

## Electrochemical Activation of Screen Printed Carbon Electrode for the Determination of Antibiotic Drug Metronidazole

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Metronidazole (MTZ) is a potential drug for the treatment of antibiotic and antiprotozoal medications. However, the drug over dosage or contaminated water from the drug industry makes the human to fatal disease. Therefore, in this work we have concentrated the determination of metronidazole by the electrochemical technique. Thereby, we have utilized the activated screen printed carbon electrode (ASPCE) for the determination. This electrode was prepared by simple electrochemical cyclic voltammetry technique. Wherein, the SPCE was pre-anodized in the phosphate buffer solution and directly used for the determination. This electrode provides the better performance when compared with bare electrode. Moreover, it provides the selective and sensitive determination towards the MTZ with linear concentration ranges 0.05 - 563  $\mu\text{M}$ ; 753 - 2873  $\mu\text{M}$  and the lowest detection limit 0.01  $\mu\text{M}$ . The developed disposable sensor electrode is low cost and revealed high repeatability and reproducibility.

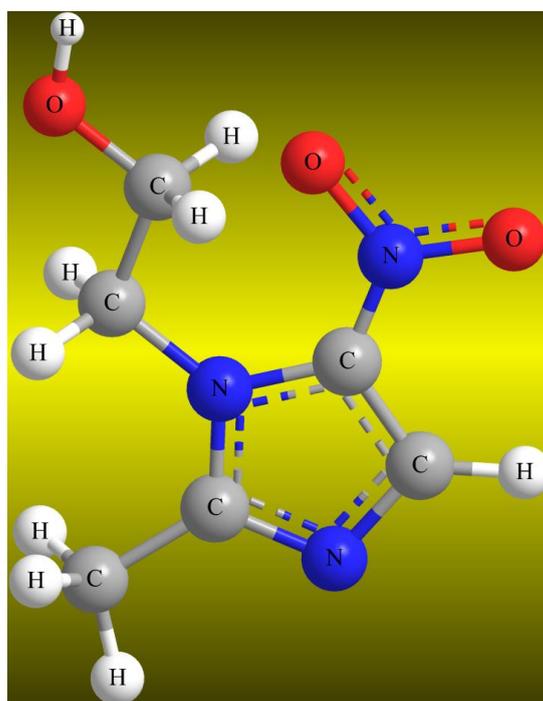
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**Keywords:** Antibiotic drug, Metronidazole, Electrochemical detection, ASPCE

### 1. INTRODUCTION

Metronidazole (1-(2hydroxyethyl)-2methyl-5nitroimidazole, MTZ) is one of the nitroimidazole antimicrobial drug [1, 2] used for the medication of dracunculiasis, giardiasis, trichomoniasis [3] and amebiasis [4, 5]. It is also used for the elimination of parasites additives in

poultry and fish. However, the over dosage of metronidazole leads to mutagenic and carcinogenic [6, 7] and also will cause seizure, optical neuropathy, neutropenia, encephalopathy. Furthermore, the widespread use of metronidazole is becoming the adversary to the ground water and soil. Hence, monitoring the MTZ in environment is attaining more important to save living beings from the deadly diseases. Several analytical techniques has been reported for the determination of MTZ from biological samples such as polarography, high-performance liquid chromatography (HPLC)[8-10] gas chromatography [11, 12] mass spectrometry (GC-MS), spectrophotometry, liquid chromatography, supercritical fluid chromatography [13], fluorescent spectrophotometry [14], ultraviolet spectrometry [15], thin layer chromatography [16]. Due to the high cost, difficulty in handling, less selectivity and sensitivity restricts the extensive applications of aforementioned techniques. Therefore, the electrochemistry has emerged to determine the MTZ with highly sensitive and selective way. Here also, some problem arises with the use of working electrode such as stability, catalytic activity and reproducibility. Previously, some research groups were developed a noble metal nanoparticles (platinum, gold, iridium metal) based enzyme mimetic sensor which exhibits highly selective for the MTZ detection, however they were cost effective. Similarly, some other research group have developed the mimetic enzyme based molecularly imprinted polymer matrix for the detection of MTZ, but the use of polymer minimizes the catalytic activity. Owing to the biodegradable, poor soluble and high thermal stability properties, the biopolymer chitosan was composite with metal-carbon matrix for the MTZ sensor. However, the trimethylchitoson based biopolymer has been exposed to transfect breast cancer cell. Therefore, the enzymatic determination of MTZ based on mimetic enzyme, polymer or biopolymer was fallen down due to the aforementioned disadvantages. So we need a low cost, highly selective and disposable sensor electrode for detection of MTZ. The chemical structure of MTZ is shown in Fig.1



