



Investigation of the optimum conditions for the electrocatalytic oxidation of methanol on Ti/PbO₂ modified electrode

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Received: 10th June, 2008 ; Accepted: 15th June, 2008

ABSTRACT

Electrocatalytic oxidation of methanol on Ti/PbO₂ electrode (as anode) was investigated in different conductive electrolytes. The highest electrocatalytic activity was achieved in the presence of NaCl (2g/l) and could be attributed to indirect oxidation of methanol by the electrogenerated hypochlorite ions from the oxidation of chloride ions. In addition, contribution from direct oxidation could also be possible via reaction of methanol with the electrogenerated hydroxyl radicals adsorbed on the Ti/PbO₂ modified electrode surface. In the presence of NaOH, the electrocatalytic activity of the employed anode was not compared to that in NaCl due primarily to the absence of chloride. This indicates that methanol degradation in NaOH occurs exclusively via direct electrochemical process. However in H₂SO₄, the electrode performance was poor due partially to the absence of chloride from the conductive solution. The possibility of electrode poisoning as a result of growth of adherent film on the anode surface. Optimizing the conditions that ensure effective electrochemical degradation of methanol on Ti/PbO₂ modified electrode necessitates the control of all the operating conditions.

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KEYWORDS

Ti/PbO₂ modified electrode;
Methanol;
Direct and indirect
electrochemical oxidation.

INTRODUCTION

Titanium is a leading candidate material suitable for use in fabricating jet engine parts and other aircraft and aerospace component. In addition, the high electrical conductivity of titanium renders it a suitable material for the fabrication of current collectors used in fuel cells. These applications are limited by the formation of unstable, low conductive oxides on the surface of titanium and its alloys. This problem can be overcome by the application of a thin layer of noble metal on the titanium surface.

Various methods can be used for the application of the metallic coatings on the titanium substrates^[1]. The

electrodeposition method is the most favoured technique, as it has many advantages, but it is difficult to obtain a truly adherent electroplate on titanium due to the formation of oxide layer on the surface^[2-4].

Lead dioxide, is characterized by high oxygen overpotential, therefore it is one of the most commonly used anodes for electrochemical degradation of many pollutants^[5-8].

Nowadays the heterogeneous catalysis of electrochemical reactions occurring at the electrode-electrolyte interface has mainly concerned technological investigations related to energy storage, energy conversions (fuel cells) and environmental protection (wastewater treatment). Many fundamental investigations were

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undertaken in the last two decades on the direct oxidation of several alcohols: methanol, ethanol, ethylene glycol, butanol ... etc. This is because the above-mentioned compounds are very interesting fuels due to a lot of advantages: high solubility in aqueous electrolytes, relatively high reactivity, eases of storage and supply, and low toxicity. On the other hand, the presences 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 at the same time it formed as pollutant in wastewater of several industries such as pharmaceutical, beverages ... etc. When a suitable anode is inserted into the contaminated solution 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 organic chemicals such as methanol in the homogeneous phase.

The aim of the present study was to investigate the electrocatalytic degradation of methanol from an aqueous solution by direct and indirect electrochemical oxidation. Since effective and economical means of treatment of pollutants requires the choice of appropriate electrolysis conditions and catalytic electrode materials. The effect of different operating factors, such as type and concentration of conductive electrolyte, applied current density, initial methanol load, solution pH and others on the methanol removal efficiency and chemical oxygen demand (COD) depletion were analyzed to optimize the conditions of electrochemical oxidation of methanol. Titanium/lead oxide modified electrode was selected for this investigation.

EXPERIMENTAL

In this study a new method was developed to electroplate titanium substrate with lead. This method comprises an anodization of titanium substrate in oxalic acid solution at very high current density to form a very porous and very conductive titanium oxide layer that is accessible for subsequent electrodeposition of very adherent coatings.

Prior to the electrodeposition of lead, the titanium substrates of dimensions ($1 \times 2 \text{ cm}^2$) were pretreated by mechanical polishing using emery paper down to 4/0 grade and degreasing with acetone. After this, the substrates were degreased in an alkali soaking cleaner of composition: NaOH 50g/l, Na_2CO_3 20g/l, Na_3PO_4

20g/l and sulphonic acid 2g/l^[4,9]. The degreasing process was carried out at 50°C for five minutes, and then the titanium substrates were washed in running distilled water. The degreasing process was followed by pickling, where the substrate were immersed in a solution containing nitric acid 400g/l and hydrofluoric acid 50g/l. This was found to be a good pickling solution, because it removes the oxides and scales from the titanium surface without difficulty and renders the metal active. Finally, chemical polishing was carried out on the titanium substrates by their immersion in oxalic acid solution (100g/l) for five minutes.

