



# Electrochemical sensing of paracetamol based on sugarcane bagasse-activated biochar

Scarlett Allende<sup>a</sup>, Yang Liu<sup>b</sup>, Mohan V. Jacob<sup>a,\*</sup>

<sup>a</sup> Electronics Material Lab, College of Science and Engineering, James Cook University, Townsville, QLD 4811, Australia

<sup>b</sup> College of Science and Engineering, James Cook University, Townsville, QLD 4811, Australia

## ARTICLE INFO

### Keywords:

Biochar  
Microwave-assisted pyrolysis  
Paracetamol  
Sugarcane bagasse

## ABSTRACT

Agro-industrial waste is an abundant bio-resource that can be used as a feedstock to develop carbon nano-materials. This research identifies the specific microwave pyrolysis operating conditions to generate activated biochar from sugarcane bagasse (SCB) biomass. The optimal conditions to obtain activated biochar from SCB was by using H<sub>2</sub>SO<sub>4</sub> chemical treatment in a mass ratio 1:1 followed by microwave-assisted pyrolysis at 1.5 kW for 1 hour. The resulting carbon material attained a 278 m<sup>2</sup>/g BET surface area and a relatively pure carbon structure with a minor concentration of oxygen and silicon. The activated biochar was used to develop an electrochemical sensor using the drop-casting method. The SCB-activated biochar electrochemical sensor achieved significant electrocatalytic properties to detect paracetamol, showing 71% less charge transfer resistance in EIS and 96% higher electrocatalytic properties than the bare electrode based on CV curves. The linear range of paracetamol current responses demonstrated a considerable sensitivity with a 2.5 μM limit of detection. The modified GCE indicates a promising performance in paracetamol detection in a real sample.

## 1. Introduction

Globally, agricultural production yields approximately 23.7 billion tons of solid food residues per day (Duque-Acevedo et al., 2020). Some agro-industrial waste categories are rice straw, rice husk, coffee pulp, sugarcane bagasse, seeds, crop/tree, wheat straw, and coconut husk (Zhao et al., 2022). Particularly, the global production of sugarcane bagasse is estimated at 534 million tonnes per year, with Australia contributing 10 million tonnes per year, and a waste generation range of 8 tonnes per hectare (Hamawand et al., 2021; Khatri and Pandit, 2022). Each year, the global waste of wheat straw, hardwoods, and rice straw amounts to 709.2 million tons, 58 million tons, and 673.3 million tons, respectively (Millati et al., 2019; Sath et al., 2018). The growing demand for agricultural resources leads to increased waste production, resulting in higher greenhouse gas emissions during waste disposal and storage, e.g., methane and carbon dioxide gas (Millati et al., 2019; Sath et al., 2018). To address waste management challenges and reduce environmental risks, it is essential to develop efficient bioenergy technologies that utilize abundant agricultural feedstock and provide a shortage of energy sources (Belyakov, 2019; Li et al., 2022a).

Microwave pyrolysis is an alternative to the waste conversion

method. Microwave heating implies a volumetric absorption of electromagnetic energy (thermochemical process)- whose main by-products are char, oil, and gas (Ethaib et al., 2020). This technique offers various advantages such as high energy transfer, quick start-up, versatility in feedstock application, and rapid and efficient heating (Hadiya et al., 2022). It enables the generation of clean energy and producing high-quality carbon materials (Allende et al., 2023a). Using microwave pyrolysis contributes to waste management solutions and reduces environmental hazards.

Significant interest has gained the biochar activation due to its potential as an electrocatalytic material for sensing applications (Godwin et al., 2019; Spanu et al., 2020; Sudha et al., 2019). Microwave pyrolysis treatment of feedstock generates carbon-rich material with a microporous structure and prominent porosity formation (Allende et al., 2023b). Activated biochar development considers physicochemical properties, environmental benefits, and low-cost production (Luo et al., 2022). Biochar modification involves two stages: biomass chemical activation and thermal treatment. Prior to thermal treatment, the biomass is chemically activated using acid (H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub>, HCl, H<sub>2</sub>O<sub>2</sub>, ZnCl<sub>2</sub>), alkaline (KOH, NaOH), or sulfonation additives (H<sub>2</sub>SO<sub>4</sub>) to enhance the porosity and optimize functional groups of the biochar (Cheng et al.,

\* Corresponding author.

E-mail address: [Mohan.Jacob@jcu.edu.au](mailto:Mohan.Jacob@jcu.edu.au) (M.V. Jacob).

<https://doi.org/10.1016/j.indcrop.2024.118241>

Received 8 May 2023; Received in revised form 1 February 2024; Accepted 11 February 2024

Available online 17 February 2024

0926-6690/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

2017; Spanu et al., 2020). The chemically impregnated biomass undergoes thermochemical conversion through pyrolysis, which accelerates chemical reactions and thermal breakdown of lignocellulosic biomass components (Godwin et al., 2019). The porosity and functional groups are significantly influenced by the operating conditions during the pyrolysis process (Allende et al., 2022, 2023a). Higher pyrolysis temperatures and longer treatment times result in decreased particle size, increased BET surface area, enhanced pore volume, and higher concentrations of carboxylic or hydroxyl functional groups on the biochar surface (Godwin et al., 2019; Monticelli, 2020; Tang et al., 2020).

The use of agricultural waste for the generation of valuable carbon material is gaining interest due to its diverse applications in multiple industries. The global consumption of pharmaceutical products has increased rapidly through the years (Alfhaid, 2022; Benyekkou et al., 2020). During these products' fabrication, various pharmaceutical compounds are discharged into natural water, posing a considerable environmental risk due to the presence of toxic elements that can contaminate essential resources such as water, groundwater, food, and soil. (Benyekkou et al., 2020; Escapa et al., 2017). Paracetamol (acetaminophen) is a common drug used for its antipyretic and analgesic properties, which chemical product has been detected in recycled water (Benyekkou et al., 2020; Villota et al., 2019). Accurate and rapid detection of paracetamol is crucial for conserving environmental sources (natural water and sewage treatment plants), avoiding improper disposal, and active pharmaceutical ingredients removal in recycled water. Current detection methods are capillary electrophoresis, mass spectroscopy, fluorescence spectrum and gas chromatography (Boumya et al., 2021). The applications of those methods represent extended procedure time, complex equipment, and expensive technologies (Zafar et al., 2022). Nevertheless, activated biochar is an emerging alternative with promising properties of electrochemical sensing, e.g., high sensitivity, simplicity, reliability, inexpensive, and low time-consuming for detecting paracetamol (Boumya et al., 2021; Wang et al., 2020a).

