

Investigation of the optimum conditions for methanol electro-catalytic oxidation using titanium/platinum-rhodium modified electrode

H. H. Shaarawy^{*}; A. M. Baraka^{} & H. A. Hamed^{*}**

^{*}Chemical Eng. & Pilot Plant Dep., National Research Center (NRC), Cairo , Egypt.

^{}Chemistry Department, Faculty of Sciences , Cairo University, Cairo, Egypt.**

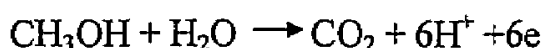
Abstract

The electrocatalytic degradation of methanol using titanium/platinum-rhodium modified electrode was investigated. The results of electrocatalytic oxidation process of the methanol were expressed in terms of remaining methanol concentration, COD, and total organic carbon removal, which were determined experimentally. Different operating conditions such as applied current density, pH, electrolysis time, temperature, ...etc were studied. The under-development modified electrode gave good results for the complete removal of methanol from its solutions.

Key words: Titanium, modified electrodes, Platinum, Rhodium, methanol, electro catalytic oxidation.

Introduction

Nowadays, the heterogeneous catalysis of electrochemical reactions occurring at the electrode- electrolyte interface, has mainly concerned technological investigations related to energy storage, and energy conversion (fuel cells and batteries)[1,2], and environmental protection (wastewater treatment)[3]. Many fundamental investigations were undertaken in the last two decades on the direct oxidation of several alcohols : Methanol[4], ethanol[5], ethylene- glycol[6,7], glycerol[8], butanol[9], and also related compounds : formic acid[10], formaldehyde[11],...etc. The reason is that the above mentioned compounds are very interesting as fuels due to a lot of advantages: including high solubility in aqueous electrolytes, relatively high reactivity, ease of storage and supply, and small toxicity. On the other hand, the presence of these substances in industrial wastewater cause serious pollution problems. Methanol is one of the most important fuel used for electricity production (fuel cells), and in the same time formed as pollutant in wastewater of several industries such as pharmaceutical, beverages, ...etc. Several mechanisms for the electrochemical oxidation of methanol were proposed in the literature [12-15]. Herrero et al. [16] suggested a dual path mechanism for methanol electrooxidation on platinum electrode, this mechanism is :



This mechanism was found to be valid if the methanol oxidation charge is larger than the corresponding CO formation charge [16].

The presence of Pt-OH layer on Pt surface, leads to several reaction mechanisms [17]. It was predicted that, the adsorption of methanol occurs

only on the base Pt sites and not on the PtOH sites, although the oxidation occurs through the energy of PtOH present on the electrode surface. The efficiency of methanol electro-oxidation is inhibited due to various factors. One of these factors is the oxides formation on the surface of platinum [18]. CO, which represents the main stable intermediate after methanol adsorption, is adsorbed on two sites on the platinum surface [19]. For smooth polished Pt, attack on adsorbed CO by water appears to be the rate limiting process, where for electrochemical roughened Pt, adsorbed CO helps to stabilize the roughened Pt surface, allowing oxidation of methanol to take place at significantly lower overpotentials. CO was identified as the poisoning species[20]. The thermally decomposed alloy electrode containing 10% Rh showed the highest anti- poisoning ability [20]. Electro-catalytic activities of binary noble metal co-deposits Pt-Pd, Pt-Rh, Pt-Ru, Pt-Ir and Pt-Au of different composition over carbon substrate were studied for the anodic oxidation of methanol in alkaline solution [20]. Electrodes are indispensable and of importance in the fields of chemical analysis and electrochemical industries. The development about the material of an electrode for practical application is continuously lasting. A good electrode must possess a superior electrode conductivity, an excellent catalytic activity to a chemical reaction expected to occur, and sufficiently prolonged life-time to be free from being spoiled or damaged. An electrode will face much crucial conditions when applied as an anode. In addition to an abrasion caused there onto by its surrounding solution, the anode electrode will be eroded by oxygen or chlorine gas formed thereon.

Owing to the possibility of processing a superior electrode chemically catalytic activity, excellent electric conductivity, corrosion durability and

chemical inertness, the modified electrodes attract the attention. Modified electrodes is the term used for the applying an catalytic thin film over electrode surface to form the so called mediator. The present work aims to study the optimum conditions for methanol electro-catalytic oxidation using titanium/platinum-rhodium thermally activated modified electrode prepared by the electro deposition technique.