The anodizing process was carried out on the pretreated titanium substrates in oxalic acid solution (100g/l) at current density of about 90 mA/cm², at ambient temperature. This high current density was chosen with the aim of obtaining porous and conductive titanium oxides on the surface of substrates. Stainless steel electrodes (austenitic type) were used as cathodes. The distance between cathode and anode was 2cm^[4,9].

Lead was chosen to be electrodeposited metal on the anodized titanium substrates, since the electrodeposited lead can be oxidized to PbO_2 which has high electrocatalytic activity owing to its high oxygen evolution overvoltage.

The optimum composition of lead electroplating bath is: lead fluoroborate $\text{Pb}(\text{BF}_4)_2$, free fluoroboric acid HBF_4 30g/l, free boric acid H_3BO_3 13.5g/l, animal glue 0.2g/l, temperature of 25-40°C, cathode current density 200A/m², anode current density 100-300 A/m²^[10]. After the electrodeposition of lead on the preanodized titanium substrates, it was oxidized to PbO_2 by anodization the electrodes in oxalic acid solution (100g/l). This acid solution was electrolyzed galvanostatically for 30 minutes at ambient temperature using an anodic current density of 100 mA/cm². The cathodes was stainless steel (austenitic type).

Chemicals used in this study were methanol, sodium chloride, sodium hydroxide and sulphuric acid of analytical grade.

The electrolysis of the aqueous solutions of methanol to be electrochemically oxidized was carried out in a one-compartment Pyrex glass cell of 150ml volume with the prepared Ti/ PbO_2 modified electrode as anode and austenitic stainless steel as cathode. DC power supply (model GP 4303 D, LG Precision Co. Ltd, Korea) was used. The current and potential measure-

ments were carried out using digital multimeter (Kyoritsu model 1008, Japan).

Two main parameters were measured to evaluate the electrochemical oxidation efficiency, remaining methanol concentration and COD (oxygen equivalent of the organic matter content of the methanol). Remaining methanol was measured with a liquid chromatograph (Shimazu LC-6A) while the COD was determined using the reactor digestion method⁽¹¹⁾. From these analysis the remains ratio was calculated as follows⁽¹²⁾:

$$\text{Remains\%} = [\text{COD}/\text{COD}_0] \times 100$$

COD₀:COD value before electrolysis, COD:COD value after electrolysis

$$\text{Remains\%} = (\text{remaining methanol} / \text{initial methanol}) \times 100$$

$$\text{Removal\%} = 100 - \text{Remains\%}$$

RESULTS

The initial stage in this study was to select a suitable conductive electrolyte in which a highest rate of electrocatalytic oxidation of the methanol occurs. This was carried out in the presence of 2g/l of different electrolytes, acid (H₂SO₄), base (NaOH) and salt (NaCl) under the following operating conditions: 1000 mg/l methanol with corresponding 1660 mg/l initial COD, a temperature of 25°C, pH of 3, a current density of 25 mA/cm² and a 30 min time of electrolysis. Figure 1 show the effect of different conductive electrolytes on the removal% of methanol. As clearly seen in figure 1 the electrocatalytic rate of degradation of methanol was poor in the acid electrolyte, where the removals% reached 45. This is, in fact, considered an unsatisfactory rate for practical industrial applications.

The rate of the electrocatalytic degradation of methanol was better in base (NaOH) than that in H₂SO₄ as evident from the considerable increase in removals%. The value of removals% of methanol reached 75. NaCl appears to be the most effective conductive electrolyte in which almost complete removal of the methanol was observed. In this electrolyte a maximum degradation efficiency of 99% was reached.

