

PAPER • OPEN ACCESS

## Voltammetric Study of Ascorbic Acid Using Polymelamine/Gold Nanoparticle Modified Carbon Paste Electrode

To cite this article: A N Farida *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **217** 012004

View the [article online](#) for updates and enhancements.

You may also like

- [Nano-Impact Single-Entity Electrochemistry Enables Plasmon-Enhanced Electrocatalysis](#)  
Sagar Ganguli, Ziwen Zhao, Onur Parlak et al.
- [Near-Infrared Light-Excited Photoelectrochemical Biosensing Platform for MC-LR in Aquatic Products Based on Ag<sub>2</sub>S Cubes](#)  
Chenyang Zheng and Xiaomei Chen
- [Voltammetric Sensing of Endocrine Disruptor \(Bisphenol A\) Based on a Reduced Graphene Oxide/Carbon Nanotube/Gold Nanoparticles Nanocomposite Modified Screen-Printed Electrode](#)  
Yi-Cheng Wang, Dilek Cokeliler and Sundaram Gunasekaran

**DISCOVER**  
how sustainability  
intersects with  
electrochemistry & solid  
state science research

# Voltammetric Study of Ascorbic Acid Using Polymelamine/Gold Nanoparticle Modified Carbon Paste Electrode

A N Farida<sup>1</sup>, E Fitriany<sup>1</sup>, A Baktir<sup>1</sup>, F Kurniawan<sup>2</sup>, M Harsini<sup>1\*</sup>.

<sup>1</sup>Department of Chemistry, Faculty of Science and Technology, Universitas Airlangga, Kampus C Mulyorejo, Surabaya 60115, Jawa Timur, Indonesia

<sup>2</sup>Department of Chemistry, Faculty of Natural Science, Institut Teknologi Sepuluh Nopember, Jl. Raya ITS, Keputih, Sukolilo, Surabaya 60111, Jawa Timur, Indonesia

\* muji-h@fst.unair.ac.id

**Abstract.** Polymelamine/gold nanoparticle modified carbon paste electrode (PM/AuNPs/CPE) has been developed for voltammetric study of ascorbic acid (AA). The PM/CPE was prepared onto carbon paste electrode surface via electropolymerization, then it has been deposited gold nanoparticle (AuNPs) via electrodeposition for PM/AuNPs/CPE. In pH 7.0 phosphate buffer, PM/AuNPs/CPE was oxidized during the cyclic potential sweep between 0.0 V and 1.5 V, forming polymer and gold nanoparticle at the carbon paste electrode (CPE) surface. The electrochemical behavior of ascorbic acid at the bare CPE, PM/CPE, AuNPs/CPE and PM/AuNPs/CPE were investigated. The oxidation peak potential of ascorbic acid shifts to more negative potential at PM/AuNPs/CPE. Moreover, the oxidation peak current significantly increases at PM/AuNPs/CPE. The PM/AuNPs/CPE electrode exhibits a quasi-reversible electron with a peak separation 130 mV. These phenomena indicate that PM/AuNPs/CPE shows highly-efficient catalytic activity to the oxidation of ascorbic acid.

**Keywords:** PM/AuNPs/CPE, Ascorbic Acid, Voltammetric Study

## 1. Introduction

Ascorbic acid (also called vitamin C) is an important water-soluble vitamin that widely distributed in fresh fruits and leafy vegetables. In the body, ascorbic acid is necessary for producing collagen, a protein that gives structure to bones, cartilage, muscle and blood vessels [1]. It is believed to be the primary antioxidant in human blood plasma. Otherwise, severe deficiency of ascorbic acid cause scurvy with following symptoms such as follicular hyperkeratosis, loosening of teeth, loss of hair as well as dry itchy skin and takes part in several biological reactions [2]. Therefore, it is very important and interesting to study electrochemical behavior of ascorbic acid. Various approaches have been made to study voltammetry of ascorbic acid, for example voltammetric studies of ascorbic acid using an oracet blue modified glassy carbon [3], a cyclic voltammetric study of ascorbic acid using polyglycine modified carbon paste electrode [4], and poly(glutamic acid) modified carbon paste electrode [5], and graphene oxide/gold nanoparticle [6], carbon nanotube paste electrode [7], and carbon nanotubes-ionic liquid gel modified electrode [8], and TX-100 modified carbon paste electrode [9] but they explained incomplete voltammetric study of ascorbic acid, so we describe a cyclic voltammetric studies of ascorbic acid include pH and scan rate.