Experimental

The titanium/platinum-rhodium thermally activated modified electrode was prepared according to the method described elsewhere [21]. The methanol used was of analytical grade and produced by El Naser for pharmaceutical chemicals company in Egypt (EDWIC). Synthetic solution of methanol used for experimental work with concentration of 0.5 g/l . The cell used in this investigation was made of transparent Perspex in the form of rectangular trough. The anode was supported in a vertical position midway between, and parallel to the graphite cathodes. The distance between each cathode and the anode was 2cm., the solution used in each experiment was 100ml, also the anode area was 15cm². All experiments were carried out with stirring. The electrical circuit used in the process is shown diagrammatically in Fig.(1). Analytical parameters were measured to evaluate the electro-catalytic oxidation efficiency of methanol, these parameters were: (i) remaining methanol concentration (mg l⁻¹) [23], (ii) chemical oxygen demand COD (mgO₂ l⁻¹), which is a measure of the oxygen equivalent to the organic matter content of a sample that is susceptible to the oxidation by strong chemical oxidant. COD can be related empirically to organic matter content. All required equipment including reagents, COD digestion reactor, used are supplied from Hash systems for analysis, Hach

Co., Loveland, Colorado, USA., the spectrophotometer (model 552s double – Beam UV-Visible, Bodensee Werk Perkin – Elmer and Co. GMBH, Germany) with microcomputer electronics was used in our investigation. The methanol concentration was measured with a liquid chromatograph (Shimazu LC-6A), and reactor digestion method, USEPA approved for reporting [22,23], was used for the determination of chemical oxygen demand (COD).

Studies were carried out for the determination of optimum operating conditions for the degradation of methanol from its synthetic solutions, and COD removal by electrocatalytic oxidation process using titanium/platinum-rhodium thermally activated modified electrode. The studied operating conditions were: type of conductive electrolyte, current density (mAcm^2), time of electrolysis (min.), pH, temperature ($^{\circ}\text{C}$), supporting electrolyte concentration. NaOH, and HCl were used for pH adjustment.

Results

Figs.(2,3) show the effect of supporting electrolyte type on the electro catalytic degradation of methanol using Ti/Pt-Rh thermally activated modified electrode. five electrolytes were examined (NaOH 3g/l, H_2SO_4 3g/l, NaCl 3g/l, Na_2CO_3 3g/l, and KCl 3g/l). The operating conditions of the electro-catalytic oxidation process were: current density 20mAcm^{-2} , 25°C , initial methanol concentration 0.5g/l, pH 2, and electrolysis time 15 min. It is clear from the results that NaCl show the maximum degradation for methanol i.e the methanol concentration was 0 mg/l and COD reduced to 0.0 mgO_2/l while the methanol concentration and COD value were (213,4 and 333,33), (242,06 and 378), (456,6 and 727,2), and (229, and 357,69) for

NaOH, H₂SO₄, Na₂CO₃, and KOH, respectively. From these results, it is clear that, NaCl is the most effective supporting electrolyte. For that reason, NaCl was chosen as supporting electrolyte in the following series of experiments.

The effect of current density on remaining methanol concentration and COD removal is shown in Figs.(4,5). The electro-catalytic oxidation process was carried out at pH2, 25°C, 500mg/l methanol concentration, NaCl 3g/l, and electrolysis time 15min. The results show that both methanol removal and COD drop increase with the increase of the applied current density, COD reaching zero at 20 mAcm⁻². Therefore, a current density of 20 mAcm⁻² was taken as the optimum value.

The effects of pH variation on both degradation of methanol and COD decrease were shown in Figs(6,7). Operating conditions of oxidation process were 20 mAcm⁻², 25°C, 15 min, NaCl 3g/l, and 500 mg/l methanol. These results show that the optimum pH value for degradation of methanol and COD decrease was 2.

Figs (8,9) represent the effect of electrolysis time on both degradation of methanol and COD Removal. The operating conditions were, 20mAcm⁻², pH 2, 25°C, NaCl 3g/l, and 500mg/l methanol. The results show that methanol was completely destroyed and complete removal of COD was obtained at 15min.

Figs (10,11) show the effect of NaCl concentration, on the removal of COD and degradation of methanol at operating conditions 20mAcm⁻², pH 2, 25°C, 15 min. and 500 mg/l methanol concentration. The results show that, the maximum degradation of methanol was obtained at NaCl concentration

equals to 3 g/l and any increase of NaCl concentration above 3g/l has no effect on the removal efficiency.

Figs(12,13) show the effect of initial methanol load on the degradation and COD removal. The operating conditions were: 20 mAcm⁻², 15 min., 25°C, pH 2, NaCl 3g/l. The results show that the increase of initial methanol concentration has no effect on both COD, and methanol removal till methanol concentration reaches 500 mg/l. At higher concentration the removal of both methanol and COD decreases and additional variation of operating conditions are required such as increase of current density or electrolysis time.

Table(1) shows the effect of temperature on both methanol residual concentration and COD removal at operating conditions: 20 mAcm⁻², pH 2, 15 min., NaCl 3g/l, and 500 mg/l methanol concentration. The results show that no change was obtained with temperature change. For that reason the temperature of 25°C is taken as optimum.

Table (1) Effect of temperature on both the methanol and COD removal using Ti/Pt-Rh modified electrode.

Temperature (°C)	Remaining methanol conc. (MgL ⁻¹)	COD (mg O ₂ L ⁻¹)
25	0	0
35	0	0
40	0	0
60	0	0

From the above mentioned results, the following optimum conditions for electrocatalytic oxidation of methanol using titanium/platinum-rhodium

thermally activated modified electrode were: current density 20 mAcm^{-2} , pH 2, temperature 25°C , electrolysis time 15 min, and 3g/l NaCl.

