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Effect of pH on the Development of Bio-Pt in Relation to Methanol Oxidation Reactions

Nurul Atiqah Izzati Md Ishak[1,2]*, Siti Kartom Kamarudin[2,3], Norulsamani Abdullah[1,4], Rabita Mohd Firdaus[5] and Syed Ahmad Farhan Syed Iskandar[6]
[1]Research Centre for Nano-Materials and Energy Technology (RCNMET), School of Engineering and Technology, Sunway University, Bandar Sunway, Petaling Jaya, 47500, Selangor Darul Ehsan, Malaysia
[2]Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
[3]Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
[4]Sunway Materials Smart Science & Engineering (SMS2E) Cluster, Sunway University, 47500 Petaling Jaya, Selangor, Malaysia
[5]Research Centre for Carbon Dioxide Capture and Utilisation (CCDCU), School of Engineering and Technology, Sunway University, No. 5 Jalan Universiti, Bandar Sunway, 47500 Petaling Jaya, Selangor, Malaysia
[6]Institute of Self-Sustainable Buildings for Smart Living, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
*Corresponding author (e-mail: atiqahmi@sunway.edu.my; ctie@ukm.edu.my)

The study explores the potential of plant extracts as a biosynthesis route for creating a robust electrocatalyst for methanol oxidation, utilizing their diverse bioactive reducing metabolites. In this work, the effect of pH during the synthesis of Platinum nanoparticles (Pt NPs) using *Saccharum officinarum* L. bagasse extract was investigated at pH 2, 7, 9, and 11 and compared to the original solution, which was subsequently analyzed using Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD). Note that pH has a considerable influence on chemical reduction synthesis, with a higher alkaline pH resulting in a faster reaction rate than in an acidic environment. Furthermore, the effect of pH on bio-Pt NPs production has an impact on electrochemical activities in the methanol oxidation reaction (MOR). The findings demonstrated that, while not surpassing the performance of its original media, bio-Pt NPs synthesized at pH 11 had the highest electrochemical activity for MOR, followed by pH 2, 9, and 7. This was caused by the presence of more readily accessible hydroxide ions (-OH) in more alkaline media, which absorb on Pt's surface and aid in the dehydrogenation of methanol oxidation.

Keywords: Biosynthesis; green chemistry; methanol oxidation reaction; fuel cell; electrochemistry

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Palladium (Pd), platinum (Pt), silver (Ag), and gold (Au) are examples of noble metal nanoparticles that have been significantly contributing to the fields of organic catalysis, bioelectronics, medicine, and pharmaceuticals. Studies on the synthesis of metallic nanoparticles of Ag and Au using plant extract are abundant, particularly in the field of medicine, however, rare studies reported on the synthesis of Pt using plant-mediated extract, with a focus on applications related to electrochemical energy conversion and storage [1]. Numerous applications, including electrocatalysis, hydrogen storage, fuel cells, organic catalysis, and bioelectronics, heavily rely on platinum nanoparticles (Pt NPs) [2]. Pt is an essential catalyst, particularly in redox processes and direct methanol fuel Cells (DMFCs) application [3]. Additionally, Pt has the maximum activity toward the dissociative adsorption of methanol [4]. Even though Pt makes excellent catalysts, its high cost, easy CO poisoning effect, limited availability, and slow kinetics prevent DMFCs from being widely accepted. Therefore, researchers are exploring new catalysts, morphology, size adjustments, support, alloying, and dopants to produce high-efficiency catalysts, while also exploring novel preparation routes [2].

Pt NPs are commonly produced using traditional physical and chemical methods. However, they suffer from chemical potential hazard and toxicity, high cost, are harmful to the environment, require high energy, and are non-ecofriendly by products [5-6]. Thus, due to this reason and with the growing demand for green chemistry the biosynthesis of metallic nanoparticles using plant extract seems to offer significant benefits concerning biocompatible, thermal and chemical stability, environmentally benign, cost-efficient, sustainable, renewable, single-step procedure, rapid and can be scale up [7]. Notably, plant extracts can serve as both reducing and stabilizing agents in the creation of nanoparticles due to the involvement of

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a functional group of bioactive molecules during the bio-reduction mechanism [8].

