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Electrochemical Oxidation of Sodium Dodecylbenzenesulphonate, Cetyltrimethyl-ammonium Bromide and Oleic Acid at Platinum and Cobalt Hydroxide Modified Platinum Electrodes

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Electrochemical oxidation of sodium dodecylbenzenesulphonate (SDBS), cetyl-trimethylammonium bromide (CTAB) and oleic acid has been studied at platinum (Pt) and $Co(OH)_2$ modified platinum ($Pt/Co(OH)_2$) electrode. Two methods, namely, cyclic voltammetry and constant current electrolysis have been used in this study. It was found that the electrochemical oxidation of the compounds studied was best conducted in KOH supporting electrolyte. The oxidation current of each compound studied at $Pt/Co(OH)_2$ was higher than that at Pt electrode, and percent yield of CO_2 produced from constant current oxidation of each compound studied at $Pt/Co(OH)_2$ electrode was higher than that at Pt electrode showing that electrocatalytic oxidation of the compounds studied was occurred at $Pt/Co(OH)_2$ electrode. The results suggests that the $Pt/Co(OH)_2$ electrode could be used for fatty acid and surfactant destruction in polluted water.

Keywords: mediated oxidation, modified electrode, oleic acid, SDBS, CTAB, voltammetry

1. INTRODUCTION

Water pollution by organic compounds has become main concern because of their increasing use in industries and household chemicals. Two main potential water pollutants are fatty acids and surfactants. Fatty acids are broadly used in domestic cleaning products, cosmetics, pharmaceuticals, foods and lubricants. Fatty acids used in household cleaning products normally contain C10 to C22 chains and can be toxic for fish in the environment. Therefore, degradation of fatty acids in waste water before they are introduced into environment has become very important. Several methods have been developed for fatty acid treatment such as anaerobic degradation [1,2], electrooxidation [3], chemical oxidation [4] ultrasound-assisted oxidation [5], catalyzed oxidation [5,6], photosensitized oxidation [7] and high temperature oxidation [8].

Surfactants are widely contained in many products mainly in household chemicals. Surfactants are also used in production process of wide range of products such as textiles, fibbers, food, paints, polymers, cosmetics, pharmaceutical, microelectronics, mining, and paper pulp. The use of surfactants is increasing every year. In 1984, 1987 and 1995, world surfactant production was 1.7, 1.8 and 9.3 million tons, respectively [9]. Surfactants in concentrations greater than $\underline{1}$ mg/L are harmful to humans, fish and vegetation, and they act synergistically with other toxic chemicals [2]. There are three types of surfactants namely anionic, cationic and nonionic surfactants. Cationic surfactants (CS) have strong affinity with environments because sewage sludge, soil and sediments have predominantly negative charge [10]. Surfactants can be treated by coagulation-flocculation process [9], sonochemical degradation [10], photocatalytic degradation [11,12], photoelectrochemical degradation [13], electrochemical oxidation [14], biodegradation [15] and oxidative degradation [16,17].

Mediated electrochemical oxidation has been shown to be one of effective method for destruction of hazardous organic pollutant [18,19]. However nontoxic mediator must be used to avoid contamination of solution. In this research we studied the use of $Co(OH)_2$ modified platinum electrode for destruction of fatty acid and surfactant. $Co(OH)_2$ modified platinum electrode was chosen because $Co(OH)_2$ can be easily plated of the surface of the electrode and previous study show that it can electrocatalyze ascorbic acid oxidation [20] and the Pt/Co(OH)(2) presented excellent catalytic performance in the chemoselective hydrogenation of halonitrobenzenes such as chloronitrobenzenes, bromonitrobenzene and iodonitrobenzene [21]. We expect that the electrode can also electrocatalize oxidation of fatty acid and surfactant. To study the performance of this electrode for fatty acids and surfactants destruction, three model compounds was used namely sodium dodecylbenzenesulphonate (SDBS), cetyl-trimethylammonium bromide (CTAB) and oleic acid.