**Figure 1.** The chemical structure of MTZ (2-Methyl-5-nitroimidazole-1-ethanol)

Therefore we have concentrated on the screen printed carbon electrode (SPCE) for the electrochemical sensing of MTZ. In general, the SPCE was prepared by pyrolytic carbon with some polymer materials, which attracted in sensor field due to the low cost, easily available, accessible and reproducibility. However, the SPCE is electrochemically less active and selective because of its polymeric material which restricts the electron transfer reaction at electrode-electrolyte interface and minimizes the electron transfers kinetics. Mostly, the basal planes and edge planes of SPCE have shown the electrochemical behavior comparatively the edge planes are highly active. Therefore, the SPCE was electrochemically activated to improve the edge planes [17-20, 51, 52]. Zen, Compton and Prasad group have demonstrated the various activation process of SPCE and applied in different sensors [21-27]. Followed by their reports, present study we have activated SPCE by electrochemical treatment by using the cyclic voltmmogram (CV). The activated SPCE (ASPCE) was directly applied to the detection of MTZ which revealed the linear detection range 0.05 - 563  $\mu\text{M}$ ; 753 - 2873  $\mu\text{M}$  and the lowest detection limit 0.01  $\mu\text{M}$ . Moreover, the electrochemical kinetic behavior of MTZ at ASPCE was demonstrated in various pHs.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials

The metronidazole (MTZ), nilutamide (NIL) 4-nitrobenzene (4NB), flutamide (FLA), 4-nitroaniline (4-NA), 4-nitrophenol (4-NP), glucose (Glu), uric acid (UA), dopamine (DA), ascorbic acid (AA), glutaric acid (GA), sodium hydrogen phosphate ( $\text{NaHPO}_4$ ), sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) and all other chemicals were acquired from Sigma-Aldrich chemical Co., (USA) Alfa-Aeser (USA) and Fluka chemicals (Switzerland). The screen printed carbon electrode (SPCE; working area = 0.07  $\text{cm}^2$ ) was received from Zensor R&D Co., LTD, Taiwan.

### 2.2 Preliminary treatments

Anterior to the experiment, the SPCE was pre-cleaned with ethanol and water. After that SPCE was activated by performing CV in 0.05 M phosphate buffer (PB) solution between the potential window of -0.5 to 2 V for 10 cycles. Then activated SPCE (ASPCE) was rinsed with water and dried at room temperature. Then the resulting ASPCE was directly used for the further electrochemical studies.