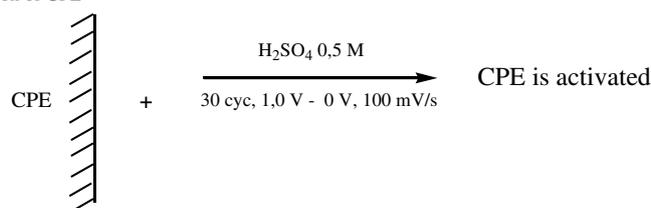
Electrochemical methods for the determination of ascorbic acid are more selective, less expensive, and less-time consuming than other methods [10]. Carbon based electrodes are among the most commonly used in voltammetric determination because of their low cost, wide potential windows, low electrical resistances, and versatility of chemical modification. The use of carbon paste as an electrode has been applied in the preparation for several purposes such as electrochemical sensors for the analysis of biologically important compounds [11].

The main objective of this work is to study electrochemical behavior of ascorbic acid utilizing the

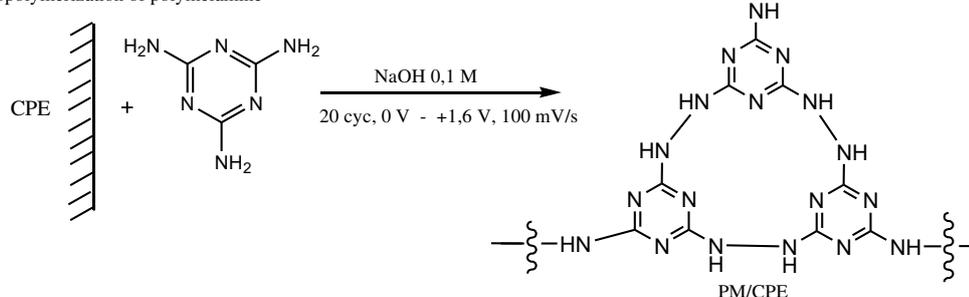


excellent properties of polymelamine/gold nanoparticle modified carbon paste electrode (PM/AuNPs/CPE). To do so, polymelamine was electrochemically polymerized at the surface of carbon paste electrode (CPE). After that, Gold nanoparticles deposited at the surface of PM/CPE via electrodeposition. The electrochemical behaviors of ascorbic acid were examined at the bare CPE, PM/CPE, AuNPs/CPE, and PM/AuNPs/CPE. From the comparison, it was found that oxidation peak potential of ascorbic acid remarkably shifts negatively at the PM/AuNPs/CPE, indicative of highly-efficient catalytic ability. Besides, the oxidation peak current of ascorbic acid significantly increases at the PM/AuNPs/CPE. This unique combined properties of polymelamine and gold nanoparticles are result into the high catalytic activity of ascorbic acid detection, and this proposed electrochemical sensor was further explored for practical application in the detection of ascorbic acid in urine sample.

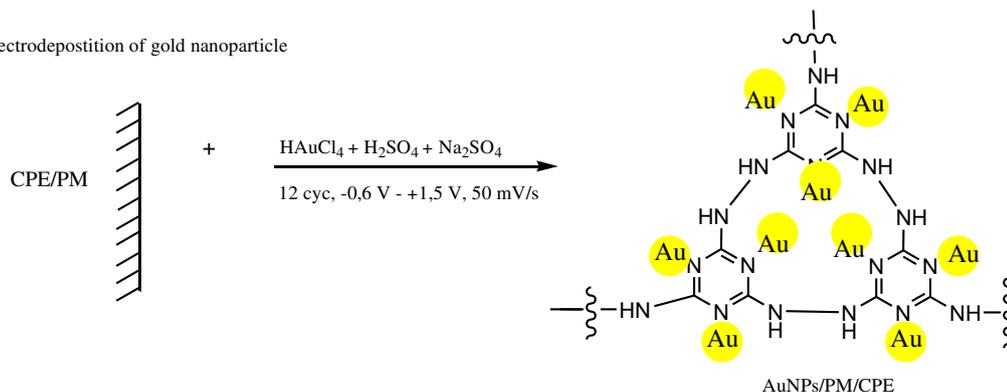
#### Step 1 Activation of CPE



#### Step 2 Electropolymerization of polymelamine



#### Step 3 Electrodeposition of gold nanoparticle



Scheme 1. Proposed reaction of activation of CPE, electropolymerization of melamine and electrodeposition of gold nanoparticle on the surface of carbon paste electrode

