

Sustainable Hydrogen Peroxide Synthesis Using Bismuth-Modified Biochar

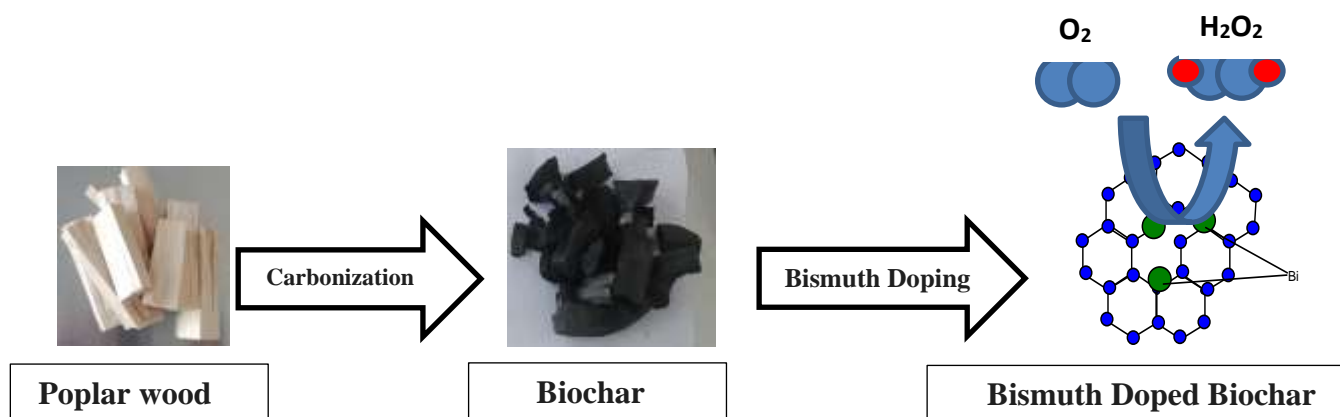
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Graphical Abstract:



Abstract:

In this work a novel biochar based renewable electrode material has been developed for the sustainable electrochemical synthesis of hydrogen peroxide via oxygen reduction. Biochar was derived from waste, Himalayan poplar wood (*Populus ciliata*) through pyrolysis at (600-1000°C). The obtained biochar was characterized by using techniques, like scanning electron microscopy (SEM) to investigate morphology, X-ray diffraction (XRD) to analyze crystal structure and degree of graphitization and Raman spectroscopy to probe internal structure. The results affirmed that the biochar obtained from poplar wood was highly porous and containing both ordered and disordered carbon framework. This biochar was further ball milled with bismuth carbonate and annealed at 600°C to get bismuth doped biochar. The XRD spectra revealed the successful incorporation of bismuth in the carbon framework of biochar. The results of electrochemical impedance spectroscopy (EIS) showed that the bismuth doped biochar has less equivalent series resistance compared to pristine biochar. Incorporating bismuth into biochar resulted in a current density of 1.1 mA/cm², exceeding the 0.5 mA/cm² achieved by undoped biochar. Moreover, the bismuth-doped biochar exhibited greater selectivity of 71.25% compared to 49.6% for the pristine biochar. These findings hold good promise for bio waste utilization to develop ecofriendly electrode material for onsite, on demand synthesis of hydrogen peroxide.

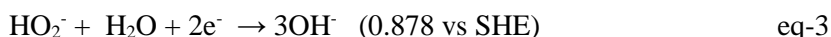
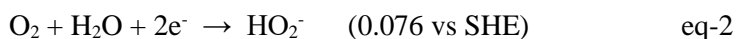
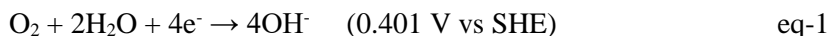
Keywords: Biochar, Pyrolysis, Doping, Hydrogen Peroxide, Sustainable, Renewable.