### 2.3 Methods

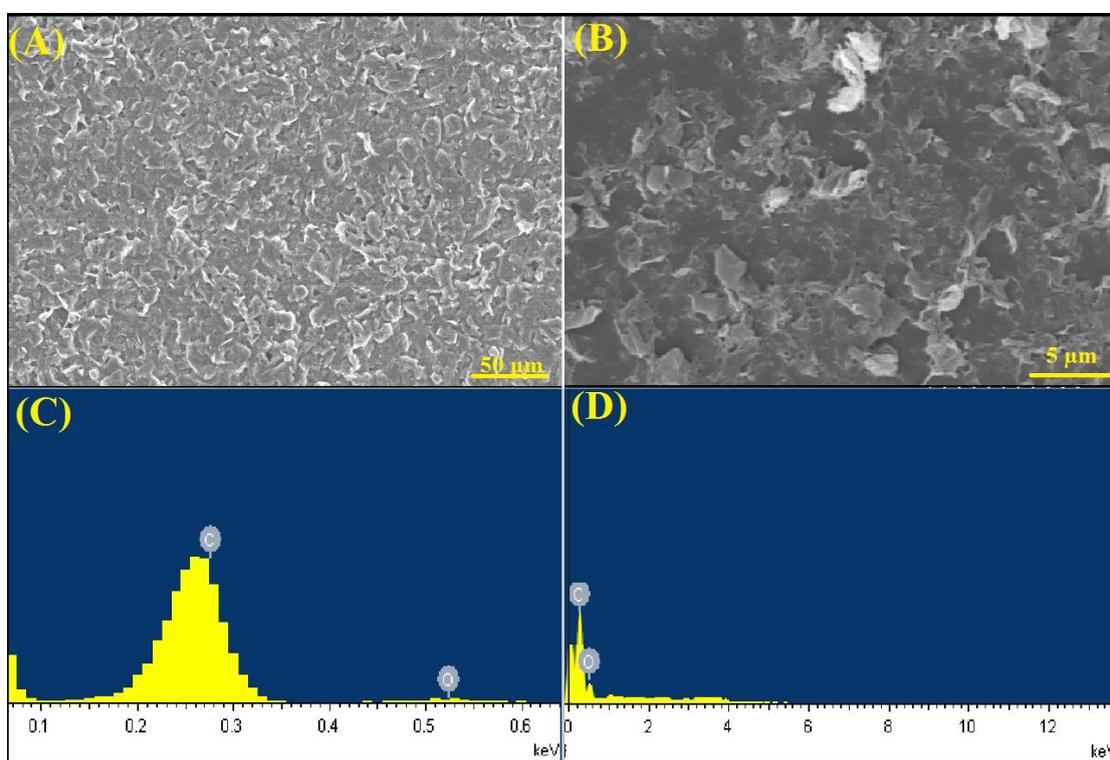
The surface morphological study was investigated by using scanning electron microscopy (SEM Hitachi S-3000 H). CV and differential pulse voltammetry (DPV) experiments were carried out using CHI 405a and CHI 900 electrochemical work station. Electrochemical studies were carried out in a typical three electrode system using bare SPCE and ASPCE as a working electrode (area 0.07  $\text{cm}^2$ ),

saturated Ag/AgCl (saturated KCl) as a reference electrode and platinum wire as a counter electrode. All the electrochemical measurements were carried out at room temperature.

### 3. RESULTS AND DISCUSSION

#### 3.1 Surface characterization of bare SPCE and ASPCE

SEM is one of the best tool to identify the structure and morphology of the materials. In order to we studied the surface morphology of the SPCE and activated SPCE by SEM analysis as it can be seen in Fig.2. Fig.2A shows the before activated SPCE surface which looks like aggregated flake-like morphologies with rough surface and its corresponding to the EDX spectrum is shown in Fig.2C. After the activation of SPCE in phosphate buffer solution, the morphologies was totally changed, which suggests that the SPCE was successfully activated and its corresponding to the EDX spectrum is shown in Fig.2D.