The plant extract has been known to reduce metal ions since the early 1900s. It is likely that phytoconstituents like flavonoid, phenolic acid, terpenoids, organic acids, and proteins are probably responsible for acting as reducing agents of metal ions (M^+) to metal (M^0) [1, 9]. Additionally, the plant extract effectively stabilizes the particle size of nanoparticles, offering a more defined size and morphology compared to certain physical and chemical methods that mostly rely on hazardous chemicals [10]. Limited studies have utilized green synthesis of plant-mediated extracts to synthesize Pt NPs for catalytic activities, with only almond seeds skin, [11], *Hibiscus sabdariffa* [12], *Polygonum salicifolium* leaves, and gum olibanum (*Boswellia serrata*) [13]. Herein, this work examined the effect of pH in Pt NPs synthesis using *Saccharum officinarum* L. at pH 2, 7, 9, and 11 and compared it with its original pure sugarcane bagasse extract which covered the acidic, neutral, and alkaline environments. Furthermore, the produced bio-Pt NPs were analyzed for their physicochemical characterizations including morphology, size, crystal structure and correlation with the electrocatalytic activities of the methanol oxidation reaction (MOR).

EXPERIMENTAL

Chemicals and Materials

Chloroplatinic acid ($H_2PtCl_6.6H_2O$), 0.1 N NaOH and 0.1 HCl were procured from MERCK. Every reagent purchased was of analytical grade and used without any further purification. Deionized water was employed in all experiments until stated otherwise.

Plant-Mediated Extract Preparation

Sugarcane bagasse (*Saccharum officinarum* L.) was initially cut into small pieces and then dried in an oven at 55 °C to eliminate residual moisture. Subsequently, the dried bagasse underwent pulverization in a sterile electric blender to produce a fine powder, which was subsequently stored in an airtight polymer plastic bag for future applications. To prepare the crude extract, 10 g of the fine powder was mixed with 100 ml of deionized water and boiled for 30 minutes at 60 ºC. After cooling, the broth was filtered using a vacuum pump through Whatman No. 1 filter paper. The resulting extract was refrigerated and utilized within one week.

Synthesis of Platinum Nanoparticle Catalyst

A 10 ml aliquot of bagasse extract was combined with a 90 ml solution of chloroplatinic acid hexahydrate (1 mM) at a ratio of 1:9. To achieve pH levels of 2, 7, 9, and 11 during synthesis, either 0.1 N HCl or 0.1 N NaOH was introduced into the solution. These conditions were compared against those using pure sugarcane bagasse extract for bio-Pt NP synthesis. The reaction mixture was stirred on a hot plate at 95°C for two hours, during which color changes from pale yellow to blackish were observed visually. Subsequently, the mixture underwent sonication for 30 minutes, followed by centrifugation for 20 minutes. The resulting pellet was washed multiple times with deionized water, redispersed, collected, and dried at 100°C for 8 hours.

Characterization Methods of bio-Pt NPs

The synthesized bio-Pt NPs underwent analytical techniques to determine their physical characteristics, including X-ray Diffraction (XRD) to ascertain their crystalline nature and Transmission Electron Microscopy (TEM) for morphological analysis. XRD patterns of bio-Pt NPs were obtained using an XRD instrument (D8 Advance/Bruker AXS Germany) operating at 40 kV and 20 mA with Cu–Ka radiation (λ = 1.5406 Å). The scanning range (2θ) spanned from 20 to 90º at a continuous speed of 0.045 degrees per minute. Morphological shape analysis was conducted via TEM using a Philips model.

Electrochemical Properties of Bio-Pt NPs Electrode

A 2 mg of bio-Pt NPs was dissolved in a solution containing 150 µL deionized water, 150 µL 2-propanol, and 50 µL of 5 wt. % Nafion® 117 solution, followed by sonication for 1 hour. The resulting solution was drop-coated onto the surface of a glassy carbon electrode (GCE) and allowed to dry at room temperature. The electro-chemical analysis of bio-Pt NPs electrode was performed by cyclic voltammetry (CV) and conducted on Autolab PGSTAT204 (Netherlands), an instrument-integrated automated electrochemical workstation. The electrochemical measurements were performed in a three-electrode system, in which glassy carbon electrode as working electrode, platinum wire as counter electrode, and Ag/AgCl as reference electrodes with a 1.0 M CH_3OH as fuel and 0.5 M H_2SO_4 as the electrolyte. The voltammetry measurements were performed at a potential window of −0.25 to 1.0 V at scan rates of 50 mV/s. The reversibility of electron transfer was studied using voltammetry techniques to assess the electro-catalytic properties of bio-reduced Pt NPs films on GCE.