Various studies have focused on synthesizing carbon materials to modify electrodes for detecting different species (Bhujel et al., 2019; Martínez-Sánchez et al., 2019; Wang et al., 2020b). However, many of these processes require the addition of metal/metal oxide and involve complex and less sustainable procedures (Li et al., 2022b). The objective of this research is to investigate the synthesis of activated biomass-derived materials and their application as metal-free sensors for detecting paracetamol. Sugarcane bagasse (SCB) serves as the biomass feedstock, sulfuric acid ( $H_2SO_4$ ) as the acidic chemical activation method, and microwave pyrolysis as the heating conversion method in this study. The analytical performance of SCB-activated biochar is examined as an electrode material when applied to a glassy carbon electrode (GCE) for the detection of paracetamol. The electrochemical performance is evaluated based on the sensitivity, selectivity, stability, and reproducibility properties of the modified GCE.

## 2. Material and methods

### 2.1. Production of activated biochar

The preparation of  $H_2SO_4$ -activated biochar involves several steps, including chemical activation and microwave pyrolysis of the raw biomass, followed by thermochemical post-treatment of the biochar. In this study, sugarcane bagasse (obtained from Wilmar Sugar Australia, Queensland) was used as the feedstock for biochar production. To eliminate impurities, the raw sugarcane bagasse (SCB) was initially washed with ethanol and then rinsed several with distilled water. Subsequently, the SCB was soaked in a 1:1 mass ratio of sulfuric acid ( $H_2SO_4$ ) for 24 hrs. After the acid treatment, the feedstock was dried overnight at 110 °C. The selection of  $H_2SO_4$  as the activating agent was based on its ability to generate carbon material with catalyst properties (El-Nemr et al., 2022; Zhou et al., 2021). To prevent over-gasification and the destruction of the biochar pore structure, a low concentration

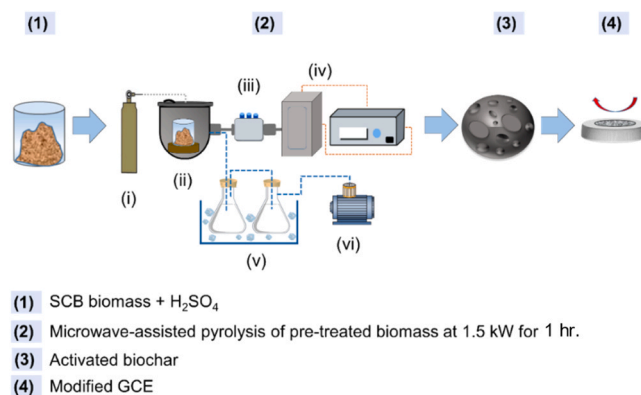


Fig. 1. Synthesis process of SCB-activated biochar using microwave pyrolysis.

of sulfuric acid (1:1 ratio) was used. Excessive addition of  $H_2SO_4$  during the microwave heating process can lead to the dehydration of excess water and undesired over-gasification of the biochar (Baharak Sajjadi et al., 2019).

Unlike previous studies on biochar-modified electrodes (Madhu et al., 2014; Wang et al., 2020b), this research utilized a larger amount of pre-treated biomass (75 g) for pyrolysis. Consequently, higher power and low microwave susceptor addition (M.S) were required to ensure the complete thermal decomposition of the lignocellulosic fibre compounds. Once chemically activated, the biomass was subjected to microwave pyrolysis at 1.5 kW for 1 hour and 10% M.S in an oxygen-free environment under negative pressure of 25 kPa. These operational conditions were established based on a previous study reported in (Allende et al., 2022), in which power range and M.S were optimised in a range of 1–3 kW and 10–20% M.S, respectively. Optimised biochar allowed the formation of microporosity volume and BET surface area.

The resulting carbon material was washed with 1 M hydrochloric acid (HCl) and thoroughly rinsed with distilled water. The selection of HCl is linked to the removal of impurities inside the biochar pores (Han et al., 2022; Wang et al., 2023). To remove moisture, the activated biochar was further heated at 110 °C in an oven for 24 hours. Fig. 1 illustrates the synthesis process of SCB-activated biochar and the components involved in microwave pyrolysis. The microwave-assisted pyrolysis system utilized in the biochar activation process comprised the following components: (i) a nitrogen flow (5 L/min) to maintain an oxygen-free environment, (ii) a chamber where the biomass was placed during the pyrolysis process, (iii) a tuner used to control the reflected power, (iv) a 3 kW microwave generator (Sairem brand), (v) a condenser system, and (vi) a vacuum pump.

### 2.2. Preparation of SCB-activated biochar/ GCE

To prepare the carbon nanocomposites, the SCB-activated biochar was ground into a fine powder with a mortar. The resulting material was then dispersed in ethanol and subjected to ultrasonication for 40 min. until reached fine and uniform particles. Before the coating, the surface of the GCE was carefully polished using 0.3  $\mu m$  and 0.5  $\mu m$  alumina slurry to ensure a smooth surface. The bare GCE was cleaned by sonicating it in ethanol and deionized water for 15 min. Subsequently, 2  $\mu L$  of a dispersible activated SCB-biochar solution with a concentration of 1.5 mg/mL was added dropwise onto the surface of the bare GCE. The modified working electrode was then dried at room temperature before conducting further testing.

### 2.3. Reagents and apparatus

The reagents used in the study included 98% sulphuric acid obtained from AJAX-Finechem (Univar) and 1 M hydrochloric acid from Sigma. Dibasic- $Na_2HPO_4$  and monobasic- $NaH_2PO_4$  were used in the

**Table 1**  
Ultimate analysis of raw feedstock and activated carbon material.

Element	N (wt %)	C (wt %)	H (wt %)	O (wt %)	H/C	O/C
Raw biomass	0.15	43.37	5.83	40.7	0.13	0.94
SCB-activated biochar	0.43	53.95	1.92	22.53	0.036	0.42

**Table 2**  
Porosity data of raw biomass with H<sub>2</sub>SO<sub>4</sub> before pyrolysis and SCB-activated biochar.

Analysis	Raw biomass+H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub> activated SCB-biochar
BET Surface Area (m <sup>2</sup> /g)	3.47	277.7
t-Plot Micropore Area (m <sup>2</sup> /g)		188.2
t-Plot micropore volume (cm <sup>3</sup> /g)	0.0013	0.075

preparation of the buffer solution (PBS, pH 7.0). The BET surface area, microporosity area and volume of the SCB-activated biochar were determined using a micromeritics 3-flex surface analyzer. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained using a JEOL 7001 F SEM and a JEOL 2100 TEM, respectively. Thermogravimetric analysis (TGA) was carried out using a Netzsch STA 449F3 Jupiter Simultaneous Thermal Analyzer. Raman spectroscopy measurements were performed using a Renishaw In-Via Micro-Raman spectrometer. Electrochemical experiments were conducted using a three-electrode system involving a platinum wire as the counter electrode, a glassy carbon electrode (GCE) as the working electrode and an Ag/AgCl reference electrode. The specifications of GCE involve an electrode of 3.0 mm diameter and a geometric area of 7.07 mm<sup>2</sup>. For the electrochemical analysis was employed PalmSens4 potentiostat (PalmSens, Netherlands).