## 2. Experimental Method

### 2.1 Reagents and material

All the chemicals were of analytical-reagent grade and used directly without further purification. Carbon nanopore was purchased from Puslitbang Bogor (Indonesia). Melamin was purchased from Merck, ascorbic acid was purchased from Sigma, hydrogen tetrachloroaurate ( $\text{HAuCl}_4$ ) was dissolved gold granule by aqua regia ( $\text{HCl}:\text{HNO}_3 = 3:1$ ). Phosphate buffer solution 0,1 M with variations pH were prepared by mixing stock solution of  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ , and adjusting with  $\text{NaOH}$  or  $\text{H}_3\text{PO}_4$ . Ultra high pure water (UHP) was used for all experiments.

### 2.2 Apparatus

All electrochemical experiments were performed with a model 201 electrochemical analyzer (Edaq e-corder 201) with a conventional three-electrode system. The working electrode was a carbon paste electrode, platinum wire as the auxiliary electrode, and  $\text{Ag}/\text{AgCl}$  as the reference electrode. Voltammetry Cyclic experiments employed from 0.0 V to +1.5 V. During all the experiments, the ascorbic acid solution was prepared freshly. The scanning electron microscopy (SEM) was used to see surface morphology electrode.

### 2.3 Preparation of bare carbon paste electrode

The carbon paste electrode was prepared by mixing 70:30 carbon nanopore:paraffin pastilles in watch glass to get homogeneous carbon paste. Then the paste entered into micro tip. Then, the carbon paste electrode was polished on a piece glossy paper to get equal surface. After that, carbon paste electrode was saved 24 hours. Before measurement, the carbon paste electrode was electrochemically cleaned by cyclic voltammetry, the potential between 0.0 V to 1.0 V vs  $\text{Ag}/\text{AgCl}$  in  $\text{H}_2\text{SO}_4$  0,5 M at scan rate 100 mV/s and 30 cycle (Scheme 1).

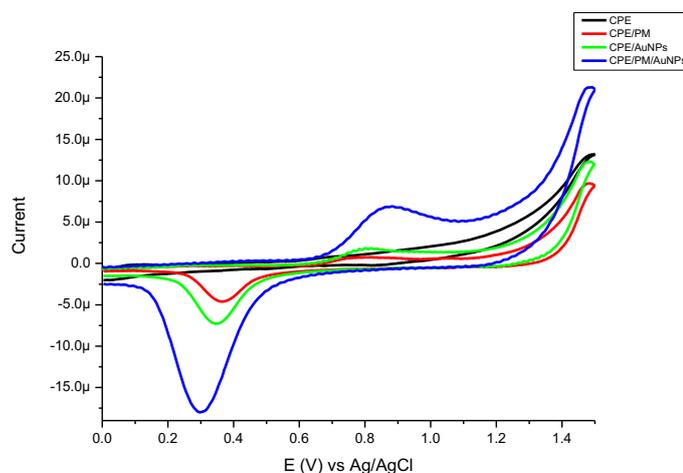
### 2.4 Preparation of modified electrode (PM/AuNPs/CPE)

The polymer-modified electrode at surface CPE was treated with cyclic voltammetry in the potential range of 0.0 – 1.6 V at 100 mV/s for 20 cycles in 1 mM melamine (0.1 M NaOH). After that, PM/CPE was save for 24 hours (Scheme 1). Then, the PM/CPE was deposited by electrodeposition of gold nanoparticles with cyclic voltammetry in the potential range of -0.6 – 1.5 V at 50 mV/s for 12 cycles in 6 mM  $\text{HAuCl}_4$  (0.1 M  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$ ). Finally, PM/AuNPs/CPE was washed with UHP to removed the physically adsorbed material (Scheme 1).