RESULTS AND DISCUSSION

Characterization TEM on Bio-Pt NPs

The effect of pH solution from 2, 7, 9, 11 and the origin of bio-Pt NPs synthesis at 100ºC is displayed in Figure 1. TEM images exhibit a spherical shape agglomerated formation of nanoparticles at all pH value except well-distributed small-size particles were formed at the original medium and alkaline pH 9.

Based on Figure 1 (a) and (e), at extreme pH alkaline and acidic environment, a high degree of Pt NPs agglomeration is clearly observed. This was believed to be due to the fast rate of synthesis reaction happening at the extreme pH condition, which may lead to uneven nucleation and growth of size particles and make the particles agglomerated. When comparing the rate of synthesis in an alkaline and acidic environment, the rate of synthesis rose in an alkaline pH that was stronger, such as pH 11. The rate of synthesis increased with increasing pH alkalinity. The synthesis duration time becomes shorter and faster reaction when the pH is alkaline, compared to the original solution, which was measured to be pH 3.5. This suggests that alkaline environments may be more conducive to promoting synthesis reactions compared to acidic environments. The higher concentration of hydroxide ions (-OH) in alkaline solutions may play a role in accelerating the rate of synthesis. Furthermore, there is a noticeable shift in the particle size decrement from 15.9 to 2.0 nm when the synthesis occurs at pH 7 instead of the original and pH 2. Conversely, a similar pattern was observed when the synthesis occurred in an alkaline pH range of 9 to a higher alkaline pH of 11, where it was discovered that the particle size had dropped from 17 nm to 4 nm. This finding implies that the particle size is influenced by pH.

Characterization XRD on Bio-Pt NPs

The crystal phase and structure of the produced bio-Pt NPs from the green reduction method of bagasse aqueous extract were ascertained using XRD analysis, as illustrated in Figure 2. The XRD peaks observed at 38.21º, 44.39º, 64.62º, and 77.59º correspond to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) Bragg's reflections, respectively, indicative of the face-centered cubic (*fcc*) structure characteristic of metallic Pt. These peaks closely resemble those of pure platinum (JCPDS 04-0802), affirming the pure crystalline nature of the synthesized bio-Pt-NPs. The intensity of the (111) orientation surpasses that of other peaks, indicating its predominance. The strong and narrow peak signifies the well-crystallized nature of the particles. However, no impurity peaks were detected, confirming the formation of pure crystalline Pt. Scherrer equation corresponding to the XRD profile (Figure 2) was used to calculate the particle size of the bio-Pt NPs at condition synthesis of pH 2, 7, 9, 11 and its origin was estimated to be 6.06, 5.49, 9.15, 5.20, and 5.23 nm, respectively.

