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Optimisation of parameters for detection of manganese ion using electrochemical method

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Abstract. An electrochemical method was detected a heavy metal ion of manganese (Mn^{2+}) based on bare gold electrode (AuE). The bare AuE was optimized including various type of electrolytes, redox indicators, pH, scan rate and accumulation time using cyclic voltammetry (CV). From the CV results, the optimal conditions of Mn^{2+} were found of Tris-HCl (0.1 M, pH 2) buffer for electrolytes supported by 5 mM Prussian blue as a redox indicator with scan rate of 100 mVs^{-1} and accumulation time of 2 s, respectively. Differential pulse voltammetry (DPV) method was detected with different concentrations of Mn^{2+} on the ranged from 0.05 to 1.0 ppm with limit of detection (LOD) of 0.075 mg L^{-1} (S/N=3). A linear regression was found of 0.9659 (r^2). The above results indicated that the bare AuE was unable to detect of Mn^{2+} below safety level. So, the proposed method suggests to detect below safety level of Mn^{2+} based on the further modification of AuE with high sensitivity, selectivity and accuracy.

1. Introduction

Manganese is the third most abundant transition element in the earth's crust as compared to other elements. Manganese plays important role as a key activation of many enzymes in the human, animals and plants [1,2]. The manganese's trace is important in cellular metabolism [3]. Manganese has been applied on manufacture industries such as batteries, fertilizers, ceramics, dietary supplements and electrical coils [1,2]. The high concentrations of manganese can cause adverse negative effects to human health, environment and the ecosystem [1]. The high level of manganese exposure which linked to neurological disorders such as Parkinson-like syndrome. Victim will suffer the manganism diseases which physical disability and body posture problems due to the low muscle stretching and flexibility [4]. In addition, Manganism also affecting the brain activities which resulted in decreased mental status, slow speech, hard to adapt new environment and lack of interest [5]. The dissolved manganese ion widely present in drinking water, foods, ad plants [6].

Due to it existent, the standard quality levels of manganese in drinking water have been fixed for domestic water was 0.05 μg mL^{-1} [3,7]. Note that, the other journal mentioned the different value on maximum concentration allowance for domestic water was 0.05 mg mL^{-1} [2]. The Ministry of Heath

Malaysia has been set the standard quality level for manganese in drinking water was 0.1 mg L^{-1} [8]. Despite on the usages of domestic water, the detection of manganese ion becomes highly important in order to monitor the uncertainty amount of manganese in domestic water such as drinking water.

Currently, various conventional methods had been used such energy dispersive X-ray florescence spectroscopy (EDXRF) [9], atomic absorption spectrometry (AES) [10,11], microwave plasma-atomic emission spectrometry (MP-AES) [12] and coupled plasma mass spectrometry (ICP-MS) [13]. These methods provided high selectivity and sensitivity for manganese ion detection but suffer from a number of drawbacks including expensive instruments, tedious, complex and time-consuming procedures, and require skilled operators. On the other hand, electrochemical techniques offer a practical alternative and have drawn growing attentions from researchers due to the advantages offered such as high selectivity and sensitivity, rapid with quality and quantity analysis, on-site detection (portable), inexpensive instrument and does not required pre-treatment of sample before analysis was conducted [7,14,15,16]. Recently, less information on detection of manganese using electrochemical methods. Latest researches only done by Roushani et al. (2017) and Ruggeri et al. (2017) which both were using glassy carbon electrode (GCE)[1,6]. No one has use the gold electrode on detection of manganese ion yet. However, the gold electrode has proven with high conductivity, electrocatalytic, good selectivity and high signal-to-noise ratio. The utilization of gold electrode in electrochemical detection of various elements have been widely reported. According to Jiang et al. (2016), the detection of arsenic (As^{3+}) using gold electrode fabricated with ultrathin SnO2 nanosheets was showed the limit of detection about 5 mg L^{-1} in 0.1 M acetate buffer (pH 5)[17]. Another experiment conducted by Giacomino et al. (2011) on the analytical performance using lateral gold electrode showed the limit of detection As^{3+} about 0.06 mg L^{-1}[18].