## 3 Results and Discussion

### 3.1 Electrochemical behaviors of Ascorbic Acid

The electrochemical behaviors of ascorbic acid were studied using cyclic voltammetry at different electrodes. Figure 1 shows the cyclic voltammogram from ascorbic acid analysis was carried out in ascorbic acid solution with a concentration of 0.2 mM in a pH 7 phosphate buffer solution at a potential range of 0.0 V to +1.5 V and a scan rate of 100 mV/s at bare CPE, PM/CPE, AuNPs/CPE, and PM/AuNPs/CPE. The anodic peak potential value ( $E_{pa}$ ), cathodic peak potential ( $E_{pc}$ ), anodic peak current ( $I_{pa}$ ), cathodic peak current ( $I_{pc}$ ) and the separation of peak potential ( $\Delta E_p$ ) values can be determined by figure 1.  $E_{pa}$ ,  $E_{pc}$ ,  $I_{pa}$ ,  $I_{pc}$ , and  $\Delta E_p$  of 0.2 mM ascorbic acid analysis are shown in Table 1.



**Figure 1.** Cyclic voltammogram of 0.2 mM ascorbic acid in pH 7 phosphate buffer in bare CPE, PM/CPE, AuNPs/CPE, and PM/AuNPs/CPE

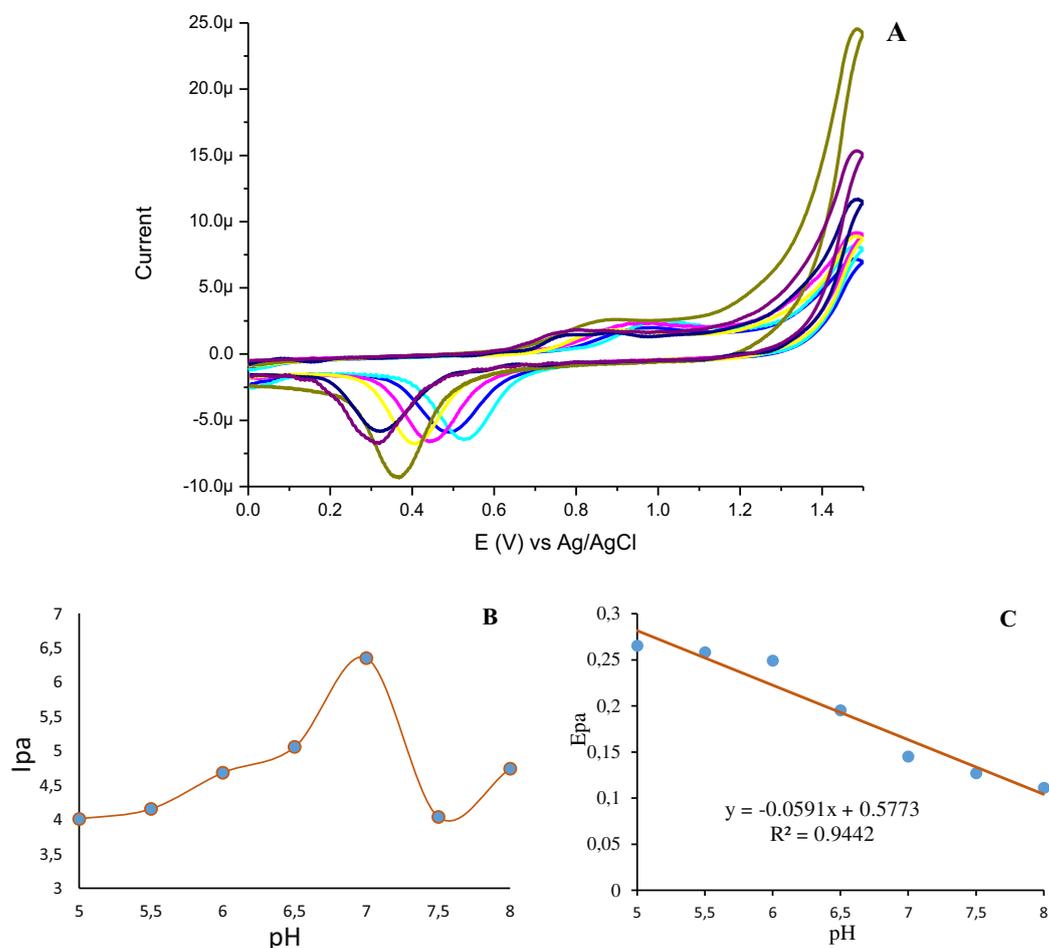
**Table 1.** The effect of variation of electrode types on analysis with 0.2 mM ascorbic acid solution on pH 7 phosphate buffer

