Integrated Chemical–Thermal Activation of Pyrolyzed Used Tire-Derived Char for Enhanced Total Organic-Carbon Adsorption from Starch Processing Wastewater

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***Abstract*—** To address environmental concerns regarding scrap tire waste in South Africa, this study enhanced pyrolyzed used tire-derived activated char (PUTDC) using an aqua-regia/KOH/CH_3CO_2K treatment. Thermal activation at 650 °C produced LPUTDCC, which demonstrated a significantly improved Brunauer-Emmett-Teller surface area of 85 m^2/g and a reduced sulfur content of 0.6 w/w %. When applied to starch manufacturing wastewater, LPUTDCC achieved 80% total organic carbon removal at pH 5. These findings indicate that LPUTDCC is an effective, low-cost adsorbent for industrial wastewater treatment. The results further suggest that blending PUTDC with commercial carbon can produce sustainable materials to mitigate environmental pollution.

***Keywords*—** Pyrolyzed used tire-derived activated char; Thermal and chemical Activations; Starch manufacturing wastewater; Adsorption**.**

I. INTRODUCTION

Non-biodegradable used tires are a major environmental threat in South Africa [1, 2]. Pyrolysis offers a circular economy solution by generating oil and pyrolyzed tire-derived char (PUTDC) while reducing greenhouse gases [3, 4]. However, the abundant char—typically 31.4-52.9 wt. % of yield—requires viable utilization strategies [5, 6]. While PUTDC is carbon-rich, its high sulfur and mineral content results in a low Brunauer-Emmett-Teller (BET) surface area (<45 m^2/g), limiting its adsorption capacity compared to commercial carbon [7, 8, 9, 10, 11].

To enhance its properties, researchers have explored physical and chemical activation [12]. This study addresses a literature gap by evaluating PUTDC activation using potassium hydroxide (KOH), potassium acetate (CH_3CO_2K), and aqua-regia (ARR) at 650 °C. The investigation uses South Africa national mineral research organisation (Mintek) macro thermogravimetric analysis system (M-TGA), X-ray diffraction (XRD), X-ray fluorescence (XRF), Raman, and total organic carbon (TOC) analyses to assess the resulting adsorbents for treating starch manufacturing wastewater (SWW), focusing on the impact of chemical concentrations and environmental variables on TOC removal.

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II. MATERIALS AND METHODS

A. Materials Sourcing and Preparation

This study utilized four primary materials: PUTDC, AquaSorb® 2000, granular commercial activated carbon (ACC) [13], and SWW. All materials were sourced from various locations within the Gauteng province of South Africa.

B. Solid Materials Sourcing

Approximately 25 kg of PUTDC was sampled from Energy Partners (Alrode, South Africa) following ISO 18283 and ISO 13909-4 guidelines, having been produced via rotary kiln pyrolysis of used tire crumb rubber from Dawhi Rubber-Recycling (Germiston, South Africa) at 450 °C for 4 hours; additionally, 5 kg of ACC was sourced from UDEC Trading (Kempton Park, South Africa).

C. Wastewater Sourcing and Handling

In this study, researchers collected 20 L of SWW from a Germiston corn-starch plant following ISO 5667-21:2010 protocols, storing the sample under an argon atmosphere and chilling it to prevent UV interference and decomposition.

D. Chemicals and Gases

The study utilized hydrogen chloride (HCl, 35%), nitric acid (HNO_3, 65%), and KOH (99%) from Protea laboratory solutions; CH_3CO_2K (99%) from Sigma-Aldrich; argon gas (99.99%) from Afrox Ltd; and deionized water for all preparations.

E. Preparation of PUTDC and KOH/CH3CO2K blends

The precursor (PUTDC) was blended with KOH and CH3CO2K solutions and thermally activated in an argon atmosphere to create various carbon materials:

- KOCC and KACC were produced using 15 wt. % KOH and 20 wt. % CH3CO2K, respectively.
- 10KOCC/2KOCC and 10KACC/2KACC were produced using

optimized 10 wt. % and 2 wt. % solutions of KOH and CH3CO2K respectively.
All samples were stored under argon to prevent reaction with moisture or air before testing.