We have not found in the literature, namely: a cyclic voltammetry study to determine the optimum conditions of the electrode, supporting electrolyte and mediators. The use of Pt electrode modified by cobalt hydroxide as the working electrode for electro-oxidation of SDBS, CTAB and oleic acid not found in the literature. The study was conducted by researchers previously limited to only a few parameters of voltage, temperature, and temperature to convert CO2 into organic compounds. They have not revealed the oxidation reactions that occur in the electrolysis cell and reduction reactions. There is no report on the rate of transfer reaction of cobalt (II) to cobalt (III), so here studied the use of multiple electrodes and electrolyte for electro-oxidation supporters SDBS, CTAB and oleic acid.

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

The chemicals used were $CoCl_2.6H_2O$, KCl, $NaClO_4$, KNO_3, KOH, oleic acid, CTAB, SDSB, HCl, Na_2CO_3 and methanol. All chemicals were of analytical grade and obtained from either Merck or

Aldrich. All chemicals were used without further purification. Milli Q water was used to make all solutions.

2.2. Apparatus

All voltammetry measurements were conducted using eDAQ (Model ED410) electrochemical analyzer using three-electrode system. Working electrodes used were either Pt disc or $Co(OH)_2$ modified platinum disc electrode (Pt/Co$(OH)_2$) having diameter of 1 mm. Auxiliary electrode was a platinum wire, and reference electrode was Ag/AgCl (3 M NaCl). Electrolysis experiments were conducted in a 200 ml homemade cell using ATTEN APS3005Si power supply using platinum sheet electrode (1 cm × 1 cm) or the modified platinum sheet electrode as anode and platinum wire as cathode. Surface morphology, structure and composition of electrodes were identified by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) model JEOL-JSM-6510LV.

2.3 Experiment

Modified Platinum electrode. Pt/$Co(OH)_2$ electrode was made by placing a platinum electrode in a solution containing 0.1 M Na_2CO_3 plus 40 mM NaK-tartrate and 4 mM $CoCl_2$ at pH = 11.6, with 0.1 M NaOH solution as supporting electrolyte and then cyclic voltammetry was conducted (100 cycle) at potential range of -250 to 750 mV versus Ag/AgCl at scan rate of 100mV/s [20].

Selection of supporting electrolyte. Cyclic voltammogram was made in voltammetric cell containing 28 mM of SDBS or CTAB or oleic acid and 25 mM cobalt (II) mediator. Four supporting electrolyte, namely KNO_3, KCl, KOH and $NaClO_4$, with concentration of 0.1 M was studied.

Electrolysis. The concentration of SDBS, CTAB and oleic acid used in electrolysis experiment was 500 ppm and the concentration of KOH as supporting electrolyte was 150 ppm. A constant current of 40 mA was used during electrolysis. Concentration of CO_2 produced was monitored every 15, 30, 45, 60 minutes.

Determination of CO_2. Carbon dioxide produced during electrolysis experiment was determined with acid base titrimetric method using HCl standard solution and two indicators, namely phenolphthalein and methyl red.

3. RESULTS AND DISCUSSION

3.1 Preparation of modified electrode

Films of cobalt hydroxide were prepared on Pt electrode using cyclic voltammetry technique. Working electrode potential was cycled in the range of –250 to 1000 mV vs Ag/AgCl at a scan rate of 100 mV s^{-1}. One hundred consecutive cyclic voltammograms (CV) of a Pt electrode in the presence of 100 mM Na_2CO_3 + 40 mM NaK tartrate + 4.0 mM $CoCl_2$ at pH 11.6, was conducted to form $Co(OH)_2$ layer on the surface of platinum electrode. Typical voltammograms obtained are presented in Figure 1. The voltammograms are similar to those reported in literature [20].