Electrode	$I_{pa}$ ( $\mu\text{A}$ )	$E_{pa}$ (V)	$I_{pc}$ ( $\mu\text{A}$ )	$E_{pc}$ (V)	$\Delta E_p$ (V)
CPE	0.621	0.200	4.294	0.400	0.200
PM/CPE	0.767	0.477	4.623	0.350	0.127
AuNPs/CPE	1.666	0.408	7.121	0.270	0.138
PM/AuNPs/CPE	4.820	0.389	15.867	0.259	0.130

Based on the Table 1. It can be seen that the values of  $I_{pa}$  and  $I_{pc}$  on ascorbic acid analysis with modified electrode has a higher peak current than without modification. In Figure 1, the cyclic voltammogram of bare CPE is smaller (lowest current response) indicates that electron transfer on the electrode surface is very slow. PM/CPE has current higher than bare CPE, this is due to the presence of amine groups that interact with ascorbic acid. But, AuNPs/CPE has current higher than the bare CPE or PM/CPE electrodes because of AuNPs which provide better conductivity as a mediator of the electron transfer process. The modification polymelamine and gold nanoparticles catalyzes the ascorbic acid oxidation [12]. If we compare all of the electrodes, the result shows that modified electrode has the highest  $I_{pa}$  and  $I_{pc}$  and the lowest  $\Delta E_p$  is PM/AuNPs/CPE.  $I_{pa}$  and  $I_{pc}$  values of PM/AuNPs/CPE produced seven times and four times higher than bare CPE. On the other hand, PM/AuNPs/CPE was chosen because it has heteroatoms such as nitrogen present in the conducting polymers interact with metal nanoparticles to form a complex to stabilize the nanoparticles because its high stability and abundant nitrogen functional groups [12,13].

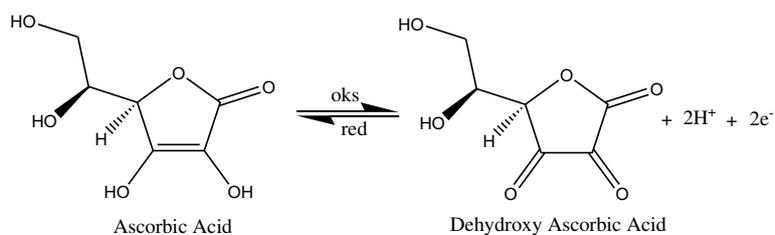
### 3.2 Effect of pH

The electrochemical reduction of ascorbic acid in pH 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, and 8.0 phosphate buffer ( $0.1 \text{ mol l}^{-1}$ ) was studied. Figure 2 (A) shows the cyclic voltammogram of ascorbic acid at PM/AuNPs/CPE with pH values. Figure 2 (B) insert shows curve the effect of pH value on the oxidation peak current of ascorbic acid ( $I_{pa}$ ). When pH value gradually increases from 5.0 to 7.0, the oxidation peak current of ascorbic acid also gradually increases. As further increasing the pH value from 7.5 to 8.0 the reduction peak current slightly decreases. Thus, pH 7.0 phosphate buffer was used for the optimal pH of ascorbic acid.



**Figure 2.** (A) Cyclic voltammogram of ascorbic acid  $2.10^{-4}$  mol  $l^{-1}$  with pH values; (B) Curve the anodic peak current ( $I_{pa}$ ) of ascorbic acid vs pH; (C) Curve anodic potential ( $E_{pa}$ ) of ascorbic acid and pH values).

