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Electrochemical Studies of Mn(II) Mediated by Li^+ Doped Indium Tin Oxide(ITO) Electrode

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An electrochemical investigation of Manganese species has been carried out by using cyclic voltammetry (CV) at Lithium doped Indium Tin Oxide (ITO) electrode. The doping of the Li^+ ion onto the Indium Tin Oxide (ITO) electrode was carried out to 10 potential cycling in the presence of 0.1M LiOH. The modified Li^+/ITO electrode used as working electrode and was applied for the detection of Mn(II) in 0.1M KCl aqueous solution using cyclic voltammetry (CV). Electrode responses were obtained for the reduction of 50μM of Mn(II) at lithium doped modified ITO electrode, and bare ITO electrode. A well defined peak appeared at -136mV vs Ag/AgCl with a current enhancement and peak potential shift toward higher potential due to the presence of Lithium doped. Besides that, the presence of Lithium doped caused an increase of the reduction peak of Mn (II) ion (current enhancement) by about 2.9 times compared to use of bare ITO electrode. The optimum physical and chemical conditions such as pH, concentration of Mn(II) ion solution, and scan rate for current enhancement would be obtained. A linear relationship ($y= 1777.3x + 42.145$, $R^2=0.995$) was observed for the plot of current (μA) versus concentration range of 10μM to 1.0mM of Manganese in 0.1M KCl using Lithium doped modified ITO electrode. Based on the background noise of 50 data points, adjacent to the reduction peak of Mn (II), and 3σ/slope, a detection limit of 1.0nM was determined.

Keywords: Manganese, Lithium ion, Indium Tin Oxide (ITO)

1. INTRODUCTION

Voltammetry is a major branch of electroanalysis in which a potential is imposed upon an electrochemical cell and the resulting current is measured. Manganese (abbreviated Mn) is one of the most abundant metals in soils, where it occurs as oxides and hydroxides, and it cycles through its various oxidation states. The most common oxidation states of manganese are +2, +3, +4, +6 and +7. The most stable oxidation state for manganese is +2, which has a pale pink color [1, 2]. Manganese

(IV) compound, potassium permanganate is a common oxidizing agent and widely used for volumetric analysis. [3, 4] Besides that, Manganese is mainly used in iron and steel production.

Indium Tin Oxide (ITO) is a transparent conducting and photoelectric material that have attracted the interest of many researchers in the field of electrochemical due to their good electrical conductivity and photo-penetrability. [5] Liquid crystal display (LCD) and light emitted diode (LED) are some of the examples for the application of Indium Tin Oxide (ITO) in electronic and photoelectric devices [6-10]. Indium Tin Oxide (ITO) also known as the degenerate n-type semiconductor and is a mixture of indium (III) oxide (In_2O_3) and tin (IV) oxide (SnO_2) [11, 12]. Indium (III) oxide (In_2O_3) is a material that widely applied to enhance the catalytic performance for dehydrogenation of ethanol and steam reforming of methanol. [13-15] Thus, we suspected that lithium doped modified ITO electrode was used to enhance the electrode conductivity, facilitating the electron transfer and improving the analytical sensitivity and selectivity.

Many research works showed that lithium doped modified glassy carbon electrode (GCE) [16, 17] increase the sensitivity of cyclic voltammetry towards the detection of many species. However, modified GCEs easily influenced to poor reproducibility because the surface of GCE need to be cleaned before used. The problem can be solved by use of disposable material, low cost and easily modified material as an electrode material [18, 19]. Thus, Indium Tin Oxide (ITO) is one of the most suitable materials that wisely used as an electrode.

Most electrochemical methods rely on the use of modified Indium Tin Oxide electrode for the detection of variety of organic and inorganic compound such as paracetamol and H_2O_2. [20, 21] In this work, the study is on the reduction of Manganese (II) at lithium doped modified Indium Tin Oxide (ITO) electrode. It is shown that the reduction of Manganese (II) at lithium doped modified Indium Tin Oxide (ITO) electrode show an enhancement in analytical response in comparison to bare Indium Tin Oxide (ITO) electrode.

2. EXPERIMENTAL

2.1. Instrumentation and apparatus

An Electrochemical analyzer of Bioanalytical System Inc. USA: Model BAS 50W was used for cyclic voltammetry (CV), chronocoulometry (CC), and chronoamperometry (CA) study. It was equipped with an electrochemical cell that consists of 3 electrodes which are Indium Tin Oxide (ITO) electrode as working electrode, a silver/silver chloride (in 3M NaCl) as reference electrode and a platinum wire as counter electrode. All the voltammetric experiments are referred at ambient temperature of 25 ± 2 °C. N_2 gas was bubbled into the solution for 15 minutes to remove the dissolved oxygen before voltammogram was recorded.