As this research is ongoing research, many parameters have been considered and optimized. The electrochemical parameters such as type electrolytic solution, redox indicator, pH, scan rate and accumulation time had been optimized using cyclic voltammetry (CV) method. The optimal parameters were used for measured the different levels of manganese towards current signals using differential pulse voltammetry (DPV) method. The proposed sensor enhances the high sensitivity and selectivity with focusing on optimization step.

2. Experimental section

2.1 Materials and chemicals

Potassium hydrogen phosphate (K_2HPO_4), potassium dihydrogen phosphate (KH_2PO_4), sodium citrate dihydrate ($C_6H_9Na_3O_9$) and sodium chloride (NaCl) were purchased from Systerm, citric acid anhydrous ($C_6H_8O_7$) was obtained from Nacalai Tesque, ammonium acetate ($C_2H_7NO_2$) was from Ajax Chemical and tris-HCl ($NH_2C(CH_2OH)_3$.HCl was from 1st Base for buffer preparation materials. Redox indicator chemicals, potassium hexacyanoferrate (III) and potassium ferrocyanide (II) trihydrate were the product of Nacalai Tesque, while methylene blue and iron (III) chloride were purchased from Systerm Chemicals and Sigma-Aldrich, respectively. Manganese (II) sulphate ($MnSO_4.H_2O$) as a target ion was obtained from Systerm.

2.2 Instrumentation

All electrochemical experiments were carried out with potentiostat/galvanostat (PGSAT) equipment (Metrohm-Autolab B.V), packaged with NOVA Autolab 1.8 software. The instrument uses three-electrode configuration systems which consist of working electrode (AuE), counter electrode (Pt wire) and reference electrode. The cyclic voltammetry pontensiostat indicate the presence of target ion through current responses, shown in cyclic voltammogram graph. Differential pulse voltammetry (DPV) determined the effect of different concentrations of target ion in the electrochemical cell by promoting the current changing in form of bell-shaped curve.

2.3 Pre-treatment of bare gold electrode (AuE)

Pre-treatment of the bare gold electrode (AuE) was performed following the method described by Siddiquee et al. (2010)[19]. Briefly, AuE was polished with $0.3 - 0.5 \, \mu$m alumina slurry for 2 minutes. Then, the electrode was gently cleaned with distilled water before further cleaned with ultrasonic cleaner for 2 minutes. After that, the electrode was dried using nitrogen gas. The dried electrode was dropped with 5 μL of redox indicator at the centre of the electrode and left for 2 minutes [20].

2.4 Preparation of redox indicator

The Prussian blue as a redox indicator was prepared by mixing potassium ferrocyanide (II) trihydrate ($C_6H_6FeK_4N_6O_3$) and iron (III) chloride ($FeCl_3$) at 1:1 ratio [21]. 5 mM Prussian blue ($C_{18}Fe_7N_{18}$) was gently dropped on the surface of gold electrode. This redox indicator acts as supporting agent to promote high current response when it submerged into the electrolytic solution containing Mn^{2+}.

2.5 Preparation of electrolytic solution

Five types of electrolytic solution including phosphate buffer saline (PBS), ammonium, citrate, tris-HCl and acetate buffers were prepared in 10 ml with concentration of 0.1 M in the presence of target ion [22,23,24]. The tris-HCl buffer was selected as the optimal buffer due to the highest current response. The preparation of tris-HCl buffer was performed by mixing 0.1 M tris-HCl ($NH_2C(CH_2OH)_3$.HCl with 0.1 M sodium chloride (NaCl) in distilled water.

