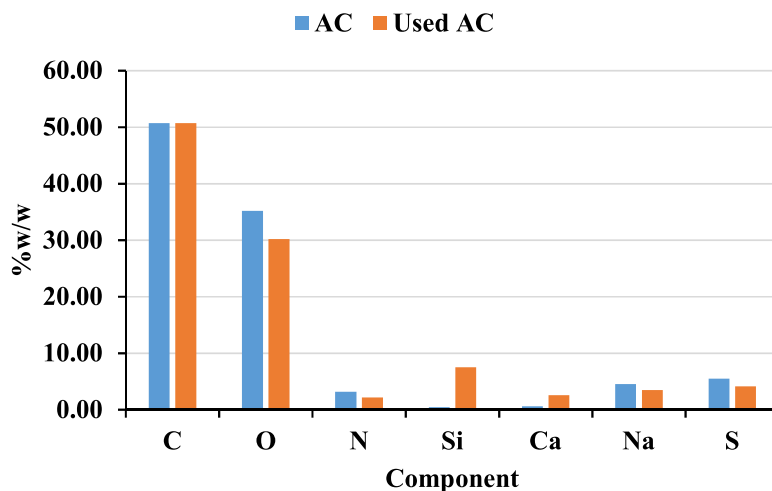


Fig. 6. EDX results of the activated carbon synthesized from the pyro-char and the spent activated carbon after the sugar mill wastewater treatment. AC = Activated char.

of carbon in the spent AC was the same as that of the unused AC), even after wastewater treatment. However, the surface area of the spent AC has been reduced to 940.62 m²/g from an initial AC surface area of 1065.44 m²/g (Table 5), due to surface adsorption of the heavy metal (cadmium) during the removal process as shown in the SEM image of the spent AC (Fig. S4 (b)).

Conclusions

The catalytic and non-catalytic pyrolysis of the motor car scrap have been studied using three operating temperatures (450, 500, 550 °C) and a fixed time of 50 min. The results showed that the HHV of the scrap tire (35.90 MJ/kg) can be compared to that of crude oil and coal because of its energy recovery potential and its suitability for the production of fuels, chemicals, and clean energy generation. The addition of catalyst (ZnCl₂) increased the yields of the chars for the pyrolysis conditions (SC450 = 59% w/w, SC500 = 52% w/w, and SC550 = 51% w/w) compared to the non-catalytic conditions at S450 = 44% w/w, S500 = 38% w/w, and S550 = 34%

w/w. More of the oil and gas fractions were produced at higher temperatures, unlike the production of char at lower temperatures. Oil and gas fractions were 33% w/w (at 500 °C) and 44% w/w (at 550 °C) respectively. Different characterization techniques used in this study showed enduring industrial applications of both the char and the activated char (carbon) with high specific heat capacity of the char of about 35 J/kg.K. The maximum removal efficiency of 90 % was established when 80 mg (wastewater treatment operated at 50 °C and 60 min) of the activated char was used for the treatment of sugar mill wastewater contaminated with heavy metal, cadmium. Therefore, the char fraction obtained during the pyrolysis processes proved to have high thermal stability useful as a fuel, for energy generation, in furnaces, reactors, and heating constructions. The produced char showed to be an excellent adsorbent for the removal of pollutants from wastewater which further contributes to waste management purposes.

CRediT authorship contribution statement

Augustine O. Ayeni: Conceptualization, Supervision, Visualization, Writing – original draft, Writing – review & editing. **Deinma T. Dick:** Data curation, Formal analysis, Writing – original draft. **Oluranti Agboola:** Methodology, Supervision, Validation, Writing – review & editing, Resources. **Rotimi Sadiku:** Data curation, Formal analysis, Resources, Software. **Michael O. Daramola:** Validation, Visualization, Writing – review & editing. **Olagoke Oladokun:** Project administration, Validation, Writing – review & editing. **Edith E. Alagbe:** Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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