



Electrochemical preparation and the characterizations of poly(3,5-diamino 1,2,4-triazole) film for the selective determination of pyridoxine in pharmaceutical formulations

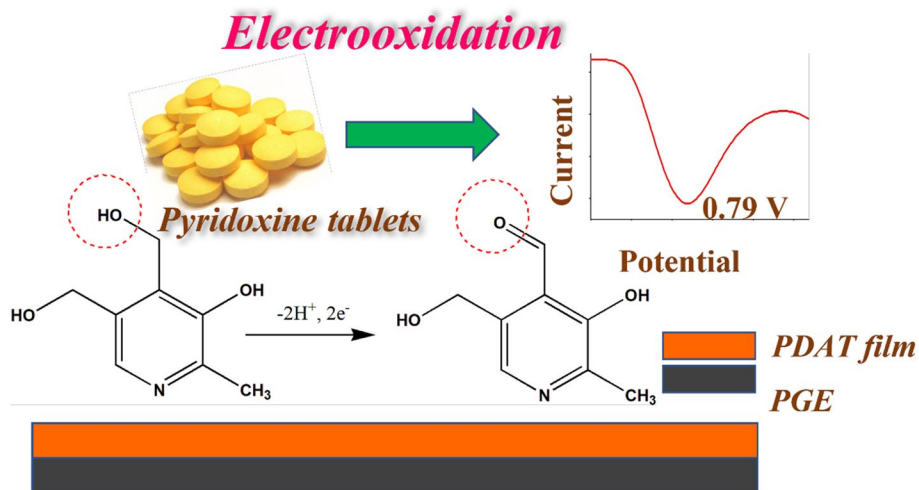
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Abstract

This work describes the synthesis and characterization of a polymeric film of 3,5-diamino 1,2,4-triazole on a pencil graphite electrode for the selective sensing of pyridoxine (PY). The PGE was modified using the electropolymerization process by the potentiodynamic method. The polymerized electrode (PDAT/PGE) was characterized by IR, SEM, AFM, cyclic voltammetry, and electrochemical impedance spectroscopy. PY undergoes irreversible oxidation at 0.79 V on PDAT/PGE in phosphate buffer of pH 5. Using the differential pulse voltammetric technique (DPV), PY showed a linear range from 5 to 950 μM with a lower detection limit of 2.96 μM . The PDAT/PGE was applied for the analytical determination of PY in pharmaceutical tablets with good recovery.

Graphical abstract



Keywords Pyridoxine · Voltammetry · 3,5-diamino 1,2,4-triazole

Introduction

Pyridoxine is a cardinal biomolecule in the human body that plays a prominent role in various cellular metabolic processes (Hellmann and Mooney 2010)(Parra et al. 2018). PY is a class of water-soluble B vitamins and is otherwise known as Vitamin B6 (Huang et al. 2021). PY also

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possesses significant functions in the central and peripheral nervous system (Calderón-Ospina and Nava-Mesa 2020). PY performs neuro-specific functions (Bender 1984), and the PY-related enzymes are actively involved in the synthesis of different neurotransmitters (Dakshinamurti et al. 1990) (Rejithamol and Beena 2020). Pyridoxal 5'-phosphate (PLP) is the active form of vitamin B6, and the PY concentration in blood plasma is usually measured in terms of PLP (Information 2015). The marginal values of PLP in plasma are 20–30 nM, and thus PY deficiency is associated with plasma PLP values of < 20 nM (Jungert et al. 2020). Several diseases, such as cardiovascular diseases, gastric disorders, diabetes, neurological disorders, immune deficiency, and cancer, are associated with low concentrations of vitamin B6 in plasma (Kim and Cho 2014) (Merigliano et al. 2018) (Kjeldby et al. 2013). According to literature reports, PY possesses anti-inflammatory properties, and thus supplementation of vitamin B6 can be used to alleviate viral infections (Santhy et al. 2020) (Kumrungsee et al. 2020) (Zhang et al. 2016). Recent studies reported that supplementation of PY significantly relieves the worse health conditions associated with Covid-19 patients, such as cardiovascular diseases, diabetes, hypertension, etc. (Huang et al. 2021) (Stach et al. 2021). PY is essential for maintaining healthy skin, and its deficiency may cause dermatitis (Kato 2012). Hence vitamin B6 has been used as a supplement to treat dermatitis and other skin diseases (Wright et al. 1943) (Mabin et al. 1995). Various cases of neuropathies have been reported in patients due to the excessive intake of vitamin B6 supplements (Gdynia et al. 2008; van Hunsel et al. 2018; Vrolijk et al. 2020). The European food safety authority has recommended lowering the upper-level dosage of vitamin B6 intake from 100 to 25 mg/day (Vrolijk et al. 2017). Hence the usage of the pharmaceutical supplements of PY has received more attention in the last few years.

