Electrochemical degradation of some pesticides in agricultural wastewater by using modified electrode

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Abstract: This work deals with the possibility of using Ti/Rh-modified electrode for the electrocatalytic oxidation process of some pesticides (malathion, imidacloprid and chlorpyrifos). The Ti/Rh-modified electrode was prepared by brushing of rhodium nitrate solution on preanodized titanium substrate and annealing. The results of the electrolytic oxidation were expressed in term of chemical oxygen demand (COD) removal, which was determined instrumentally. For the Ti/Rh-modified electrode (anode), the highest electrocatalytic activity was obtained in the presence of NaCl as conductive electrolyte. The different operating conditions of electrocatalytic oxidation process were studied which include: current density, pH, electrolysis time, initial pesticide concentration and conductive electrolyte concentration. The optimum operating conditions for the above mentioned electrode was determined..
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Keywords: Ti/Rh-modified electrode combined electrochemical oxidation, pesticides, chemical oxygen demand (COD).

1. Introduction

The ambitious plan of the Government of Egypt (GOE) to reclaim 3-4 million feddans as an additional cultivated area up to the year 2017 put further pressure on the existing limited fresh water resources. On the other hand, the vast increase in industrial horizontal and vertical expansions need more water conservation. Furthermore, the increasing population presents another red flag for the available renewable water resources. According to the limited water availability, there is a real need to search for another water sources. These sources can be found within the non-conventional water sources in Egypt. The agricultural wastewater represents one of the major non-conventional water sources in Egypt due to its volume that reaches about 16 bilion cubic meters per year (BCM/yr). Most of this volume, about 12 BCM/yr, is disposed in the Mediterranean Sea. Water quality of this major source is threatened due to several pollution causes. So, chemical treatment of this major source before using is very important [1].

Out of the world production of pesticides (3 million tonnes in 2009), 20% (equivalent to 600000 tonnes) were exported annually to developing countries, and at least 90% were used in agriculture for pest, weed and plant disease control. The remaining 10% were used for public health programmes, particularly for the control of vectors of human diseases (malaria, filariasis schistosomiasis, leishmaniasis and trypanosomiasis) [2].The amount of pesticides applied actually affecting target pests is often less than 1%, while over 99% moves into the environment to contaminate the land, water and air [2]. These toxic compounds have been implicated in various disorders and diseases including cancer, adverse reproductive outcomes, peripheral neuropathies, neurobehavioral disorders, impaired immune functions and allergic sensitization reactions, particularly of the skin, cumulative inhibition of cholinesterase activity because of long-term low doses of exposure [2].

Millions of tons of pesticides applied annually are used in modern agriculture to increase production through controlling harmful effects caused by the targets organisms including insects, fungi, bacteria, viruses as well as grasses grown in between the economical crops [3].

Polluted drainage water from a dump of toxic chemical waste containing organophosphoric pesticides and their natural degradation products was treated with electrochemical oxidation in order to investigate the applicability of the technique in remediation of natural complex polluted water [4].
This work aims to study the possibility of using Ti/Rh-modified electrode for the electrocatalytic degradation of some pesticides.

2- Experimental

2.1 Preparation of the Titanium/ Titanium oxide/ Rhodium oxide ($Ti/TiO_2/Rh_2O_3$) electrode

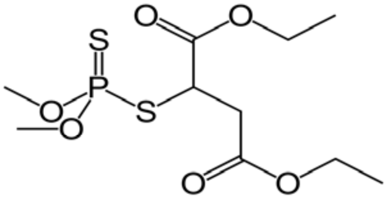
The Ti substrate (IMI 115) of dimension 1.5 x 6 cm^2 were pretreated by mechanical polishing, using sand papers down to 4/0 grade, and degreasing with acetone. After this, the substrates were degreased in an alkali soaking cleaner of the following composition: NaOH 50 g/L, Na_2CO_3 20 g/L, Na_3PO_4 20 g/L, and sulphonic acid 2 g/L [6]. The degreasing process was carried out at 50ºC for 5 min, and then the Ti substrates were washed in running distilled water. The degreasing process was followed by pickling, where the substrates were immersed in a solution containing nitric acid (400 g/L) and hydrofluoric acid (50 g/L). This was found to be a good pickling solution, because it removed the oxides and scales from the Ti surfaces without difficulty and rendered the metal active. Finally, chemical polishing was carried out on the Ti substrates by their immersion and boiling in oxalic acid solution (100 g/L) for 5 min. The anodizing process was carried out on the pretreated Ti substrates in oxalic acid solution (80-100 g/L) at current density ranging from 15-25 mA/cm^2, at ambient temperature. These high current densities were chosen with the aim of obtaining porous and conductive Ti oxides on the surface of the substrates. Stainless steel electrodes (austenitic) were used as cathodes. The distance between the cathode and anode was 2 cm [7]. The rhodium oxide is deposited on the treated Ti substrate by brushing of the nitrate solution [195 g/L $Rh(NO_3)_3.2H_2O$, Aldrich], followed by heat treatment for 4 min at 673 K. This procedure was repeated until the desired oxide loading (7 ± 1 mg cm^{-2}) was achieved. Then the electrode is annealed at the same temperature for 1 h [8].