Discussion

The results of the study of the possibility of the use of titanium/platinum-rhodium thermally activated modified electrode, prepared by electro deposition technique for methanol electrocatalytic oxidation are presented in figs.(2-15). This electrode was used as anode in the electro catalytic oxidation process. The simulated effluent of methanol contained mainly NaCl as supporting electrolyte at pH 2. The results of the electro catalytic oxidation process were expressed in terms of residual methanol concentration and COD removal. The effect of different operating conditions such as : type of supporting electrolyte, current density, pH, temperature, electrolysis time, initial methanol concentration and supporting electrolyte concentration. Taking into consideration the effect of initial methanol concentration on the removal of methanol and COD, it can be concluded that, Ti/Pt-Rh modified electrode had highest efficiency in the methanol electrocatalytic oxidation process. When this electrode was used as anode in the electrocatalytic oxidation process, more concentrated methanol effluents can be treated and complete removal of methanol and COD can be obtained. This may be attributed to the assumption that, the electronic structure of the electrode greatly influences its electrocatalytic activity.

Also , it was reported [24] that, organic matters oxidation can be accomplished by indirect electrochemical route, when the contaminated stream is pumped against a suitable anode at which chlorine or ClO^- is generated (if necessary with prior addition of Cl^- ions). These species (Cl_2 ,

ClO^-) are powerful oxidizing agents capable of destroying a wide range of biological microorganisms as well as many organic chemicals in the homogeneous phase. The indirect homogeneous oxidation mechanism means that, mass transport limitations are not so serious, and even very dilute impurities can be removed.

From the previous considerations, it can be predicted that the removal of methanol from its simulated solution may proceed by direct electrochemical oxidation rather than indirect electrochemical oxidation. The oxidation by the electrocatalytic process was carried out at considerable low current densities not more than 20mAcm^{-2} . At these low current densities there is a great possibility of electrogeneration of Cl_2 and ClO^- in the solutions. These species are powerful oxidizing agents capable of destroying, oxidation and removal of methanol from its simulating solutions.

On the other hand, when H_2SO_4 , KOH , NaOH , and Na_2CO_3 were used as supporting electrolytes in the present investigation, the efficiency of the methanol and its COD removal was relatively low. This may be due to the low current densities used in the oxidation process. This means that the amount of the formed oxygen and/ or intermediate species at these low current densities is not enough to perform a complete electrocatalytic oxidation of methanol, but partial oxidation may occur.

All these remarks confirm the assumptions that the electrogenerated Cl_2 , ClO^- may play the main role in the electro catalytic process of methanol, and its removal from its simulated solutions containing NaCl as supporting electrolyte at low pH values.