F. Preparation of blend of PUTDC with aqua-regia

To prepare the leached PUTDC samples (LPUTDCs) for activation, ARR (1:3 HNO3 to HCl) was applied at a 1:1 ratio to reduce ash content. This preparatory step was used exclusively for this experimental study and is not intended for the proposed commercial production process. The resulting samples were stored under argon before being activated at 650 °C for wastewater treatment testing.

Various adsorbents were synthesized at a uniform activation temperature of 650 °C by treating a PUTDC precursor with a range of activating agent:

- PUTDCC: Raw PUTDC without activating reagents.
- KOCCC, 10KOCC, 02KOCC: PUTDC activated with 15 wt. %, 10 wt. %, and 2 wt. % KOH, respectively.
- KACCC, 10KACC, 02KACC: PUTDC activated with 20 wt. %, 10 wt. %, and 2 wt. % CH3CO2K, respectively.
- LPUTDCC: PUTDC activated using an ARR.

G. Thermal Activation Experiments

In this study, carbonization was performed using MINTEK's in-house M-TGA under a 10 ml/min argon flow [5]. Samples (10–30 g) of PUTDC, KOCC, KACC, or LPUTDC were heated to an optimal temperature of 650 °C [14] at 10 °C/min. This peak temperature was maintained for a 4-hour isothermal stage before controlled cooling and preservation in an argon environment for subsequent analysis.

H. Procedure for Adsorption Studies

In this investigation, batch experiments were conducted using an adsorption column (450 mm height, 2.205×10-4 m3 total volume packed) with 65 g of char. SWW was pumped at 3.3 ml/min with a 30-minute residence time [15, 16, 17]. Uniform flow was maintained via a 200 µm distribution plate and a 50 µm filter, allowing for the subsequent determination of adsorption capacity and TOC removal.

I. Characterization Study of Different Samples

Various analytical methods were applied to the ACC, PUTDC, and activated chars (KOCCC, LPUTDCC, etc.). Proximate and ultimate analyses followed ISO standards [18], while XRF determined inorganic proportions in ash [ASTM D4326-13]. XRD analysis was performed to determine proportions of crystalline and amorphous phases in the solid samples [19]. Structural features were further examined via Raman spectroscopy [20] and BET surface area measurements through N2 adsorption at -196 °C. Finally, TOC removal performance in SWW was quantified using a Teledyne-Tekmar TOC analyzer [21].

J. Uncertainty for TOC Removal %

TOC removal efficiency was calculated using Equation 1, despite measurement uncertainties from adsorbent mass (plus/minus 1.5 g), volume, and concentration ([22]. These cumulative errors can impact final results for materials with low adsorption capacities. TOC removal efficiency was quantitatively determined using the following standard equation:

$$\text{TOC Removal (\%)} = \frac{c_i - c_f}{c_i} \times 100 \qquad \text{Eq. 1}$$

where and represent the initial and final TOC concentrations (ppm), respectively

To ensure robust results, all novel experiments were run in triplicate, with standard deviation used to determine experimental error. A 95% confidence interval identified statistically significant changes, and all reported data represents the average results, with corresponding error bars on figures. Confidence intervals for each product fraction were calculated using Equation 1:

$$CI = \bar{x} \pm \left(t_{score} \times \frac{\sigma}{\sqrt{n}}\right) \qquad \text{Eq. 2}$$

In this formula, x is the sample mean, sigma (σ) is the standard deviation, n is the sample size, and t_ is 4.303 for 2 degrees of freedom at a 95% confidence level.

III. RESULTS AND DISCUSION

A. Proximate and Ultimate Analyses

Proximate analysis shows that ACC has the highest fixed carbon (87.5%) and lowest ash yield (4.1%), resulting in superior material properties, while PUTDC and its derivatives have higher ash yields (up to 29.2%) and lower fixed carbon (50.6%–54%). Impurities like residual sulfur (~2%) in PUTDC from rubber vulcanization reduce surface area and active sites [9; 11]. Although ACC has higher moisture (3.4% and volatile matter (4.9%) than PUTDC (both 1.9%), its levels are the lowest among all samples, correlating with superior material properties [11].