2.6 Analytical procedure

Data analysis were conducted using electrochemical sensor (potentiostat/galvanostat) machine. Total volume of the electrolytic solution containing the target ion was in the electrochemical cell is 10 mL [23,25]. The optimisation of buffer, redox indicator, pH, scan rate and accumulation time were performed using cyclic voltammetry (CV) method under electrochemical technique. Current responses from five type of buffers and three types of redox indicator with different pH were obtained to select the best buffer and redox indicator for further optimisation.
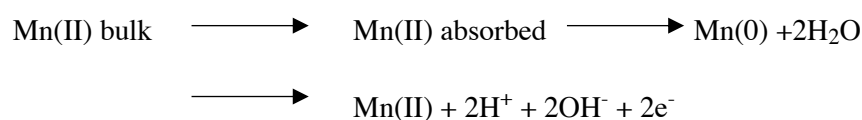
The initial electrochemical measurements of cyclic voltammetry method were 0.0 V to 1.7 V for potential applied; 0.8 V stop/start potential; 100 mVs^{-1} scan rate and 10 s accumulation time. First, each of the buffers was tested with different pH values ranging from 2 to 9. After pre-treatment of the AuE, the dried electrode was submerged into the 10 mL of 0.1 M electrolytic solution of different type of buffer containing 0.1 ppm of the manganese. Then, the AuE supported with different type of redox indicator (5 mM, 5 μL) was submerged into the selected electrolytic solution containing manganese for selection of the buffer and best redox indicator. The pH, buffer and redox indicator that yield the highest current response were then used for optimisation of the scan rate and accumulation time. The scan rate of the experiment was set from $50 - 350$ mVs^{-1} with interval scan rate was 50 mVs^{-1} while the accumulation time was from $5 - 40$ s with 5 s interval time. The optimised parameters obtained from the CV measurement were applied to DPV method to determine the effect of different concentrations to current signals. The linear range (LOR) of manganese was investigated from 0.05 to 1.0 ppm with 0.2 ppm interval of concentration. The peak formed at 0.67 V after 10 s deposition time. The concentration of manganese was inversely proportional with current response.

3. Results and discussion

3.1. Effect of pH

To test the effect of pH on detection of 0.1 ppm of manganese ion, we ranged the pH from pH 2 to pH 9 for the electrolytic solution. Adjustment of the pH was made by using 0.1 M of hydrochloric acid and 0.1 M of potassium hydroxide. From the result shown in Figure 1, the behaviours of Mn^{2+} under different pH of the electrolytic solution can be observed where the current responses increased with the decrease of pH of the electrolytic solution. For the oxidation, the complex mechanisms of Mn^{2+}

involved between the bulk and the solid (electrode) caused the peak to increase as the pH decreased. Thorough understanding of these mechanisms is still under debate. All the peaks were formed higher at oxidation range due to hydrogen evolution potential which more positive response compared to potential located at the reduction range of Mn^{2+} [26]. On the other hand, reduction peak was a good quantitative measurement to determine the concentration of Mn^{2+} in the solution [6]. This is due to the concentration of Mn^{2+} depending on the acidity of the solution as shown in Figure 1. Highest peak indicates the high deposition of Mn^{2+}. The oxidation peak was observed at applied potential of 1.6 V for all the pH range tested except for pH 2 where the peak shifted slightly to lower potential (1.59 V) while the reduction peak was observed at 0.52 V. The shifting of the current potential was due to the mass transfer of the photon on the surface of the electrode [6]. Other factor might be due to excess of hydrogen ion (H^+) in the solution as low pH value was applied. According to the proposed mechanism suggested by Roushani et al. (2017), H^+ was one of the products during the electrochemical reaction [1].

$$Mn(II) \text{ bulk} \longrightarrow Mn(II) \text{ absorbed} \longrightarrow Mn(0) + 2H_2O$$