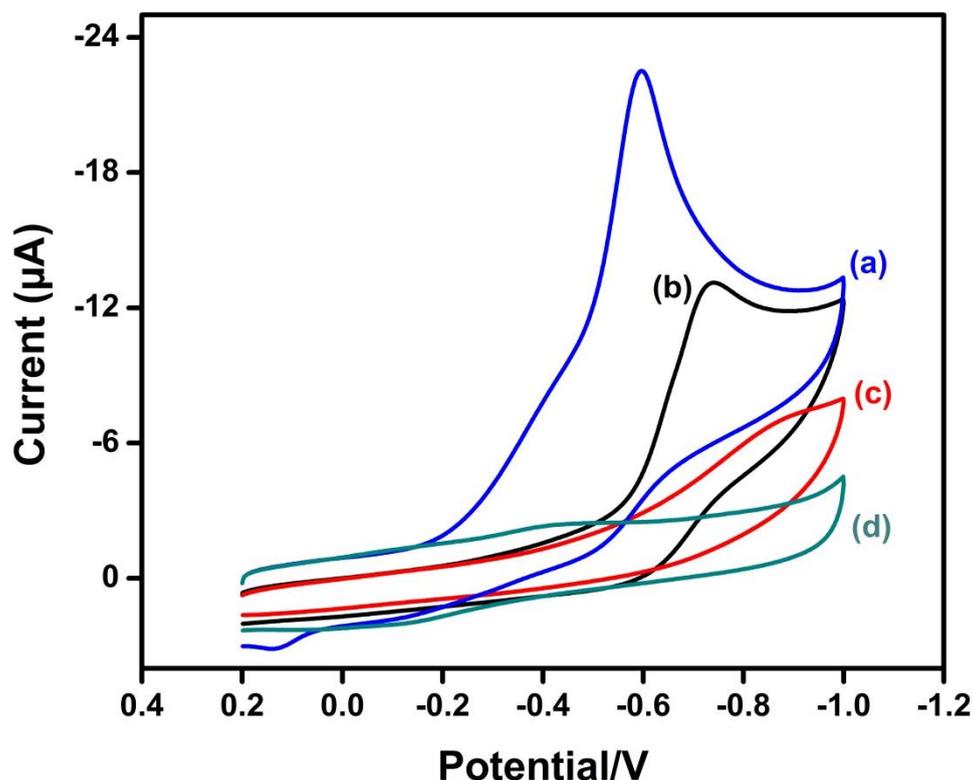


**Figure 2.** SEM images of (A) SPCE (B) ASPCE and corresponds to the EDX spectrum of C and D.

#### 3.2 Electrochemical behavior of metronidazole on the bare SPCE and ASPCE

Fig. 3 shows the CV responses of bare SPCE and ASPCE in the presence (b, a) and absence (c, d) of 200  $\mu$ M MTZ in 0.05 M phosphate buffer (PB) solution (pH 7) at scan rate of 50 mV/s. The bare SPCE and ASCPE show the different electrocatalytic behavior in the PB solution. The bare SPCE

shows low background current for the electrochemical double layer capacitance and then strong reduction behavior at high potentials. On the other hand, the ASPCE reveals good capacitance behavior with sharp cathodic peak current at the potential of  $-0.56$  V. This sharp cathodic peak current and lower potential is experienced from the electrochemically active oxygen functional groups. These active groups are highly participated in the reduction of MTZ.

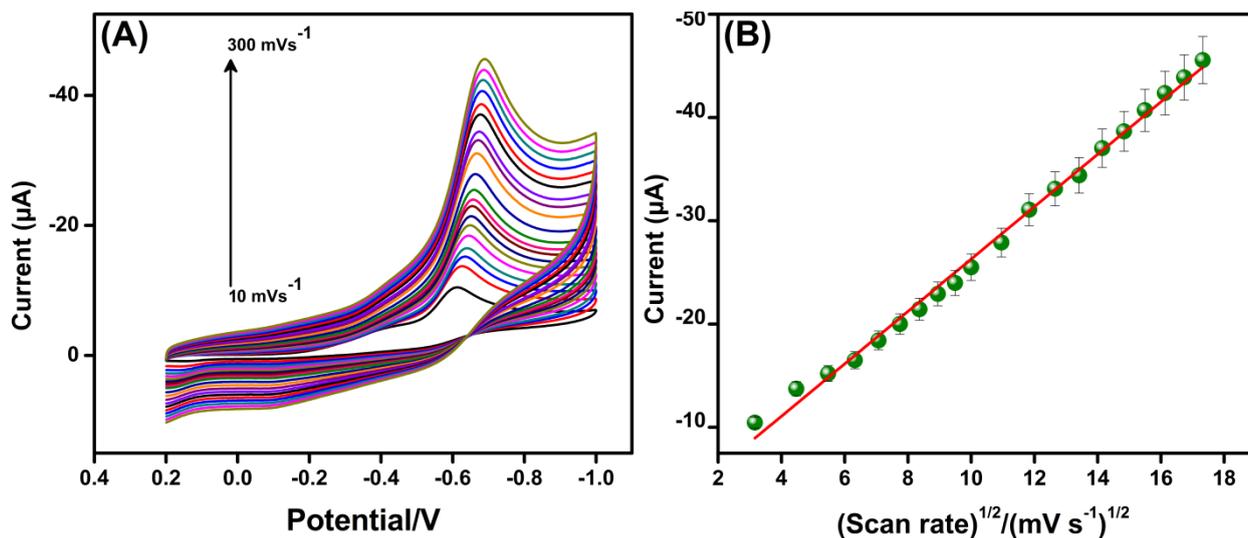


**Figure 3.** (A) CVs response of bare SPCE (b) ASPCE (a) in the presence of  $200 \mu\text{M}$  MTZ and bare SPCE (c) ASPCE (d) in the absence of MTZ at a scan rate of  $50 \text{ mV/s}$ .