2.2. Preparation of Li^+/ITO electrode

The ITO glass was cut into 1 x 4cm in pieces. Then the ITO glass is cleaned through ultrasonication in acetone, 0.1M NaOH and deionized water, sequentially, for 15 min each and dry it

[19]. The doping of the Li^+ ion onto the ITO electrode was carried out by subjecting the electrode to level- 10 potential cycling in the presence of 0.1M LiOH between +600mV to -600mV during cyclic voltammetry.

2.3. Chemicals and reagents

All the chemicals used such as KCl, $MnCl_2$, LiOH, HCl, NaOH and acetone are received from the manufacturers. The deionized water used for the preparation of solution is from reverse osmosis (RO) water model Elken (BIO PURE).

3. RESULTS & DISCUSSION

3.1. Current enhancement

A pronounced reduction current of Mn(II) at -136 mV vs Ag/AgCl is increased by about 2.9 times at Li^+ doped modified Indium Tin Oxide electrode (Li^+/ITO) and peak shifted by 127 mV towards higher potential as compared to that obtained at bare indium tin oxide (ITO) surface (Fig.1). These are evidences of partitioning effect attributed to the presence of Li^+/ITO electrode.

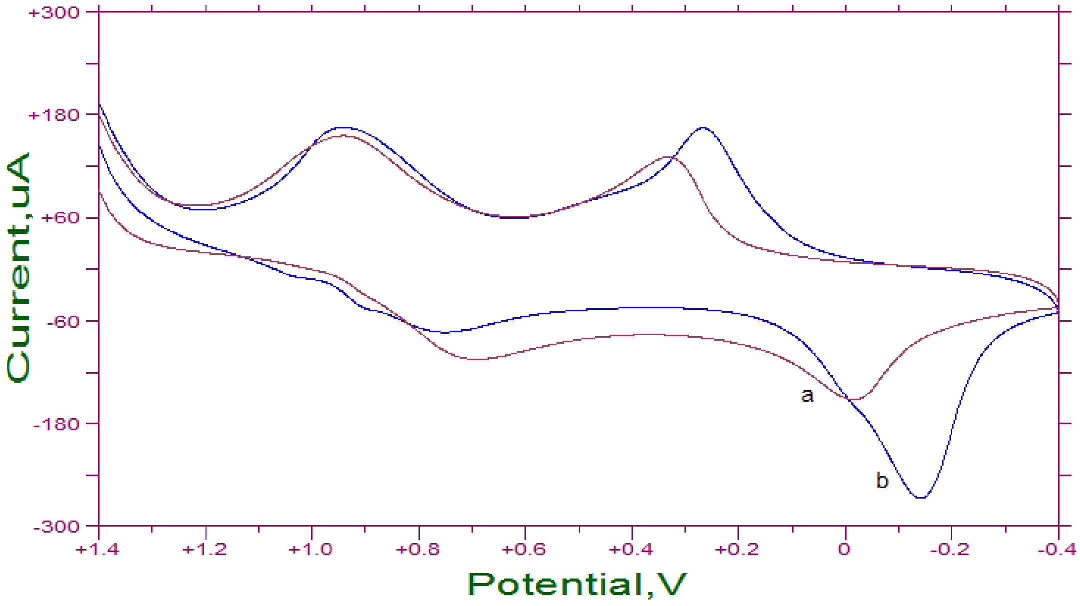


Figure 1. Cyclic voltammograms of 50.0μM Mn(II) obtained in 0.1M KCl using (a) bare ITO electrode and (b) Li^+ doped ITO electrode vs Ag/AgCl at a scan rate of 100mV/s at 25°C.

3.2. Effect of varying pH

The effect of solution pH on the electrochemical response of the modified Li^+ doped ITO electrode was studied in the pH range from 1 to 6.9 using cylic voltammetry as shown in Figure 2. pH study showed that the reduction current of Mn (II) was high under unadjusted condition of pH 6.9 but falls with decrease pH value. The optimum pH for Mn (II) is at pH 6.9. The effect of solution pH was not studied under alkaline condition because Mn(II) react with NaOH will give a result of pale yellow precipitate.