$$\longrightarrow Mn(II) + 2H^+ + 2OH^- + 2e^-$$

pH 9 shows the lowest current responses for both the oxidation and reduction peaks. For a clear comparison of oxidation and reduction peak for all range of pH value tested, the current value by which the oxidation and reduction peaks were observed at different pH was plotted as depicted in Figure 1. The oxidation peak was higher in every point of pH value compared to the reduction peak. Among the all pH values, the pH 2 (oxidation peak) showed the most influent by giving the good signal as supporting electrolyte. However, as this research focusing mainly on analytical rather than mechanism of Mn^{2+} electrochemical reaction, thus reduction current response marked by pH 2 was selected as optimal pH condition for further investigation.
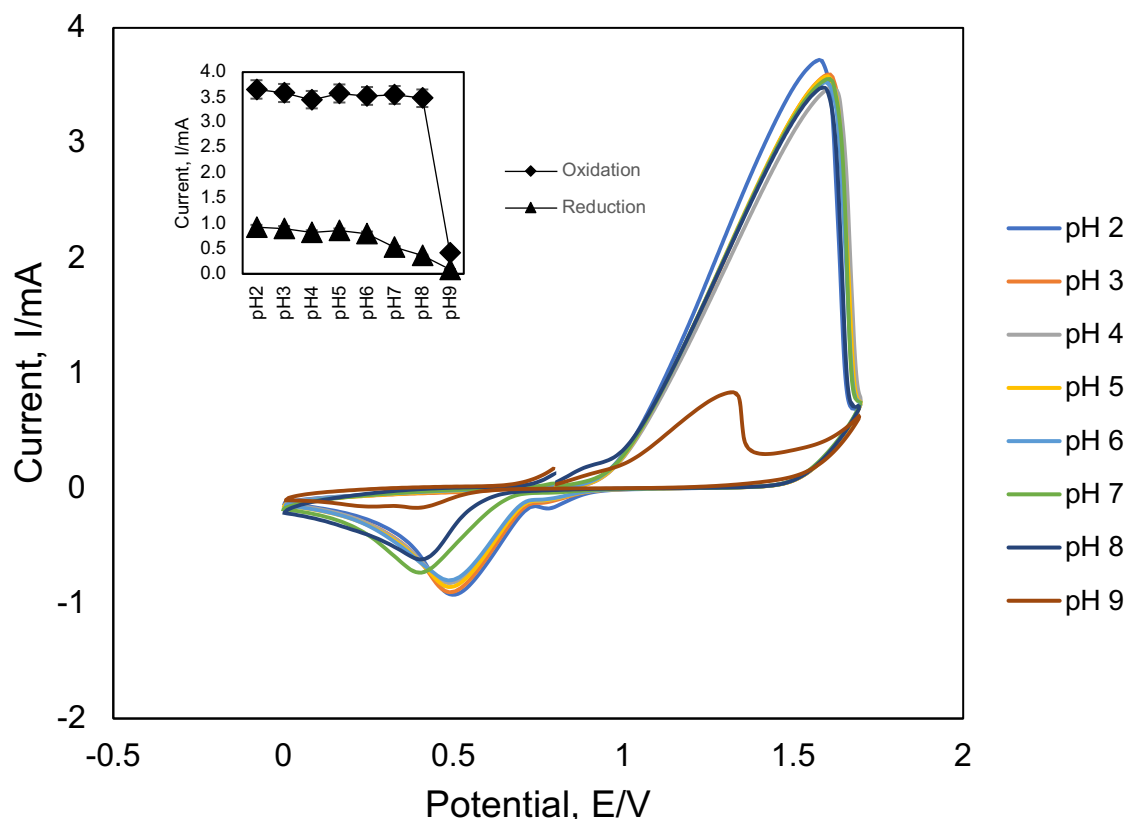
Fig. 1. Cyclic voltammetry test for optimisation of the pH value range from pH 2 to pH 9 for 0.1 M tris-HCl buffer supported by 5 mM Prussian Blue under 100 mVs^{-1}. 0.1 ppm of manganese was directly dilute into the buffer solution and optimised within range 0.0 V to 1.7 V for at least three times experiment was conducted (n>3).