From the analytical point of view, it is of utmost importance to develop highly efficient and accurate sensors to determine the PY concentrations from biological and pharmaceutical samples. Since more advanced scientific methods are used in clinical and pharmaceutical industries, the demand for developing disposable and portable devices is increasing. According to literature reports, multiple techniques have been employed to determine PY, including spectrophotometry, chromatography, spectrofluorimetry, etc. (Gatti and Gioia 2005; Sorouraddin et al. 2005). But these analytical techniques are more expensive, require lengthy procedures, and could be considered as the limitations (Hadi Beitollahi and Fariba Garkani Nejad 2019). However, compared to all the analytical techniques mentioned above, electrochemical methods have more advantages as it offers easy operating procedure, fast response, and a cost-effective detection platform for various analytes (Sharma and Arya 2019). Hence splendid research is going

on for the development and application of sensing devices based on electrochemical methods in environmental, food, pharmaceutical, clinical fields, etc. (Antherjanam and Saraswathyamma 2021; Krishnan and Saraswathyamma 2021; Li et al. 2015; Madrakian et al. 2014).

In electrochemical detection methodologies, PGEs have attracted more attention than other carbon-based electrodes and are widely utilized in many electroanalytical applications (David et al. 2017). PGEs are one of the highly economical electrodes which possess various characteristics suitable for electrochemical sensor fabrication (Kolahi-Ahari et al. 2020). The easy preparation methods, high sensitivity, and low background current highlight its demand in the area of electrochemical sensors (Sankaranarayanan and Venkateswaran 2020) (Ganesh et al. 2018). Chemically modified electrodes are used to increase the sensitivity and selectivity of the electrochemical sensors (Zuo et al. 2012). The applications of electropolymer as modifiers in the fabrication of electroanalytical devices are reported in previous literature (Sajid et al. 2015) (Muti et al. 2013a). The thickness and morphology of the polymers can be carefully controlled using electropolymerization techniques, and polymerization can be done by in situ methods by a simple procedure (Imisides et al. 1991) (Vedhi et al. 2009). Also, the polymers obtained via electropolymerization techniques were highly pure, and even these polymers can be prepared in an aqueous solution, which is not possible in chemical polymerization methods (Gvozdenović et al. 2014). Hence the use of electropolymer is of great interest in modifying various electrode surfaces in electrochemical applications. Conducting as well as insulating polymers can be generated using electropolymerization by potentiodynamic method, and their applications in the surface modification are also reported (Yuqing et al. 2004) (Gvozdenović et al. 2014) (Bonyadi and Ghanbari 2021). Conducting polymers are one of the attractive materials used for the modification of various electrodes in electrochemical sensor developments (Lee et al. 2012; Meng et al. 2021). Conducting polymers offers more stability and excellent electrical properties that extend its applicability in the fabrication of electrochemical sensors (Chen et al. 2013; Nie et al. 2013). The organic compounds with heterocyclic rings and nitrogen-containing aromatic compounds are promising scaffolds for synthesizing conducting polymers (Waltman and Bargon 1986; Yadav et al. 2013). Hence triazoles and triazole-derived compounds are appropriate materials for the generation of conducting polymers, and it has been proven in literature reports (Danyıldız et al. 2017; Revin and John 2012).

In this report, we have introduced a conducting polymer of 3,5-diamino 1,2,4-triazole (DAT) for the electrochemical determination of PY in pharmaceutical samples. PGE was used as the electrode substrate, and the PDAT film was generated on the PGE surface by cyclic voltammetry. DAT has

been previously used to fabricate electrochemical sensors for pharmaceuticals, biomolecules, environmental pollutants, etc. (Calam 2021; Kesavan and Abraham John 2014; Kumar et al. 2017). The mechanism of electropolymerization was investigated by ATR-IR spectroscopy and its morphological studies were done by SEM and AFM techniques.

Moreover, electrochemical studies were done by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analysis. The obtained PDAT/PGE sensors showed high sensitivity and stability towards the electrooxidation of PY. In addition, this is the first work reported for the electropolymerization of DAT on PGE, according to our knowledge. The results suggested that the PDAT/PGE might be a reliable sensor for the sensitive determination of PY in pharmaceutical formulations.

Experimental

Reagents and materials

DAT, monosodium dihydrogen phosphate (NaH_2PO_4), and disodium orthohydrogen phosphate (Na_2HPO_4) were obtained from Merck. PY was purchased from Loba Chemie. Analytical grade chemical reagents were utilized for preparing all solutions and all solutions were made up in Millipore water. PGE of 0.7 mm diameter manufactured by Cello writing Aids Pvt. Ltd. was procured from a local supermarket. PY tablets containing 100 mg per tablet were purchased from a pharmaceutical shop.

Instrumentation

The electrochemical analyzer of model CHI 610E, CH Instruments, USA, was used for all voltammetric studies. The experimental setup consists of a three-electrode system with Pt wire as the counter electrode and Ag–AgCl (1 M KCl) electrode as the reference electrode. The modified electrode (PDAT/PGE) was used as the working electrode. These electrodes were placed in an electrochemical cell containing 10 mL supporting electrolyte for the electrochemical studies. Scanning electron microscopic images (SEM) were obtained using the JEOL model: JSM 6490La. ATR-IR analysis of the electrodes was done using Perkin Elmer Spectrum Two IR Spectrometer. The ATR-IR analysis was performed in a range of 500–4500 cm^{-1} . EIS analyses were performed using the Autolab bi-potentiostat PGSTAT 302N instrument. A potential amplitude of 0.1 V in a frequency range of 0.1–1000 Hz was used for the EIS analysis. AFM analysis in tapping mode was done using Bruker Dimension Edge atomic force microscope.