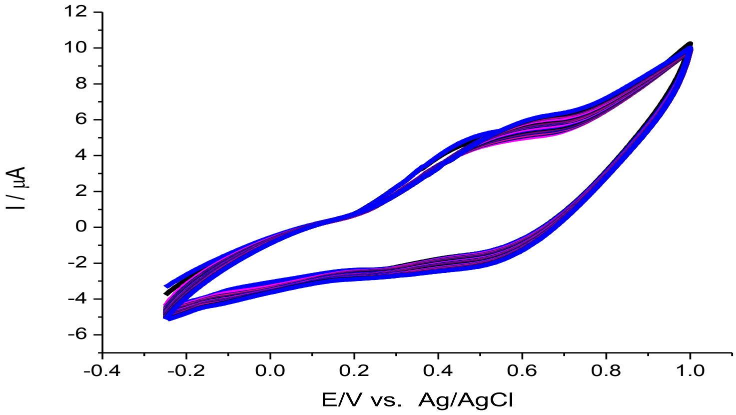

Figure 1. Cyclic voltammograms of 4.0 mM $CoCl_2$ + 40 mM NaK tartrate + 100 mM Na_2CO_3 solution at Pt electrode (15 cycles) in potential range of –200 and 1000 mV obtained using scan rate of 100 mV s^{-1}.

The surface morphology of the modified electrode was studied using SEM/EDX technique. SEM/EDX image of Pt/$Co(OH)_2$ is shown in Figure 2. EDX measurement confirm that the particle contain cobalt. Figure 2 shows that layer of relatively uniform $Co(OH)_2$ particle with an average diameter of 1 µm have been form on the surface of Platinum electrode.

3.2 Effects of supporting electrolyte

Several supporting electrolyte have been studied for the oxidation of SDBS, CTAB and oleic acid. Solution of 0.1 M of KCl, $NaClO_4$, KNO_3 and KOH has been studied as supporting electrolyte for the oxidation processes. It was found that KOH was the best supporting electrolyte because it gave the highest oxidation current of the analyte.

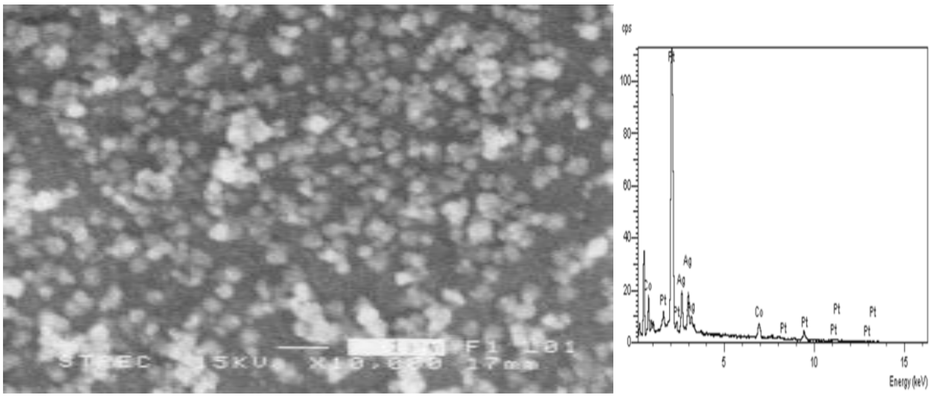

Figure 2. SEM/EDX image of Pt /$Co(OH)_2$ with magnification of 10,000 times.

3.3 Electrochemical oxidation of SDBS

Figure 3 shows cyclic voltammograms (CVs) of SDBS obtained from solution of 24 mM SDBS in 0.1 M KOH using both Pt and Pt/Co(OH)$_2$ electrodes. Because no peaks were found in background solution of 0.1 M KOH using both electrodes (CVs were not shown), the oxidation peak in Figure 3 was due to oxidation of SDBS. At both electrodes, oxidation of SDBS started to occur at potential around 0.1 V. Clear oxidation and reduction peaks were found using Pt/Co(OH)$_2$ electrode indicating that SDBS oxidation was mediated by Co(OH)$_2$. Oxidation current at Pt/Co(OH)$_2$ electrode was much higher than that of Pt electrode. For comparison, at potential of 0.5 V, oxidation current at Pt/Co(OH)$_2$ electrode was 138 μA while oxidation current at Pt electrode was 38 μA. This indicates that oxidation of SDBS was more efficient at Pt/Co(OH)$_2$ electrode than at Pt electrode.