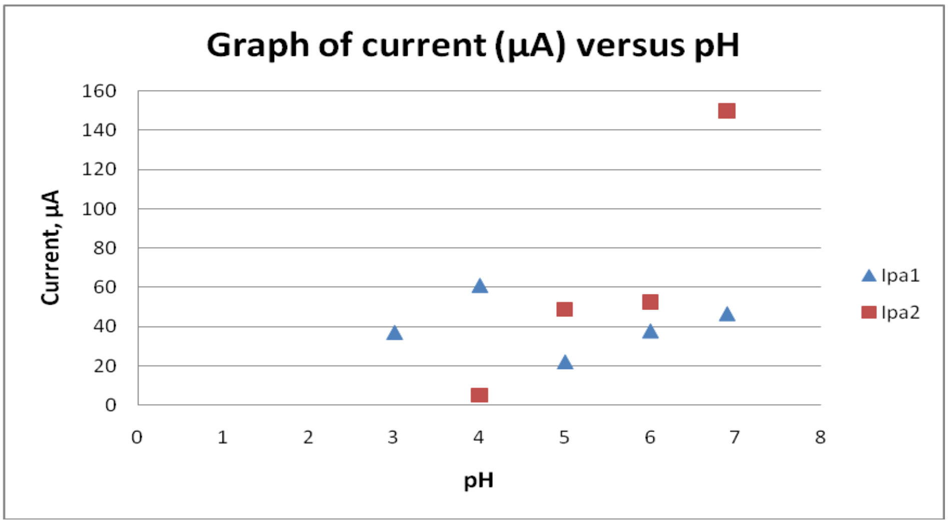
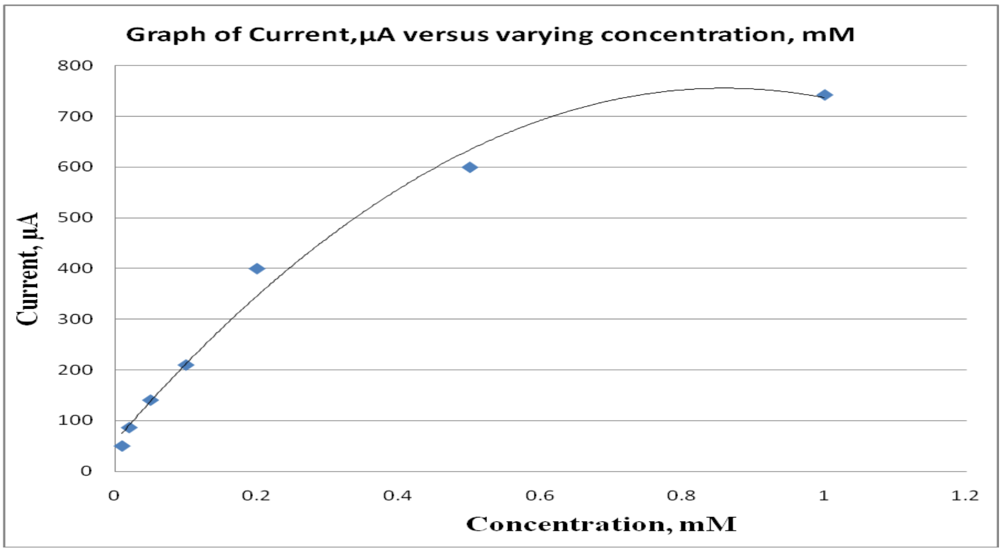


Figure 2. Graph of current versus varying pH condition of 50.0μM Mn(II) in 0.1M KCl for modified Li^+ doped ITO electrode vs Ag/AgCl at scan rate of 100mV/s.

3.3. Effect of varying Mn(II) concentration

The effect of varying concentration Mn (II) ion from 10μM to 1.0mM of Mn(II) in 0.1M KCl with Li^+ doped modified Indium Tin Oxide electrode was studied.