2.3 Electrocatalytic degradation procedures:

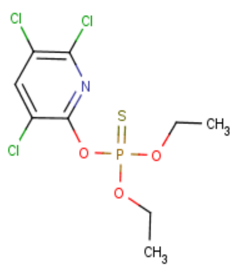
The electrolysis of aqueous solutions (250 mL) containing the pesticides and the electrolyte solution to be treated electrochemically was carried out in a one-compartment Pyrex glass cell of 250 ml volume with three plates electrodes of 12 cm^2 which consists of the prepared Ti/ TiO_2/Rh_2O_3 electrode as anode and two graphite electrodes as cathodes. DC power supply GW (model: GPR-181 OHD, Taiwan) was used. The current and potential measurements were carried out using two digital mutimeters (BK Mini-Pro Multimeter, model: 2405A, Taiwan). All experiments were carried out with magnetic stirring.

2.4. Chemicals

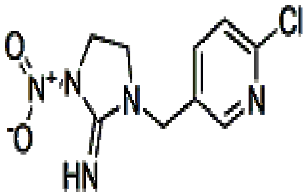
Chemicals used for degradation are different types of pesticides; malathion, chlorpyrifos and imidacloprid.



Common name: Malathion
IUPAC name: Diethyl (dimethoxy thio phosphryl thio)succinate



Common name: Chlorpyrifos
IUPAC name: O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate



Common name: Imidacloprid
IUPAC name: 1-(6-chloro-3-pyridyemethyl) –N-nitroimidazolidine-2-yliedeneamine

2.5. Analytical measurements

Analytical parameters were measured to evaluate the electro-catalytic oxidation efficiency of above-mentioned organic (pesticides) compounds, these parameters were:

A. Chemical Oxygen Demand COD (mg O_2 /l), which is a measure of the oxygen equivalent to organic matter content of a sample that is susceptible to the oxidation by strong chemical oxidant. COD can be related empirically to organic matter. COD during the electrolysis was determined by an open reflux (COD reactor, ECO 6, VELP SCIENTIFICA, Italy), dichromate titrimetric method as described in standard methods [9].This method for the determination of COD may be used were sample chloride concentration is known to be less than 2000 mg/l. This means that, in the present investigations the interferences of Cl$^-$ ions present in the solution and the electro-generated species may occur. To eliminate the effect of these interferences, two different **methods were taken into considerations [10].The first was carried out by adding sodium bisulphate ($Na_2S_2O_5$) to the organic compound (pesticides)** solutions and heating before measurements of COD. The added of sodium bisulphate destroys the hypochlorite with evolution of chlorine gas. The second includes the measurements of COD for blank solutions, which are free from the under test organic compound. These blank solutions were treated under the same operating conditions used in the electro-catalytic oxidation of organic (pesticides) compound solutions. From the measurements of COD values of blank and organic (pesticides) compound solutions after treatment, the value of COD is corresponding to the organic compound present in solution that could be evaluated. The COD values obtained from the two methods were matched with each other. The equation used to calculate the COD removal efficiency in the experiments is:

COD Removal % = [$COD_{\circ}$ - COD_{final} / $COD_{\circ}$] x 100

Where, $COD_\circ$ (initial) and COD_{final} of the pesticide solutions are calculated in mg/l

B. The average current efficiency (ACE) is calculated by the following equation [11];

ACE% = $(COD_\circ - COD_t)$ FV/8 It

Where COD^o and CODt are the chemical oxygen demand at initial time and given time t (g O_2 /L), respectively, I the current (A), F the Faraday constant (96487 C/ mol), t the treatment time (s), V is the volume of solution (L) and 8 is the oxygen equivalent mass (g/eq).