The preliminary results in this study have indicated that NaCl is the best conductive electrolyte among all the investigated electrolytes, for the electrochemical degradation of methanol on Ti/PbO₂ modified electrode. In this electrolyte, the modified electrode (Ti/PbO₂) exhibited its highest electrocatalytic activity. Therefore, NaCl was selected as the conductive electrolyte in which

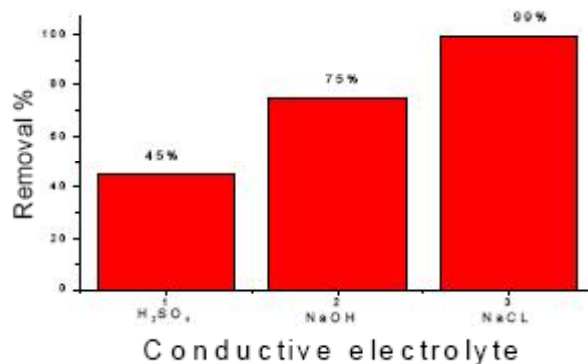


Figure 1: Effect of conductive electrolyte on the removal % of methanol on Ti/PbO₂ modified electrode

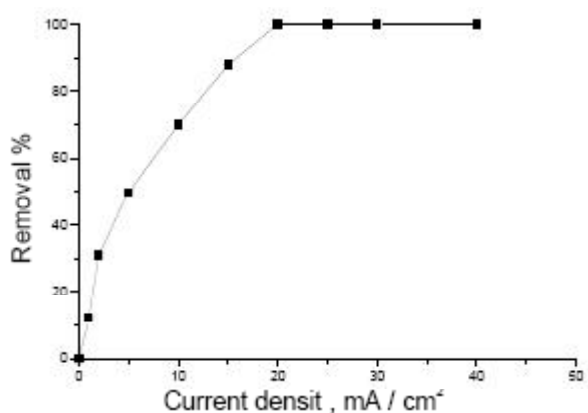


Figure 2: Effect of current density on the removal % of methanol on Ti/PbO₂ modified electrode.

all the following experiments were carried out.

A series of experiments were carried out in NaCl to investigate the effect of different operating factors on the rate of the electrochemical degradation of methanol.

1. Effect of current density

Different current densities (0-45mA/cm²) were applied to investigate the electrocatalytic degradation of methanol in NaCl solution (2g/l) at 1000 mg/l initial methanol concentration with corresponding initial COD of 1660 mg/l. This was carried out for 30 min electrolysis time at a solution pH of 3 and a temperature of 25°C. The obtained results were depicted in figure 2 as a relation between the removals% of methanol and applied current density. As shown from the plot of figure 2, the increase of the removals% of the methanol was sharp at low current density, followed by a gradual increase with increasing current density up to 20mA/cm² at which complete removal of methanol took place.

It has been indicated from this test that the Ti/PbO₂ modified electrode exhibited its highest electrocatalytic

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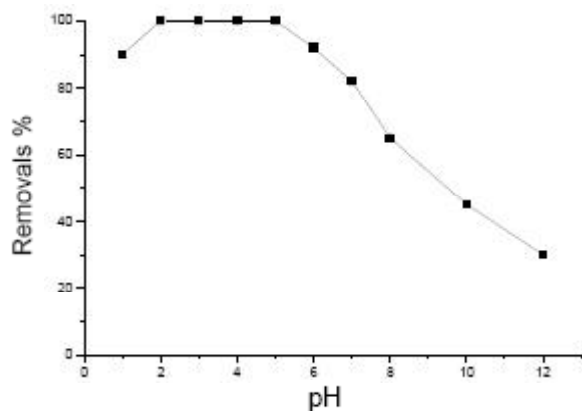


Figure 3 : Effect of pH of solution on the removal % of methanol on Ti / PbO₂ modified electrode

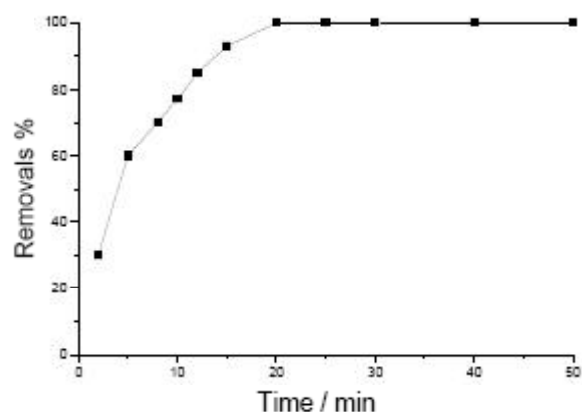


Figure 4 : Effect of electrolysis time on the removal % of methanol on Ti / PbO₂ modified electrode