Ultimate analysis indicates ACC has the lowest carbon (73.4%) and sulfur (0.5%) but the highest oxygen (22.4%), while PUTDC samples have higher carbon (85%–94.5%). High sulfur in some PUTDC chars may be due to in-situ capturing by potassium compounds, whereas lower sulfur (0.9%–2.5%) in PUTDC blended with KOH/CH_3CO_2K or leached with ARR is attributed to the volatilization of sulfur species during thermal treatment.

B. XRF Analysis

XRF analysis of all samples revealed that while ACC ash is predominantly SiO_2 (55.6%) and Al_2O_3 (18.5%), the PUTDC samples are rich in ZnO (up to 39.9%) and SiO_2 (43.9%). Acid leaching significantly increased Fe_2O_3 and Cr_2O_3 proportions in the LPUTDC (32.5% and 6.3%) and LPUTDCC (49.4% and 10.1%) samples due to corrosion, while the potassium-treated chars (KOCC, KOCCC, KACC, KACCC) showed high K_2O content (up to 27.8%) and corresponding low percentages of other oxides compared to raw PUTDC.

The ash from a PUTDC sample primarily consists of SiO_2 and ZnO, aligning with previous studies [9, 10, and 11]. Ash from the ACC sample, however, is mainly composed of SiO_2 and Al_2O_3.

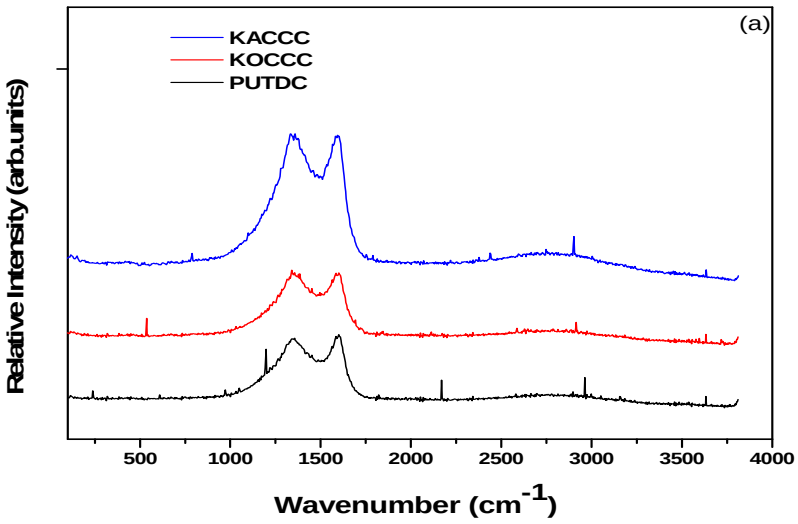
Blending PUTDC results in decreased proportions of SiO_2 and ZnO relative to pure PUTDC. Contamination from stirrer

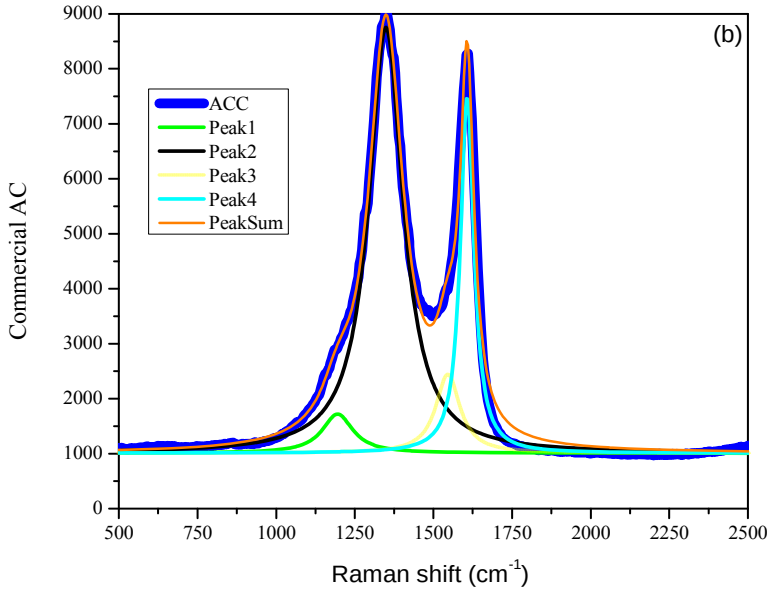
equipment during acidic leaching led to elevated Fe_2O_3 and Cr_2O_3 in some samples, which inversely lowered measured SiO_2 and ZnO. Mineral matter dissolution from PUTDC via reactions like $Fe_2O_3+6HCl=2FeCl_3+3H_2O$, $ZnO+2HCl=ZnCl_2+H_2O$, $Ca(OH)_2 + 2HCl = CaCl_2 +2H_2O$ and $Al_2O_3 + 6\ HCl = 2AlCl_3 + 3H_2O$ also decreased elemental composition of mineral matter in the leached pyrolyzed used tire-derived activated char (LPUTDCC).