Electropolymerization of DAT

The electropolymerization of DAT was carried out in an electrochemical cell containing three electrode systems with PGE as the working electrode, Ag–AgCl (1 M KCl) as the reference electrode, and Pt wire as the counter electrode. PGE was covered by a teflon tape exposing a length of 5 mm, and the uncovered portion was used for the polymerization process. The opposite side of the exposed part of PGE is used for electrical contact. PDAT film was generated on PGE using CV in a monomer solution containing 15 mM DAT dissolved in 0.1 M KCl. Chloride ion containing electrolytes have been used in various electropolymerization process according to the literature reports (S. Chen et al. 2018; Zembrzuska et al. 2019). The CV was done in a potential range of -0.8 to 1.6 V at a scan rate of 100 mV/s. After ten cycles, the obtained PDAT/PGE was thoroughly washed with millipore water and used for further studies.

Electroanalytical measurements

CV and DPV were used for the study of electrochemical oxidation and quantification of PY on PDAT/PGE. CV was performed by sweeping the potential from 0.5 V to 1.2 V with a scan rate of 100 mV/s. DPV measurements were also done in the potential window of 0.5 to 1.2 V. The CV and DPV measurements were performed by adding a known volume of PY to 10 mL 0.1 M PBS pH 5 contained in an electrochemical cell.

Results and discussions

Morphological studies of PDAT/PGE

Figure 1A and 1B display the SEM images of PGE and PDAT/PGE. The graphite flakes are noticeable on the surface of PGE, whereas flake-like morphology is not there in the case of polymer-coated PGE. This indicated the successful polymerization of DAT on the bare graphite surface. The 2D and 3D AFM images of unmodified PGE and PDAT/PGE are given in Fig. 2. From the AFM data obtained, R_q of the PGE and PDAT/PGE were $0.0536 \mu\text{m}$ and $0.0625 \mu\text{m}$ respectively, where R_q is the root mean square roughness value. The increase in R_q value of PDAT/PGE indicates the formation of a polymeric film on pencil graphite surface after the modification process.

Electrochemical characterization of PDAT film

The PDAT/PGE and PGE were electrochemically studied by the fundamental electroanalytical technique, CV and EIS using 5×10^{-3} M potassium ferricyanide in 0.1 M KCl