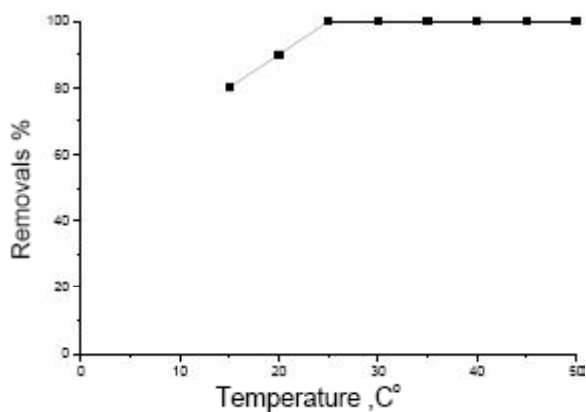


Figure 5 : Effect of temperature on the removal % of methanol on Ti / PbO₂ modified electrode

activity towards the degradation of methanol in NaCl at 20mA/cm² applied current density. Therefore, this value is considered the optimum current density for the electrolytic process.

2. Effect of solution pH

The solution pH was varied from 1 to 12 in order to determine its effect on the electrocatalytic degradation of methanol on Ti/PbO₂ modified electrode. Figure 3 presents the removals% as a function of pH. The operating factors: 2g/l NaCl, 1000 mg/l initial methanol concentration, current density of 20mA/cm², 30 min time of electrolysis and temperature of 25°C. The results of figure 3 indicated that the highest electrocatalytic activity was attained under acidic conditions of pH range from 2-5.

3. Effect of electrolysis time

Investigation of the effect of time of electrolysis on the electrocatalytic degradation of methanol was carried out under the following operating factors: 2g/l NaCl, 1000 mg/l initial methanol concentration, pH was 3 and temperature of 25°C. The obtained results are depicted in figure 4, as the dependance of the removal% of methanol on the time of electrolysis. The plot of Figure 4 showd that the increase of removals% was sharp after the first 5 min. followed by gradual increase with time reaching maximum after 20 min. of electrolysis.

4. Effect of temperature

The effect of temperature on the electrocatalytic oxidation of methanol was carried out under the following operating conditions: 2g/l NaCl, 1000mg/l initial methanol concentration, 20mA/cm² current density, 20 min. electrolysis time and pH of 3. Figure 5 shows the variation of removals% of methanol as a function of temperature. At low temperatures below 25°C, the methanol degradation was not complete. The rate of methanol degradation as enhanced significantly with increasing the solution temperature to 25°C at which complete methanol degradation was obtained and further increase in temperature above 25°C did not bring any effect.

5. Effect of conductive electrolyte concentration

In this investigation the operating conditions were: 1000mg/l initial methanol concentration, 20mA/cm² current density, 20 min. time of electrolysis, pH of 3 and temperature of 25°C, the concentration of NaCl varies from 0 to 6 g/l. Figure 6 presents the effect of NaCl concentration on the removals% of methanol on Ti/PbO₂ modified electrode. The plot of this figure indicated that the removal% of methanol increased with increasing NaCl concentration up to 2g/l, above which there was no additional effect of NaCl. This means that,

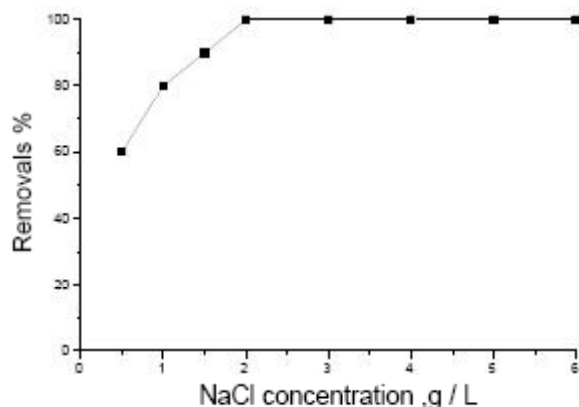


Figure 6: Effect of NaCl concentration on the removal % of methanol on Ti/PbO₂ modified electrode

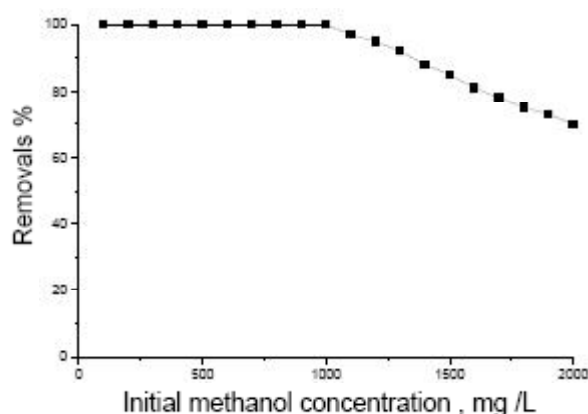


Figure 7: Effect of initial methanol concentration on the removal % of methanol on Ti/PbO₂ modified electrode

complete degradation of methanol was achieved in the presence of 2g/l NaCl.