### 3. Result and discussion

#### 3.1. Characterisation of H<sub>2</sub>SO<sub>4</sub> activated SCB-biochar

The CHNSO elemental composition of activated biochar is vital to understanding its electrochemical behaviour. Table 1 shows the elemental analysis of the sugarcane bagasse treated with sulphuric acid before the pyrolysis process and the activated SCB-biochar. After H<sub>2</sub>SO<sub>4</sub> impregnation and microwave pyrolysis, the carbon content of the activated biochar is increased by 24%, and the oxygen concentration is decreased by 45%. The chemical activation before microwave pyrolysis can reduce the carboxylic group and increase lactonic compounds (Baharak Sajjadi et al., 2019). The significance of the presence of functional groups lies in their electro-charge interaction with various molecules, especially on the surface of functionalized biochar, as observed in the case of paracetamol. On the other hand, the activation can produce high oxidation of H<sub>2</sub>SO<sub>4</sub>, generating a high C=O form and reducing the functional groups of oxygen-containing (Liu et al., 2020). SCB-activated biochar shows lower H/C and O/C ratios than nonactivated biochar. A low H/C ratio involves higher biochar carbonization, low cellulose and hemicellulose content compounds and a high aromatic structure (Hassan et al., 2020). Furthermore, a low O/C value comprises a decrease in the hydrophilic and polarity properties of the biochar, which is linked to the volatilization of polar functional groups (Godwin et al., 2019; Peiris et al., 2019). Sulphur is not detected in raw biomass or biochar.

Table 2 shows the BET analysis of SCB-activated biochar. The chemical activation by H<sub>2</sub>SO<sub>4</sub> impregnation and microwave pyrolysis led to an increased surface area of up to 278 m<sup>2</sup>/g and 0.075 cm<sup>3</sup>/g pore volume. The acid impregnation in the raw biomass increases the

formation of oxygen-containing functional groups on the modified biochar surface. The chemical activation generates sulphuric oxidation and carbon gasification, benefiting an increase in specific surface area and pore volume (Baharak Sajjadi et al., 2019; Spanu et al., 2020). The biomass nature and the pyrolysis parameters are crucial to developing biochar surface area properties, e.g., the morphology structure of lignocellulosic biomass (tubular) promotes microporosity formation. The greater surface area is related to the raw sugarcane bagasse's high lignin content and the prolonged pyrolysis time (Leng et al., 2021; M. Waqasa et al., 2018).

The SEM images of activated biochar reveal the disintegration of lignocellulosic fibres as shown in Fig. 2 (a1) and (a2). The thermochemical activation process resulted in the formation of crystalline rods measuring approximately 5–10 nm in width. Fig. 2 (b1) and (b2) depict layered semi-organized carbon clusters, with no observation of individual carbon sheets. This biochar structure can be favourable to improve the sensing signal between the molecule and the biochar surface due to the stability and electrocatalytic properties of the biochar. The impregnation of SCB with sulphuric acid promoted the formation of pores due to carbon gasification (Baharak Sajjadi et al., 2019; Monticelli, 2020). On the other hand, the application of high microwave power evidenced high biochar quality in terms of carbon elemental content, and uniform and larger pores formation. These properties are succeeded by the large volatiles released at a high heating rate throughout the biochar surface- rapid thermal breakdown of the lignocellulosic fibre compounds (Wallace et al., 2019; Zhang et al., 2022). Fig. 2 (c1), (c2) and (c3) show the EDS of activated biochar. The results indicate a relatively pure carbon structure with a minor concentration of O and Si.

Thermogravimetric analysis (TGA) of activated biochar is shown in Fig. 3(a). The curve reveals biomass weight loss started between 150 °C and 350 °C. Below 350 °C occurs moisture content reduction (thermal dehydration process), whose mass loss is attributable to the elimination of adsorbed water and the decomposition of some simple organic components. The second stage was observed between 350 °C and 450 °C, which involves the principal removal of volatile matter and fibre decomposition (cellulose and hemicellulose). The final mass loss was associated with the breakdown of lignin compound over 450 °C to 800 °C— char combustion (Chen et al., 2019; Díaz et al., 2021; Elkhailifa et al., 2022). Fig. 2(b) reveals the Raman spectroscopy curve of activated SCB-biochar. The D and G peaks were observed at ~1350 cm<sup>-1</sup> and ~1550 cm<sup>-1</sup>, respectively. The D band intensity is related to existing defects in the structure (Muzyka et al., 2018), and the G peak is associated with graphitization grade (Khan et al., 2017). A small 2D peak was detected at 2700 cm<sup>-1</sup>, exhibiting the existence of graphite and some layers of graphene (Merlen et al., 2017). 2D and D+D' are linked to sp<sup>2</sup> graphitic presence (Muhammad Hafiz et al., 2014). The 2D' band specifies two or more graphene layers in the material composition (Muzyka et al., 2018).

#### 3.2. Electrochemical characterisation

The interfacial performance of the modified GCE was evaluated by the electrochemical impedance spectra (EIS). Fig. 4 shows the electron transfer kinetic properties at the surface of the bare and modified GCE. EIS diagram consists of a semi-circular and linear part. The semicircle diameter denotes the charge-transfer resistance (R<sub>ct</sub>), which describes the conductivity property (resistance electron movement). The linear section at low frequency symbolizes the diffusion process (Foroughi, 2021; Randviir and Banks, 2013; Zamfir et al., 2020). A decreased charge transfer resistance (R<sub>ct</sub>) was observed in modified GCE (0.35 kΩ to 0.1 kΩ), representing lower mass transport resistance and improving the electron transfer kinetics. The results of the two studied electrodes are in accordance with the proposed equivalent circuit (inset figure), which denotes the electrolyte resistance (R<sub>s</sub>), charge transfer resistance property (E<sub>et</sub>), double layer capacitance (C<sub>dl</sub>) and Warburg impedance