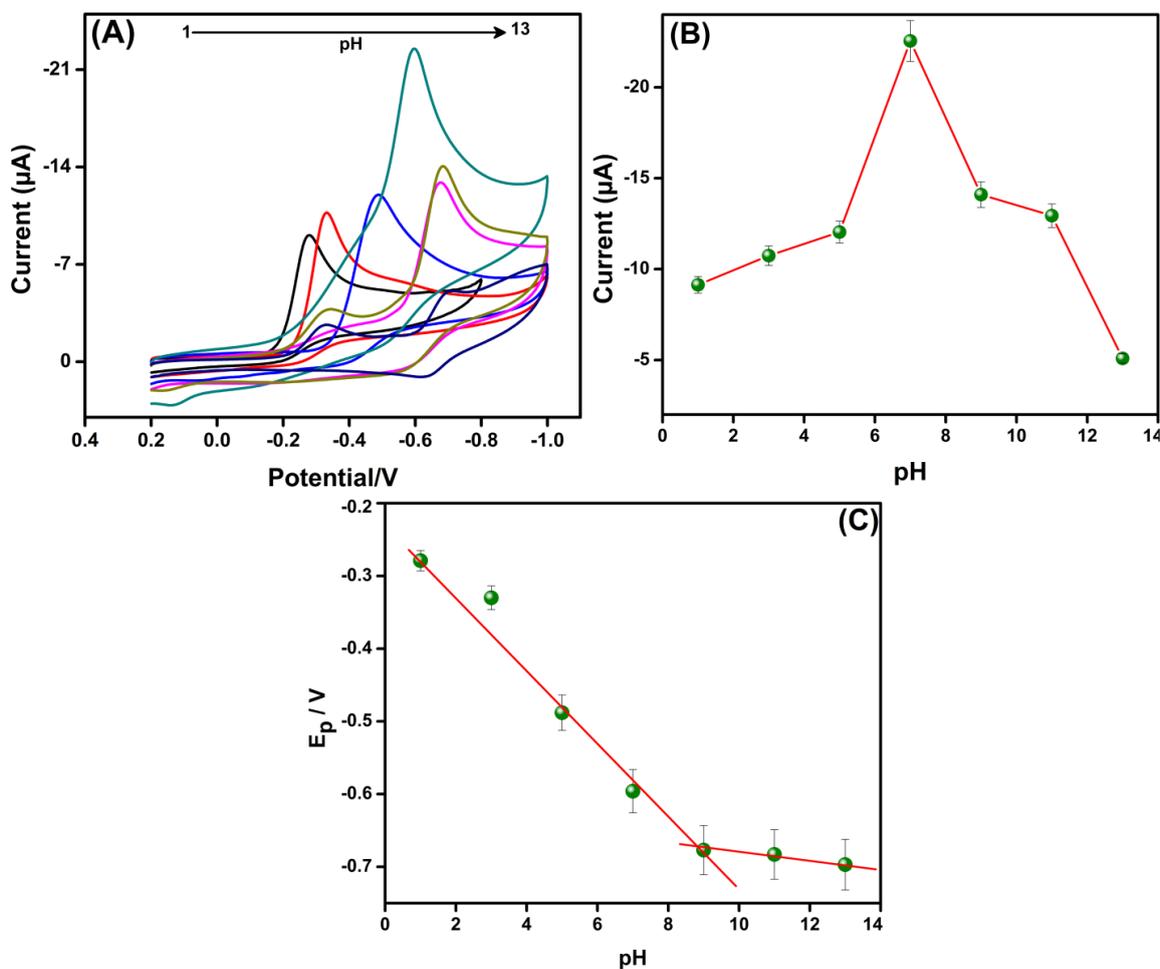
In Fig 3, the cathodic sweep indicates that reduction of MTZ to phenylhydroxylamine and the reverse scan rate there is no oxidation peak was observed corresponds to the reduction peak, which indicates irreversible electrochemical process. The ASPCE revealed the reduction peak potential is  $-0.58$  V whereas the bare SPCE showed  $-0.77$  V, and also the obtained cathodic peak current is much higher when compared to bare SPCE. The obtained result suggests that the ASPCE is more favorable and excellent electron mediator for the detection of MTZ than that of bare SPCE.

