

# Cyclic voltammetry in electrochemical oxidation of amoxicillin with Co(III) as mediator in acidic medium using Pt, Pt/Co and Pt/Co(OH)<sub>2</sub> electrodes

H. Herlina<sup>1,2,\*</sup>, Muhammad Ali Zulfikar<sup>1</sup>, and B. Buchari<sup>1</sup>

<sup>1</sup>Bandung Institute of Technology, Analytical Chemical Department, Indonesia

<sup>2</sup>Medan Institute of Technology, Electrical Engineering Department, Indonesia

**Abstract.** Amoxicillin is one of penicillin antibiotic groups with active  $\beta$ -lactam which the presence in surface water and wastes not only affects water quality but also causes long-term adverse effects on ecosystems and human health due to their resistance to natural biodegradation. The processing of organic waste electrochemically has the advantages of cheap and efficient cost, waste gas that does not contain toxic and hazardous materials. Have been studied the process of amoxicillin electro-oxidation mediated by a cobalt (III) in a cyclic voltammetry study using a platinum, Pt/Co(OH)<sub>2</sub> and Pt/Co as working electrodes in acidic medium HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> as supporting electrolytes solution. The voltammogram of Pt, Pt/Co and Pt/Co(OH)<sub>2</sub> electrodes showed that higher current was found in medium of HNO<sub>3</sub> 0.1 M and it can be used to oxidize the amoxicillin wastes, the two anodic and cathodic peaks can be observed at potential of 200-800 mV (vs Ag/AgCl). The presence of cobalt (III) ions in the system caused the decrease of oxidation current, indicated the presence of degradation to amoxicillin.

## 1 Introduction

The most commonly antibiotics been used is the amoxicillin group, which is a type of semi-synthetic penicillin with antimicrobial properties derived from the beta-lactam ring. Some researchers have found the presence of amoxicillin in urban wastewater. [1-4] The existence of antibiotics in the environment comes from various sources such as industrial antibiotics, hospital waste and excretion from humans and livestock. Arslan-Alaton et al [5] have reported that the concentration of penicillin in antibiotic waste is real in the range of 400 mg/L. Antibiotic waste has high COD values and low BOD values, so biological processes are not suitable for antibiotic waste treatment. In the long run the existence of antibiotic waste in the environment will cause bacterial resistance so that will endanger public health [5-11].

Direct electrochemical processes and indirect (mediated) have been widely used to degrade pollutants, including pharmaceutical waste and antibiotic waste. In their research Sirés and Brillas [12] have reported the electrochemical oxidation process against pharmaceutical waste from drugs such as 17 $\beta$ -estradiol, 17 $\alpha$ -ethinylestradiol, diclofenac, clofibrac acid, enrofloxacin, ibuprofen, ketoprofen, oxytetracycline hydrochloride, sulfamethoxazole, paracetamol and tetracycline using electrode Pt, Ti /RuO<sub>2</sub>, Ti/ SnO<sub>2</sub>, Ti/IrO<sub>2</sub>, Ti/RuO<sub>2</sub>-IrO<sub>2</sub>, and BDD [12-17].

Another electrochemical process, the mediated electrochemical oxidation (MEO), is the most promising

waste treatment method for the degradation of organic compounds. This is because the method is able to completely decompose organic compounds into carbon dioxide and water using a mediator, without emitting toxic chemicals, oxidation / reduction reactions can take place at room temperature and pressure, secondary waste can be minimized to avoid additional treatment methods. [18-22]

The research that has been done is an attempt to degrade the presence of amoxicillin in the environment with several measurement parameters such as potential, temperature, current density, and total CO<sub>2</sub> conversion, but not much has been revealed about the reaction of oxidation and reduction that occurs inside the electrochemical cell. A cyclic voltammetric study was conducted to determine the optimum conditions of the working electrode and the mediator in acidic medium as supporting electrolyte solutions to see the oxidation and reduction reactions occurring in amoxicillin with 3 working electrodes Pt disc, Pt/Co and Pt/Co(OH)<sub>2</sub> electrodes to degrade amoxicillin mediated by a cobalt (III). This method utilizes electron transfer for the reduction/oxidation reaction in analyte. This method can be used to degrade (oxidize) organic pollutants directly or indirectly (mediated). Mediated electrochemical oxidation method is a method that utilizes oxidizers from electrooxidation mediator to oxidize organic pollutants into simple degradation products, and final product is carbon dioxide. The main advantage of this method is the repeated use of the oxidator when the degradation process is carried out with an ex-cell system. Another

\* Corresponding author: [herlina@itm.ac.id](mailto:herlina@itm.ac.id)

advantage is that it can be performed at ambient temperature and atmospheric pressure and optimum oxidizing forces in acidic conditions. [18,19,23].