1. Introduction

Hydrogen peroxide is enlisted among the 100 most important chemicals due to its diverse applications and green nature. The global annual production of hydrogen peroxide is about 4 million metric tons with an anticipation to be more than 6 million tons in 2026 (Qu, Wu, & Ng, 2023). Its major uses are as oxidant, bleaching agent, disinfectant and for the manufacture of other oxy chemicals (S. Chen et al., 2018);(Martins, Plazl, Strmcnik, & Genorio, 2023). Recently its potential as an energy storing chemical is under study. Though its energy density is $1/10^{\text{th}}$ of that of gasoline, it has zero carbon dioxide emission, making it a promising alternative to conventional fuels (Tang et al., 2021). At present, most of hydrogen peroxide is manufactured through auto oxidation of anthraquinone with considerable negative impact on environment due to the release of large amount of organic solvents, metal catalysts and waste water (Perry et al., 2019). To overcome the limitations of anthraquinone process there is a need for the development of alternate methods for the synthesis of this valuable reagent.

Direct synthesis of hydrogen peroxide by reacting oxygen and hydrogen in the presence of suitable catalyst looks simple in theory, but has limitations of selectivity and danger of combining hydrogen and oxygen (Y. Wang, Zhong, Yang, Feng, & Alonso-Vante, 2023). Recent studies have shown that electrochemical synthesis of hydrogen peroxide by the partial reduction of oxygen could be a potential alternate of anthraquinone process due to its sustainability and use of renewable energy sources like solar and wind energy (Sun et al., 2018);(Perry et al., 2019).

Electrochemical oxygen reduction reaction (ORR) is a major reaction in fuel cells, metal-air batteries and water splitting. In electrochemical ORR, oxygen is reduced at the electrode surface. The mechanism of ORR is complex and involves a number of intermediate steps which depends on the specific conditions and catalysts used. Based on the number of electron transferred the ORR took place either by direct four electron pathway (acidic medium) or by two electron pathway (basic medium). The two electron pathway involve the formation of peroxide species in first step which is further reduced to hydroxyl ion (Ma et al., 2019).



For energy conversion applications, four-electron ORR is more desirable reaction mechanism due to high energy output but certain amount of dissolved oxygen is converted into hydrogen peroxide via two electron reduction process. This undesired formation of hydrogen peroxide during oxygen reduction reaction in fuel cell has enticed to investigate the potential of this reaction for the sustainable, onsite, on demand synthesis. However the slow kinetics of reaction (activity) and the formation of other products (selectivity) are the major challenges for the electrochemical synthesis of hydrogen peroxide through oxygen reduction approach (Xia et al., 2021).

To overcome these limitations, investigations are going on to develop novel electro catalytic materials with high activity and selectivity. The electro catalytic materials can be broadly classified into three categories: First the Platinum group metals, second, transition metals based and third, carbon based electro catalytic materials. Platinum group catalysts have high activity but their rare availability restrict their scope for large scale economic applications.

There are a number of reports that carbon based electro catalytic materials have certain advantages over metal based catalysts due to their green nature, low cost, high selectivity, and surface tailoring ability (Li et al., 2020). Different carbon materials like carbon nanotubes, graphene, doped graphene, carbon black, and biomass based carbon materials (biochar) has been investigated for the electrochemical synthesis of hydrogen peroxide (Sa, Kim, & Joo, 2019);(Han et al., 2019; Z. Wang et al., 2021). In present work a novel biochar based electrode material is prepared and its potential for the electrochemical production of hydrogen peroxide has been investigated.

Biochar is an easily available renewable carbonaceous material derived by the controlled pyrolysis of biomass. It has multiple applications due to its unique properties like, high porosity, tune-able electrical conductivity, surface functionality, thermal stability, and high absorption (capability). Beside this, production (of biochar) is cost effective and contributes towards carbon sequestration as it fixes more than 50% of carbon liable for emission as (CO_2). Biochar has been extensively investigated for its agricultural and environmental applications, however in recent past it is under study for its electric and electro catalytic applications like water splitting, oxygen reduction, fuel cell and as a super capacitor material (Gao, Wang, Zheng, Zhao, & Yu, 2020). The properties of biochar are mainly dependent on its feedstock, temperature of pyrolysis, rate and duration of pyrolysis and heteroatom doping. Wood based biochar, compared to other sources, has distinguished properties like high carbon content, surface area, porosity and electrical conductivity which making it a potential material for electrical and electrochemical applications.