(a)



(b)

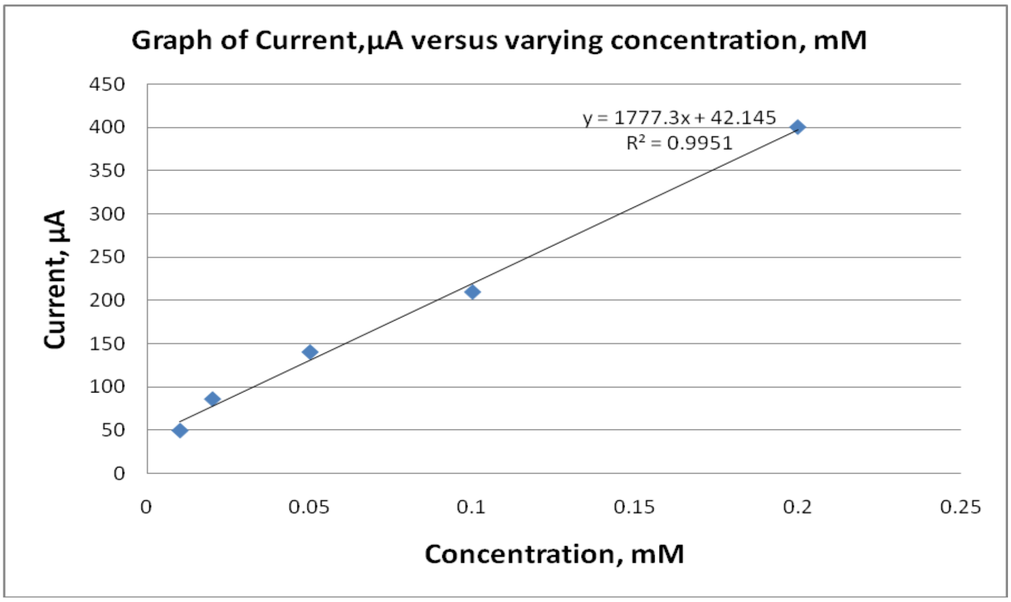


Figure 3. Calibration graph of current versus varying concentration of Mn(II) in 0.1M KCl for modified Li^+ doped ITO electrode vs Ag/AgCl at scan rate of 100mV/s from (a) 10µM to 1mM and (b) 10µM to 0.2mM.

The dependence of the voltammetric response to Indium Tin Oxide (ITO) electrode doped with lithium ion in the addition of Mn(II) from 10µM to 0.2mM of Mn (II) in 0.1M KCl showed a linear relationship (y= 1777.3x + 42.145, R=0.995) with an excellent sensitivity respond of 1777.3µA/mM as compared to 64.7 µM/mM at the CNT/Li^+/GC electrode [15]. Based on the slope and the background noise level, using 3σ/slope, the detection limit of Mn(II) of 1.0nM was obtained which appears to be better than those of 7µM at CNT/Li^+/GC electrode.[15] Thus, it proved that lithium doped modified Indium Tin Oxide (ITO) electrode is more sensitive and a good electrode sensor towards the detection of lower concentration of Mn(II) as compared to that of CNT/Li^+/GC electrode.

3.4. Effect of varying scan rate

Figure 4 shows the scan rate study of Lithium doped Indium Tin Oxide electrode. The log cathodic peaks current vary approximately linearly with a slope 0.84 and the log of scan rate over the range $5mVs^{-1}$ to $200mVs^{-1}$, which suggest that the reaction is a complex surface reaction. According to the literature review of M.Rahdi et al, the effect of varying scan rate for Mn(II) also suggested is a complex surface reaction by using CNT/Li^+/GC electrode. [15]

3.5. Effect of temperature

The effect of temperature for reduction process of Mn(II) was studied from ranges of temperature 10 to 80° C. Based on Arrhenius plot of ln peak current versus 1/T, activation energy can be calculated from the slope of the plot using Arrhenius equation (Equation 1 & 2). The activation energy calculated is 20.79 kJ/mol, which is quite comparable to the activation energy of 17.23 kJ/ obtained by using CNT/Li^+ modified glassy carbon electrode. [15]