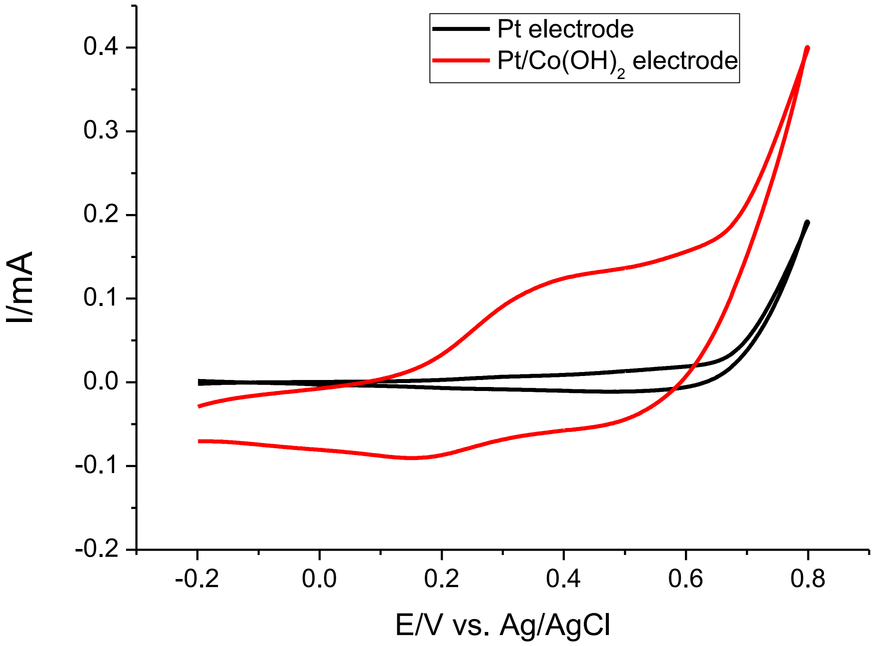

Figure 3. Cyclic voltammograms of 24 mM SDBS in 0.1 M KOH on Platinum and Pt/Co(OH)$_2$ electrodes.

To further evaluate performance of both Pt and Pt/Co(OH)$_2$ electrode for oxidation of SDBS, constant current (40 mA) oxidation of 500 ppm SDBS was conducted using each electrode as anode. In both cases Pt wire electrode was used as cathode. Carbon dioxide produced from oxidation process was determined volumetrically and percent yield of carbon dioxide produced was plot against time of electrolysis. The plot for SDBS oxidation is shown in Figure 4. As expected, percent yield of carbon dioxide produced increase as time of electrolysis increase. Percent yield of carbon dioxide produce using Pt/Co(OH)$_2$ electrode is higher than that of Pt electrode, showing that Pt/Co(OH)$_2$ electrode is more efficient for SDBS oxidation than Pt electrode. These results are in good agreement with the CVs data.