Structurally biochar is a multiphase complex carbon material and contains both amorphous as well as graphitic forms of carbon. The presence of these ordered and disordered carbon structures enhance the development of surface defects at grain boundaries. The common defect sites are surface edge sites and atomic vacancies. These defect sites provide a unique environment and act as active sites for 2 electrons oxygen reduction. In addition porous structure of biochar results in large surface area which facilitating adsorption and desorption of dissolved oxygen (S. Chen et al., 2018). This results in faster reaction kinetics and improved overall efficiency of the reaction.

Previous research suggests that doping biochar with heteroatoms can improve its electro catalytic properties through a synergistic effect. These incorporated heteroatoms create more defect sites, improve charge flow, and act as binding sites for substrates (Li et al., 2020). Building on this concept, biochar was doped with bismuth using annealing method. To best of our knowledge there is no report of bismuth doped biochar for electrochemical synthesis of hydrogen peroxide.

2. Experimental

2.1. Chemicals and Instrumentation

Analytical-grade bismuth carbonate was used as the primary precursor for catalyst synthesis. Nafion-117 solution (5% w/w) was procured from Sigma Aldrich and utilized as a binder in electrode preparation. Morphological characterization was performed using a Cube II model scanning electron microscope (Emcraft). Structural analysis was carried out with an X-ray diffraction analyzer (Powder D-8 Advance, Bruker). Raman spectroscopy measurements were conducted using the MNSTEX PRI-100 spectrometer. Electrochemical analyses, including cyclic voltammetry and impedance spectroscopy, were performed using a Gamry Reference 3000 workstation. For rotating ring-disk electrode (RRDE) studies, a CHI700E Series bipotentiostat coupled with a RRDE-3A setup was employed. Elemental composition of the samples was determined using a EuroEA elemental analyzer.

2.2. Preparation and doping of Biochar

Poplar wood was collected from a local woodwork shop. The wood was chipped (5cm in length and 1cm thickness). Before carbonization the wood sticks were washed and dried at 80°C till constant weight was achieved. Dry wood chips were carbonized at 1000°C . in a tube furnace under nitrogen environment at a heating rate of 5°C per minute. The obtained biochar was named as pristine biochar (P-BC). This P-BC was ball milled with bismuth carbonate in 2:1 respectively for two hours. The obtained homogeneous powder was annealed at 600°C for two hours. The obtained doped biochar was named as Bismuth doped biochar (Bi-BC).

2.3. Physical Characterization

The morphology and structural features of P-BC were investigated by using Scanning Electron Microscopy (SEM). Identification of crystal structure and degree of graphitization was found by using X-ray Diffraction

Analysis. Raman spectroscopy was carried to find out the internal structure of biochar. The elemental analysis (C,H,O,N) of P-BC were also carried out by elemental analyzer.

2.4. Electrochemical Characterization

Electrochemical impedance spectroscopy (EIS) was employed to probe the interfacial properties and charge transfer kinetics of the P-BC and Bi-BC. Cyclic voltammetry(CV) was carried out to assess the electro catalytic activity of materials towards the Oxygen Reduction Reaction (ORR). Linear sweep voltammetry (LSV) was carried out using rotating ring disc electrode(RRDE) to find the selectivity towards hydrogen peroxide and the number of electron transferred.

To perform these measurements “catalytic ink” was first prepared from the biochar samples. For this purpose 3.3mg of the synthesized biochar was mixed with 1ml of isopropyl alcohol. Then 10 μ L of Nifion-117 solution was added to it. The mixture was sonicated for 20min to get homogeneous ink-like suspension. A small volume (0.6 μ L) of the prepared catalyst ink was carefully pipetted out onto a glassy carbon disk electrode and dried in an oven (S. Wang et al., 2022).