6. Effect of initial methanol dosage

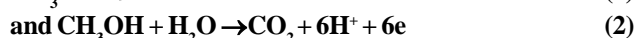
This test was carried out under the following operating factors: 2g/l NaCl, 20mA/cm² current density, 20 min. time of electrolysis, pH of 3, temperature of 25°C and initial concentration of methanol varied from 1000 to 2000 mg/l. The obtained results are depicted in figure 7, where the removals% was plotted against the initial methanol concentration. The plot of this figure indicated that the total removal of methanol can be achieved in the presence of initial methanol load up to 1000mg/l. However, increasing the methanol concentration above this level resulted in the decrease in the removals% of methanol. Although the degradation of methanol decreases with increasing the initial methanol concentration, good removal efficiency was achieved at a relatively high methanol load as indicated from the plot of figure 7. For example, the removals% of methanol at

2000mg/l initial concentration was ≈70% .

The results of this investigation have indicated that the operating factors play a fundamental role in electrochemical degradation of methanol and controlling these factors leads to efficient electrocatalytic oxidation on the Ti/PbO₂ modified electrode.

DISCUSSION

Nowadays, the heterogeneous catalysis of electrochemical reaction occurring at the electrode-electrolyte interface, has mainly concerned technological investigations related to energy storage, energy conversions^[13,14] and environmental protection (wastewater treatment)^[15]. Methanol is one of the most important fuels used for electricity production (fuel cells) and at the same time formed as a pollutant in wastewater of several industries such as pharmaceutical, beverages,etc. Several mechanisms for the electrochemical oxidation of methanol were suggested in the literature^[16-19]. Herrero et al.^[4] suggested a dual path mechanism for the electrochemical oxidation of methanol on platinum electrode, this mechanism is:



This mechanism was found to be operative if the methanol oxidation charge is larger than the corresponding CO formation charge.

The electrocatalytic oxidation of methanol from liquid (usually aqueous) phases through electrochemical processes is based on the possibility of choosing suitable electrodes and potential/current potentials selectively to destroy these impurities. Degradation of some organic compounds by indirect electrochemical oxidation has been carried out.

It was previously reported^[20-23] that, when a suitable anode is inserted into the contaminated solution chlorine or ClO⁻ is generated (if necessary with prior addition of Cl⁻ ions). These species (Cl₂, ClO⁻) are powerful oxidizing agents capable of destroying a wide range of biological microorganisms as well as many organic chemicals in the homogeneous phase. Among common organic impurities that can be oxidized in this way are phenols, mercaptanes, aldehydes, alcohols, carboxylic acids, dyes ...etc.

If NaCl solution is electrolyzed in an individual cell, Cl₂ formed at the anode disproportionates in the presence of OH⁻ ion generated at the cathode:

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The resultant hypochlorite can be further oxidized to chlorate:

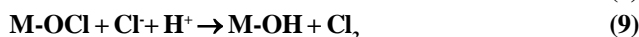


However, this leads to the requirement of nine Faradays per mole of chlorate, whereas only six are needed if a chemical disproportionation route is followed:

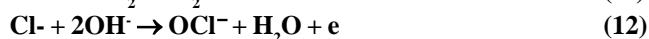


On the basis of the above reactions, we can see from reaction (4) that the hypochlorite is favoured by keeping the chloride concentration as high as possible. In addition, high current densities are employed owing to the fact that the current-voltage curve for reaction (4) is flatter than the chlorine evolution. Reaction (5,6) can be suppressed by working at low temperature, and the resultant liquor can be used directly for bleaching and disinfection purposes.