$$K = Ae^{-Ea/RT} \qquad (1)$$

$$\text{In } k = \text{In } A - Ea/R\ (1/T) \qquad (2)$$

$$\text{In } k \quad \alpha \quad 1/T$$

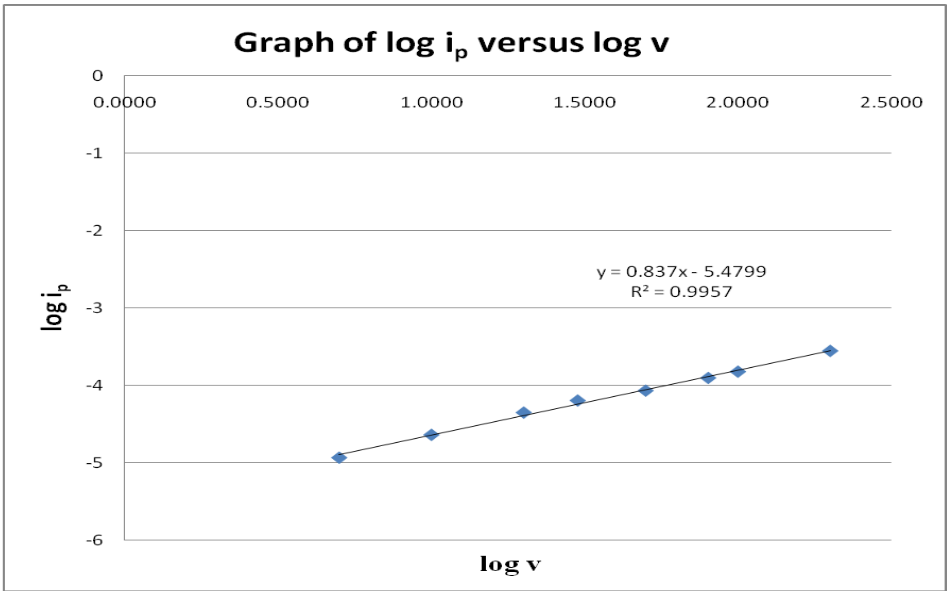


Figure 4. Plot of log I_p (cathodic current) versus log v of of Mn(II) in 0.1M KCl for modified Li^+ doped ITO electrode vs Ag/AgCl from scan rate of 5mV to 200mV/s.

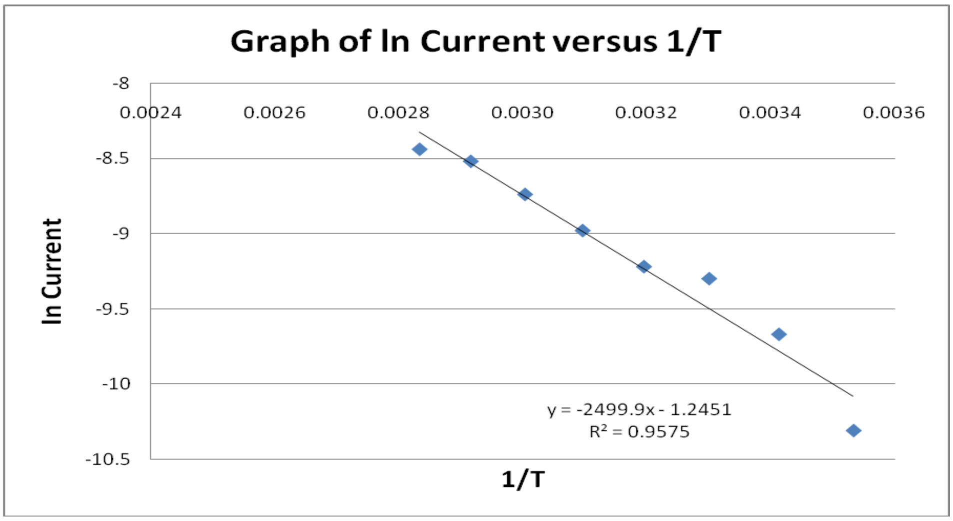


Figure 5. Plot of In I_p (cathodic current) versus 1/T of of 50μM Mn(II) in 0.1M KCl for modified Li^+ doped ITO electrode vs Ag/AgCl from temperature 10^0C to 80^0C.

3.6. Chronoamperometry and Chronocoulometry

By using Chronocoulometry, for lithium doped modified ITO electrode in 50µM Mn(II) in 0.1 M KCl, the value of surface charge calculated was about 53.65µ C/cm^2. (Figure 6) Besides that, the diffusion coefficient (D) of the Mn(II) ion in 0.1M KCl at lithium doped ITO electrode by using Chronocoulometry equal to 5.75 x 10^{-6} cm^2/s was determined. For diffusion control process, current versus time in accordance to Cottrell equation [22], a monotonic rising and current transient (current dependent of t$^{-1/2}$) should be observed. However, Figure 7 shows a non-monotonic rising current transient versus time dependent of power -1/2 was observed instead indicating presence of a non diffusion controlled process. It supported the earlier finding of a complex surface process based on the scan rate study.