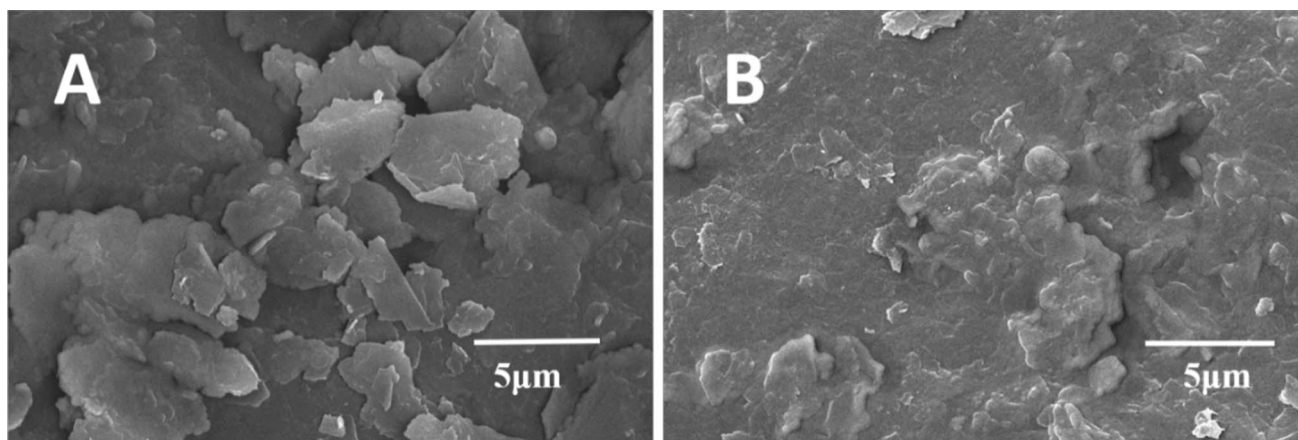


Fig. 1 SEM images of **A** bare PGE and **B** PDAT/PGE

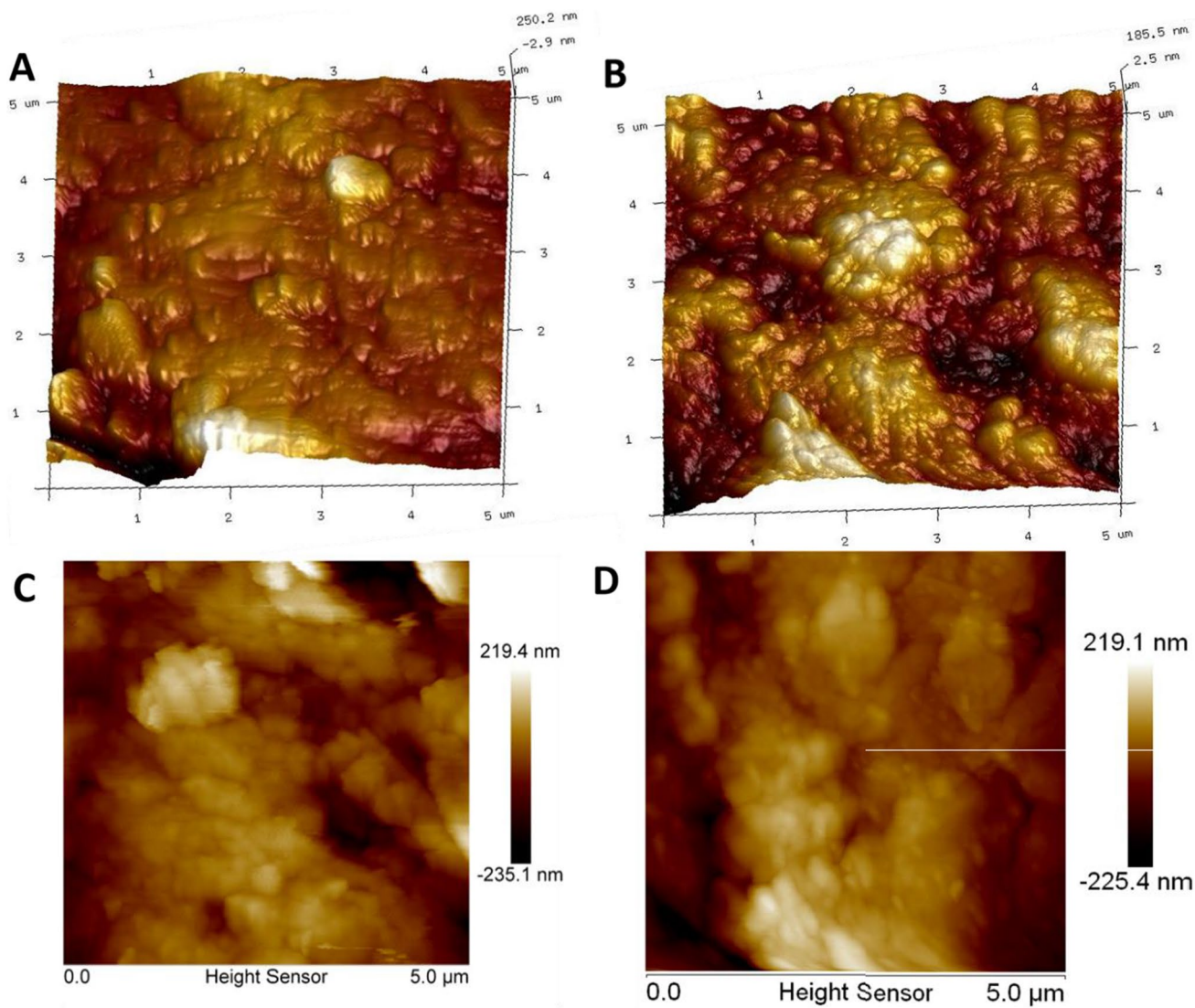


Fig. 2. 3D AFM images of **A** PGE, **B** PDAT/PGE and 2D AFM images of **C** PGE, **D** PDAT/PGE

as the redox probe. CV images are displayed in Fig. 3A, and the electrochemical behavior of the redox probe was observed on both electrodes. The current response of redox peaks gets increased in the case of PDAT/PGE than PGE in the CV measurements. Thus, the polymer film on the PGE is more conducting than the bare graphite surface; consequently, the modified PGE enhances the electron transfer rate of the redox reaction. EIS is a fundamental electroanalytical technique used to study the electrochemical behavior of the electrode surface (Sharma et al. 2020). Figure 3B represents the Nyquist plot for the PGE and PDAT/PGE in 5×10^{-3} M potassium ferricyanide in 0.1 M KCl solution. The Randles circuit for the electrodes is given in the inset of Fig. 3B and R_1 is the resistance of the electrolyte solution, R_2 represents the charge transfer resistance of the electrode, Q is the constant phase element and W is the Warburg impedance (Antherjanam and Saraswathamma 2022). The Warburg component denotes the diffusion of ion in the electrochemical oxidation reactions and the R_1 is independent

on the frequency (Balasubramani et al. 2020; Randviir and Banks 2013). The Nyquist plot with Randles circuit fitted data is given in supplementary figure S1. The semicircle in the higher frequency region of the Nyquist plot represents the charge transfer limited process (Shishkanova and Sinica 2022). From Fig. 3B, PGE represents the largest diameter, and PDAT/PGE showed the smallest diameter for the semicircle. Hence it is concluded that the polymeric film of DAT on PGE is more conducting than bare PGE.

ATR-IR analysis of DAT, PGE, and PDAT/PGE

The formation of PDAT film on PGE can be explained using the ATR-IR spectra of DAT, PDAT/PGE, and bare PGE. The IR spectrum of the monomer DAT is given in figure S2A. DAT showed peaks at 1578 cm^{-1} and 1068 cm^{-1} corresponding to C=N and N-N stretching frequencies. However, the peaks due to C=N and N-N stretching are slightly shifted to 1651 cm^{-1} and 1046 cm^{-1} , respectively (Tabanlıgil