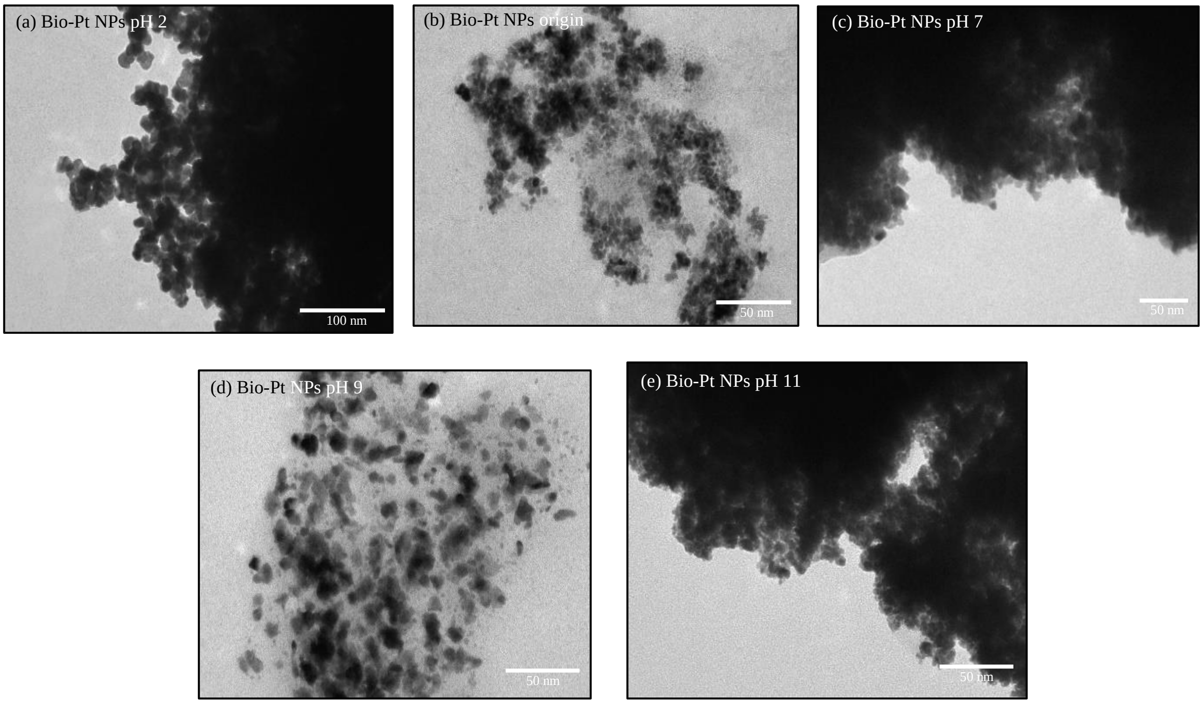

Figure 1. TEM image of bio-Pt NPs at various pH level of 2, 7, 9, and 11 and their origin.

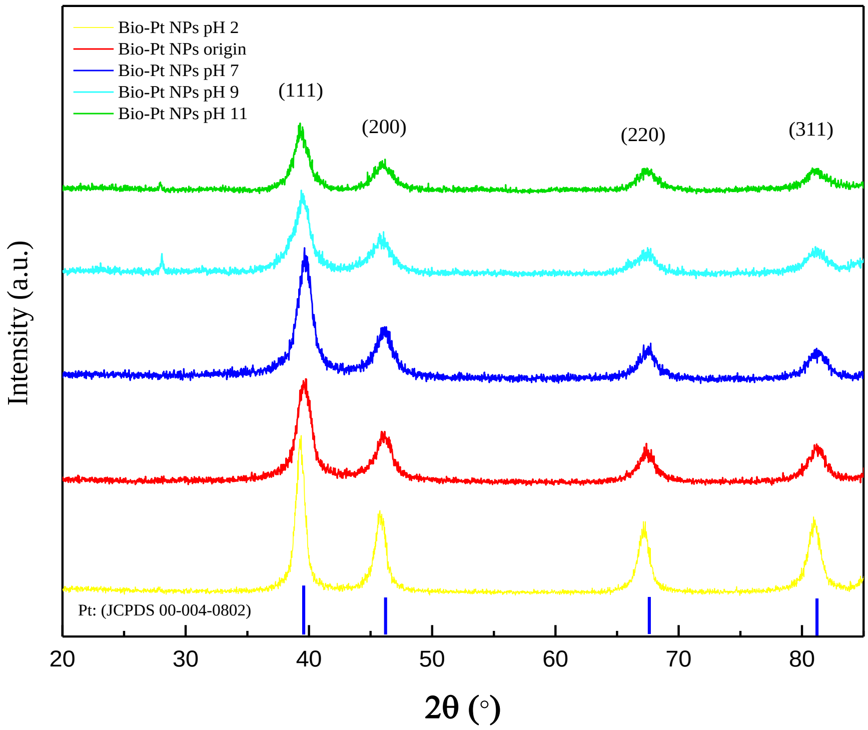

Figure 2. XRD pattern of bio-Pt NPs using bagasse extract at different pH.

Electrocatalytic Activities of Bio-Pt NPs in the Methanol Oxidation Reaction

The electrocatalytic activity of bio-Pt NPs at different pH was investigated in 0.5 M H_2SO_4 with or without 1 M CH_3OH. Figure 3 (a) illustrates CV performed in 0.5 M H_2SO_4 to measure the electro-chemical surface area (ECSA) of all bio-Pt NPs by integrating the area of H_2 peak desorption using the equation (1):

$$\text{ECSA } (\text{m}^2/\text{g}_{\text{Pt}}) = \frac{Q_H}{m_{Pt}\ x\ c} \qquad (1)$$

The charge for hydrogen adsorption/desorption on Pt (Q_H) is expressed in C cm^{-2}, while m_{Pt} denotes the Pt loading in mg cm^{-2}. Here, c = 210 µC/cm^2 represents the charge needed to oxidize a monolayer of H_2 onto the Pt surface [14]. The number of accessible active sites for electron transfer to and from the electrode surface can be determined using ECSA [15].