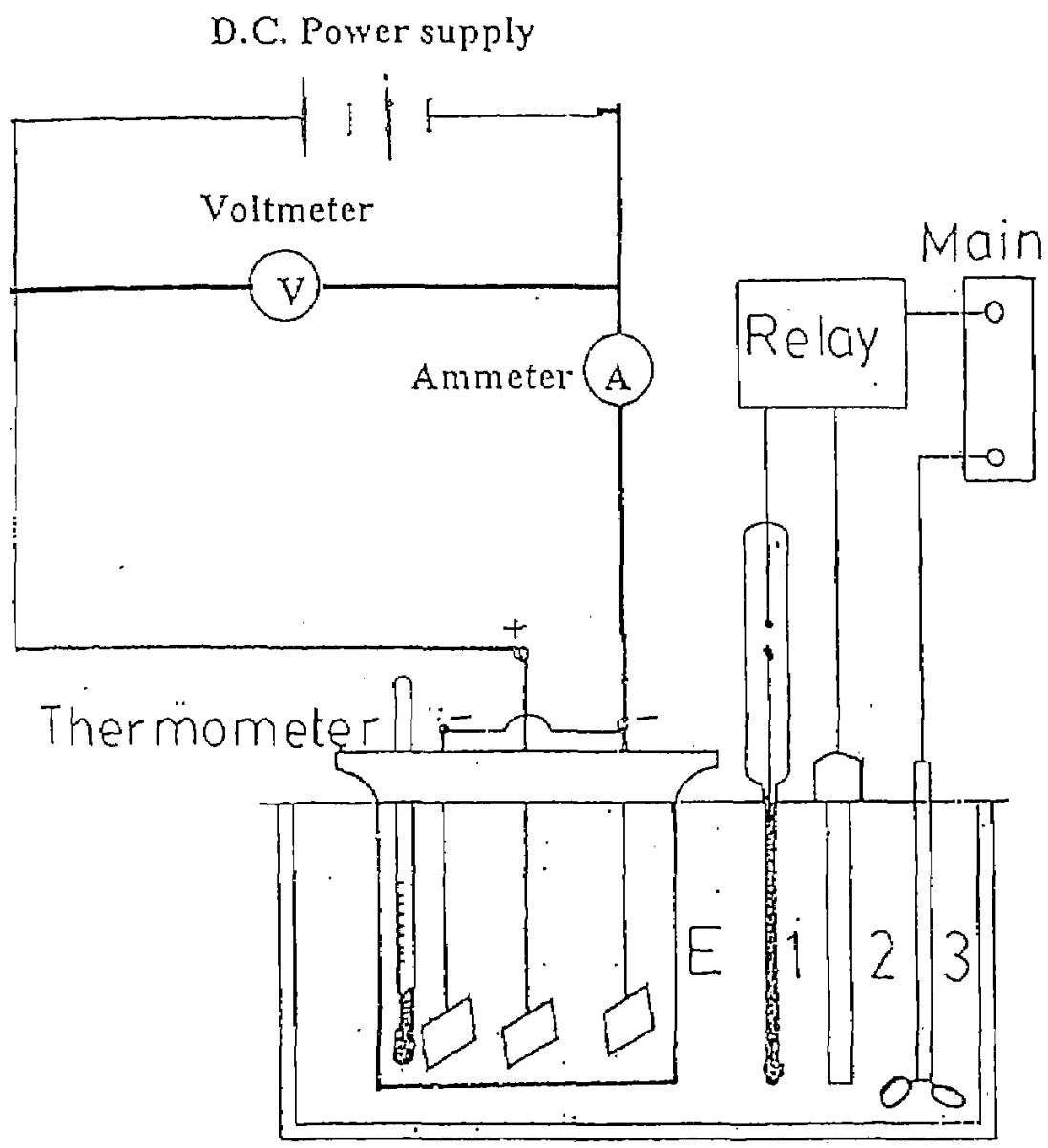
Conclusions

Thermally activated modified electrodes are of great importance in chemical industries. Titanium/platinum-rhodium thermally activated modified electrode was used in the electrocatalytic oxidation of methanol. It is concluded that, this modified electrode has a great efficiency in the oxidation of methanol at low current densities, short electrolysis time. Low pH value in the presence of NaCl as supporting electrolyte at room temperature. In addition, this modified electrode may be used in many applications such as: the electrocatalytic oxidation of different types of dyestuffs, bleaching of textile fibers, electrochemical polymerization. Also, they could be used as electrocatalysts in fuel cells and electrolysis of water for hydrogen production.

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|---|-------------------|---|---------------------|
| E | Electrolysis Cell | 1 | Contact Thermometer |
| 2 | Heater | 3 | Stirrer |

Fig (1) Circuit diagram for electrocatalytic wastewater treatment technique.

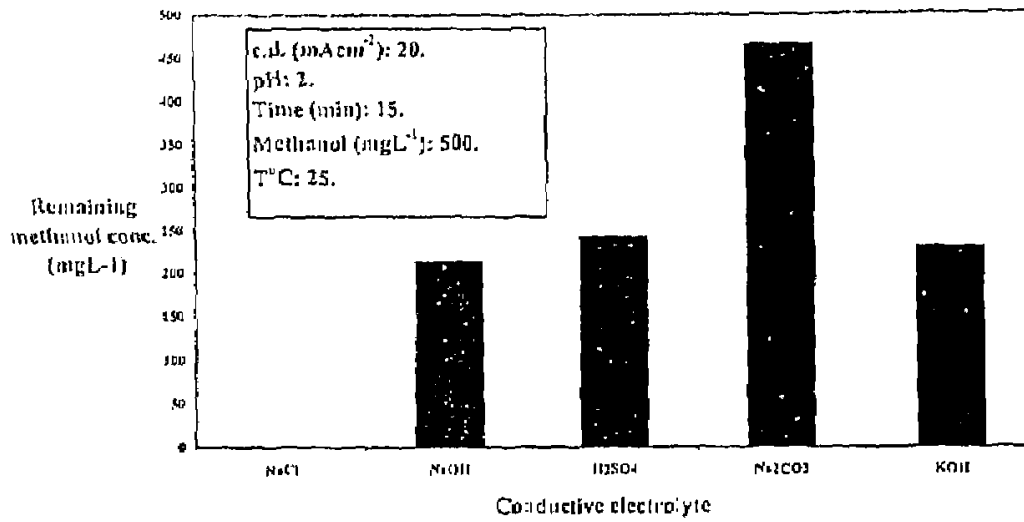


Fig.(2) Effect of conductive electrolyte type on the methanol removal using Ti/Pt-Rh modified electrode.