Cyclic voltammetry (CV) of the dried spot of ink was carried out to evaluate the oxygen reduction ability of the prepared electro catalytic samples. The potential window used for CV measurements was from 0.4V to -0.8V with respect to reference Ag/AgCl electrode. The CV measurements were performed in 0.1 M oxygen-saturated potassium hydroxide (KOH) solution with a typical three-electrode system in which the glassy carbon ring-disk was used as the working electrode. A Pt-wire electrode and a Ag/AgCl electrode (saturated KCl, 0.198 V vs. SHE) were used as the counter electrode and reference electrode respectively. All the electrochemical measurements were performed at room temperature (H.-X. Zhang et al., 2019).

The LSV measurements of P-BC and Bi-BC biochar samples were carried out in the potential range of -0.0V to -0.8V at a scan rate of 10mv/sec. The potential of ring electrode was fixed at 0.3V vs Ag/AgCl. The electrolyte solution was purged with oxygen for 20 minutes before each LSV run.

The selectivity for the hydrogen peroxide synthesis (eq-4) and the number of electron transferred (eq-5) was calculated from the ring current I_{ring} , the disc current I_{disc} and the collection efficiency of the ring electrode N_c by using the formula (Harraz, Weng, & Surendranath, 2023);(Meng, Li, Huo, Huang, & Xiang, 2017).

$$\% \text{H}_2\text{O}_2 = 100 \frac{2i_{ring}/N_c}{i_{disc} + i_{ring}/N_c} \quad \text{eq-4}$$

$$n = \frac{4 I_d}{I_d + \frac{I_r}{N_c}} \quad \text{eq-5}$$

3.RESULT AND DISCUSSION

3.1. Surface Analysis:

Surface morphology of the biochar was examined with the help of Scanning Electron Microscopy (SEM). The images shown in Fig.1 (a & b) reveal that biochar produced was highly porous with numerous ridges and grooves in continuous carbon structure. This porous structure is very crucial for its application in the electrochemical synthesis of hydrogen peroxide (H_2O_2). Large number of pores and grooves increase the overall surface area and thus provides more space for the reactant molecules to interact with electrode surface (Deng, Gong, Gong, & Wang, 2022);(Z. Chen et al., 2023).This becomes more crucial for electrochemical generation of hydrogen peroxide due to low solubility of oxygen (8ppm) in water. The large pore size also facilitates the desorption of hydrogen peroxide produced and prevents its further reduction.