### 3.3 Effect of scan rate and pH

The effect of scan rate on the ASPCE was investigated by CV in the presence of  $200 \mu\text{M}$  MTZ containing  $0.05 \text{ M}$  PBS. The reduction peak current of MTZ is increased when increasing the scan rate from  $10$  to  $300 \text{ mV}$  (Fig. 4A) and the peak potential is slightly shifted to cathodic direction. This behavior indicated that the MTZ at ASPCE is irreversible reduction process.



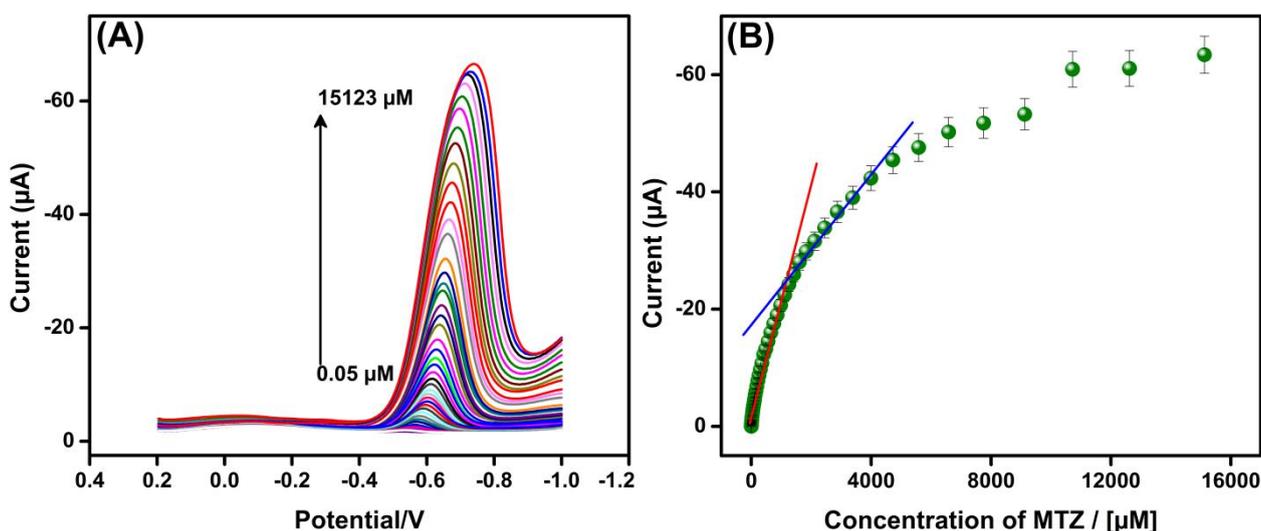
**Figure 4.** (A) CV responses of ASPCE in the presence of 200 μM MTZ with various scan rates ranging from 10 to 300 mV/s. (B) The corresponding linear plot for the reduction peak vs. square root of the scan rate for MTZ.



**Figure 5.** (A) CV responses of ASPCE in the presence of 200 μM MTZ for the various pH from (1-13). (B) The relationship between pH and reduction peak current of MTZ. (C) The linear plot between peak potential vs. different pH value.