C. XRD Analysis

The XRD results reveal that while all samples are predominantly amorphous (63.0%–92.8%), varying mineral compositions were observed, characterized by quartz (3.2%–10.7%) and wurtzite (0.1%–4.7%) across all samples, significant sphalerite in KACC (16.9%), and increased concentrations of kalicinite, diopside, and arcanite in the chemically treated and carbonized derivatives. The XRD analysis shows that ACC is primarily composed of amorphous carbon, whereas PUTDC-based samples contain mineral phases such as wurtzite, sphalerite, and zinc oxide (ZnO), consistent with literature [9, 10, and 11]. Chars activated at 650 °C remain predominantly amorphous but include traces of various minerals; specifically, chromite in LPUTDCC resulted from aqua-regia equipment corrosion [9, 11].

Potassium-rich kalicinite was identified in KOH and CH_3CO_2K blends, likely forming via CO_2 reaction and concentrating as volatile matter is released at high temperatures [14]. These elevated processing temperatures facilitate rapid volatilization, which restricts zinc-sulfur reactions, favoring H_2S gas formation and potential zinc loss [9, 10, and 11].





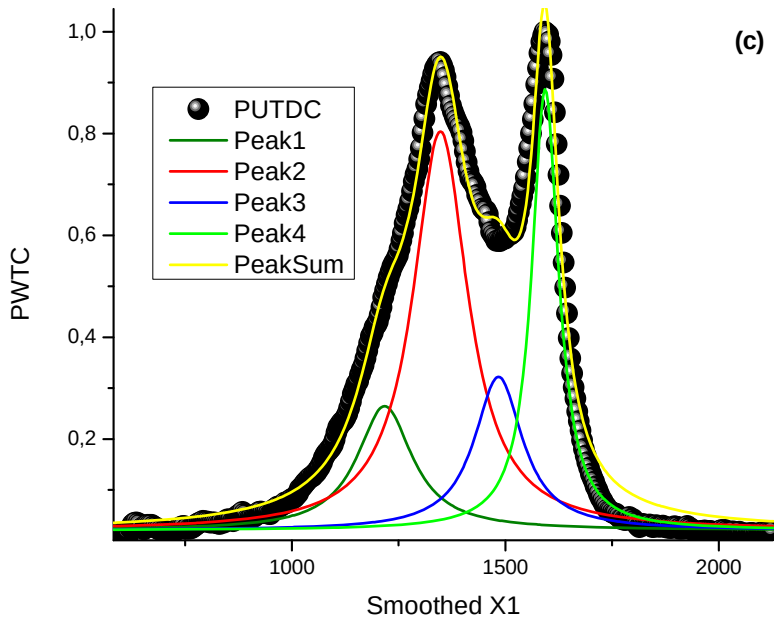


Fig. 1. Normalized Raman spectra for ACC and PUTDCC (a), curve fitting of KACCC, KOCCC, PUTDC; (b) curve fitting of ACC (c) curve fitting (smoothed) of PUTDC

A. BET Surface Area and Pore Characteristics

Figure 2 shows that ACC possesses the highest BET surface area (816.0 m^2/g) and pore volume (0.38 cm^3/g), while PUTDC and its various treated derivatives exhibit significantly lower values, with surface areas ranging from (18.9 to 85.3 m^2/g) and pore volumes between (0.01 and 0.21 cm^3/g).