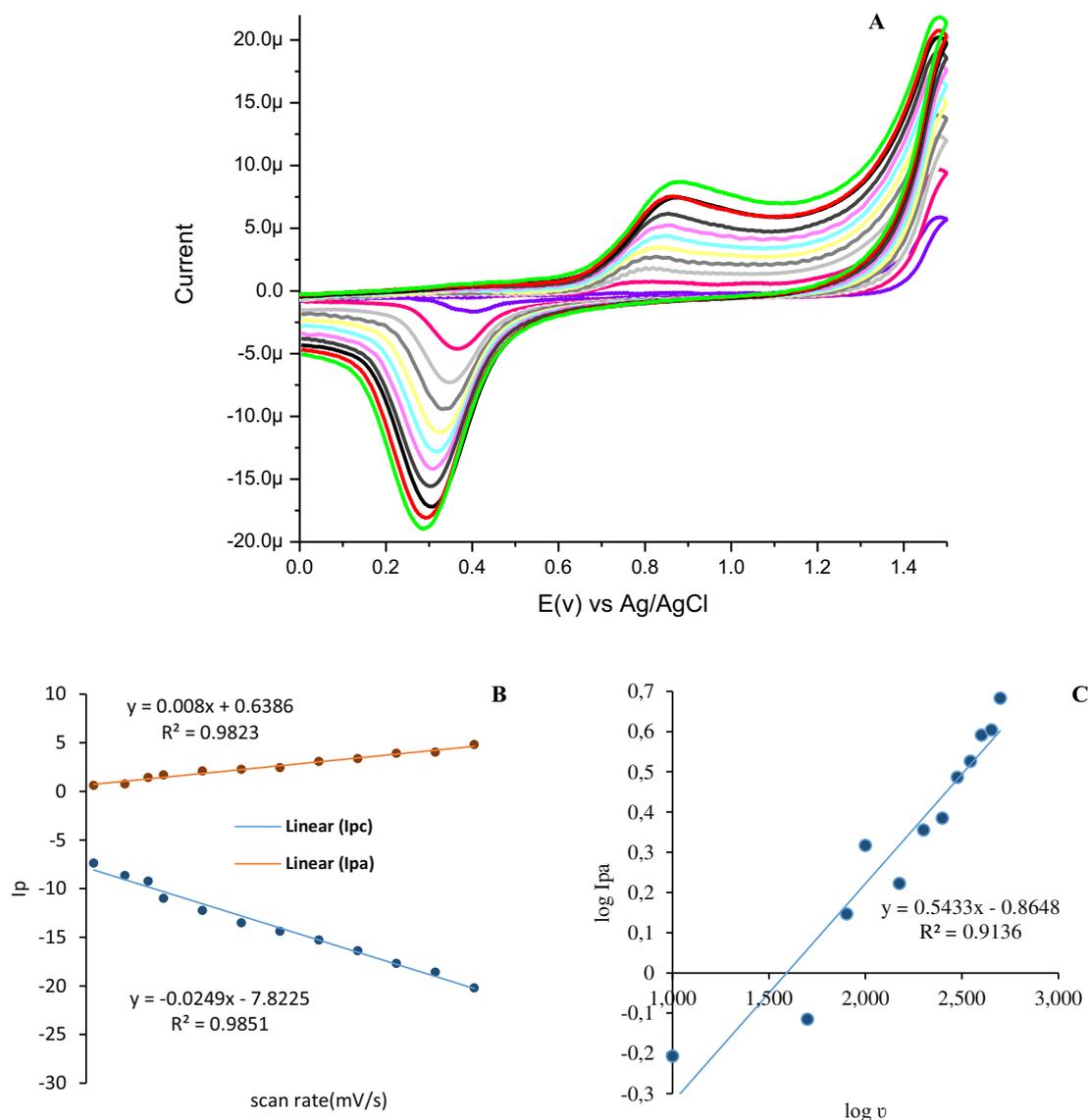
Figure 2 (C) shows curve the anodic peak potential ( $E_{pa}$ ) is shown to shift linearly in the more negative direction as the pH increases which proves that the proton takes part in the reaction on the surface of the electrode. The equation in the curve is  $E_p(V) = -0,059x + 0.7651$ . The slope value of -0.059 refers to the same number of protons and electrons. This is equal with the Nernst equation,  $E_p(V) = -0,059 (m/n) pH + E^0$ , where m and n are the number of protons and electrons. So that there is compatibility with the mechanism of ascorbic acid in Figure 3.



**Figure 3.** Oxidation-reduction reaction of ascorbic acid

### 3.3 Effect of scan rate

The effect of scan rate to studied kinetic aspects, reaction mechanisms, and scan rate optimization of ascorbic acid analysis on the surface of PM/AuNPs/CPE electrodes using cyclic voltammetry techniques. Measurements of scan rate optimization were carried out three times repetition in 0.2 mM ascorbic acid in phosphate buffer pH 7 with a potential range of 0.0 V to +1.5 V at scan rates of 10, 50, 80, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mV/s. The voltammogram of ascorbic acid 0.2 mM in PBS (0.1 mol L<sup>-1</sup>) pH 7 in variation scan rate can be seen in Figure 4 (A).



**Figure 4.** (A) Cyclic voltammogram ascorbic acid 0.2 mM in pH 7 phosphate buffer at various scan rates, (B) Curve between the scan rate and the anodic peak current value ( $I_{pa}$ ) and the cathodic peak current ( $I_{pc}$ ) and (C) The relationship curve between  $\log I_{pa}$  and  $\log v$ .