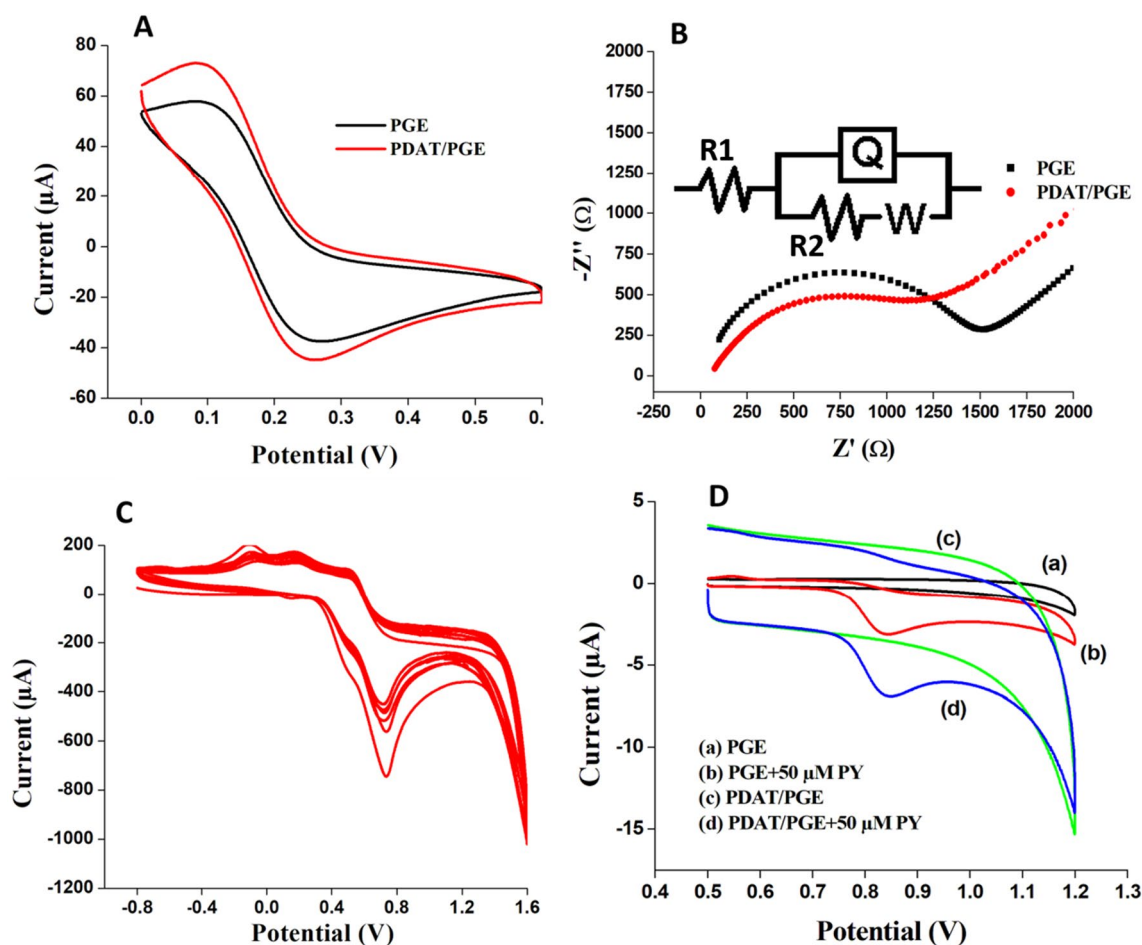


Fig. 3 A CV of bare PGE and PDAT/PGE in 5 mM ferricyanide in 0.1 M KCl at 100 mV/s B Nyquist plot of bare PGE and PDAT/PGE in 5 mM ferricyanide in 0.1 M KCl and corresponding Randles circuit is given in inset C CV of electropolymerization of DAT on PGE

D CV of PY on PGE and PDAT/PGE at 100 mV/s in PBS pH 5

Calam 2019). The band due to C–N stretching is observed at 1143 cm^{-1} on DAT and 1151 cm^{-1} on PDAT/PGE (Calam 2020). C–H stretching bands are observed at 3107 cm^{-1} and 2989 cm^{-1} on DAT and PDAT/PGE, and the peaks are in good agreement with the reported literature (Calam 2020). IR bands in the range of 3300 cm^{-1} are observed on DAT, indicating the presence of the aromatic -NH_2 group in the monomer (Ismail et al. 2015). But on comparison of the IR spectra of PGE and PDAT/PGE (Figure S2B and S2C), no new peaks were observed on PDAT/PGE corresponding to the -N-H stretching of primary aromatic amine. This justified the involvement of the NH_2 group in the polymerization process, as reported in the previous literature. Further, a new peak is obtained on PDAT/PGE at 1439 cm^{-1} , which corresponds to N=N stretching, and this peak is not visible in the spectrum of DAT (Aydođdu et al. 2014; Muti et al. 2013b; Revin and John 2011). The presence of N=N stretching in the modified electrode successfully proved the generation of PDAT film on the PGE.

Mechanism of formation of PDAT film on PGE

The CV of electropolymerization of DAT (Fig. 3C) showed strong oxidation peak at 0.49 V and cathodic peaks at 0.51 V, 0.18 V, and -0.11 V. These peak potentials are observed to be slightly shifted from the reported polymerization of DAT on bare GCE (Kumar et al. 2017). Following the reported mechanism in (Kesavan and Abraham John 2014; Kumar et al. 2017), the anodic peak at 0.49 V corresponds to the oxidation of the aromatic primary NH_2 group to form a radical cation (Antherjanam and Saraswathyamma 2021). Then the radical cations undergo polymerization through the -NH-NH- linkage. At 0.74 V, the -NH-NH- further undergo dimerization to form another radical cation. Then the unstable radical cations get dimerized to form PDAT film on the PGE. According to the reported mechanism, the plausible mechanism of electro generation of DAT film on PGE is given in figure S3.