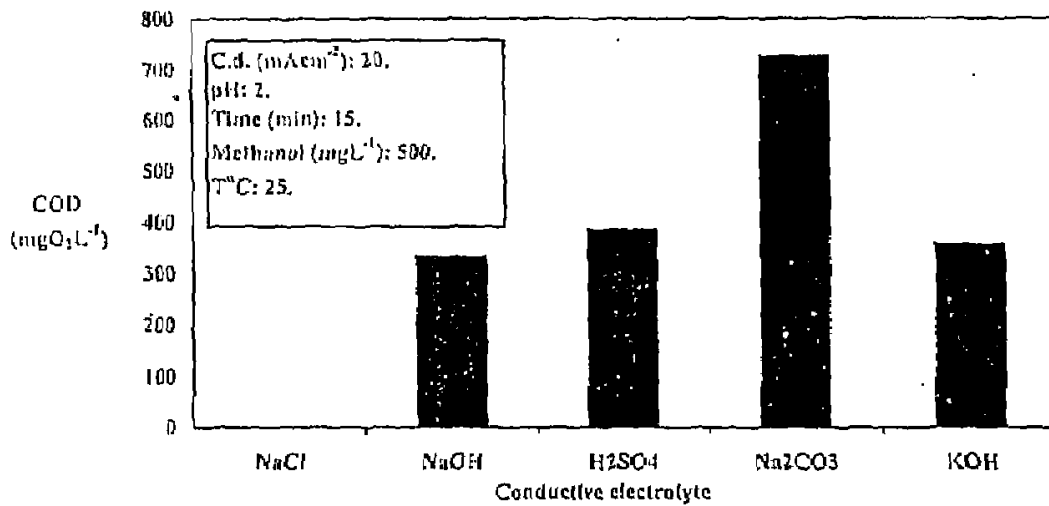


Fig.(3) Effect of conductive electrolyte type on the COD removal of methanol using Ti/Pt-Rh modified electrode.

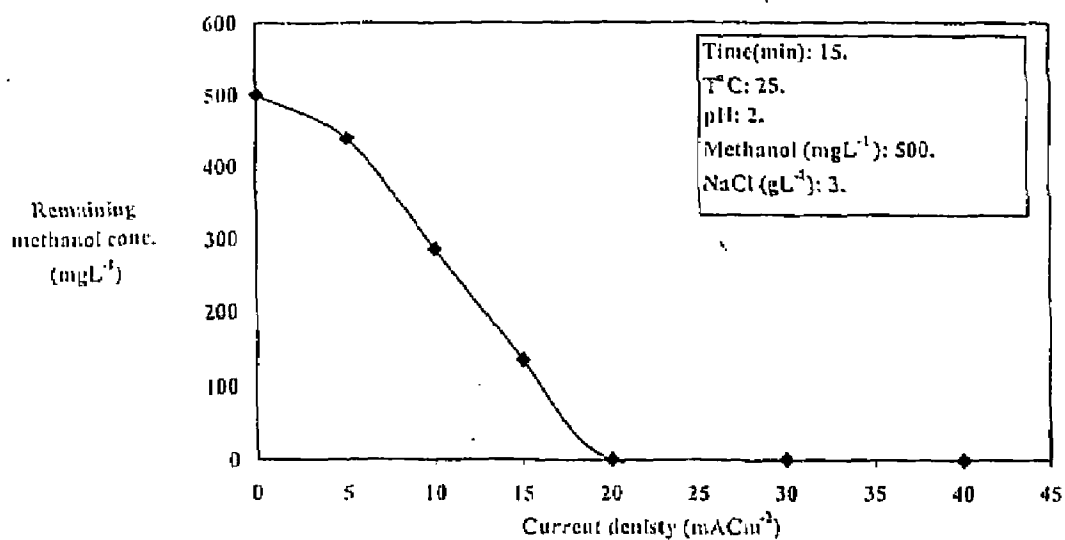


Fig. (4) Effect of current density on the methanol removal using Ti/Pt-Rh modified electrode.

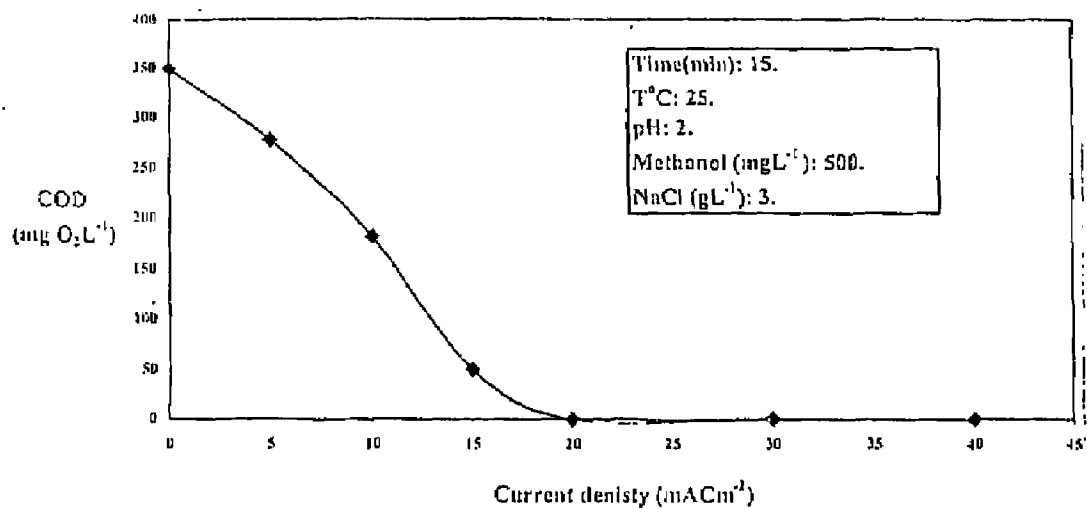


Fig.(5) Effect of current density on COD removal of methanol using Ti/Pt-Rh modified electrode.