The scan rate is related to the increase in the diffusion rate of the species to the electrode. A high scan rate causes the thinness of the diffusion layer to be produced so that the transfer of electrons to the electrode surface becomes easier and the resulting peak current is also greater. On the other hand, at a small scan rate, the thickness of the diffusion layer is produced, which inhibits the electron transfer process on the surface of the electrode and the resulting peak current is small. Based on Figure 4, it is known that the scan rate affects the peak values of anodic and cathodic currents, the peak of the current increases with the higher scan rate given. The relationship curve between the scan rate and the anodic peak current value ( $I_{pa}$ ) and the cathodic peak current ( $I_{pc}$ ) are shown in Figures 4 (B).

Relevant studies indicated that the electro-catalysis of ascorbic acid was greatly involved with the slope value of  $\log I_{pa} - \log v$  [14]. The relationship curve between  $\log I_{pa}$  and  $\log v$  (Figure 4 (C)) shows the reaction that occurs on the surface of the working electrode. The criteria that show the diffusion-control reaction on the working electrode surface are if the relationship between  $\log I_{pa}$  and  $\log v$  shows a linear result with a slope value close to 0.5. For slope values equal to 1 indicates the adsorption reaction and if the slope value is between 0.5 to 1.0, it is included in the process of mixing diffusion and adsorption [14]. In the analysis of 0.2 mM ascorbic acid with PM/AuNPs/CPE electrodes produced a slope of 0.5433 which indicates that the reaction that occurs on the surface of the electrode is a mixture of diffusion and adsorption reactions but diffusion control is more dominant.

$E_{pa}$  and  $E_{pc}$  values experience a potential shift as the scan rate increases used in the ascorbic acid analysis process. Large and small potential values are influenced by electron transfer kinetics, if the electron transfer kinetics is slow, the magnitude of the peak potential separation will be greater and increase in accordance with the increase in scan rate. Determination of the optimum scan rate in ascorbic acid analysis is based on  $I_{pa}/I_{pc}$  values and  $\Delta E_p$  values. The reaction on the surface of the working electrode is said to be reversible if the  $I_{pa}/I_{pc}$  value approaches 1 and if the anodic and cathodic peak potential separation values ( $\Delta E_p$ ) are less than 59 mV/n, then the redox reaction includes reversible reactions [15]. If the anodic and cathodic peak potential separation values ( $\Delta E_p$ ) are greater than 59 mV, the redox reaction is said to be a quasi-reversible reaction [16]. On the contrary the working electrode is said to be irreversible if the  $I_{pa}/I_{pc}$  value is less than 1 and  $\Delta E_p$  is greater than 59 mV. The results of the analysis of the effect of the scan rate on ascorbic acid showed the scan rate underwent a quasi-reversible reaction because the  $I_{pa}/I_{pc}$  value was less than 1 and  $\Delta E_p$  was greater than 59 mV and The most optimum result of ascorbic acid analysis is the scan rate of 100 mV/s because it has  $I_{pa}/I_{pc}$  1.051  $\mu$ A which closed to 1 and  $\Delta E_p$  is 0.130 V.

#### 4. Conclusion

The experimental results reported here clearly demonstrated that the oxidation of AA was facilitated by the electrodeposition AuNPs and electropolymerization polymelamine on carbon paste electrode. The PM/AuNPs/CPE electrode exhibits a quasi-reversible electron with a peak separation 130 mV. The result shows that PM/AuNPs/CPE for ascorbic acid is optimum at PBS pH 7.0. The anodic peak potential shifted towards the negative shifts in the oxidation potential. The best of scan rate's ascorbic acid on the surface of PM/AuNPs/CPE is 100 mV/s.