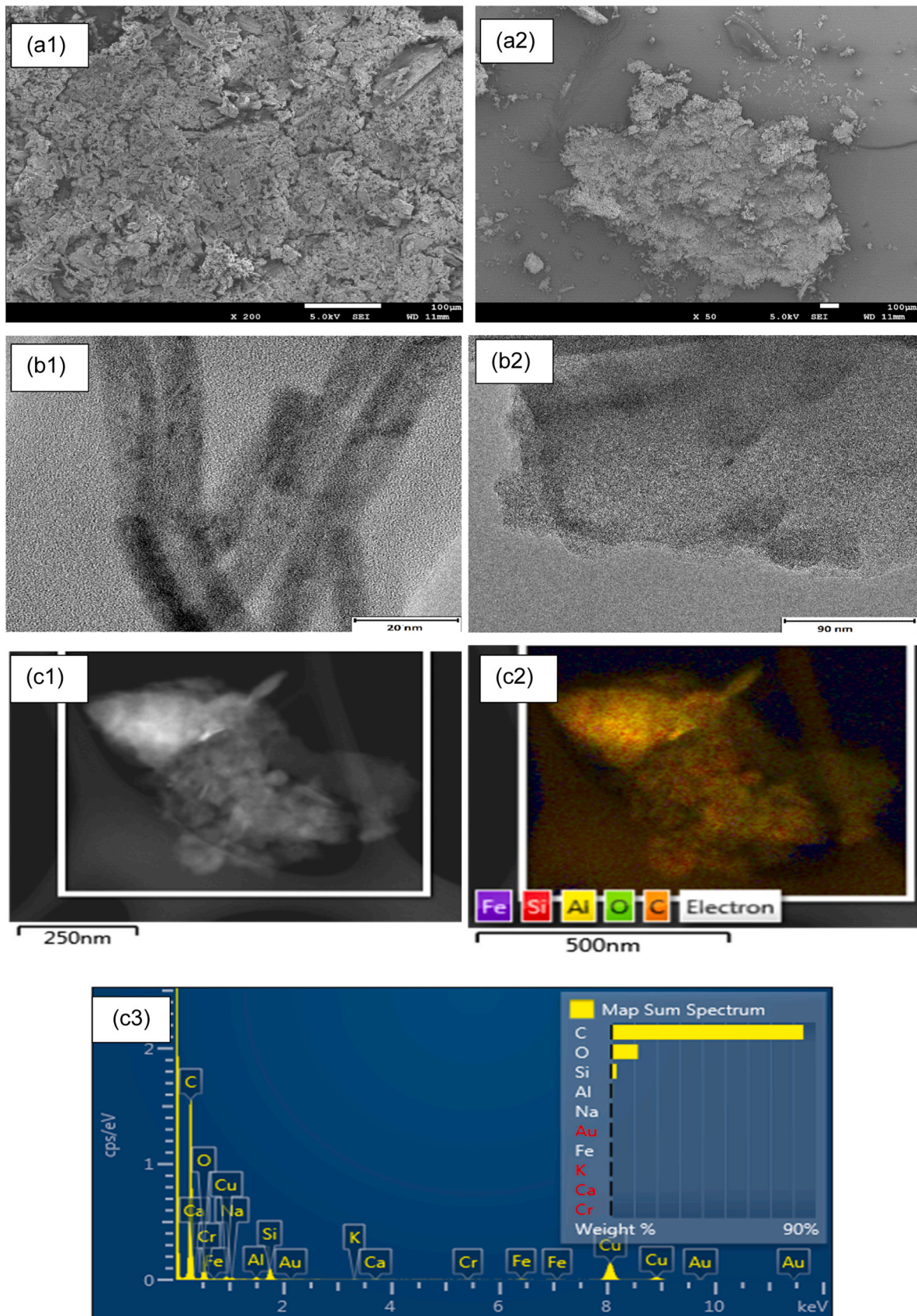


Fig. 2. Images of (a1) (a2) SEM, (b1) (b2) TEM, and (c1) (c2) (c3) TEM- EDS of SCB-activated biochar generated after the H<sub>2</sub>SO<sub>4</sub> activation and 1.5 kW microwave pyrolysis process for 1 hour.

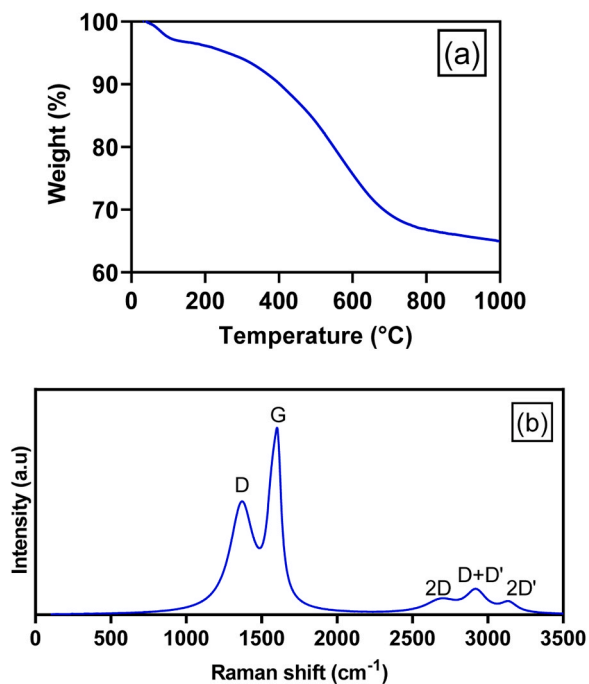


Fig. 3. (a) Thermogravimetric analysis and (b) Raman spectra curves of SCB-activated biochar.

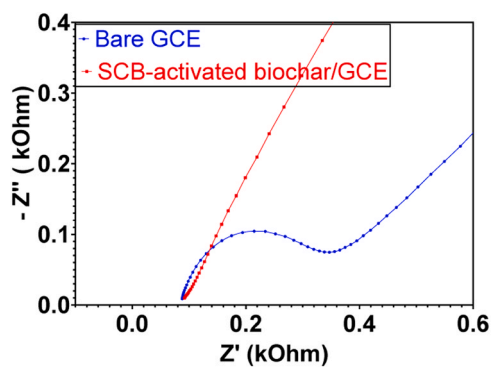


Fig. 4. Nyquist plot of the bare electrode and SCB-activated biochar/GCE in 0.1 M KCl containing 5 mM  $K_3[Fe(CN)_6]$  at 5 mV potential amplitude and 0.1 Hz to 100 kHz frequency range.

(Zw).

The Cyclic voltammetry (CV) curves of the bare and modified GCE in 0.1 M PBS with and without the presence of paracetamol are shown in Fig. 5. In a blank solution, oxidation responses were not observed for non-modified and modified electrodes. There is a considerable difference between the capacitance of bare GCE and SCB-activated biochar/GCE, whose property is related to a higher porosity of the SCB-activated biochar contrasted to the specific surface of the bare GCE. CV curve of the bare electrode showed a pair of oxidation peaks. The first peak could indicate acetaminophen oxidation to semiquinone radical formation. Then, the second peak could be assigned to the complete oxidation of a quinone (Chikere et al., 2019; Luk et al., 2021). The evidence of only one oxidation peak on modified GCE can be attributed to the large surface area of SCB-activated biochar provides a well-defined oxidation peak at

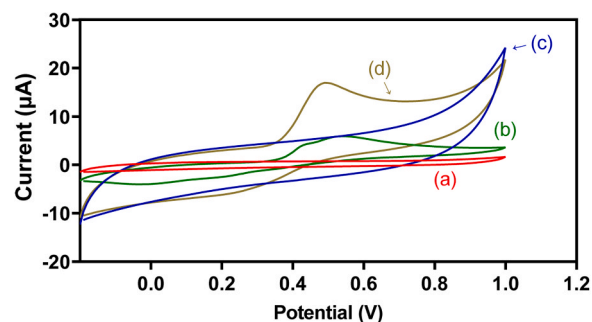


Fig. 5. Cyclic voltammetry (CV) curve of the bare electrode and modified GCE in the non-existence (a and c) and the existence of 0.5 mM concentration of paracetamol (b and d) in 0.1 M PBS at 0.05 V/s scan rate.