3.2. Effect of different buffers and redox indicators

The current response obtained from the CV measurement of five types of buffer is shown in Figure 2. For this measurement, the buffer concentration and pH were fixed at 0.1 M and 2.0, respectively while 0.5 mM Prussian blue was used as the redox indicator. The buffer provides a complete circuit by acting as electrolytic solution. The volume of the electrolytic solution was fixed at 10 mL with the presence of 0.1 ppm manganese [23]. The selection of manganese concentration was made based on the standard quality level of manganese in drinking water according to the Ministry of Health, Malaysia (2010)[8]. The manganese was diluted directly in the electrolytic solution and tested with bare gold electrode supported by the Prussian blue on the surface of the electrode. Two peaks were formed which located at 1.6 V for oxidation peak while reduction peak was formed at 0.5 V. The current response for oxidation and reduction peaks was 3.439 mA and 0.888 mA, respectively. The sharp of anodic peaks at oxidation range indicates that the process was diffusion-controlled (Filipe and Brett, 2003)[7]. With the highest peak points recorded, 0.1 M tris-HCl buffer (pH 2) was selected as the optimal buffer for further investigation.
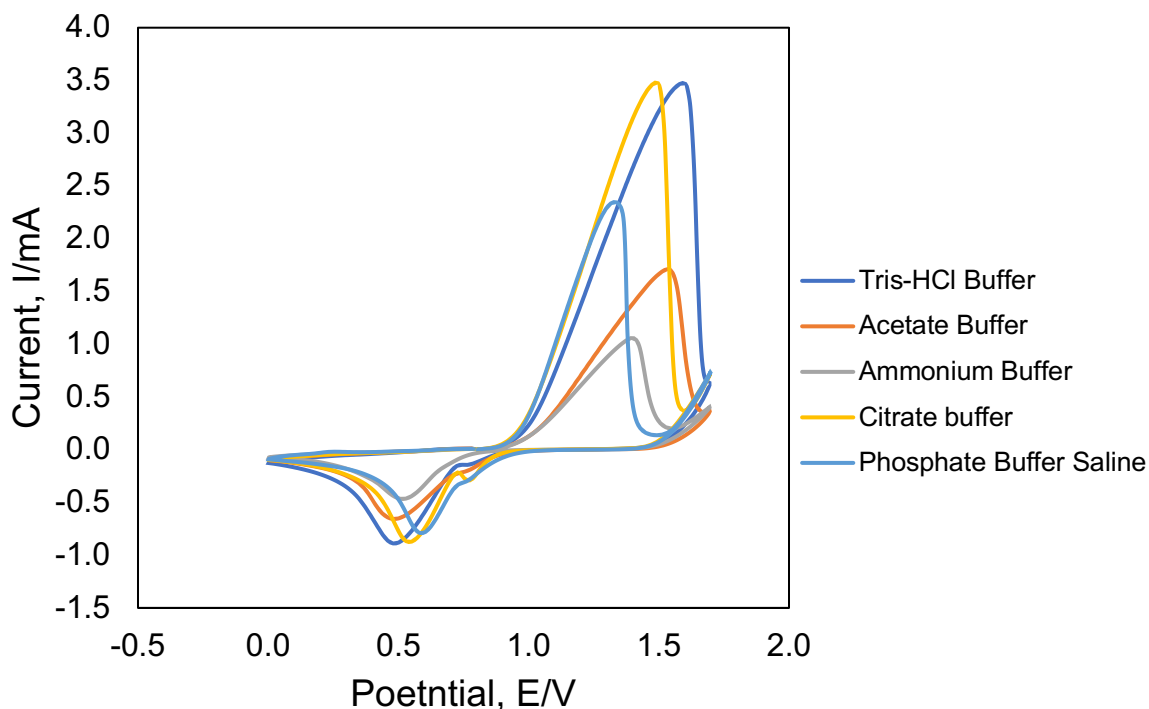
Fig. 2. The cyclic voltammetry test of five types of buffer (0.1 M, pH 2) with 5 mM Prussian blue in the presence of 0.1 ppm in the electrolytic solution. Prussian blue was dropped onto the bare gold electrode under potential range of 0.0 V to 1.7 V. The scan rate was 100 mVs^{-1} while the accumulation time was 5 s. This experiment was repeated at least 3 times for each buffer (n>3).