Electrochemistry of PY on PDAT/PGE and PGE

Figure 3D represents the CV of $50\text{ }\mu\text{M}$ PY on PGE and PDAT/PGE in PBS pH 5 in a potential scanning from 0.5 to 1.2 V at 100 mV/s . An oxidation peak for PY was obtained on the bare PGE and PDAT/PGE at 0.83 V. However, the current response of PY was increased on PDAT/PGE than on the bare PGE surface. According to previous literature, the electrooxidation of PY occurs through a two proton-two electron transfer (Cherian et al. 2021). Thus, the alcoholic group opposite the nitrogen in the pyridine ring is oxidized to the aldehyde group, as this hydroxyl group is highly reactive compared to other hydroxyl groups present in the ring structure of PY (Rejithamol and

Beena 2020). The suggested mechanism of electrooxidation of PY is given in supplementary figure S4.

Optimization studies

Supporting electrolyte

As DPV is more sensitive than CV, analytical quantification of PY was done using the DPV method (Vadivaambigai et al. 2015). Among the different supporting electrolytes studied (0.1 M KCl , $0.1\text{ M H}_2\text{SO}_4$, $0.1\text{ M acetate buffer pH } 5.6$, $0.1\text{ M PBS pH } 5$), a better current response for $25\text{ }\mu\text{M}$ PY was obtained on PDAT/PGE in PBS pH 5 (Data given in supplementary table T1). The pH of the PBS was also optimized from pH 4 to 8 (supplementary figure S5 A), and a better current response was obtained for PBS pH 5. Hence all further analytical studies were optimized with PBS pH 5. The oxidation peak current increased from pH 4 to 5 and then gradually decreased with a further increase in pH. This showed the involvement of the pH of the electrolyte in the electrooxidation of PY on PDAT/PGE. Thus, at higher pH, the deprotonation of PY will occur, slowing down the oxidation process, and therefore peak current decreases (Cherian et al. 2021). The influence of pH in the electrooxidation of PY was corroborated by the negative shift of peak potentials with the increase in pH (figure S6) (Zhang et al. 2017). Also, the plot of pH of the supporting electrolyte against peak potentials was linear with the following linear regression equation.

$$E_{\text{pa}} = 1.1164 + -0.06192\text{ pH}, R^2 = 0.99861$$

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Thus, the slope obtained of 61.92 mV/pH was almost equal to the Nernstian slope. Therefore, an equal number of protons and electrons are involved in the electrooxidation of PY (Filik et al. 2017). Hence the mechanism mentioned above of the electrochemical oxidation of PY on PDAT/PGE is validated.

Further, the effect of DAT concentration on the electrooxidation of PY was also examined ($5\text{--}20\text{ mM}$). The oxidation peak with more peak current was obtained for 15 mM DAT concentration (result displayed in supplementary S5 B). After all, the polymerization cycles were also varied from 5 to 20 cycles to find out the best result for the electrochemical oxidation of PY. The polymerization cycle was then finally selected as ten cycles, providing the best outcome for the electroanalysis of PY (supplementary Figure S5C).

Scan rate study

CV was used to examine the dependence of scan rate on the oxidation potential of PY. Figure 4A shows the cyclic voltammogram of $50\text{ }\mu\text{M}$ PY in 0.1 M PBS of pH 5 from varying scan rates of $10\text{--}120\text{ mV/s}$. The voltammogram indicates

that the oxidation current of PY is increased with an increasing scan rate. Also, the peak potentials are shifted to more positive values as the scan rate increases, which is attributed to the irreversible nature of the oxidation process (Sartori et al. 2010). The peak currents of PY against the square root of scan rate ($v^{1/2}$) were plotted (Fig. 4B), and they showed good linearity, implying a diffusion-controlled nature of the electrooxidation process (Stanković and Kalcher 2015). In addition, the logarithm of peak current showed linear dependence with the logarithm of scan rate with a slope of 0.445 (Figure S7A). This validated the diffusion-controlled electrochemical reaction of PY on PDAT/PGE, as the slope obtained is almost equal to the theoretical value of 0.5 (Deepa G. Patil, Naveen M. Gokavi and Nandibewoor, 2016). The total number of electrons (n) participated in the electrochemical oxidation of PY was calculated using the equation, $E_{pa} = (2.303RT/\alpha nF) \log v + \text{constant}$ where α is the electron transfer rate constant and is assumed to be 0.5 for an irreversible electrode reaction (Figure S7B) (Oliveira et al. 2013). The other terms involved in the equations are E_{pa} : the oxidation peak potential (V), F , the Faraday's constant (96,485 C/mol), R , the gas constant (8.314 J/K mol), and T , the temperature (K). The number of calculated electrons was 2.36, which is approximately equal to 2.

Electroanalysis of pyridoxine on the modified electrode

DPV profiles of PY in the concentration range of 5–950 μM in 0.1 M PBS (pH 5) using the PDAT/PGE is displayed in Fig. 5A. As seen from the figure, the oxidation peak currents of PY increase successively with the concentration.