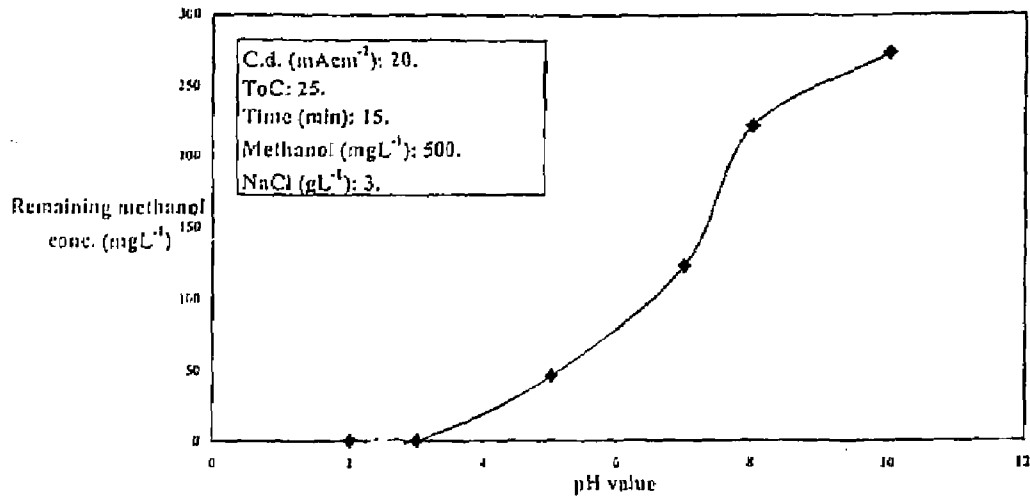


Fig.(6) Effect of pH value on the methanol removal using Ti/Pt-Rh modified electrode.

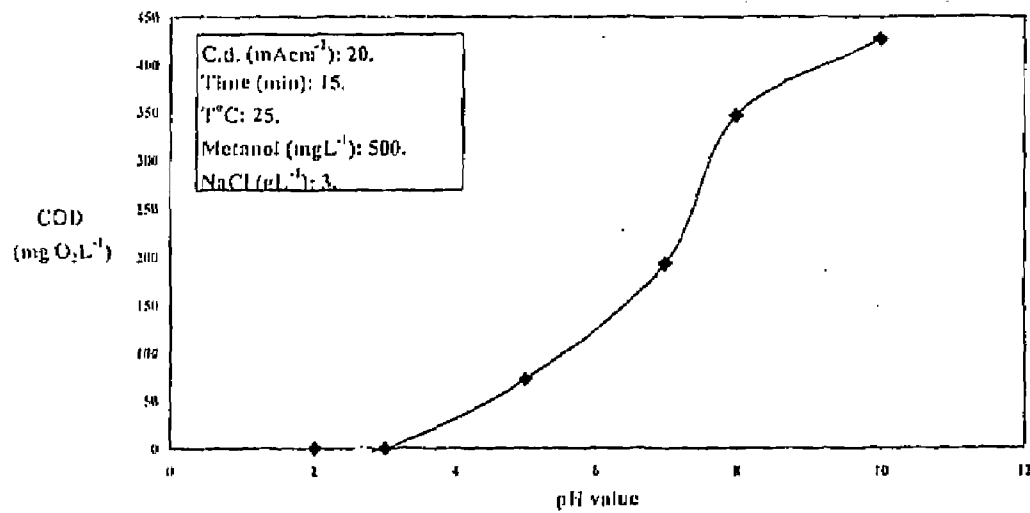


Fig.(7) Effect of pH value on COD removal of methanol using Ti/Pt-Rh modified electrode.

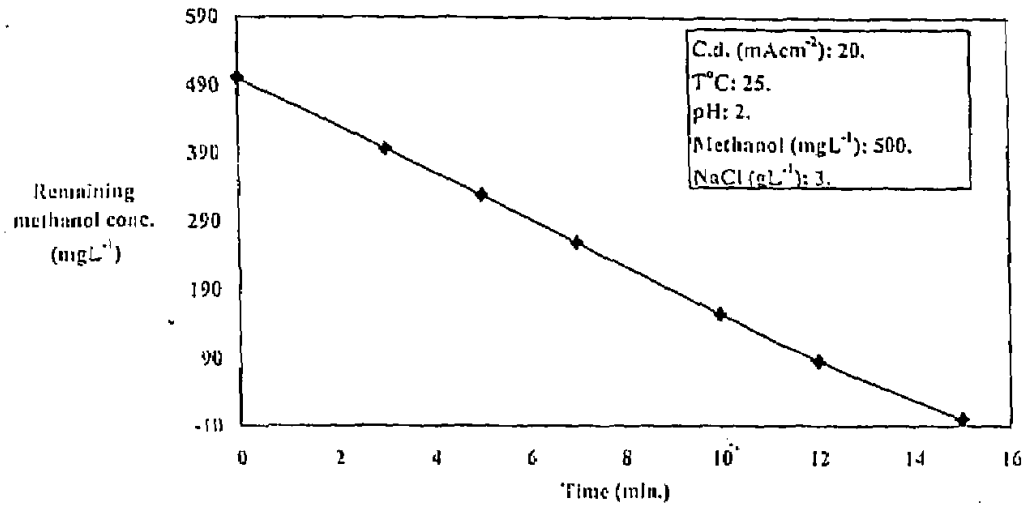


Fig. (8) Effect of time of electrolysis on methanol removal using Ti/Pi-Rh modified electrode