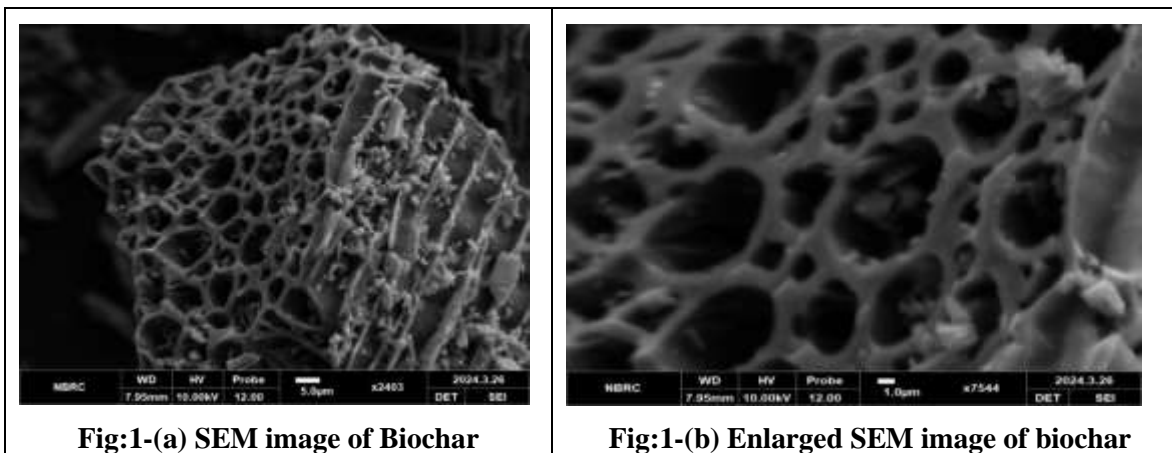


Fig:1-(a) SEM image of Biochar

Fig:1-(b) Enlarged SEM image of biochar

3.2. Raman Spectra

The Raman spectra of pristine biochar showed the presence of two characteristic bands one at 1590cm^{-1} and the other around 1330cm^{-1} as shown in Fig.2. The band located around 1350cm^{-1} is called disordered band (D band) where as bands at 1590cm^{-1} is due to the presence of graphitic phase and is called G band . The G band is due to the stretching vibration of sp^2 hybridized carbon atoms within the graphene sheets present in the biochar carbon matrix. The degree of disorder (ID/IG) of more than one was obtained due to the higher intensity of d band compared to G band. The disordered carbon atoms provide abundant active sites for reactant adsorption and reaction, while the graphitic domains contribute to improve electrical conductivity for efficient electron transfer during the electrochemical process (Xin et al., 2021).

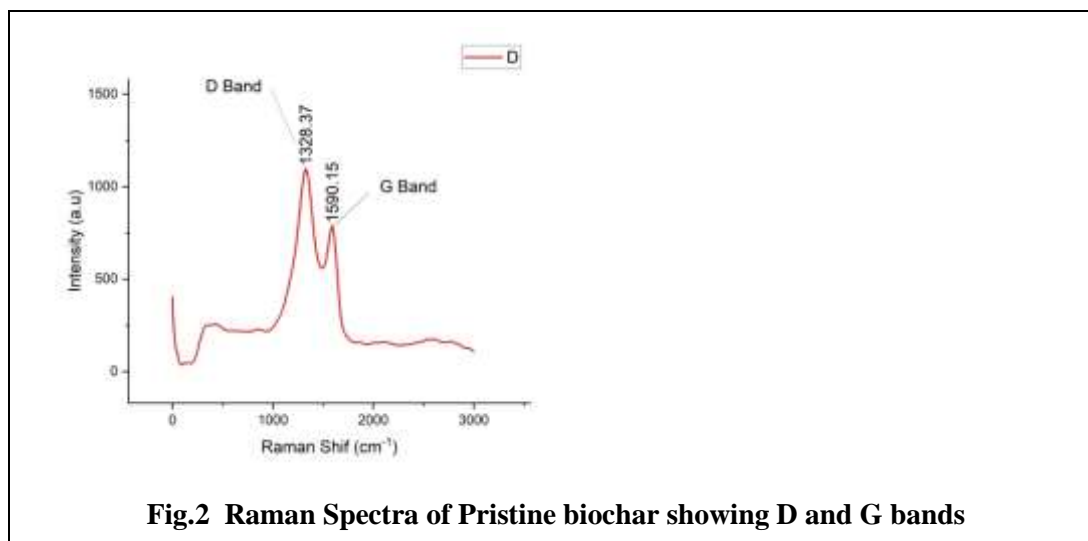


Fig.2 Raman Spectra of Pristine biochar showing D and G bands

3.3. Elemental Analysis:

Elemental analysis of P-BC revealed the presence of carbon (98.43%) and nitrogen (1.56%). Notably, hydrogen and oxygen were not detected. This indicated that carbonization at high-temperature (1000°C) effectively drove off all the hydrogen and oxygen originally present in the feedstock. This gave the biochar a stable and robust carbon structure suitable for electrochemical applications (Chaves Fernandes et al., 2020).

3.4. XRD Analysis:

The XRD spectra of P-BC and Bi-BC was showed in Fig.3. P-BC showed two distinct peaks 23.5 degrees 2θ and 43 degrees. The large peak (002) at 23.5 degree 2θ is most probably due to the presence of disordered carbon atoms in biochar. This random arrangement of carbon atoms is responsible for high surface area and porosity of the carbon atoms. The peak (001) at 43 degrees 2θ is associated with the scattering of X-rays form well-ordered graphitic carbon atoms. Presence of such carbon atoms gives the biochar with high electrical conductivity. These results support the finding of the Raman spectra of biochar.