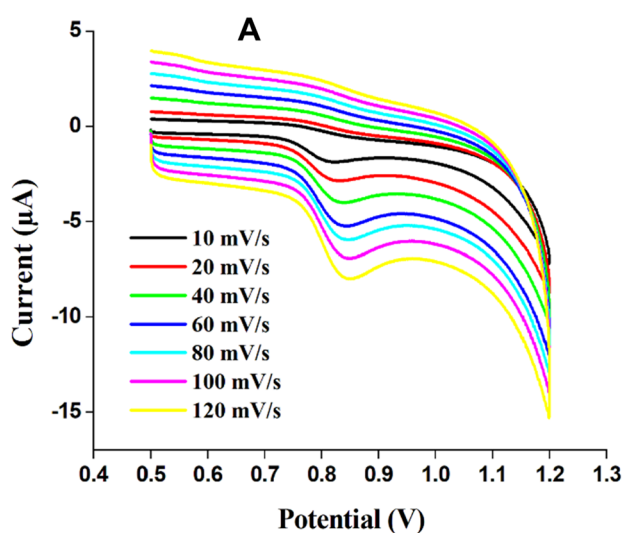


Figure 5B shows the calibration curve of different concentrations of PY obtained from the oxidation peak currents. The anodic peak current increased linearly with two slopes ranging from 5–450 μM and 450–950 μM , respectively, with a LOD of 2.96 μM at a signal-to-noise ratio of 3.

Interference studies

Selectivity is an important parameter to be studied in the development of electrochemical sensors, as this could identify the interfering species that may influence the analytical determination of analytes. DPVs of the PDAT/PGE in 0.1 M PBS pH 5 containing 50 μM PY with addition of NaCl (5 mM), KCl (5 mM), trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) (0.1 mM), MgSO_4 (0.1 mM), riboflavin (100 μM), folic acid (80 μM), ascorbic acid (80 μM), CaCl_2 (80 μM), FeCl_3 (80 μM), glucose (1.25 mM), and urea (5 mM) is presented in Fig. S8. The modified electrode showed a signal change of only less than 10% for the quantification of PY in the presence of excess amounts of the species mentioned above. Thus, the PDAT/PGE is selective for the electrochemical analysis of PY in real samples.

Reproducibility and stability studies

The reproducibility of the electrodes towards the electrooxidation of PY was measured from the DPV response of three independently fabricated electrochemical sensors in 0.1 M PBS pH 5. The RSD of the three electrodes' electrochemical response was calculated and was about 5.93%. Also, three different PDAT/PGE was kept in water in the refrigerator for 15 days, and the stability of the electrode was studied

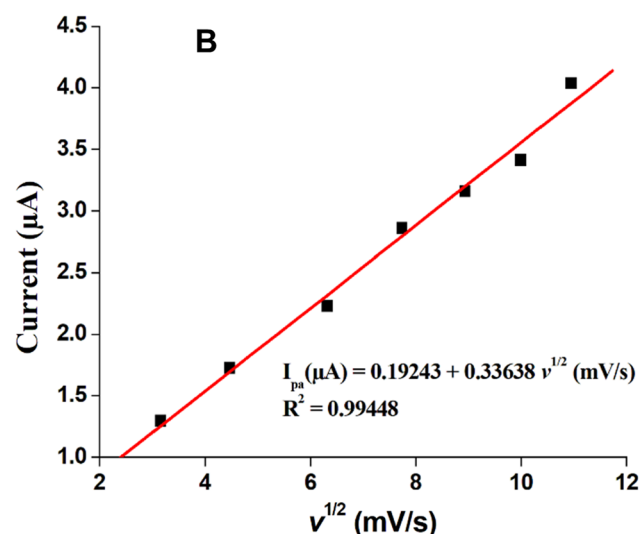


Fig. 4 A Effect of scan rates on the anodic peak currents for 50 μM PY on PDAT/PGE B linear plot for the anodic peak current towards the square root of scan rate