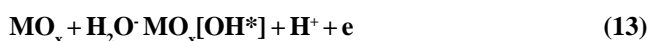
Lassali et al.^[24] reported in detail on the electrocatalytic activity for chlorine evolution, and indicated the possible electrochemical routes involving the chloride ion at an anode as follows :



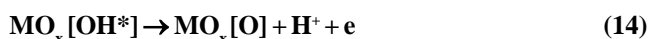
Moreover, it was reported^[25], that hypochlorite ion could be generated in aqueous chloride medium electrolysis, according to the following reaction sequence :



The direct electrochemical oxidation of organic compounds could generally occur via a mechanism in which the first step is the oxidation of water molecules on the electrode surface (MO_x), giving rise to the formation of hydroxyl radicals according to the following equation^[7,26,27] :



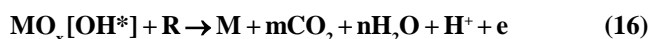
The produced hydroxyl radicals can, if it is possible oxidize the underlying oxide lattice to a higher state forming the so-called higher oxide:



The only role of the formed higher oxide is the participation in the formation of selective oxidation of the organic pollutants (R) without complete incineration:



It is to be noted that the above route can take place only if the transition of the underlying oxide to a higher oxidation state is possible and the electrodes of this class are called "active electrodes". However, if this is not possible the electrogenerated hydroxyl radicals could directly oxidize the organic compound to carbon dioxide and water; predominantly cause the combustion of the organic compound:



and this class of electrodes are called "non-active electrodes".

On the basis of the above view, the lead dioxide anode employed in this investigation is characterized by high oxygen overvoltage on which OH^* are generated from the oxidation of water according to equation (13). However, PbO_2 does not have a higher oxidation state; consequently it is classified as "non-active electrode". It was reported that lead dioxide electrode is hydrated^[7] and the electrogenerated hydroxyl radicals are expected to be more strongly adsorbed on its surface. This in turn, makes lead dioxide anode very reactive towards organics oxidation leading to complete degradation of the methanol by reaction with hydroxyl radicals forming carbon dioxide and water.

The results of the present investigation have shown that the electrocatalytic oxidation of methanol on lead dioxide anode occurred very efficiently in the presence of NaCl as a conductive electrolyte. The degradation rate of methanol in NaOH was not as good as that in the NaCl containing solution. However, the lead dioxide electrode performed deficiently towards the electrochemical degradation of methanol in the presence of H_2SO_4 .

In the NaCl solution, the oxidation of the methanol could occur directly via reaction of methanol with the electrogenerated hydroxyl radicals adsorbed on the lead dioxide surface. In addition, indirect electrochemical oxidation may possibly take place involving the participation of the electrogenerated hypochlorite ions produced from the naturally occurring chloride ions in the processed water. This in turn, contributes to higher degradation rate of methanol from its solution.

The reduced degradation efficiency in the presence of NaOH could be attributed primarily to the absence of chloride which ensures that the electrocatalytic degradation of methanol occurs primarily by direct oxidation on the lead dioxide anode. It was reported in the literature that in the absence of the chloride the oxygen

evolution was the major anodic reaction, but the oxygen formation in solution did not produce a significant oxidation^[28]. On the other hand, the low degradation of methanol observed in H₂SO₄ solution could be correlated partially to the absence of chloride that, once again, guarantees direct oxidation process. The poor performance of the lead dioxide electrode in the presence of H₂SO₄ might also be attributed to growth of an adherent film on the anode surface that poisoned the electrode.

It has been indicated from the above discussion that the presence in the conductive electrolyte of ions (such as chloride) capable of generating species of powerful oxidizing power and the conditions at the electrode surface play a paramount rule in the electrocatalytic degradation of methanol on modified electrodes.

CONCLUSIONS

The electrochemical oxidation of methanol has been investigated in different conductive electrolytes and under several operating condition using Ti/PbO₂ electrode. From the obtained results the following conclusions can be drawn:

1. The electrocatalytic activity of the anode depends on the conductive electrolyte.
2. The highest electrocatalytic activity was achieved in the presence of NaCl (2g/l) in which degradation of the methanol occurs by direct as well as indirect oxidation.
3. In NaOH the electrocatalytic effect was not as good as that in NaCl. The electrochemical degradation of methanol occurred via direct oxidation process only due to the absence of chloride.
4. The electrode showed poor electrocatalytic activity in the presence of H₂SO₄, due to the absence of chloride as well as the possibility of the electrode poisoning as a result of forming adherent film on the anode surface.
5. Controlling the operating conditions could lead to complete electrocatalytic degradation of methanol.

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