BET analysis demonstrates that ACC, with a 4.1% ash content, possesses superior BET surface area and pore volume relative to all PUTDC-based materials (up to 29.2% ash). The reduced porosity in the 12.8% ash PUTDC is linked to high inorganic impurity levels [9.10, 11], highlighting the need for textural enhancement to improve its wastewater treatment efficacy [10, 11]. Thermal activation at 650 °C yielded only marginal gains for LPUTDC; however, the LPUTDCC sample experienced a substantial improvement, exceeding a 100% increase in both surface area and pore volume, though it remained below ACC benchmarks.

Analysis of the 10% and 2% KOC/KACC samples revealed that decreasing the concentration of activating agents (KOH or CH_3CO_2K) while increasing activation temperatures enhanced the surface area. Excessive alkali use can trigger inorganic precipitation and increase the % ash yield, thereby obstructing pores [3, 6, 7, 12, 17, 21], while extreme temperatures may lead to mesopore collapse [11]. Conversely, optimized KOH concentrations can maximize textural development, indicating that adsorption capacity is a function of both improved surface area and the presence of active surface functional groups [3, 6, 7, 12].

B. Adsorption Capacity of Activated Chars

LPUTDCC was assessed for SWW adsorption based on its sulfur content, BET surface area, and pore volume. LPUTDCC shows higher TOC removal than raw PUTDC but lower removal than ACC, yet it is considered a desirable mesoporous activated carbon consistent with its characteristics and SWW adsorption capacity. Initial TOC uptake was rapid for up to 60 minutes, with approximately 80% adsorbed after 120 minutes, potentially due to contact with active acidic surface sites and uptake into internal pores. TOC adsorption on LPUTDCC increased slightly as temperature rose but decreased above 50°C, possibly due to volatilization of HCl and HNO_3 or starch granule swelling [24]. Rapid adsorption was observed at pH 5.5, with decreased adsorption below pH 4.6 or above pH 9, suggesting adsorption mainly occurs on acidic surface sites, consistent with other researchers' findings [25].

Figure 3d demonstrates that TOC removal efficiency improved as LPUTDCC dosage increased, likely due to a higher availability of acidic active adsorption sites. This increase in active sites is further linked to the reduction of mineral matter during aqua-regia leaching of PUTDC, findings that align with the study by Zainal and Halim [11].