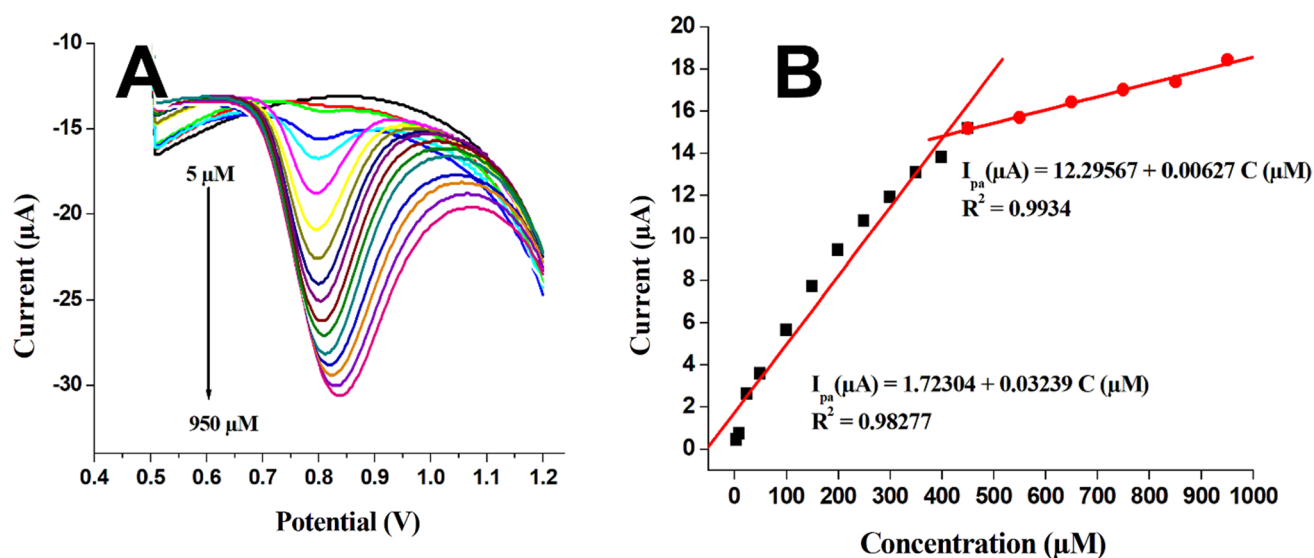


Fig. 5 **A** DPV response of the PDAT/PGE towards different concentrations of PY. **B** Calibration plot for PY in 0.1 M PBS pH 5

in 0.1 M PBS pH 5 containing 50 µM PY. The electrodes showed excellent stability with an RSD of 5.3%. Hence the modified electrode was proved to be highly efficient in developing an electrochemical device for the real-time monitoring of PY. The analytical performance of the PDAT/PGE and other recently reported electrochemical sensors for PY for the pharmaceutical application has been listed in Table 1 for comparison. Thus, the analytical performance of PDAT/PGE towards the electrochemical quantification of PY in

pharmaceutical samples is better than the reported sensors in Table 1.

Real sample analysis

The PDAT/PGE was applied for the analytical quantification of PY from commercially available vitamin B6 tablets using DPV at optimized conditions. The PY tablets were made into a fine powder, and a 5 mM tablet solution was

Table 1 Comparison table

Electrode	Electrolyte	Linear range (µM)	LOD (µM)	Storage stability	References
ssDNA/GCE	0.1 M NaOH	0.1–6000	40	–	Liu et al. (2012)
PGE	0.2 M NaOH	10–2500	7.06	–	David et al. (2015)
PGE	ABS pH 4	5–1000	2.81	–	David et al. (2015)
Au-CuO/GCE	PBS pH7	0.79–18.4	0.15	5 days	Kumar et al. (2015)
MWCNT-Mn Salen/GCE	PBS pH7	1–300	0.42	10 days	Sonkar et al. (2017)
La-Co ₃ O ₄ /SPE	PBS pH7	1–600	0.4	–	Nejad et al. (2019)
MWCNT/GCE	PBS pH7	8–1000	0.0028	30 days	Zeybek and Üğ̈e, (2021)
SnO ₂ -TiO ₂ /GCE	PBS pH7	0.1–31.4	0.035	–	Manoj et al. (2019)
ZnFe ₂ O ₄ /SPE	PBS pH7	0.2–350	0.07	15 days	Hengameh Zabolostani et al. (2021)
NiCo ₂ O ₄ -Zn/Al-LDH/GCE	PBS pH7	0.2–200	0.086	15 days	Amini and Asadpour-Zeynali (2020)
Zeolite-carbon black/GCE	PBS pH 6.6	0.3–5.9	0.09	–	Porada et al. (2021)
Magnetite/paper electrode	McIlvaine buffer pH 4.0	200–2000	29.5	–	Pereira et al. (2022)
Mesoporous carbon/SPE	PBS pH7	1–200	0.42	–	Apetrei et al. (2016)
Unmodified BDD	PBS pH 6	7–47	3.76	–	Kuzmanović et al. (2016)
Au/CPE	PBS pH 2	1.9–257	0.074	15 days	Motaghedifard et al. (2016)
MIP/carbon fiber paper electrode	PBS pH 3	0.6–700	0.01	15 days	Cherian et al. (2021)
PDAT/PGE	PBS pH 5	5–950	2.96	15 days	This work

Table 2 Analytical application of the developed sensor in pharmaceutical samples with spiked PY concentrations ($n=3$)

Sample	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
Sample 1	25	23.36	93.45	3.48
Sample 2	50	51.15	102.30	7.11
	25	24.28	97.1	7.19
	100	105.7	105.7	2.94

prepared by transferring a suitable amount of powdered tablet into 10 mL of deionized water. Then two different concentrations of the tablet solutions were spiked into PBS pH 5, and the recoveries of the tablet from the spiked solutions were estimated (Table 2).

Conclusion

Pencil graphite electrode, PGE modified with poly 3,5-diamino 1,2,4- triazole (PDAT) were prepared and used for the electrochemical determination of pyridoxine, PY in phosphate buffer solution. Electropolymerization technique was employed for the modification process and to our knowledge this is the first work reporting the electropolymerization of DAT on PGE surface. Cyclic voltammetry and differential pulse voltammetry were used for the analytical determination of PY. The developed sensor has advantages such simple fabrication procedure, cost effectiveness, wide linear range, good selectivity, etc. for the electrochemical quantification of PY. The remarkable stability and reproducibility make the proposed method a promising tool for the determination of PY in pharmaceutical samples. Moreover, the electrode was also favourably employed in the monitoring of PY in pharmaceutical samples with acceptable range of recoveries.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11696-023-02777-5>.

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Author's contribution SA contributed to Proposed the topic, conducted experiments, organized data, and wrote the original draft. BS contributed to supervised the experiments, scrutinized the data, and edited the whole manuscript.

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Declarations

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

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