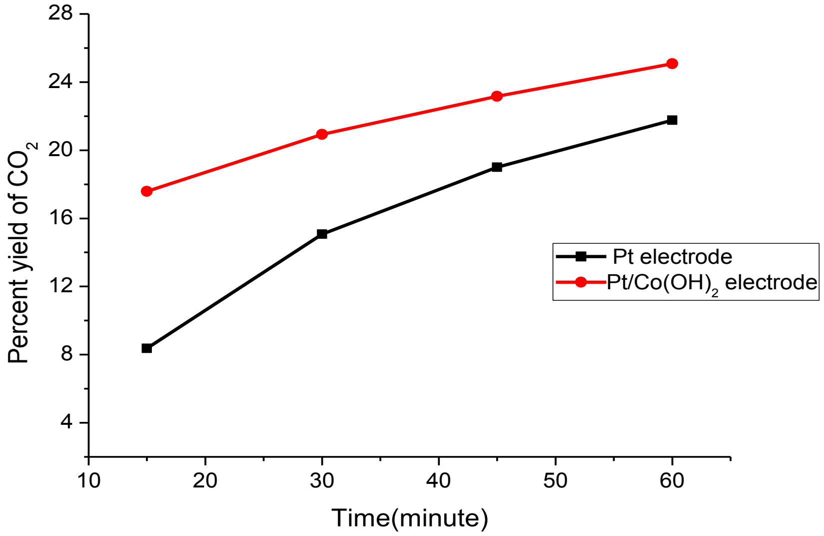

Figure 4. Percent yield of CO_2 produced from oxidation of 500 ppm SDBS

3.3 Electrochemical oxidation of CTAB

Oxidation of CTAB on Pt and Pt/Co(OH)$_2$ electrodes was also studied in the same way. The CVs of CTAB obtained from solution of 24 mM CTAB in 0.1 M KOH using Pt and Pt/Co(OH)$_2$ electrodes are shown in Figure 5. At both electrodes, oxidation of CTAB started to occur at potential around 0.1 V. Similar to the CVs of SDBS, the CV of CTAB at Pt/Co(OH)$_2$ electrode has clear oxidation and reduction peaks indicating that CTAB oxidation was also mediated by Co(OH)$_2$. Oxidation current of CTAB at Pt/Co(OH)$_2$ was also much higher than that at Pt electrode showing electrocatalytic effects of the mediated oxidation process. At potential of 0.5 V, the oxidation current of CTAB at Pt/Co(OH)$_2$ was 164 μA which is higher than that of SDBS at the same electrode showing that oxidation of CTAB at the modified electrode was more efficient than that of SDBS at the same electrode. The oxidation current of CTAB at Pt electrode was 17 μA, much lower than that at the modified electrode, indicating a less efficient oxidation of CTAB at Pt electrode.

Constant current (40 mA) oxidation of 500 ppm CTAB at Pt and Pt/Co(OH)$_2$ electrodes was also conducted to evaluate the efficiency of CTAB oxidation. Plot of percent yield of CO_2 produced from CTAB oxidation *versus* time of electrolysis is shown in Figure 6. As expected, percent yield of CO_2 produced increase with time of electrolysis. As expected from the CVs of CTAB at Pt and Pt/Co(OH)$_2$ electrodes, percent yield of CO_2 produced at the modified electrode was higher than that at Pt electrode showing a more efficient CTAB oxidation at the modified electrode. Interestingly, the difference of percent yield of CO_2 produced at Pt and Pt/Co(OH)$_2$ electrode was not more than 3%. Percent yields of CO_2 produced from CTAB oxidation at Pt and Pt/Co(OH)$_2$ electrodes were much higher than those from SDBS oxidation at both electrodes showing that CTAB was more easily oxidized than SDBS.