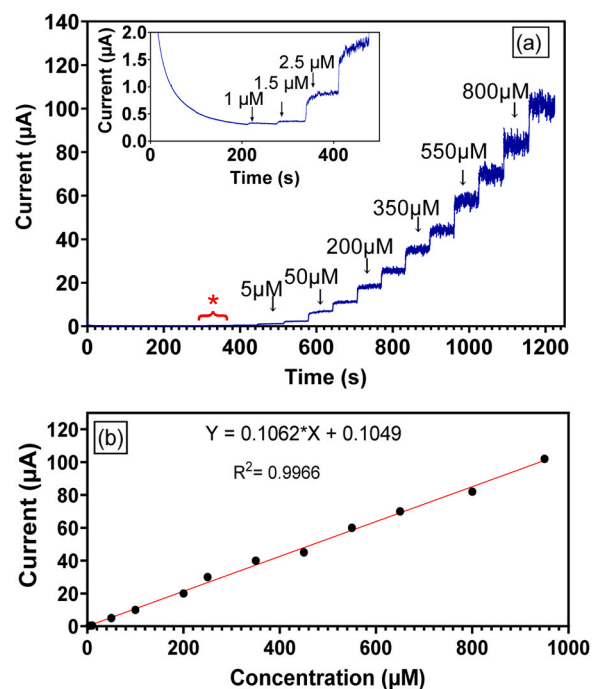


Fig. 6. (a) Chronoamperometry current response of modified GCE with activated SCB-biochar at different concentrations of paracetamol in stirring 0.1 M PBS; (b) linear calibration plot for paracetamol concentration vs. current response.

the lower potential in an irreversible reaction (El-Azazy et al., 2022; Fu et al., 2018; Shanbhag et al., 2022). In this analysis, only the predominant oxidation current peak is considered on bare GCE. Bare glassy carbon showed a current oxidation peak of  $\sim 6.2 \mu\text{A}$  for 0.5 mM paracetamol was recorded at 0.55 V. An increased oxidation peak in SCB-activated biochar/GCE ( $17 \mu\text{A}$ ) was detected at 0.49 V. The CVs response in modified GCE showed a beneficial effect on paracetamol oxidation, demonstrating that the existence of SCB-activated biochar improved the catalytic activity of the electrode.

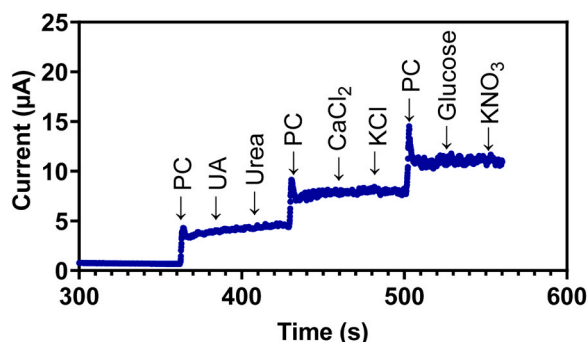
### 3.3. Electrochemical detection of paracetamol at $H_2SO_4$ activated SCB-biochar/ GCE

The chronoamperometry technique was used to analyse the sensitivity of activated SCB-activated biochar/GCE at different paracetamol concentrations. The current-time response investigated was set at the optimal of 0.8 V. This optimisation was investigated using DPV measurements at various potentials in a range of  $-0.5 \text{ V}$  to  $+1.5 \text{ V}$ , where the maximum oxidation peak current was achieved at an upper limit

**Table 3**

Analytical performance of various modified electrodes for paracetamol detection.

Electrode	Linear range concentration ( $\mu\text{M}$ )	LOD ( $\mu\text{M}$ )	Reference
NiCu-CAT/GCE	5–190	5	(Wang et al., 2020a)
DMBQ-MCNTPE	5–500	1	(Karimi-Maleh et al., 2014)
GCE-M221-Fe <sub>3</sub> O <sub>4</sub>	50–2000	16	(Mulyasuryani et al., 2019)
AGCE	0.1–100	0.72	(Câmpean et al., 2011)
GO/GCE	0.1–430	0.021	(Alagarsamy, 2018)
AuNCs/BC	0.003–50	1	(Yu et al., 2022)
SCB-activated biochar/GCE	5–950	2.5	This work



**Fig. 7.** Interference studies of activated SCB-activated biochar/GCE for paracetamol detection in the presence of various interfering components in 0.1 M PBS at 0.8 V potential.

potential of 0.8 V (decreased current peak observed below this limit). Hence, the potential value of 0.8 V was selected for paracetamol detection. Consecutive addition of paracetamol in 0.1 M PBS was evaluated in the experimental part. Fig. 6 indicates a correlation curve between the paracetamol concentration and its current response. The linear regression is given by the equation  $I(\mu\text{A}) = 0.1062(\mu\text{M}) + 0.1049$ ,  $R^2 = 0.9966$  for the range of concentration from 5  $\mu\text{M}$  to 950  $\mu\text{M}$ . Table 3 shows the performance comparison of SCB-activated biochar/GCE with other published electrodes for paracetamol detection. This work achieved a limit of detection (LOD) of 2.5  $\mu\text{M}$  ( $S/N = 3$ ). The LOD was tested as the lowest paracetamol concentration that the modified electrode can consistently detect, which

was calculated by  $\text{LOD} = 3(\text{SD}/b)$ . This ratio comprises the standard deviation of the intercept of the blank solution (SD) and the average slope of the regression line (b).

The analytical performance of SCB-activated biochar/GCE was competitive compared to sensors found in the literature due to low LOD value and wide linear range, which indicates that the modified electrode has promising electrochemical characteristics to be applied in real samples.

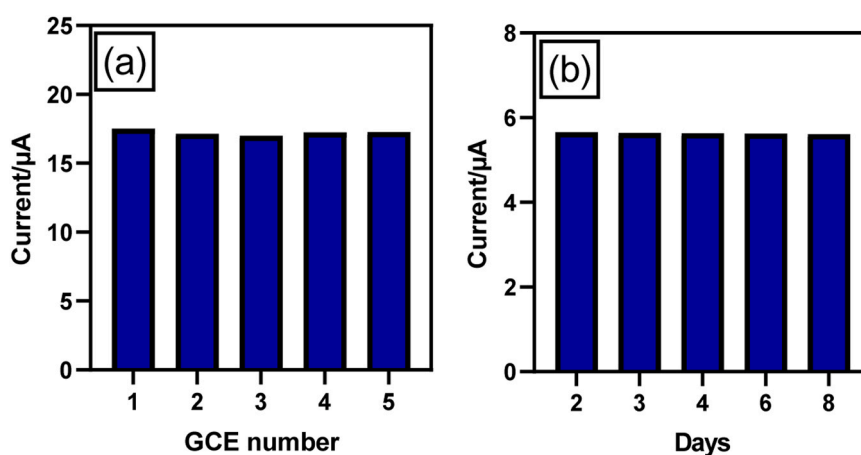
#### 3.4. Selectivity, stability, and reproducibility of the modified electrode

Selectivity of modified GCE for paracetamol detection was studied by the chronoamperometric response in the coexistence of common interference species, e.g., uric acid (UA), urea, calcium chloride (CaCl<sub>2</sub>), potassium chloride (KCl), glucose and potassium nitrate (KNO<sub>3</sub>). Fig. 7 shows the current-time response for the 0.5 mM paracetamol injections and various interfering molecules. The results demonstrated that adding 0.5 mM of interfering substances had not affected the current peak oxidation of paracetamol. Hence, SCB-activated biochar/GCE has favourable anti-interference properties and selectively detects paracetamol.