C. The energy consumption (EC) is calculated by the following:

EC = UIt / 3.6 $(COD_\circ - COD_t)$ V

Where U is the voltage applied (V) and other parameters are as defined as before [11].

D. The optimum operating conditions for the electrocataltic degradation processes:

Several parameters were studied for investigation the optimum conditions for the degradation synthetic agricultural wastewater (which prepared from pesticides). The studied operating conditions were: current density, conductive electrolyte concentration, pH and initial pesticide dose. HCl and NaOH were used for pH adjustment in case of using NaCl as conductive electrolyte.

3- Results

A series of experiments was carried out in NaCl solution to investigate the effect of different operating factors on the rate of the electrochemical degradation of the investigated pesticides on the Ti/Rh modified electrode.

3.1. Effect of applied current density

Different current densities of values 50,100, and 250 mA/ cm^2 were applied to investigate the electro-catalytic degradation of the investigated pesticides in 2 g/L NaCl solution and pH of 3. Figures (1-3) show that the variation of COD removal % of pesticides as a function of electrolysis time at different current densities for the investigated pesticides.

The plots of figure (1) indicated that:

i) For each pesticide and at a given current density, the COD removal % increased with the increase of electrolysis time reaching a limiting value (especially at 250 mA/ cm^2).

ii) At a given time of electrolysis, the COD removal % increased with the increase of applied current density. The maximum COD removal% was obtained at a current density of 250 mA/ cm^2 and they were: 78, 81 and 69 for the pesticides imidacloprid, malathion and chlorpyrifos respectively. The values of $t_{1/2}$ deduced from the plots of figure (1) at a current density of 100 mA/ cm^2 were: 53.2, 48.7 and 69.7 minutes for the pesticides imidacloprid, malathion and chlorpyrifos respectively. It is indicated from this investigation that, the Ti/Rh modified electrode exhibited its highest activity towards the degradation of the investigated pesticides in NaCl solution at 100 mA/ cm^2 of applied current density. Therefore, this value is considered the optimum current density for the electro-catalytic degradation of the investigated pesticides.

3.2. Effect of pH of solution

Figure (2) shows the variation of COD removal % of the pesticide as a function of time at different pH values (3, 7.2 and 10). These experiments were carried out in NaCl solution (2g/l) on Ti/Rh modified electrode. As shown from the plots of figure (2) that, at a given pH value, the COD removal % increased with the increase of electrolysis time reaching to a limiting value. At a given electrolysis time, the COD removal % decreased with increase of value of solution, where the maximum values of COD removal% were obtained at pH of 3 for the pesticides. For this reason, the pH value of 3 was taken as optimum.

3.3. Effect of conductive electrolyte concentration

In this investigation, the experiment was carried out in different NaCl concentration of 1, 2 and 5 g/L containing 1% as initial concentration of each pesticide under the following operating conditions: pH of 3 and current density of 100 mA/cm^2. Figure (3), shows the variation of COD removal % of pesticides as a function of electrolysis time for the investigated pesticides (imidacloprid, malathion and chlorpyrifos), respectively on Ti/Rh modified electrode. Inspection of the plots of figure (3), revealed that:

i) At a given NaCl concentration, the COD removal% increased with increase of electrolysis time reaching limiting values.

ii) Also, at a given electrolysis time the COD removal% noticeable increase with increase of NaCl concentration from 2 to 5 g/L. The values of COD removal% obtained in presence of 2 g/L NaCl were: 78, 81 and 69 for the pesticides imidacloprid, malathion and chlorpyrifos respectively.

3.4. Effect of initial pesticide dosage

The results so far have indicated that the maximum electrochemical degradation of the investigated pesticides was obtained at 250 mA/cm^2 in 2g/L NaCl solution of pH 3. Figure (4) shows the effect of different initial pesticides concentrations (0.5%, 1% and 5%) on the variation of COD removal % as a function of electrolysis time under the optimum operating conditions mentioned above. Inspection of the plots of figure (4), revealed that:

i) At a given time of electrolysis, the COD removal% are decreased with increasing initial concentration from 0.5 -5% respectively.

ii) COD removal % in the presence of 0.5% and 1% of initial concentrations is near to each other.

iii) At a given initial loaded concentrations, the COD removal % increased with increase of the electrolysis time with a rate depending on both of nature of each pesticide and its initial concentration.