#### References

- [1] Zhu, Shuyun., Li, Haijuan., Niu, Wenxin., Xu, Guobao. 2009 Simultaneous electrochemical determination of uric acid, dopamine, and ascorbic acid at single-walled carbon nanohorn modified glassy carbon electrode. *J Bios and Bioelec.* **25**:940-943.
- [2] Sivanesan, A., Kannan, P., and John, S.A. 2007 Electrocatalytic oxidation of ascorbic acid using a single layer of gold nanoparticles immobilized on 1,6-hexadithiol modified gold electrode. *J Electrochim. Acta.* **52**:8118.
- [3] Zare, R, Hamid., Rajabzadeh,N., Nasirizadeh,N. 2006 Voltammetric studies of an oracet blue modified glassy carbon electrode and its application for the simultaneous determination of dopamine, ascorbic acid and uric acid. *J.Electroanal.Chem.* **589**:60-69.
- [4] Gilbert,O., Swamy,Kumara, B.E., Chandra, U.,B.S. Sherigara. 2009 Simultaneous detection of dopamine and ascorbic acid using polyglycine modified carbon paste electrode: A cyclic voltammetric study. *J.Electroanal.Chem.* **636**:80-85.

- [5] Ganesh, P.S., Swamy,Kumara, B.E. 2015 Simultaneous electroanalysis of norepinephrine, ascorbic acid and uric acid using poly(glutamic acid) modified carbon paste electrode. *J.Electroanal.Chem.* **752**:17-24.
- [6] Yola, Mehmet, L., Atar, Necip., Ustundag, Zafer., Solak, Ali, O.,. 2013 A novel voltammetric sensor based on p-aminothiophenol functionalized graphene oxide/gold nanoparticles for determining uercetin in the presence of ascorbic acid. *J.Electroanal.Chem.* **698**:9-16.
- [7] Keyvanfard, Mohsen., Shakeri, Razieh., Maleh, Karimi,H., Alizad, Khadijeh. 2013 Highly selective and sensitive voltammetric sensor based on modified multiwall carbon nanotube paste electrode for simultaneous determination of ascorbic acid, acetaminophen and tryptophan. *J.Materials Sci Eng C.* **33**:811-816.
- [8] Zhao, Yifang., Gao, Yuqian., Zhan, Dongping., Liu,Hui., Zhao, Qiang., Kou,Yuan., Shao,Yuanhua., Li,Meixian., Zhuang,Qiankun., Zhu,Zhiwei. 2005 Selective detection of dopamine in the presence of ascorbic acid and uric acid by a carbon nanotubes-ionic liquid gel modified electrode. *J.Talanta.* **66**:51-57.
- [9] Chandrashekar, B.N., Swamy,Kumara,B.E., Gururaj, K.J., Cheng, Chun. 2017 Simultaneous determination of epinephrine, ascorbic acid and folic acid using TX-100 modified carbon paste electrode: A cyclic voltammetric study. *J.Mole. Liq.* **231**:379-385.
- [10] Mazloun-Ardakani, M., Ali Sheikh-Mohseni, M., Fatemeh, M.B., 2014 Nanomolar detection limit for determination of norepinephrine in the presence of acetaminophen and tryptophan using carbon nanotube-based electrochemical sensor. *J Springer.* **20**:431-437
- [11] Gholamian, F., Ali-Sheikh-Mohseni, M., Naeimi,H.,. 2012 Simultaneous determination of phenylhydrazine and hydrazine y a nanostructured electrochemical sensor. *J Materials Sci Eng.* **32**:2344-2348.
- [12] Wei,M., and Deng-Ming,S., 2007 Simultaneous determination of ephinephrine and dopamine with poly(L-arginine) modified electrode. *J Anal Chem.* **35**:66-70.
- [13] Su, Y-L., and Cheng, S-H., 2015 Sensitive and selective determination of gallic acid in green tea samples based on an electrochemical platform of poly(melamine) film. *J Anal Chim Acta.* **901**:41-50.
- [14] Swamy K B.E., Ganesh, P.S., 2015. Simultaneous electroanalysis of norepinephrine, ascorbic acid and uric acid using poly(glutamic acid) modified carbon paste electrode. *J Electroanal. Chem.* **752**:19.
- [15] Wang, Z., Liu, J., Liang, Q., Wang, Y., Luo, G., 2002. Carbon nanotube-modified electrodes for the simultaneous determination of dopamine and ascorbic acid. *J Analyst.* **127**:653–65.
- [16] Hu, S.Y., Wang, X., Wang, L., Xu, J., Xiang, W., Sun., 2012 Electrochemical detection of hydroquinone with a gold nanoparticle and graphene modified carbon ionic liquid electrode. *J Sensors Actuators. B. Chem.***168**:27-33.

#### Acknowledgement

The authors would like to thank the RISTEK DIKTI (Grant: Program Unggulan Perguruan Tinggi (PUPT) 2018.