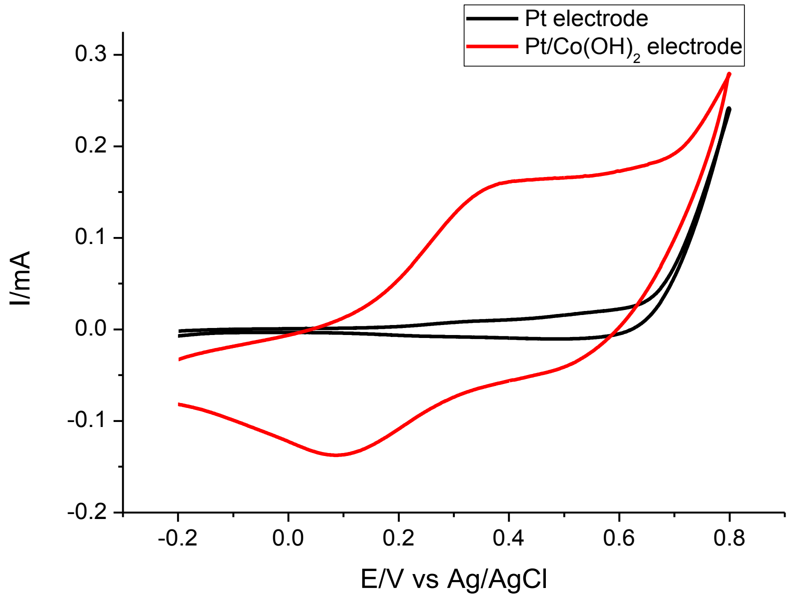

Figure 5. Cyclic voltammograms of 24 mM CTAB in 0.1 M KOH on Platinum and Pt/Co(OH)$_2$ electrodes.

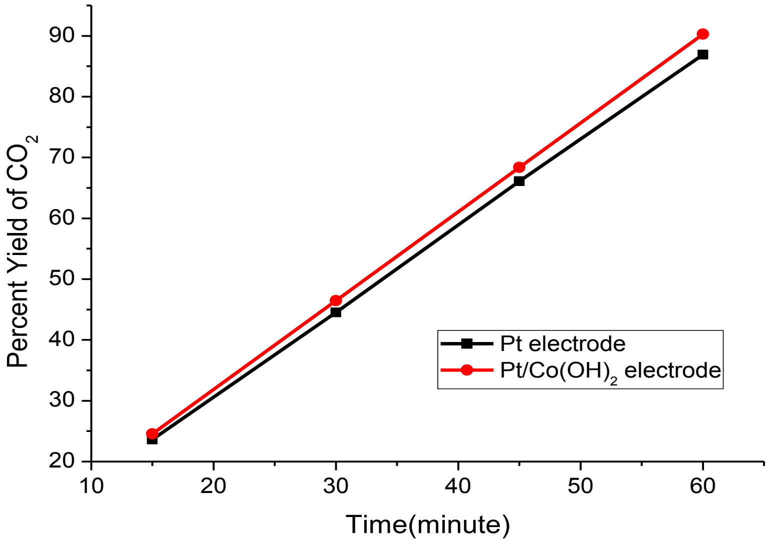

Figure 6. Percent yield of CO$_2$ produced from oxidation of 500 ppm CTAB

3.3 Electrochemical oxidation of oleic acid

Figure 7 shows the cyclic voltammogram of 24 mM oleic acid in 0.1 M KOH supporting electrolyte. It has a reversible peak with oxidation and reduction potential of 0.208 V and 0.155 V, respectively. Similar to the results found for SDBS and CTAB, the oxidation current of oleic acid at Pt/Co(OH)$_2$ electrode was higher than that at Pt electrode showing electrocatalytic oxidation of oleic acid at Pt/Co(OH)$_2$. At potential of 0.5 V, oxidation current of oleic acid at Pt/Co(OH)$_2$ and Pt electrodes was 41 mA and 9 mA, respectively. However, the oxidation currents of oleic acid at both electrode was much lower compare to those of SDBS and CTAB indicating less efficient oxidation of oleic acid at both electrode. Constant current oxidation (40 mA) of 500 ppm of oleic acid at Pt and Pt/Co(OH)$_2$ electrodes confirm this conclusion.