4-Discussion

The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorptions step. Basically two different processes occur at the anode; on anode having high electro-catalytic activity, oxidation occurs at the electrode surface (direct electrolysis); on metal oxide electrode, oxidation occurs via surface mediator on the anodic surface, where they are generated continuously (indirect electrolysis). In direct electrolysis, the rate of oxidation is depending on electrode activity, pollutants diffusion rate and current density. On the other hand, temperature, pH and diffusion rate of generated oxidants determine the rate of oxidation in indirect electrolysis. In indirect electro oxidation, chloride salts of sodium or potassium are added to the wastewater for better conductivity and generation of hypochlorite ions [5]. The reaction of anodic oxidation of chloride ions to form chlorine is given as:

$2Cl \rightarrow Cl_2 + 2e^{`}$ (1.1)

The liberated chlorine form hypochlorous acid

$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl$ (1.2)

And further dissociated to give hypochlorite ion

$HOCl \rightarrow H^+ + OCl^-$ (1.3)

The generated hypochlorite ions act as main oxidizing agent in the pollutant degradation. The direct electro-oxidation rate of organic pollutants depends on the catalytic activity of the anode, on the diffusion rate of the organic compounds in the active points of anode and applied current density. A generalized scheme of the electro-chemical conversion/combustion of organics of pollutant on noble oxide coated catalytic anode (MO_x) is given below. In the first step, H_2O is discharged at the anode to produce adsorbed hydroxyl radicals according to the reaction:

$MO_x + H_2O \rightarrow MO_x(^{\cdot}OH) + H^+ + e^{`}$ (1.4)

In the second step, generally the adsorbed hydroxyl radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radicals to the oxide forming the higher oxide MO_{x+1}.

$MO_x(^{\cdot}OH) \rightarrow MO_{x+1} + H^+ + e^{`}$ (1.5)

At the anode surface, the "active oxygen" can be present in two states. Either as physisorbed (adsorbed hydroxyl radicals $^{\cdot}OH$ or/and as chemisorbed (oxygen in the lattice, MO_{x+1}). In the absence of any oxidizable organics, the "active oxygen" produces dioxygen according to the following reactions:

$MO_x(^{\cdot}OH) \rightarrow MO_x + 1/2\, O_2 + H^+ + e^{`}$ (1.6)

$MO_{x+1} \rightarrow MO_x + 1/2\, O_2$ (1.7)

When NaCl is used as supporting electrolyte Cl^- ion may react with $MO_x(^{\cdot}OH)$ to form adsorbed OCl radicals according to the following reaction:

$MO_x(^{\cdot}OH) + Cl^- \rightarrow MO_x(^{\cdot}OCl) + H^+ + 2e^{`}$ (1.8)

Further, in presence of Cl^- ion, the adsorbed hypochlorite radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hypochlorite radical to the oxide forming the higher oxide MO_{x+1} according to the following reaction and also $MO_x(^{\cdot}OCl)$ simultaneously react with chloride ion to generate active oxygen (dioxygen) and chlorine according to the following reactions:

$MO_x(^{\cdot}OCl) + Cl^- \rightarrow MO_{x+1} + Cl_2 + e^{`}$ (1.9)

$MO_x(^{\cdot}OCl) + Cl^- \rightarrow MO_x + 1/2\, O_2 + 1/2\, Cl_2 + e^{`}$ (1.10)

In the presence of oxidizable organics the physisorbed "active oxygen" ($^{\cdot}OH$) should cause predominantly the complete combustion of organics and chemisorbed will participate in the formation of selective oxidation products according to the following reactions:

$1/2\, R + MO_x(^{\cdot}OH) \rightarrow 1/2\, ROO + H^+ + e^{`} + MO_x$ (1.11)

$R + MO_{x+1} \rightarrow RO + MO_x$ (1.12)