The reproducibility and stability properties of the modified electrode were assessed by the differential pulse voltammetry (DPV) method at 6 mV step potential— shown in Fig. 8. The DPV technique provides clarity and accuracy to detect oxidation peaks using minimal paracetamol concentrations. The reproducibility was evaluated by the successive detections of five modified GCE in response to 0.5 mM paracetamol concentration. The relative standard deviation (RSD) from the oxidation current response of five modified GCE was 2.5%, confirming an acceptable reproducibility and consistent current performance for the five modified electrodes. The stability was studied considering the oxidation current of one modified GCE after 2, 3, 4, 6 and 8 days of its fabrication and storage at room temperature. The RSD obtained in the stability test was 2.32%. Electrochemical results of SCB-activated biochar showed a stable current response through the storage time.

## 4. Conclusion

The large generation of agricultural waste and the lack of carbon sources make sugarcane bagasse biomass an excellent candidate for resource recovery, particularly from biochar. The synthesis of the SCB-activated biochar using chemical pre-treatment and microwave pyrolysis developed clustered semi-organised carbon layers with improved surface area up to 278 m<sup>2</sup>/g and increased carbon concentration by 24%. The electrochemical analysis of the modified GCE showed high electron transfer, electric conductivity, and potential redox behaviour.



**Fig. 8.** (a) reproducibility analysis of five SCB-activated biochar/GCE (b) and representation of modified GCE stability in the presence of 0.5 mM paracetamol contained in 0.1 M PBS (pH-7).

Fabrication of biosensors using biochar has received significant attention due to its practical electrode synthesis method, eco-friendly advantages, and potential electrochemical activity. Current detection methods represent extended procedure time, complex equipment, and expensive technologies. The biochar modified to possess electrocatalytic properties is well-suited for detecting paracetamol and proves to be ideal for identifying traces of pharmaceutical materials in wastewater. The use of the modified glassy carbon electrode (GCE) for paracetamol detection has shown commendable sensitivity, with a limit of detection (LOD) of 2.5  $\mu\text{M}$ . This underscores the promise of SCB-activated biochar/GCE for practical applications. Thus, developing carbon material from agricultural waste using microwave-assisted pyrolysis allowed electrochemical feasibility and an environmentally friendly alternative for paracetamol sensing in media such as wastewater.

### CRedit authorship contribution statement

**Scarlett Allende:** Writing – original draft, Visualization, Validation, Investigation, Formal analysis. **Yang Liu:** Writing – review & editing, Validation. **Mohan V. Jacob:** Writing – review & editing, Supervision, Conceptualization.

### 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.

### Data availability

Data will be made available on request.

### Acknowledgement

The authors greatly appreciate the support from Wilmar Sugar Australia for supplying the sugarcane bagasse. This project was funded by the James Cook University Postgraduate Research Scholarship and Cooperative Research Centre for Developing Northern Australia (Government's Cooperative Research Centre Program, CRCP).