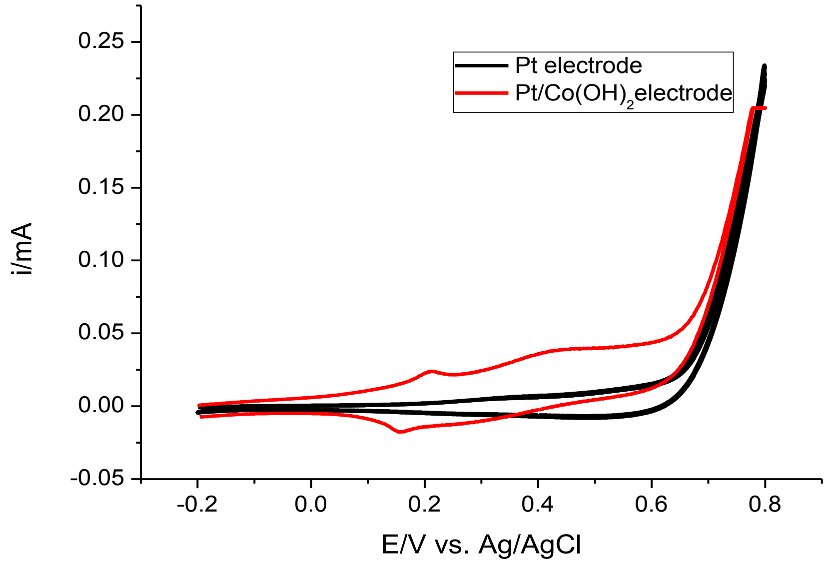

Figure 7. Cyclic voltammograms of 24 mM oleic acid in 0.1 M KOH on Platinum and Pt/Co(OH)$_2$ electrodes.

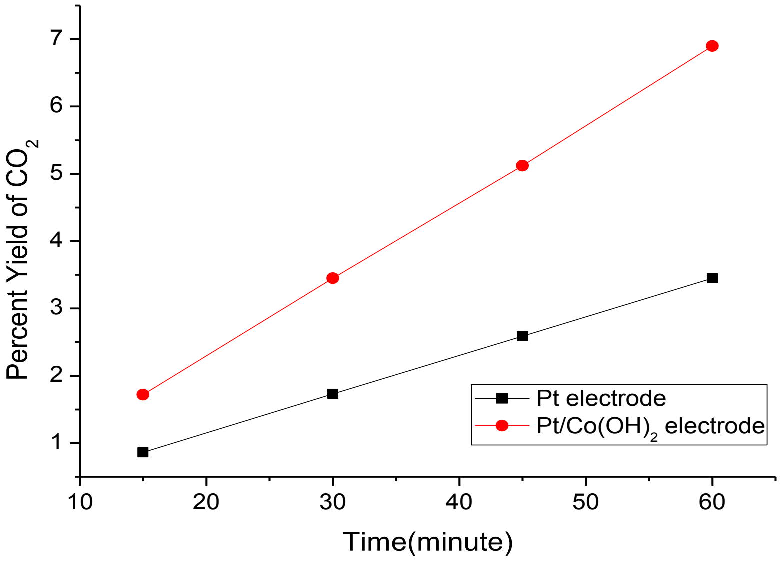

Figure 8. Percent yield of CO$_2$ produced from oxidation of 500 ppm CTAB

Percent yield of CO$_2$ produced from oxidation of 500 ppm oleic acid is shown in Figure 8. As expected, percent yield of CO$_2$ produce from the oxidation of oleic acid increase with oxidation time. The yields are higher at Pt/Co(OH)$_2$ than those at Pt electrode showing a more efficient oxidation of oleic acid at the modified electrode. However, the maximum yield obtained with Pt/Co$(OH)_2$ electrode was about 7% which is much lower than the maximum yield obtained from SDBS and CTAB.

4. CONCLUSION

It has been shown that SDBS, CTAB and oleic acid can be electrochemically oxidize more efficiently at Pt/Co$(OH)_2$ electrode than at Pt electrode. It indicated that Co$(OH)_2$ plated on the surface of Pt electrode mediated electron transfer process at Pt/Co$(OH)_2$ electrode leading to electrocatalytic oxidation of SDBS, CTAB and oleic acid. This suggests that the Pt/Co$(OH)_2$ electrode could be used for fatty acid and surfactant destruction in polluted water.

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