Bio-Pt NPs were discovered to have ECSA values of 10.26, 0.59, 17.23, 29.36, and 12.61 m^2 g^{-1} for pH 2, 7, 9, 11, and its origin as portrayed in Figure 3 (a) and (b). According to Figure 3 (c) and (d), the original bio-Pt NPs generated the highest current density of 72.0 mA cm^{-2} in the presence of methanol, followed by the bio-Pt NPs pH 11, bio-Pt NPs pH 2, bio-Pt NPs pH 9, and bio-Pt NPs pH 7 at 64.10, 18.37, 10.62, and 2.13 mA cm^{-2}, respectively. These results suggest that the ECSA values of bio-Pt NPs are influenced by the pH of the environment, with higher values observed at alkaline pH levels as compared to acidic and neutral. Additionally, the bio-Pt NPs exhibited significantly higher current densities in extremely acidic (pH 2) and alkaline (pH 11) conditions compared to neutral pH, indicating their potential for enhanced electrocatalytic activity in specific environments. Moreover, it was discovered that pure sugarcane bagasse extract had a pH of 3.5, indicating that it was slightly acidic in nature. The acidic nature of the extract may also contribute to its ability to enhance the electrocatalytic activity of bio-Pt NPs in acidic conditions. The significant phenolic content found in sugarcane bagasse was thought to be a contributing factor in the extract's acidic character [3, 16].