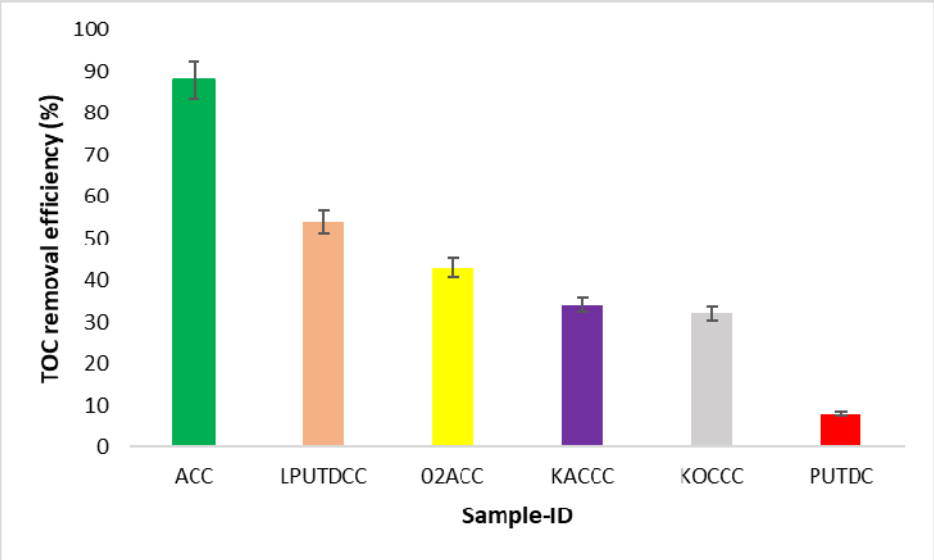


Fig. 2. Average TOC removal percentage using different adsorbents

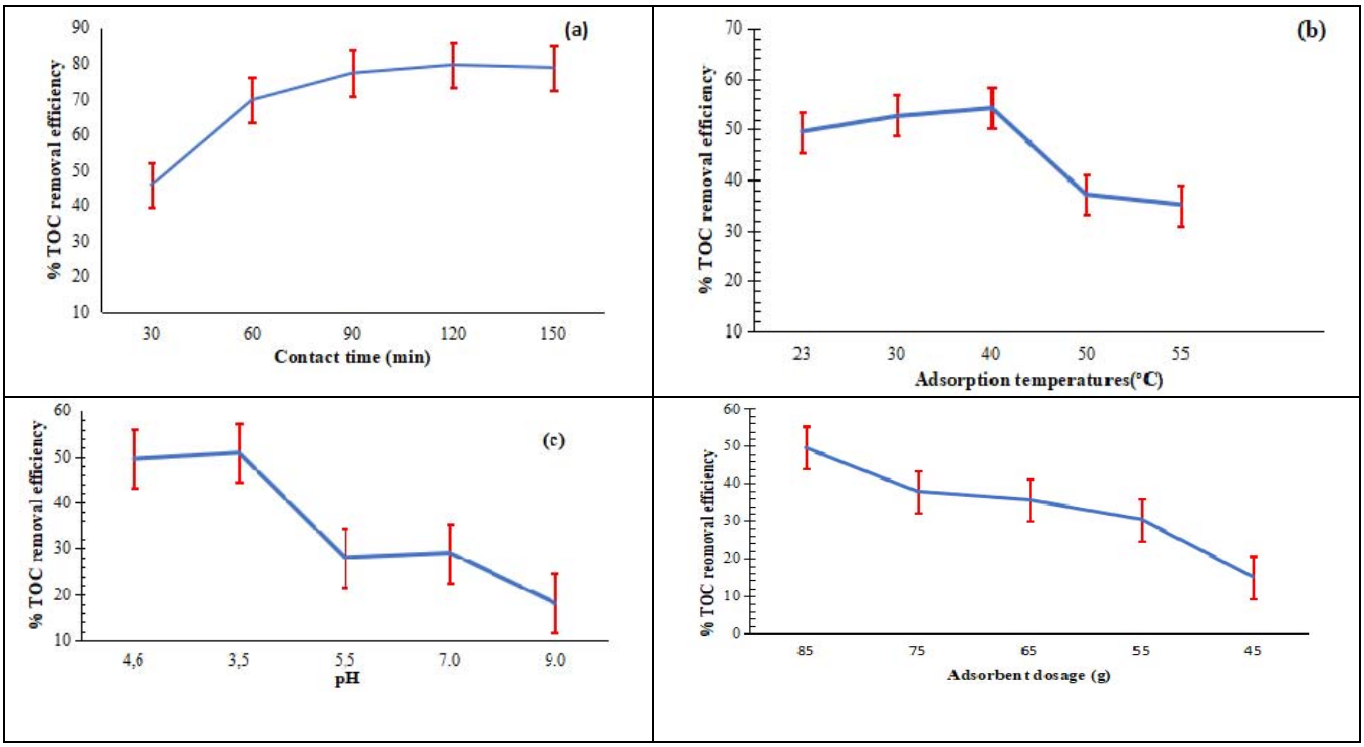


Fig. 3. Average results of the influence of (a) contact time, (b) adsorption temperatures, (c) pH and (d) adsorbent dosage on TOC removal using LPUTDC

IV. CONCLUSIONS

Specific chemical and thermal treatments were shown to convert PUTDC into a mesoporous adsorbent. Lower concentrations of activating agents resulted in better-quality char, and acid leaching effectively reduced ash content. The LPUTDCC achieved 80% TOC removal efficiency under optimal conditions, suggesting it could be an economical alternative for wastewater treatment. Nitric acid or hydrochloric acid leaching effectively will enhance char surface area, porosity, and acidity, creating an economical adsorbent or blend component for wastewater treatment

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