The XRD spectra of Bi-BC showed the presence of peaks at $2\theta = 27.8^\circ$, which is attributed to the Bi plane of (0, 1, 2). Peaks at $2\theta = 31.68, 32.77, 34.38, 36.21, 46.28, 53.9, 55.62$ and 56.33° , suggested the existence of Bi_2O_3 in different planes (Kang et al., 2023);(Zhu et al., 2020). These results showed the successful incorporation of Bi into carbon framework. However it was observed that doping biochar with bismuth disrupted its original structure, potentially creating more defect sites within the material.

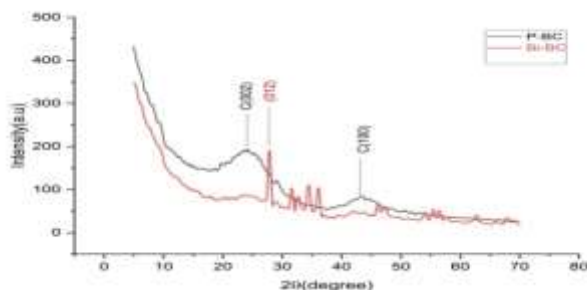


Fig.3- XRD Spectra of P-BC and Bi-BC

3.5. Electrochemical Characterization

3.5.1. Electrochemical impedance (EIS)

The charge transfer ability under practical operating conditions was found using EIS study. The Nyquist plot Fig.4 show that both the P-BC and Bi-BC have low Equivalent charge transfer resistance (ESR). However Bi-BC showed less ESR due to the metallic nature of bismuth. The combination of Bi and biochar might created a synergistic effect, where the presence of Bi not only enhances the conductivity but also altered the biochar's surface chemistry in a way that facilitated electron transfer process. These results are supported by the findings of (Lyu et al., 2019).

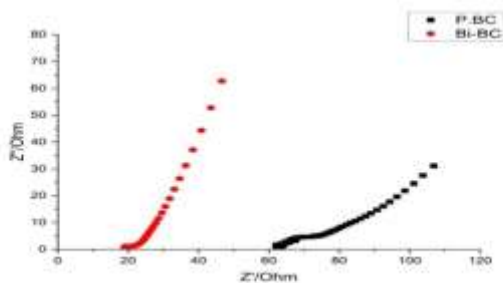


Fig.4 Electrochemical impedance spectra (Nyquist plot) of P-BC and Bi-BC

3.5.2. Cyclic Voltammetry (CV) Study.

The cyclic voltammetry (CV) comparison of P-BC and Bi-BC has been shown in the Fig.5. it show a significant difference in their electrochemical performance for oxygen reduction, evidenced by the observed current densities .The Bi-BC exhibits a current density of 1.1 mA, substantially higher than the 0.05 mA recorded for the P-BC sample. This pronounced enhancement in current density for the bismuth-doped biochar suggests that the doping of bismuth substantially improves the redox activity and electron transfer capabilities of the biochar. The increased current density could be attributed to the catalytic properties of

bismuth, which may facilitate more efficient electrochemical reactions, or to a possible increase in the surface area and conductivity of the doped biochar (W. Zhang et al., 2020).

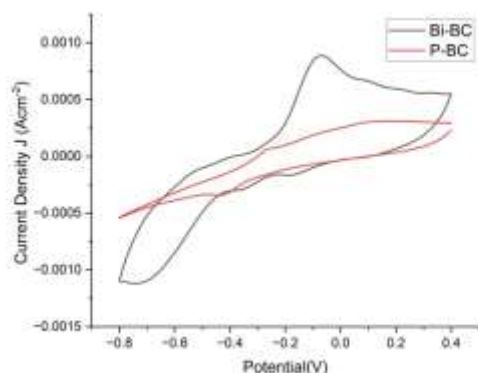


Fig.5 CV scan curve of P-BC and Bi-BC in 0.1M KOH solution saturated with oxygen

3.5.3. Linear sweep voltammetry

The linear sweep voltammetry (LSV) study utilizing a rotating ring-disk electrode (RRDE) revealed a significant enhancement in the electrochemical performance of bismuth-doped biochar (Bi-BC) compared to pristine biochar (P-BC), as showed in Fig. 6. The higher ring current observed for the bismuth-doped biochar indicates a more efficient catalytic activity towards the synthesis H_2O_2 . This improved performance can be attributed to the catalytic properties of bismuth, which facilitate more effective electron transfer and reaction kinetics.