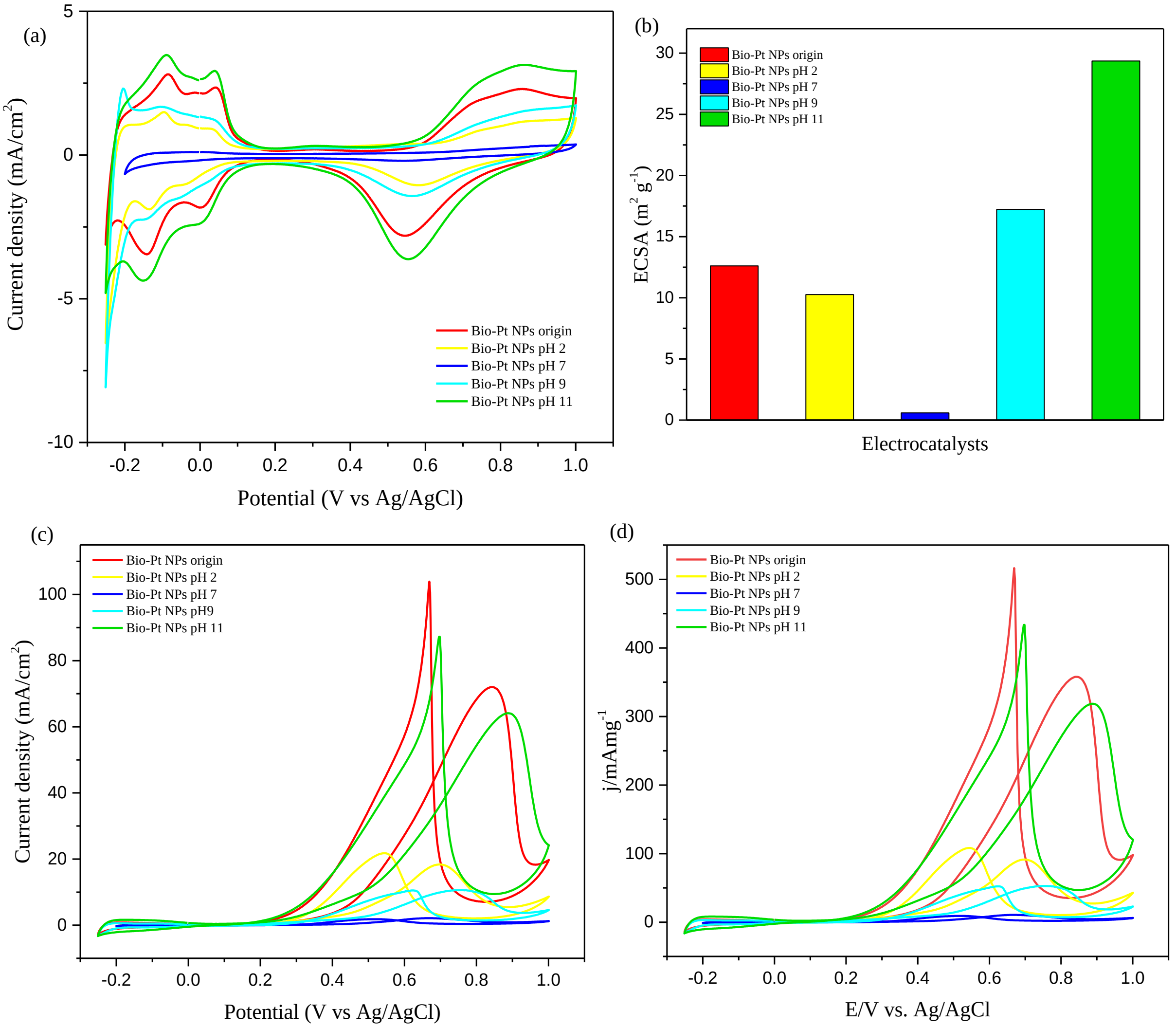

Figure 3. (a) represents the H_2 absorption and desorption in 0.5 M H_2SO_4, (b) the ECSA value for each bio-Pt NPs, (c, d) cyclic voltammetry in MOR performance for bio-Pt NPs in 0.5 M H_2SO_4 + 1.0 M CH_3OH at pH of 2, 7, 9, 11 and its origin.

Table 1 compares the methanol oxidation reaction activities of all samples at different pH in the presence of 1.0 M methanol and 0.5 M H_2SO_4. Remarkable mass activity (357.87 mA $mg^{-1}{}_{Pt}$) is demonstrated by the original bio-Pt NPs, and under high alkalinity (pH 11), 318.61 mA $mg^{-1}{}_{Pt}$ is produced as a result. This result suggested that in an extreme alkaline medium with a pH of 11, more accessible OH ions are present, thus aiding in the dehydrogenation of methanol molecules to oxidize from CO_{ads} formation [17].

Table 1. Methanol oxidation reaction performance for all bio-Pt NPs at various pH in 0.5 M H_2SO_4 and 1 M methanol.

Electrocatalyst	**ECSA (m^2 g^{-1})**	**Peak potential, E_p (V vs Ag/AgCl)**	**Current density (mA cm^{-2})**	**Mass activity (mA $mg^{-1}{}_{Pt}$)**
Bio-Pt NPs origin	12.61	0.84	72.00	357.87
Bio-Pt NPs pH 2	10.26	0.70	18.37	91.28
Bio-Pt NPs pH 7	0.59	0.66	2.13	10.59
Bio-Pt NPs pH 9	17.23	0.75	10.62	52.79
Bio-Pt NPs pH 11	29.36	0.89	64.10	318.61

CONCLUSION

This study investigates the effect of pH variations across acidic, neutral, and alkaline environments on the biosynthesis and reduction of Pt NPs using sugarcane bagasse (*Saccharum officinarum* L.) extract. Synthesis was conducted at pH levels of 2, 7, 9, and 11, with comparison to pure sugarcane bagasse extract, to analyze the formation of bio-Pt NPs in terms of rate of reaction, physicochemical properties, and their correlation with electrocatalytic activity in methanol oxidation. The results revealed that the bio-Pt NPs formed in pH 11 exhibited the highest rate of reaction and superior electrocatalytic activities with a current density/mass activity of 64.10 mA cm^{-2}/318.61 mA $mg^{-1}{}_{Pt}$ and high ECSA value of 29.36 m^2 g^{-1} compared to the other pH levels. This enhancement is attributed to the increased accessibility of -OH molecules adsorbed on the Pt catalyst surface, enhancing overall efficiency in methanol oxidation. Additionally, morphological studies unveiled a spherical structure with a crystallite size of 5.23 nm in the bio-Pt NPs synthesized at pH 11. Despite the faster reaction rate, bio-Pt NPs synthesized at extreme alkaline conditions (pH 11) displayed comparable current density/mass activity for methanol oxidation to the original bio-Pt NPs 72.0 mA cm^{-2}/357.87 mA $mg^{-1}{}_{Pt}$. Overall, these findings highlight the importance of considering environmental factors, such as pH, when optimizing the electrocatalytic properties of bio-Pt NPs for diverse applications.

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