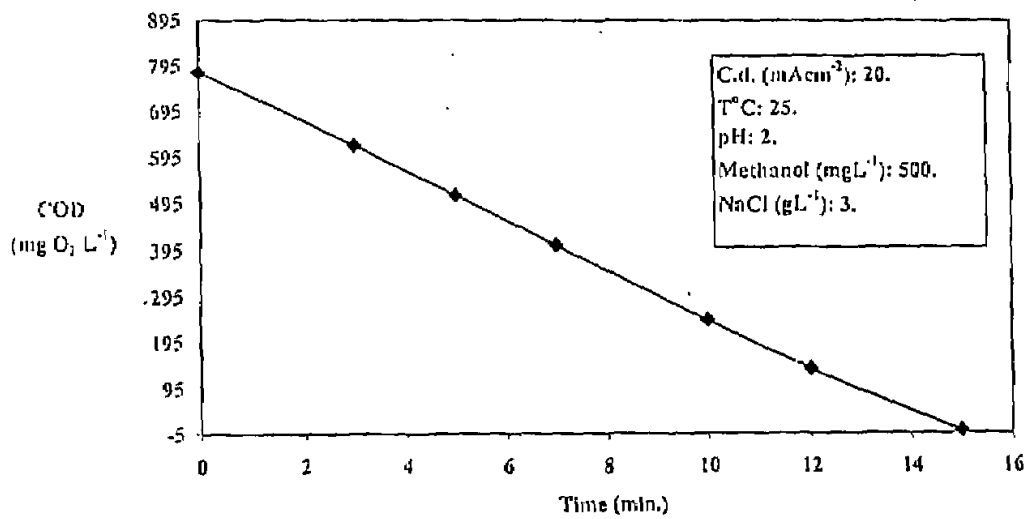


Fig. (9) Effect of electrolysis time on COD removal of methanol using Ti/Pi-Rh modified electrode.

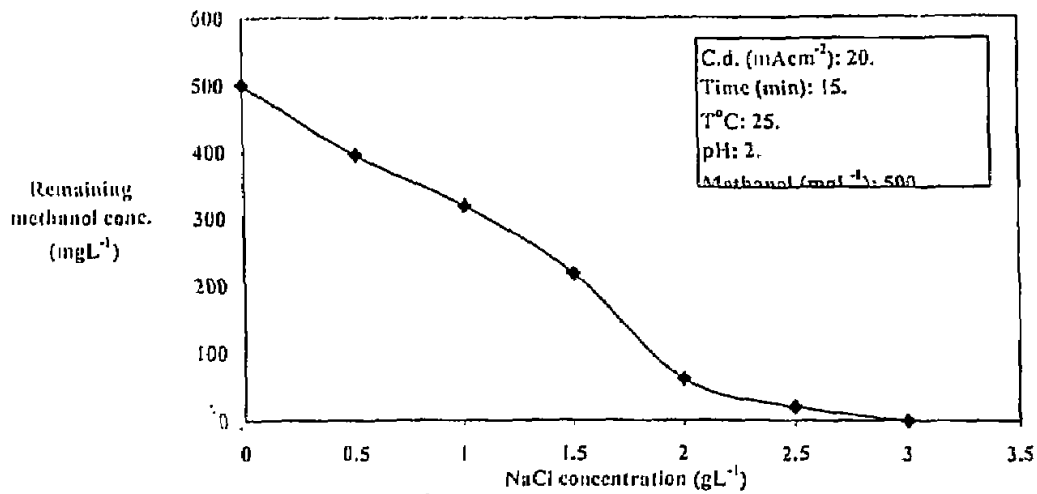


Fig.(10) Effect of NaCl concentration on methanol removal using Ti/Pt-Rh modified electrode.