### References

- Alagarsamy, P., 2018. Amperometric Determination of Acetaminophen (paracetamol) Using Graphene Oxide Modified Glassy Carbon Electrode. *Int. J. Electrochem. Sci.* 13, 7930–7938.
- Alfhaid, L.H.K., 2022. Adsorption of paracetamol in contaminated water through pH-responsive polymer-brush-grafted mesoporous silica nanoparticles. *Int. J. Environ. Anal. Chem.* 1–17.
- Allende, S., Brodie, G., Jacob, M.V., 2022. Energy recovery from sugarcane bagasse under varying microwave-assisted pyrolysis conditions. *Bioresour. Technol. Rep.* 20, 101283.
- Allende, S., Brodie, G., Jacob, M.V., 2023a. Breakdown of biomass for energy applications using microwave pyrolysis: A technological review. *Environ. Res.* 226, 115619.
- Allende, S., Liu, Y., Zafar, M.A., Jacob, M.V., 2023b. Nitrite sensor using activated biochar synthesised by microwave-assisted pyrolysis. *Waste Dispos. Sustain. Energy.*
- Baharak Sajjadi, T.Z., Danuta Leszczynska, Jerzy Leszczynski, Wei Yin Chen, 2019. Chemical activation of biochar for energy and environmental applications: a comprehensive review. *Rev. Chem. Eng.* 35, 777–815.
- Belyakov, N., 2019. Chapter Nineteen - Bioenergy, in: Belyakov, N. (Ed.). *Sustainable Power Generation*. Academic Press, pp. 461–474.
- Benyekkou, N., Ghezzar, M.R., Abdelmalek, F., Addou, A., 2020. Elimination of paracetamol from water by a spent coffee grounds biomaterial. *Environ. Nanotechnol., Monit. Manag.* 14, 100396.
- Bhujel, R., Rai, S., Baruah, K., Deka, U., Biswas, J., Swain, B.P., 2019. Capacitive and Sensing Responses of Biomass Derived Silver Decorated Graphene. *Sci. Rep.* 9, 19725.
- Boumya, W., Taoufik, N., Achak, M., Barka, N., 2021. Chemically modified carbon-based electrodes for the determination of paracetamol in drugs and biological samples. *J. Pharm. Anal.* 11, 138–154.
- Câmpean, A., Tertiş, M., Sândulescu, R., 2011. Voltammetric determination of some alkaloids and other compounds in pharmaceuticals and urine using an electrochemically activated glassy carbon electrode. *Open Chem.* 9, 688–700.
- Chen, R., Zhao, X., Jiao, J., Li, Y., Wei, M., 2019. Surface-Modified Biochar with Polydentate Binding Sites for the Removal of Cadmium. *Int. J. Mol. Sci.* 20, 1775.
- Cheng, B.H., Zeng, R.J., Jiang, H., 2017. Recent developments of post-modification of biochar for electrochemical energy storage. *Bioresour. Technol.* 246, 224–233.
- Chikere, C.O., Faisal, N.H., Kong Thoo Lin, P., Fernandez, C., 2019. The synergistic effect between graphene oxide nanocolloids and silicon dioxide nanoparticles for gallic acid sensing. *J. Solid State Electrochem.* 23, 1795–1809.
- Díaz, M.J., Ruiz-Montoya, M., Palma, A., de-Paz, M.-V., 2021. Thermogravimetry Applicability in Compost and Composting Research: A Review. *Appl. Sci.* 11, 1692.
- Duque-Acevedo, M., Belmonte-Ureña, L.J., Cortés-García, F.J., Camacho-Ferre, F., 2020. Agricultural waste: Review of the evolution, approaches and perspectives on alternative uses. *Glob. Ecol. Conserv.* 22, e00902.
- El-Azazy, M., Ahsan, I., Bensalah, N., 2022. Electrochemical Analysis of Sulfoxazole Using Glassy Carbon Electrode (GCE) and MWCNTs/Rare Earth Oxide (CeO<sub>2</sub> and Yb<sub>2</sub>O<sub>3</sub>) Modified-GCE Sensors. *Molecules* 27.
- El-Nemr, M.A., Yilmaz, M., Ragab, S., El Nemr, A., 2022. Biochar-SO prepared from pea peels by dehydration with sulfuric acid improves the adsorption of Cr<sup>6+</sup> from water. *Biomass-. Convers. Biorefinery.*
- Elkhalifa, S., Parthasarathy, P., Mackey, H.R., Al-Ansari, T., Elhassan, O., Mansour, S., McKay, G., 2022. Biochar development from thermal TGA studies of individual food waste vegetables and their blended systems. *Biomass-. Convers. Biorefinery.*
- Escapa, C., Coimbra, R.N., Paniagua, S., García, A.I., Otero, M., 2017. Paracetamol and salicylic acid removal from contaminated water by microalgae. *J. Environ. Manag.* 203, 799–806.
- Ethaib, S., Omar, R., Kamal, S.M.M., Biak, D.R.A., Zubaidi, S.L., 2020. Microwave-Assisted Pyrolysis of Biomass Waste: A Mini Review. *Processes* 8, 1190.
- Foroughi, S.H.D.S.J.D.M.M., 2021. Simultaneous voltammetric determination of tramadol and paracetamol exploiting glassy carbon electrode modified with FeNi<sub>3</sub> nanoalloy in biological and pharmaceutical media. *Anal. Chem.* 6, 8797–8808.
- Fu, L., Xie, K., Zheng, Y., Zhang, L., Su, W., 2018. Graphene Ink Film Based Electrochemical Detector for Paracetamol Analysis. *Electronics* 7, 15.
- Godwin, P.M., Pan, Y., Xiao, H., Afzal, M.T., 2019. Progress in Preparation and Application of Modified Biochar for Improving Heavy Metal Ion Removal From Wastewater. *J. Bioresour. Bioprod.* 4, 31–42.
- Hadiya, V., Popat, K., Vyas, S., Varjani, S., Vithanage, M., Kumar Gupta, V., Núñez Delgado, A., Zhou, Y., Loke Show, P., Bilal, M., Zhang, Z., Sillanpää, M., Sabyasachi Mohanty, S., Patel, Z., 2022. Biochar production with amelioration of microwave-assisted pyrolysis: Current scenario, drawbacks and perspectives. *Bioresour. Technol.* 355, 127303.
- Hamawand, I., da Silva, W., Seneweera, S., Bundschuh, J., 2021. Value Proposition of Different Methods for Utilisation of Sugarcane Wastes. *Energies* 14, 5483.
- Han, Y., Zheng, J., Jiang, C., Zhang, F., Wei, L., Zhu, L., 2022. Hydrochloric acid-modified algal biochar for the removal of *Microcystis aeruginosa*: Coagulation performance and mechanism. *J. Environ. Chem. Eng.* 10, 108903.
- Hassan, M., Liu, Y., Naidu, R., Parikh, S.J., Du, J., Qi, F., Willett, I.R., 2020. Influences of feedstock sources and pyrolysis temperature on the properties of biochar and functionality as adsorbents: A meta-analysis. *Sci. Total Environ.* 744, 140714.
- Karimi-Maleh, H., Moazampour, M., Ahmar, H., Beitollahi, H., Ensafi, A.A., 2014. A sensitive nanocomposite-based electrochemical sensor for voltammetric simultaneous determination of isoproterenol, acetaminophen and tryptophan. *Measurement* 51, 91–99.
- Khan, A., Savi, P., Quaranta, S., Rovere, M., Giorcelli, M., Tagliaferro, A., Rosso, C., Jia, C.Q., 2017. Low-Cost Carbon Fillers to Improve Mechanical Properties and Conductivity of Epoxy Composites. *Polymers* 9, 642.
- Khatri, P., Pandit, A.B., 2022. Systematic review of life cycle assessments applied to sugarcane bagasse utilization alternatives. *Biomass-. Bioenergy* 158, 106365.
- Leng, L., Xiong, Q., Yang, L., Li, H., Zhou, Y., Zhang, W., Jiang, S., Li, H., Huang, H., 2021. An overview on engineering the surface area and porosity of biochar. *Sci. Total Environ.* 763, 144204.
- Li, J., Li, L., Suvarna, M., Pan, L., Tabatabaei, M., Ok, Y.S., Wang, X., 2022a. Wet wastes to bioenergy and biochar: A critical review with future perspectives. *Sci. Total Environ.* 817, 152921.
- Li, Y., Xu, R., Wang, H., Xu, W., Tian, L., Huang, J., Liang, C., Zhang, Y., 2022b. Recent Advances of Biochar-Based Electrochemical Sensors and Biosensors. *Biosens. (Basel)* 12.
- Liu, C., Wang, W., Wu, R., Liu, Y., Lin, X., Kan, H., Zheng, Y., 2020. Preparation of Acid- and Alkali-Modified Biochar for Removal of Methylene Blue Pigment. *ACS Omega* 5, 30906–30922.
- Luk, H.-N., Chou, T.-Y., Huang, B.-H., Lin, Y.-S., Li, H., Wu, R.-J., 2021. Promotion Effect of Palladium on BiVO<sub>4</sub> Sensing Material for Epinephrine Detection. *Catalysts* 11, 1083.
- Luo, S., Yang, M., Wu, Y., Li, J., Qin, J., Feng, F., 2022. A Low Cost Fe(3)O(4)-Activated Biochar Electrode Sensor by Resource Utilization of Excess Sludge for Detecting Tetrabromobisphenol A. *Micro (Basel)* 13, 115.
- Waqasa, M., Aburiazzaiza, A.S., Minadad, R., Rehan, M., Barakat, M.A., Nizami, A.S., 2018. Development of biochar as fuel and catalyst in energy recovery technologies. *J. Clean. Prod.* 188, 477–488.
- Madhu, R., Sankar, K.V., Chen, S.-M., Selvan, R.K., 2014. Eco-friendly synthesis of activated carbon from dead mango leaves for the ultrahigh sensitive detection of toxic heavy metal ions and energy storage applications. *RSC Adv.* 4, 1225–1233.
- Martínez-Sánchez, C., Montiel-González, F., Rodríguez-González, V., 2019. Electrochemical sensing of acetaminophen using a practical carbon paste electrode modified with a graphene oxide-Y<sub>2</sub>O<sub>3</sub> nanocomposite. *J. Taiwan Inst. Chem. Eng.* 96, 382–389.