## 2 Methods

The study was divided into several stages including making the reference electrode Ag/AgCl and working electrodes Pt, Pt/Co and Pt/Co(OH)<sub>2</sub>, and the next step was a cyclic voltammetry study in acidic medium as the supporting electrolyte for the electro-oxidation process of amoxicillin mediated Co(III). The equipment used in this research is glass equipment commonly used in the laboratory and instrument equipment used is Voltammeter with EC software ver.1.60.70 for cyclic voltammetry analysis using 3 electrodes ie laboratory prepared electrode, references electrode Ag/AgCl made self and Pt wire as auxiliary electrodes.

The chemicals used are chemicals with quality pro-analysis (pa), cobalt chloride (Aldrich), cobalt nitrate (Aldrich), HNO<sub>3</sub> (Merck 65%), H<sub>2</sub>SO<sub>4</sub> (Aldrich 96%), NaCl, amoxicillin trihydrate, aqua DM, K<sub>3</sub>Fe(CN)<sub>6</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub> (Aldrich), and Pt wire and Ag wire.

Preparation of reference electrode was made from silver (Ag) wire as anode and Pt wire as cathode, electrolyzed in NaCl 0.1 M with potential 2.2 V for 5 min.

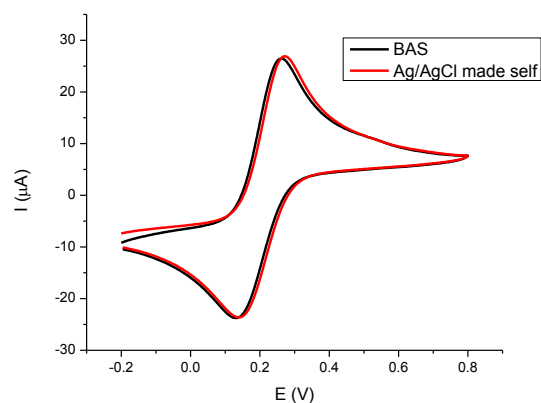
The Pt/Co electrode of work is prepared by electrodeposition cobalt onto the platinum disc metal surface, wherein the anode and cathode used are Pt wire electrodes. The source of the cobalt metal ion used is 0.05 M cobalt chloride.

The preparation of Pt/Co(OH)<sub>2</sub> electrode, made by placing Pt wire in a solution containing 0.1 M Na<sub>2</sub>CO<sub>3</sub>, 40 mM NaK-tartrate and 4 mM CoCl<sub>2</sub> at pH 11. [24] The coating process of the Pt electrode with cobalt hydroxide was carried out with a cyclic voltammium technique of 100 cyclic at a potential of -250 mV up to 800 m V at scanrate 100 mV/s. [25, 26] Then Pt/Co(OH)<sub>2</sub> electrodes were characterized in 0.1 M NaOH solution by cyclic voltammetry.

All electrodes are characterized in 0.1 M supporting electrolyte solution HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, as a blank to qualitatively the background current from the electrolyte solution and shortly before measurement of N<sub>2</sub> gas is flowed into the electrochemical cell to free the solution from dissolved oxygen due to the presence of dissolved oxygen in the solution, will cause the oxygen undergoes a redox reaction on the electrode surface so that the oxygen peaks will be visible on the voltammogram. This characterization is performed by cyclic voltammetry which is often used in qualitative test on electrode characterization. Next to the 3 electrochemical cells containing a 0.1 M supporting electrolyte solution were added a solution of Co(NO<sub>3</sub>)<sub>2</sub> 0.01 M; amoxicillin 1 mM; and a mixture of Co(NO<sub>3</sub>)<sub>2</sub>. and amoxicillin. Characterization is carried out at a potential range of -200 mV to 1800 mV using the three working electrodes above, with scanrate 100mV/s.

## 3 Results and Discussion

Characterization of reference electrode Ag/AgCl made self was compared to commercial reference electrode BAS in K<sub>3</sub>Fe(CN)<sub>6</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub> solution with NaCl as supporting electrolytes at scanrate 100 mVs<sup>-1</sup> as shown in Fig. 1 below:



**Fig. 1.** Cyclic voltammogram of BAS and Ag/AgCl in K<sub>3</sub>Fe(CN)<sub>6</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub> solution 0.01 M with NaCl 0.1 M as supporting electrolyte at scanrate 100 mV/s.