3.3. Effect of scan rate

Optimisation of the scan rate from 50 mVs^{-1} to 350 mVs^{-1} was conducted to determine the adsorption of the ion in the bare gold electrode. Based on Figure 3, the current response increases with the scan rate. However, for the oxidation peak, unstable current responses were observed as the current movement became faster as the scan rate is increasing. This demonstrated the kinetic of current where the current response is controlled by the diffusion factor [23]. The bell shaped of the current response was changed to a linear line as the scan rate was above 100 mVs-1 on oxidation formation. According to Liu et al. (2011), this indicates that the current response was unstable, which might be due to over-oxidation [27]. On the other hand, for the reduction, stable current responses were observed, and the peak shifted to lower potential value as the scan rate increases. Based on Figure 3, the comparison among the peaks formed at reduction was identified by linear graph. As the increasing scan rate was applied, the peak currents getting higher. The results will influence the next optimisation experiment.
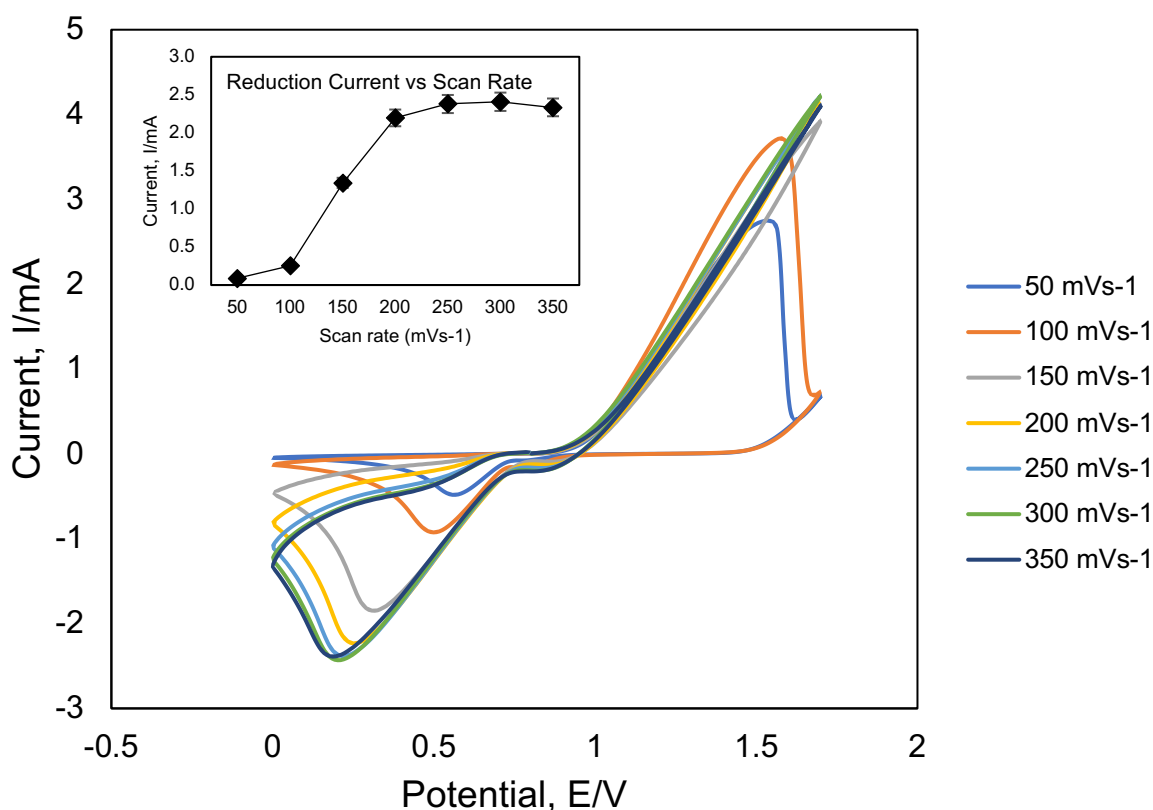
Fig. 3. Cyclic voltammetry test for optimisation of the scan rate range from 50 mVs^{-1} to 350 mVs^{-1} for 0.1 M tris-HCl buffer supported by 5 mM Prussian blue in the presence of 0.1 ppm of manganese ion. Optimisation of the scan rate was conducted at least three times (n>3).