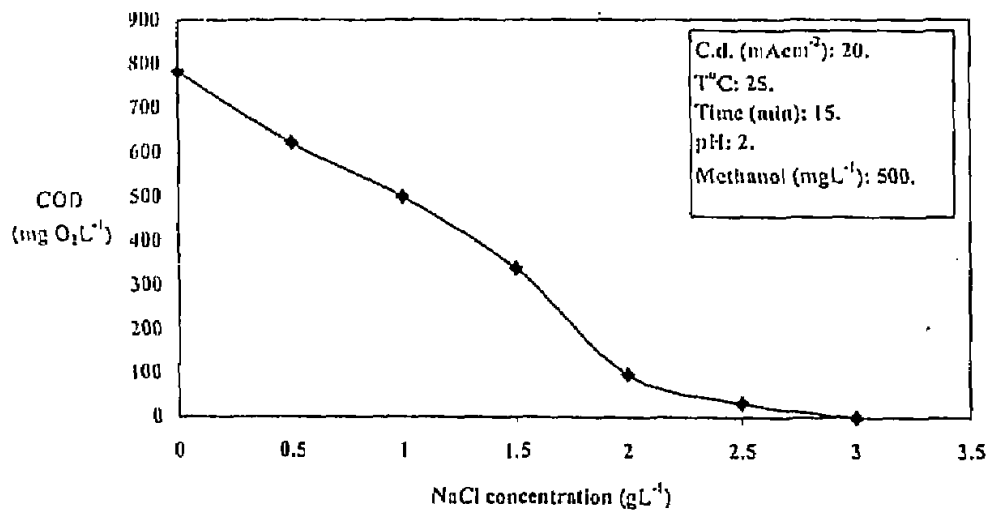


Fig. (11) Effect of NaCl concentration on COD removal of methanol using Ti/Pt-Rh modified electrode.

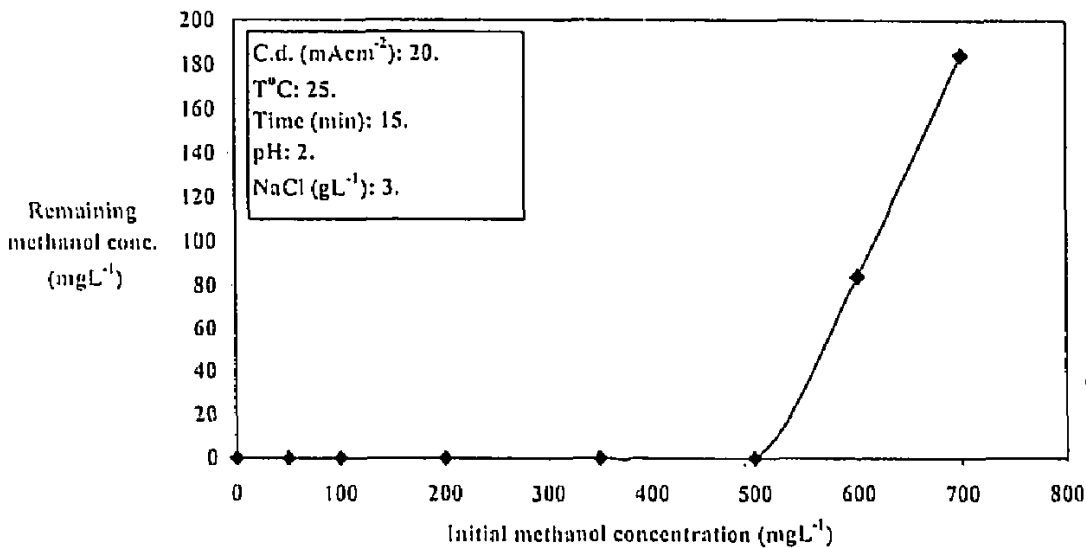


Fig.(12) Effect of initial methanol load on methanol removal using Ti/Pt-Rh modified electrode.

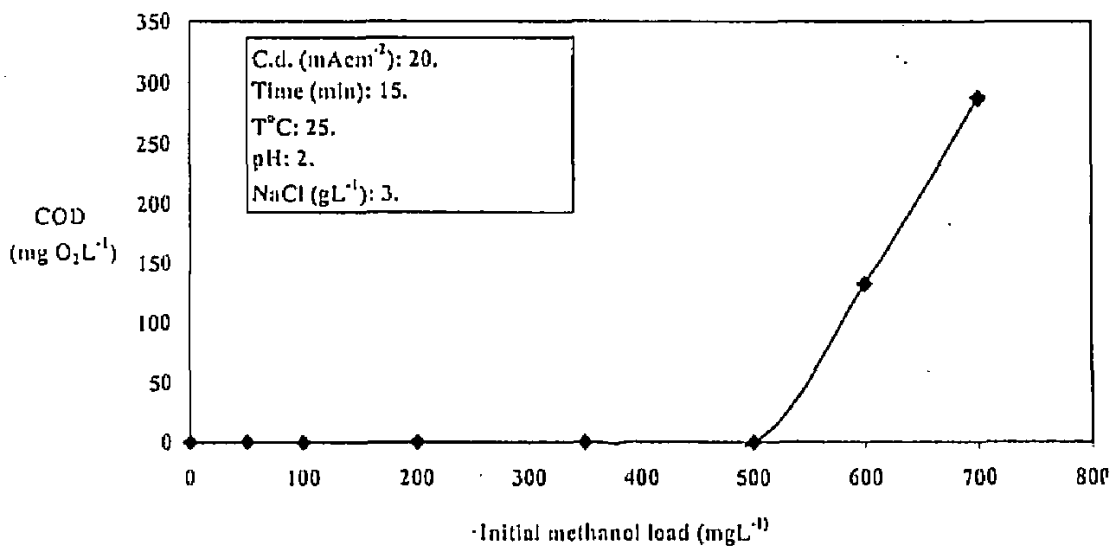


Fig. (13) Effect of initial methanol load on COD removal of methanol using Ti/Pt-Rh modified electrode.