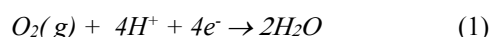
There was no significant difference between BAS and Ag/AgCl and the potential for a reversible couple in a system was shown at the table 1:

**Table 1.** Data characterization of Ag/AgCl compare to BAS.

Electrode	Parameter					
	Epa (mV)	Epc (mV)	Ipc (μA)	Ipa (μA)	E° (mV)	Ipc/Ipa
BAS	262	144	-25.83	30.65	203	0.8427
Ag/AgCl	278	148	-25.92	29.58	213	0,8763

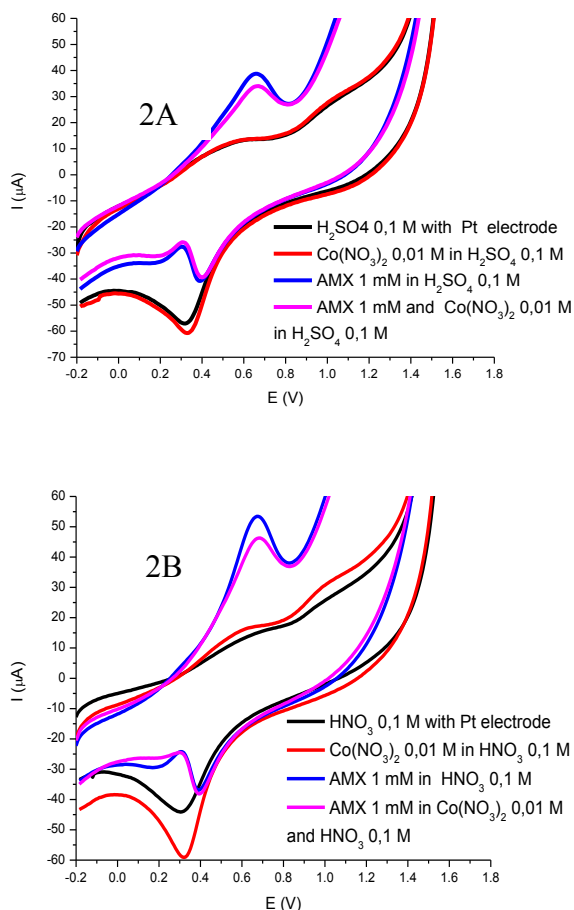
The electrocatalytic oxidation of amoxicillin can be detected by an electrochemical method based on anodic oxidation. Amoxicillin produces a substantial anodic current at Epa 656 mV (vs Ag/AgCl) using platinum disc electrode in HNO<sub>3</sub> medium with a decrease in the reduction peak in the direction of scanning back, which is a typical electrocatalytic process. While the mediator, Co(II) was oxidized to Co(III) at Epa 1,5866 V (vs Ag/AgCl).

H<sub>2</sub>O<sub>2</sub> can be formed in the system from the two-electron reduction of oxygen (directly injected as pure gas or bubbled air) at the cathode surface in acidic/neutral media, according to Eq. (1) with E° = 0.68 V/SHE [13,15].



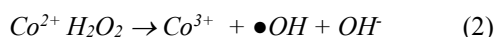
Therefore, in a cyclic voltammetric measurement, a nitrogen gas injected into the solution for a period of time, to free the solution of dissolved oxygen because in the presence of dissolved oxygen, it will cause the oxygen to undergo a redox reaction on the electrode surface so that the oxygen peaks will be visible on the voltammogram. Peaks of the oxygen would interfere the

analysis if it gives a peak at a potential similar to the analytical potential. And to prevent dissolved oxygen into the solution, before the measurements N<sub>2</sub> gas are flowed over the surface of the solution.