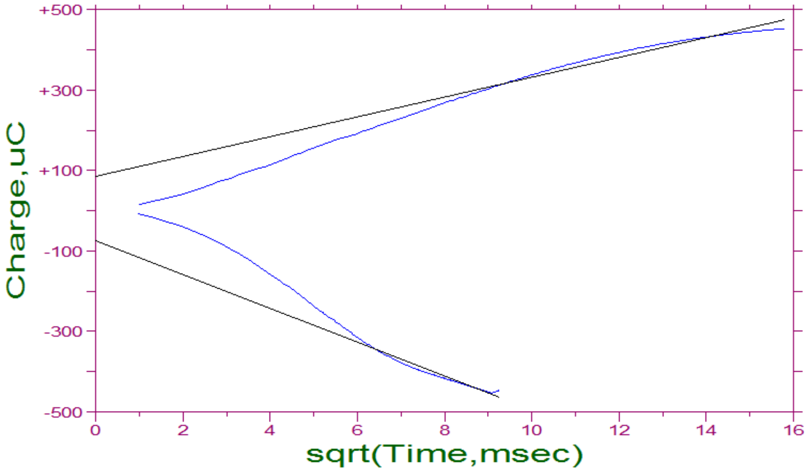


Figure 6. Anson plot of charge versus t$^{1/2}$ for the reduction of 50µM Mn(II) in 0.1M KCl by using Lithium doped ITO electrode vs Ag/AgCl at scan rate of 100mV/s.

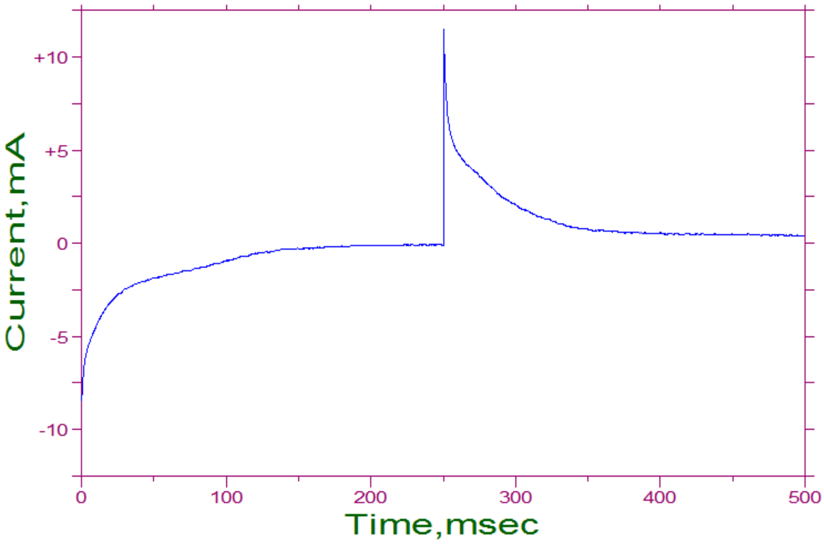


Figure 7. CA run of 50µM Mn(II) in 0.1M KCl for Lithium doped ITO electrode vs Ag/AgCl at scan rate of 100mV/s.

3.7. Reproducibility study of Li^+ doped modified ITO electrode

It was found that based on four replicates, the reduction current of Mn(II) resulted a relative standard deviation (RSD) with a value of 2.9%. Since it is less than 3%, it shows that the Li^+ doped ITO electrode is also characterized by good reproducibility.

3.8. Determination of Mn(II) in Lake water

10µM Mn(II) was spiked into the mixture solution of 5ml of supporting electrolyte, KCl and 5ml of lake water by using the Li^+ doped ITO electrode for the determination of Mn(II) in the solution. The percentage of recovery determined for Mn(II) was 99.4%. The percentage of recovery which is close to 100% showed that the Li^+ doped ITO electrode is suitable for the use of determination of Mn(II) in lake water sample.

4. CONCLUSION

The lithium doped modified Indium Tin Oxide (ITO) electrode was proven to has sensitive electrode towards the detection of Mn(II) ion. The presence of lithium doped modified ITO electrode causes an increase of reduction current of Mn(II) ion by about 2.9 times if compared with bare ITO electrode. The sensitivity of current enhancement was strongly dependent on the pH, scan rate, temperature, and concentration of Mn (II) ion solution. Based on the varying scan rate study and chronoamperometry, the reaction appears to be complex surface reaction. Diffusion coefficient of 5.75 x $10^{-6}cm^2/s$ of Mn(II) under the voltammetry conditions mentioned above was estimated using Chronocoumetry. The sensitivity, expressed as the slope of the linear region of calibration curve was 1777.33 µA/mM with a correlation coefficient of 0.995. The detection limit of 1.0nM and activation energy of 20.79 kJ/mol was determined.

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