3.4. Effect of accumulation time

Current responses for electrochemical measurement with different accumulation time ranging from 2 s to 40 s were obtained through CV method. The selection of range for accumulation time was made below one minute to fulfil the objective of rapid detection. Accumulation time of 2 s shows the highest current peak which is located at 1.6 V (oxidation range) and 0.46 V (reduction range) as shown in Figure 4. From the same figure, increasing the accumulation time from 2 s to 15 s, gradual decreased of the current peak was observed. As the accumulation time was further increased above 15 s, the current peak increased slightly until 25 s. Then, above 25 s, the current peak was fallen rapidly, and the started to reach a plateau afterward. Based on this observation, stable and high current peak can be obtained in 2 s of accumulation time for oxidation and reduction current responses, suggesting that the method employed in this study capable of detecting the target ion in as fast as 2 s. Therefore, the 2 s was selected for analysis of different concentrations of manganese ion with DPV method. Specifically, reduction peak for 2 s was selected as optimal accumulation time based on the peak responses showed equilibrium state from 2 s until 25 s indicated that Mn^{2+} saturated on the surface of the electrode [1].
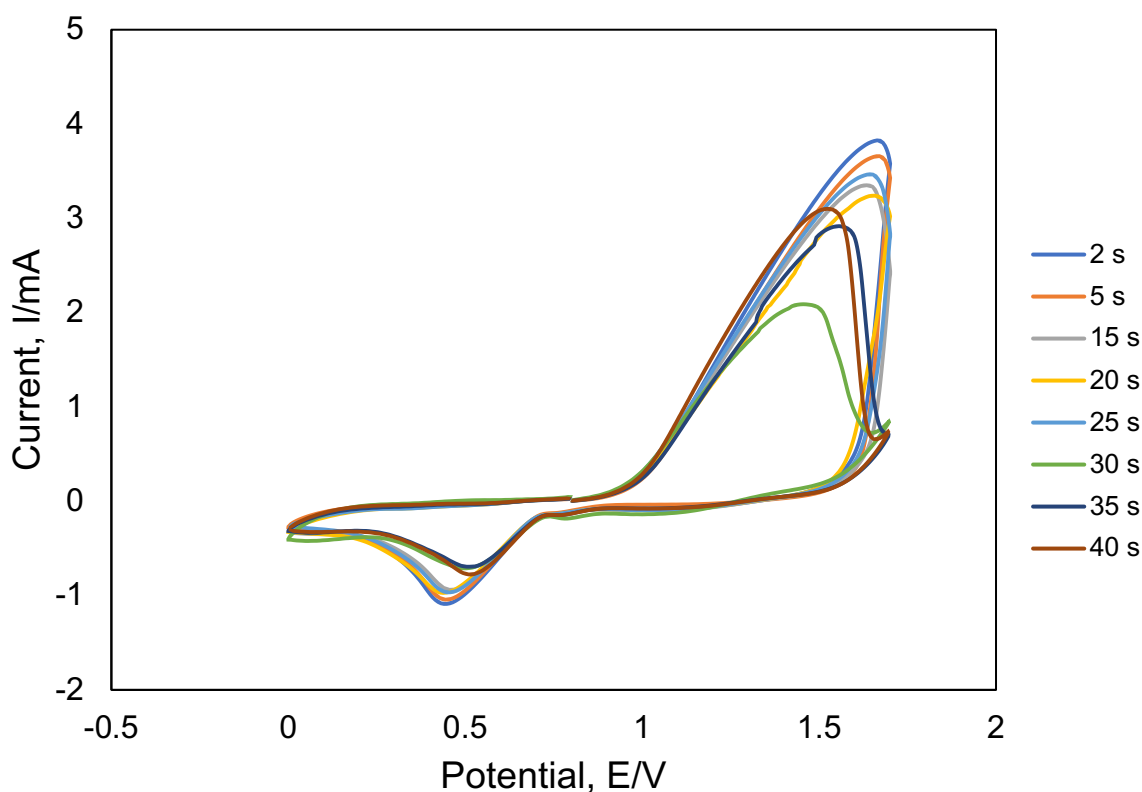
Fig. 4. Cyclic voltammetry test for optimisation of accumulation time from 2 s – 40 s. The experiment was conducted more than 3 times (n>3).