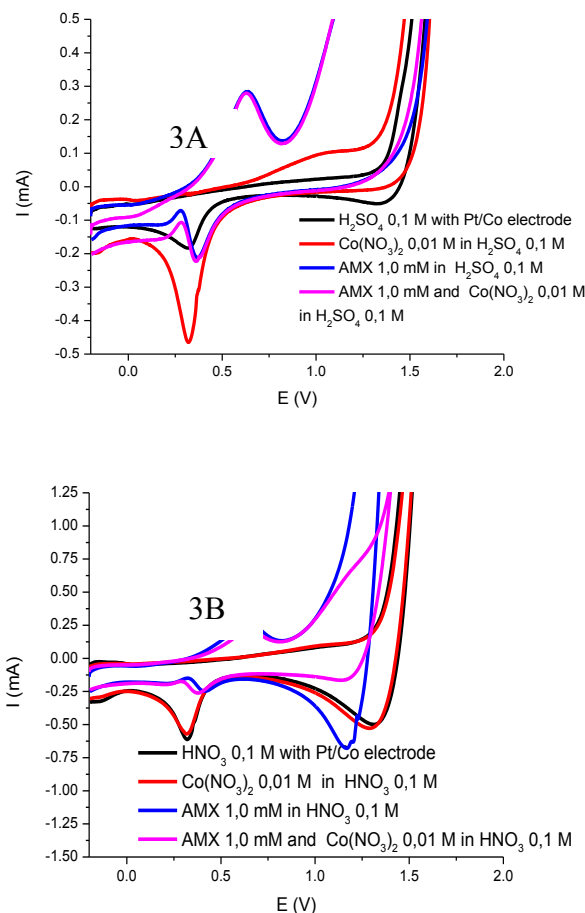


**Fig. 2.** Voltammogram of a mixed solution of 1.0 mM amoxicillin solution, 0.01 M cobalt nitrate and 0.1 M electrolyte support solution (A) H<sub>2</sub>SO<sub>4</sub> (B) HNO<sub>3</sub> using a working electrode disc Pt, scan rate 100 mVs<sup>-1</sup>.

From Fig. 2 the cyclic voltammogram of supporting electrolytes both sulfuric acid and nitric acid produces a low oxidation peak around 487 mV (Ag/AgCl) using Pt disc electrode, which probably results from the formation of peroxides derived from the oxygen reduction reaction in acid medium, as well as the peak derived from the mediator. The reaction that occurs between the mediator and the peroxide causes the decreased of oxidation peak of amoxicillin. This suggests a degradation of amoxicillin in electrochemical cells occurs



Similar to electro-Fenton, Sun and Pignatello [27] that the reaction can be efficiently applied in acidic condition with pH 2.8-3.0 where precipitation from mediator does not take place yet.



**Fig. 3.** Voltammogram of a mixed solution of 1.0 mM amoxicillin solution, 0.01 M cobalt nitrate and 0.1 M electrolyte support solution (A) H<sub>2</sub>SO<sub>4</sub> (B) HNO<sub>3</sub> using a working electrode Pt/Co, scan rate 100 mVs<sup>-1</sup>.

Figure 3 shows the use of Pt/Co electrodes in electrochemical cells provide a higher oxidation current peaks than disc Pt electrodes. And in the nitric acid medium, amoxicillin is more oxidized than sulfuric acid, and the oxidation peak is more less using Pt/Co than using disc Pt because on Pt/Co provide more mediator in a system and the data can be seen on Table 2 and Table 3 below.

**Table 2.** The cyclic voltammogram data of a mixture of 1.0 mM amoxicillin solution, 0.01 M cobalt nitrate in H<sub>2</sub>SO<sub>4</sub> 0.1 M as supporting electrolyte with 3 working electrodes, Ag/AgCl as reference electrode and Pt wire as auxiliary electrode with scanrate 100mVs<sup>-1</sup>.