- Merlen, A., Buijnsters, J.G., Pardanaud, C., 2017. A Guide to and Review of the Use of Multiwavelength Raman Spectroscopy for Characterizing Defective Aromatic Carbon Solids: from Graphene to Amorphous Carbons. *Coatings* 7, 153.
- Millati, R., Cahyono, R.B., Ariyanto, T., Azzahrani, I.N., Putri, R.U., Taherzadeh, M.J., 2019. Chapter 1 - Agricultural, Industrial, Municipal, and Forest Wastes: An Overview. In: Taherzadeh, M.J., Bolton, K., Wong, J., Pandey, A. (Eds.), *Sustainable Resource Recovery and Zero Waste Approaches*. Elsevier, pp. 1–22.
- Monticelli, D.S.G.B.C.D.D., 2020. Biochar as an alternative sustainable platform for sensing applications: A review. *Microchem. J.* 159.
- Muhammad Hafiz, S., Ritikos, R., Whitcher, T.J., Md. Razib, N., Bien, D.C.S., Chanlek, N., Nakajima, H., Saisopa, T., Songsiririthigul, P., Huang, N.M., Rahman, S.A., 2014. A practical carbon dioxide gas sensor using room-temperature hydrogen plasma reduced graphene oxide. *Sens. Actuators B: Chem.* 193, 692–700.
- Mulyasuryani, A., Tjahjanto, R.T., Andawiyah, Ra, 2019. Simultaneous Voltammetric Detection of Acetaminophen and Caffeine Base on Cassava Starch—Fe<sub>3</sub>O<sub>4</sub> Nanoparticles Modified Glassy Carbon Electrode. *Chemosensors* 7, 49.
- Muzyka, R., Drewniak, S., Pustelny, T., Chrubasik, M., Gryglewicz, G., 2018. Characterization of Graphite Oxide and Reduced Graphene Oxide Obtained from Different Graphite Precursors and Oxidized by Different Methods Using Raman Spectroscopy. *Materials* 11, 1050.
- Peiris, C., Nayanathara, O., Navarathna, C.M., Jayawardhana, Y., Nawalage, S., Burk, G., Karunanayake, A.G., Madduri, S.B., Vithanage, M., Kaumal, M.N., Mlsna, T.E., Hassan, E.B., Abeyundara, S., Ferez, F., Gunatilake, S.R., 2019. The influence of three acid modifications on the physicochemical characteristics of tea-waste biochar pyrolyzed at different temperatures: a comparative study. *RSC Adv.* 9, 17612–17622.
- Randviir, E.P., Banks, C.E., 2013. Electrochemical impedance spectroscopy: an overview of bioanalytical applications. *Anal. Methods* 5, 1098–1115.
- Sadh, P.K., Duhan, S., Duhan, J.S., 2018. Agro-industrial wastes and their utilization using solid state fermentation: a review. *Bioresour. Bioprocess.* 5 (1).
- Shanbhag, Y.M., Shanbhag, M.M., Malode, S.J., Dhanalakshmi, S., Mondal, K., Shetti, N. P., 2022. Direct and Sensitive Electrochemical Evaluation of Pramipexole Using Graphitic Carbon Nitride (gCN) Sensor. *Biosensors* 12, 552.
- Spanu, D., Binda, G., Dossi, C., Monticelli, D., 2020. Biochar as an alternative sustainable platform for sensing applications: A review. *Microchem. J.* 159.
- Sudha, V., Senthil Kumar, S.M., Thangamuthu, R., 2019. Hierarchical porous carbon derived from waste amla for the simultaneous electrochemical sensing of multiple biomolecules. *Colloids Surf. B Biointerfaces* 177, 529–540.
- Tang, Y.-H., Liu, S.-H., Tsang, D.C.W., 2020. Microwave-assisted production of CO<sub>2</sub>-activated biochar from sugarcane bagasse for electrochemical desalination. *J. Hazard. Mater.* 383, 121192.
- Villota, N., Lombrana, J.I., Cruz-Alcalde, A., Marcé, M., Esplugas, S., 2019. Kinetic study of colored species formation during paracetamol removal from water in a semicontinuous ozonation contactor. *Sci. Total Environ.* 649, 1434–1442.
- Wallace, C.A., Afzal, M.T., Saha, G.C., 2019. Effect of feedstock and microwave pyrolysis temperature on physio-chemical and nano-scale mechanical properties of biochar. *Bioresour. Bioprocess.* 6, 33.
- Wang, J., Liu, S., Luo, J., Hou, S., Song, H., Niu, Y., Zhang, C., 2020a. Conductive Metal-Organic Frameworks for Amperometric Sensing of Paracetamol. *Front. Chem.* 8.
- Wang, J., Yang, J., Xu, P., Liu, H., Zhang, L., Zhang, S., Tian, L., 2020b. Gold nanoparticles decorated biochar modified electrode for the high-performance simultaneous determination of hydroquinone and catechol. *Sens. Actuators B: Chem.* 306, 127590.
- Wang, Q., Yue, Y., Liu, W., Liu, Q., Song, Y., Ge, C., Ma, H., 2023. Removal Performance of KOH-Modified Biochar from Tropical Biomass on Tetracycline and Cr(VI). *Mater. (Basel)* 16.
- Yu, Q., Zou, J., Xiong, Q., Peng, G., Gao, F., Fan, G., Chen, S., Lu, L., 2022. Electrochemical Sensor Based on Biochar Decorated with Gold Clusters for Sensitive Determination of Acetaminophen. *Int. J. Electrochem. Sci.* 17, 220438.
- Zafar, M.A., Liu, Y., Allende, S., Jacob, M.V., 2022. Electrochemical sensing of oxalic acid using silver nanoparticles loaded nitrogen-doped graphene oxide. *Carbon Trends* 8, 100188.
- Zamfir, L.G., Puiu, M., Bala, C., 2020. Advances in Electrochemical Impedance Spectroscopy Detection of Endocrine Disruptors. *Sens. (Basel)* 20, 6443.
- Zhang, Y., Fan, S., Liu, T., Fu, W., Li, B., 2022. A review of biochar prepared by microwave-assisted pyrolysis of organic wastes. *Sustain. Energy Technol. Assess.* 50, 101873.
- Zhao, L., Sun, Z.-F., Zhang, C.-C., Nan, J., Ren, N.-Q., Lee, D.-J., Chen, C., 2022. Advances in pretreatment of lignocellulosic biomass for bioenergy production: Challenges and perspectives. *Bioresour. Technol.* 343, 126123.
- Zhou, Z., Yao, D., Li, S., Xu, F., Liu, Y., Liu, R., Chen, Z., 2021. Sustainable production of value-added sulfonated biochar by sulfuric acid carbonization reduction of rice husks. *Environ. Technol. Innov.* 24, 102025.