3.5. Determination of different concentrations Mn^{2+} ion

After optimisation step using cyclic voltammetry method, parameters of (0.1 M, pH 2) Tris-HCl buffer, 5 mM Prussian blue, 100 mVs^{-1} scan rate and 2 s accumulation time were found as the optimal condition for detection of manganese ion. These parameters were applied for obtaining the current responses when different concentrations of manganese were added by using DPV method. Figure 5 shows the concentrations of manganese proportional to current responses when the linear of range (LOR) from 0.05 ppm to 1.0 ppm were tested. The linear regression of manganese concentration proportional to current peaks was y = 2.5799x + 26.594 with R^2 = 0.9659 with limit of detection (LOD), S/N=3 was 0.075 mg L^{-1} based on Figure 5(B). The linear regression was selected from every peak point represented different concentrations which showed the line less distributed as the gold electrode supported by Prussian blue. However, the peaks showed positive reduction potential when the peak started to increase as increasing amount of manganese were added [26].
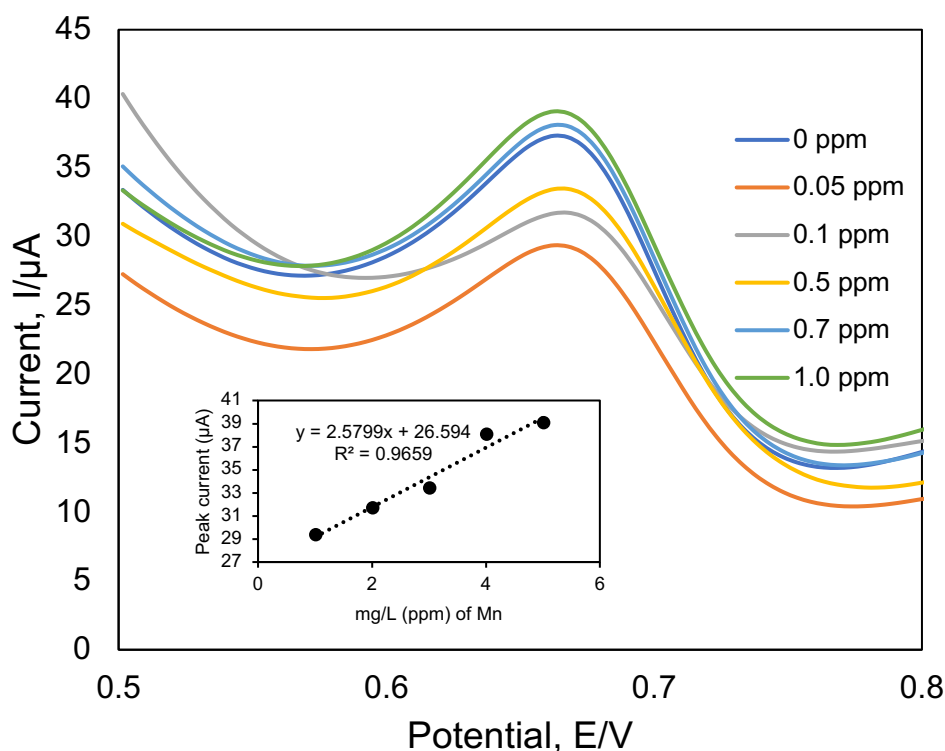
Fig. 5. Differential pulse voltammetry test for different concentrations of manganese from 0.05 ppm to 1.0 ppm in 0.1 M tris-HCl buffer supported by 5 mM Prussian Blue under 100 mVs^{-1}. This experiment was repeated at least three times (n > 3).

4. Conclusion

Electrochemical measurement of manganese ion conducted at the optimized conditions of buffer, redox indicator, pH, scan rate and accumulation time enabled rapid detection of the target ion in 2 s with a satisfactory current response. The use of Prussian blue as redox indicator has increased the current response with shifted peaks of current. The optimization process enabled detection of manganese ion at various concentration when the linear of range (LOR) from 0.05 ppm to 1.0 ppm were tested. The linear regression of manganese concentration proportional to current peaks was y = 2.5799x + 26.594 with R^2 = 0.9659 with limit of detection (LOD), S/N=3 was 0.075 mg L^{-1}. This research shows the importance of optimization for all the parameters before further modification is applied. The electrochemical method employed in this study can be applied for on-spot detection of dangerous heavy metal ions such as manganese ion in the drinking water.

Acknowledgement

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