The resultant peak current was plotted with respect to the square root of scan rate which gives a good linearity (Fig.4B). Hence, we have confirmed the reduction of MTZ is diffusion controlled process. The pH of the electrolyte solution plays vital role in the electrochemical reaction so we have studied the MTZ reduction in different pH solutions (pH 1– 13) at ASPCE with 200  $\mu\text{M}$  of MTZ. Fig.5 shows CV responses of MTZ reduction peak for all pH solutions with different current intensity. Amidst the other pH, a sharp peak with high current response was observed in pH 7. Fig 5(C) shows the plot of peak potential vs. pH which shows two linearity for pHs 1-9 and 9-13. The first linear equation is almost equal to the Nernstian behavior which means the equal number of electrons and protons are transferred from 1-(2hydroxyethyl) – 2 methyl 5 nitroimidazole to 1 – (2hydroxyethyl) – 2methyl 5 hydroxyamide imidazole. In higher pHs (9 to13), the ASPCE doesn't responded for the reduction of MTZ. The peak current also decreased when increasing pH from 9 to13. This behavior indicated that the MTZ have high activity at lower pHs because the number proton  $\text{H}^+$  is higher in lower pHs. This protons are quenches the nitrogroup and facilitates to fast reduction at low overpotentials. However, at higher pH value the number of proton is low thereby the nitrogroup doesn't allows to reduce fast. Moreover, the pH of the electrolyte is no longer active at higher pHs. Fig 5B shows the plot of peak current vs. pH wherein the pH 7 only shows high electrocatalytic current thereby we have chosen pH 7 for the further studies.

### 3.4 Determination of MTZ



**Figure 6.** (A) DPV s of MTZ at ASPCE in 0.05 M PBS with various concentrations from 0.05-15123  $\mu\text{M}$  (B) Linear plot of peak current vs. concentration of MTZ.

Differential pulse voltammetry (DPV) is very powerful techniques and it has better resolution and much higher current sensitivity compared to conventional CVs. So, we chose DPV technique for the determination of MTZ. Fig.6A reveals the DPV response of various concentration of MTZ (from 0.05 to 15123  $\mu\text{M}$ ) at activated SPCE containing 0.05 M PBS. A well-defined cathodic peak current was observed even in the very lowest addition of MTZ (0.05  $\mu\text{M}$ ) at the potential of  $-0.56\text{ V}$ , and the

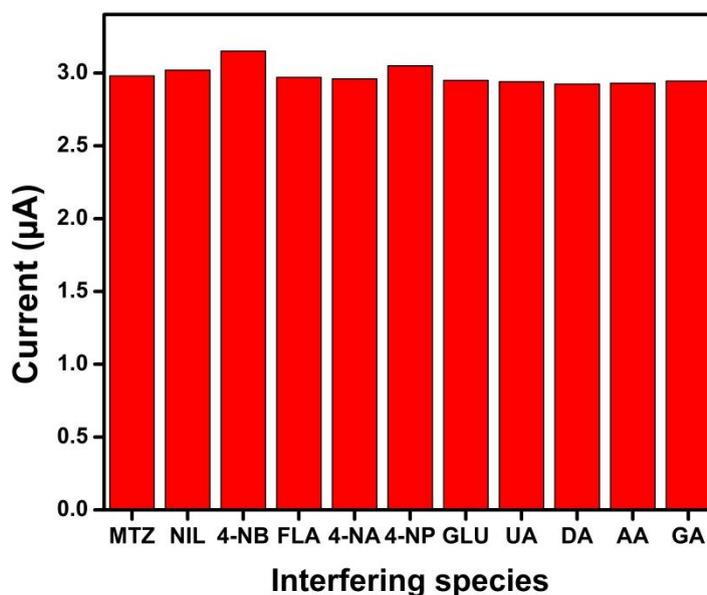
cathodic peak current is linearly increases with increasing the concentration of MTZ from lower to higher concentration. Moreover, the increasing the concentration of MTZ the peak potential was also shifted to more negative potential. From the Fig.6A, the calibration plot was derived and it can be seen in Fig.6B. From the calibration plot two linear ranges were obtained. The first linear range with higher sensitivity was obtained from 0.05 to 563  $\mu\text{M}$ , with a linear regression equation of  $I_{pc} (\mu\text{A}) = 0.0274x + 0.835$  with a correlation coefficient of  $R^2 = 0.972$  and the second linear range was 753 -2873  $\mu\text{M}$ , with a linear regression equation of  $I_{pc} (\mu\text{A}) = 0.041x + 14.554$  with a correlation coefficient of  $R^2 = 0.981$ . From the plot of lower linear concentration, the limit of detection (LOD) was calculated to be 10 nM. These two linear ranges phenomenon was already reported previously [28-33 (other modified electrodes with two linear ranges), 40, 50, (MTZ)]. It may be caused by the rapid formation of reduction products of MTZ formed on the ASPCE surface. When the MTZ concentration is high, a huge amount of reduction products was formed on the surface of the ASPCE, which prevented the adsorbing and reduction of MTZ; this is may be reason for the sensitivity was decreased. However, we achieved very lower LOD and good linear response range for the detection of MTZ. The obtained analytical parameters such as LOD and wide linear response ranges, which are very comparable with the other modified electrodes available on the previously reported towards the detection of MTZ and the results, are listed in Table 1. It is obvious that the LOD, wide linear response of the ASPCE is comparable results for previously reported various modified electrodes for MTZ determination. Hence, the ASPCE is more suitable for the sensitive electrochemical determination of MTZ sensor.