The improved catalytic activity of Bi-BC suggests that bismuth atoms create active sites that are more favorable for the synthesis of H_2O_2 , potentially by altering the electronic structure and increasing the density of states at the Fermi level. Furthermore, the presence of bismuth might improve the dispersion of the biochar, exposing more active surface area for the reactions to occur.

The selectivity for hydrogen peroxide (H_2O_2) generation (calculated by using eq-4) was 71.25% compared to 49.6% for the P-BC. This substantial increase in selectivity underscores the effectiveness of bismuth doping in tuning the catalytic properties of biochar. The number of electron transferred (calculated by using eq-5) was 2.57 for Bi-BC compared to 3.00 for P-BC showing that the doping of bismuth altered the reaction mechanism of oxygen reduction towards the formation of H_2O_2 rather than water formation (Xin et al., 2021);(Meng et al., 2017).

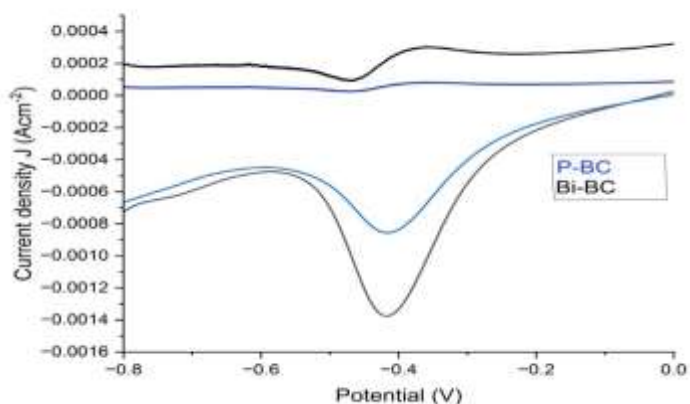


Fig.6 LSV (RRDE) curves of the ORR P-BC and Bi-BC in an O₂-saturated 0.1 M KOH at a rotation speed of 1600 rpm (10 mVs⁻¹).

Table 1 Selectivity and number of electron transferred during the ORR.

Sr. No	Sample Name	Disc Current Acm ⁻²	Ring Current Acm ⁻²	Selectivity (%)of H ₂ O ₂	Number of electron transferred (n)
1	P-BC	0.00085	0.000078	71.25	2.57
2	Bi-BC	.0013	.0002	49.6	3.00

Conclusion:

In this study, a novel electrode material derived from waste wood was successfully prepared through the carbonization of poplar wood. Characterization using SEM, XRD, and Raman spectroscopy revealed that the resulting biochar is a highly porous material containing both graphitic and non-graphitic carbon phases. The incorporation of bismuth into the biochar matrix through doping significantly enhanced its activity and selectivity for hydrogen peroxide generation. The bismuth-doped biochar-based electrode exhibited promising activity in the electrochemical production of hydrogen peroxide, demonstrating its potential as an efficient and sustainable electrode material for other electrochemical applications.

CRedit authorship contribution statement

Sajid Hussain: Conceptualization, Methodology, Formal analysis, Investigation, Writing- Original draft.

Dr. Ch. Jamil Anwar: writing- Review Editing, supervision, project administration.

Dr. Amara Dar: Conceptualization, Methodology, supervision,

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Declaration of generative AI and AI-assisted technologies in the writing process:

During the preparation of this work the author(s) used Chat GPT 3.5 in order to improve language in some sections. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

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