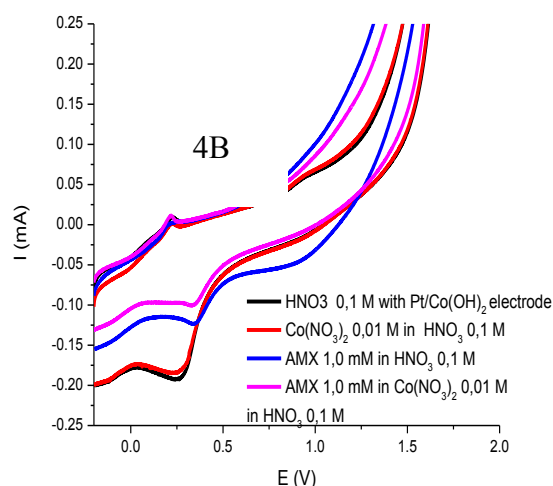
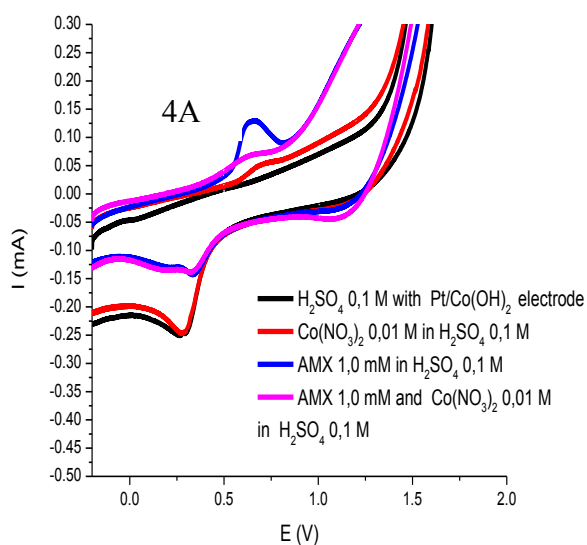
Electrode	AMX + H <sub>2</sub> SO <sub>4</sub>		AMX + Co(NO <sub>3</sub> ) <sub>2</sub> + H <sub>2</sub> SO <sub>4</sub>	
	Epa (mV)	Ipa (mA)	Epa (mV)	Ipa (mA)
Pt	648	0.0178	648	0.0139
Pt/Co	624	0.2032	620	0.1970
Pt/Co(OH) <sub>2</sub>	658	0.0128	616	0.0040

**Table 3.** The cyclic voltammogram data of a mixture of 1.0 mM amoxicillin solution, 0.01 M cobalt nitrate in HNO<sub>3</sub> 0.1 M as supporting electrolyte with 3 working electrodes, Ag/AgCl as reference electrode and Pt wire as auxiliary electrode with scanrate 100mVs<sup>-1</sup>.

Electrode	AMX + HNO <sub>3</sub>		AMX + Co(NO <sub>3</sub> ) <sub>2</sub> + HNO <sub>3</sub>	
	Epa (mV)	Ipa (mA)	Epa (mV)	Ipa (mA)
Pt	656	0.0269	664	0.0202
Pt/Co	638	0.1879	636	0.1262
Pt/Co(OH) <sub>2</sub>	660	0.0118	658	0.0092

Based on the voltammogram above Fig 2, Fig 3 and Fig 4, amoxicillin belongs to a reversible electroactive compound because it can provide an oxidation peak in range 600 mV and provide a reduction peak in range 200 mV respectively, with Ipc/Ipa equals to 1. [17, 28] A comparison of amoxicillin voltammograms with and without the addition of Co (II) proves that the Co (III) formed can oxidize amoxicillin. This is can seen by the high oxidation peak currents of amoxicillin in the acid supporting electrolyte solution and lower on the amoxicillin voltammogram by the addition of Co (II). Given the increase in the applicable potential difference, the Co (II) species will oxidize to Co (III) on the electrode surface. The presence of Co (III) species as a mediator oxidizes amoxicillin on the electrode surface so that the measured peak oxidation value of amoxicillin becomes lower compared with no Co (II) addition. The resulting voltammogram seen that in the use of Pt coated cobalt electrode and Pt/Co(OH)<sub>2</sub> providing a higher current response than Pt disc electrode

Figure 4 shows the voltammogram using Pt/Co(OH)<sub>2</sub> electrode in electro-oxidation of amoxicillin with and without the presence of Co(III):



**Fig. 4.** Voltammogram of a mixed solution of 1.0 mM amoxicillin solution, 0.01 M cobalt nitrate and 0.1 M electrolyte support solution (A) H<sub>2</sub>SO<sub>4</sub> (B) HNO<sub>3</sub> using a working electrode Pt/Co(OH)<sub>2</sub>, scan rate 100 mVs<sup>-1</sup>.

An electrochemically formed cobalt hydroxide coated with cyclic voltammetry on platinum wire in alkaline [25,26] medium pH 11 while treatment for electro-oxidation amoxicillin in acidic medium. The electrodes of this show electrocatalytic the activity for the oxidation of amoxicillin is about 660 mV (vs. Ag/AgCl), it is longer than the two previous working electrodes, which allows the electrode to work on the acid medium. However, with the presence of a mediator, the anodic current peak decreased and its oxidation potential is more shifted to the left.

## 4 Conclusion

Pt/Co, Pt/Co(OH)<sub>2</sub> and Pt disc electrodes can be used to oxidize amoxicillin in acidic medium HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> as supporting electrolytes and may be further employed to degrade antibiotic in real waste by electrochemical oxidation process mediated by metal ions in acidic conditions.

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