**Table 1** Comparative study of ASPCE for MTZ detection with other electrodes

Electrode	LOD (nM)	Linear range ( $\mu\text{M}$ )	Ref.
HMDE	36	0.23-1.8	[34]
Gr-IL/GCE	47	0.1-25	[35]
SWCNT/GCE	63	0.1-200	[36]
Pt nanosphere/polyfurfural film/GCE	50	2.5-500	[37]
3D gold nanotube/CPE	63	0.1-200	[38]
Copper-poly(cysteine)GCE	370	0.5-400	[39]
p-GR-Ag/GCE	28	0.05-10 and 10-4500	[40]
Graphene/ionic liquid/GCE	47	0.1-25	[41]
Poly(chromotrope 2B)/GCE	330	10-400	[42]
MWCNTs/CTS-Ni/GCE	25	0.1-150	[43]
SWCNT-IL/CPE	12 ( $\mu\text{M}$ )	50-5000	[44]
DMIP/CPE	91	0.4-200	[45]
$\alpha$ -Cyclodextrin/CPE	20	0.5-103	[46]
BDD electrode	65	0.2-4.2	[47]
CP electrode	29	1-500	[48]
$\beta$ -CD-GNPs/poly(1-cys)/GCE	14	0.1-600	[49]
Pretreated Au electrode	150	0.5-10 and 20-800	[50]
ASPCE	10	0.05-563 and 753-2873	This work

### 3.5 Interference study

The selectivity is very important study for the newly developed electrochemical sensor. In order to investigate, the selectivity of the ASPC electrode is evaluated with 10-fold excess concentration of potentially co-interfering nitro compounds such as nilutamide (NIL), 4-nitrobenzene (4NB), flutamide (FLA), 4-nitroaniline (4NA), 4-nitrophenol (4NP), glucose (Glu), uric acid (UA), dopamine (DA), ascorbic acid (AA), glutaric acid (GA) were selected for the selectivity studies as it can be seen Fig.7. From the Fig.7, there is no considerable peak current change being observed even in the 10fold excess concentration aforementioned interfering compounds, which suggests that the prepared ASPCE has good anti-interference ability. Therefore, the proposed ASPC electrode is good selective manner for MTZ detection and it is identified as the better electrode for practical applications.



**Figure 7.** The calibration plot of MTZ reduction in the presence of co-interfering compounds; NIL, 4-NB, FLA, 4-NA, 4-NP, GLU, UA, DA, AA, GA containing 0.05 M PBS (pH 7)

### 3.6 Repeatability and stability studies

The CVs were chosen for the repeatability and stability studies. For the storage stability studies, the ASPCE in presence of 50 µM MTZ have been taken and the cathodic peak current was monitored periodically in two weeks. Only 8 % of cathodic peak current response was decreased from its original peak current response after two week, which suggests good storage stability of the ASPC electrode. For the repeatability studies, we have carried out in a single ASPCE for 5 consecutive measurements with RSD of 2.18 %, suggesting its appreciable repeatability of the sensor.

#### 4. CONCLUSION

In summary the ASPCE is successfully prepared by the electrochemical activation process and applied to the determination of MTZ. This electrode is highly stable and sensitive to the determination of MTZ when compared with bare SPCE. Moreover, the electrochemical behavior of MTZ was demonstrated in various pHs at ASPCE. The developed disposable sensor electrode exhibited the wide linear range and lowest detection limit. This result is supported the developed sensor electrode is suitable for the commercial applications. Moreover, the developed ASPCE provides good selectivity, high stability, reproducibility and lower detection limit.

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