The physisorbed route of oxidation is the preferable way for waste treatment. It is probable that dioxygen participates also in the combustion of organics according to the reactions, such as formation of organic radicals by a hydrogen abstraction mechanism: $RH + {}^{\cdot}OH \rightarrow R + H_2O$; reaction of organic radical with dioxygen formed at the anode: $^{\cdot}R + O_2 \rightarrow ROO^{\cdot}$ and further abstraction of a hydrogen atom with formation of an organic hydrogen peroxide (ROOH) and another radical; $ROO^{\cdot} + R^{`}H \rightarrow ROOH + R^{`}$. Since the organic hydrogen peroxides formed are relatively unstable, decomposition of such intermediates leads to molecular breakdown and formation of subsequent intermediates with lower carbon numbers. These sequential reactions continue until the formation of carbon dioxide and water. In this case the diffusion rate of organics on the anode area controls the combustion rate. In the same way indirect electrochemical oxidation mechanism has been proposed for metal oxide with chloride as supporting electrolyte for wastewater treatment. The role of hypochlorite in electrochemical treatment of pesticide via chlorine generation is:

$$\text{Pesticide} + OCl^- \rightarrow CO_2 + H_2O + Cl^- \quad (1.13)$$

3.5. Calculation of electrical yield (Current Efficiency)

The current efficiency is defined as the ratio between the electrical charge that actually used to oxidize the organic compounds and the total consumed electrical charge [12]. Table (1) represents the current efficiency values and the energy consumption values of the under test electrode used for the electrolysis degradation of the pesticides at their optimum operating conditions.

3.6. Conclusion

The electrochemical treatment of simulated wastewater containing the investigated pesticides (malathion, imidacloprid and chlorpyrifos) has been investigated under several operating conditions using Ti/Rh modified electrode. The highest electrocatalytic activity at applied current density of 250 mA/cm^2, pH of 3 and supporting electrolyte of 2 g/L of NaCl. In the present investigation, it could be concluded that, the use of the under test modified Ti/Rh electrode in the electro-catalytic degradation of some organic compounds (pesticides) lead to low energy consumption and low cost of the process, so these electrode could be applied for treatment of agricultural wastewaters containing organic compounds such as pesticides.

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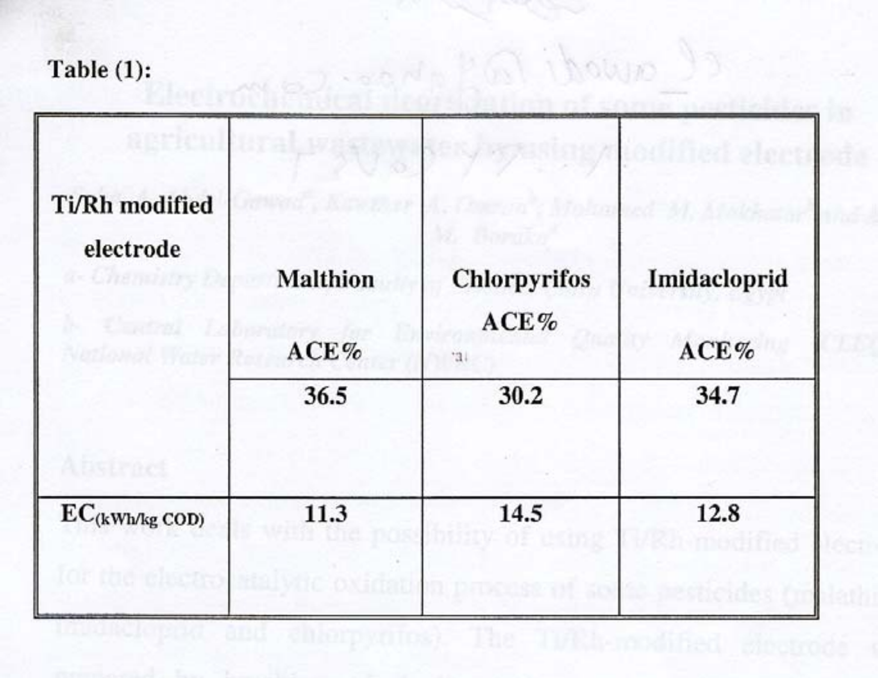

Table (1):

Ti/Rh modified electrode	**Malthion ACE%**	**Chlorpyrifos ACE%**	**Imidacloprid ACE%**
	36.5	**30.2**	**34.7**
EC$_{(kWh/kg\ COD)}$	**11.3**	**14.5**	**12.8**

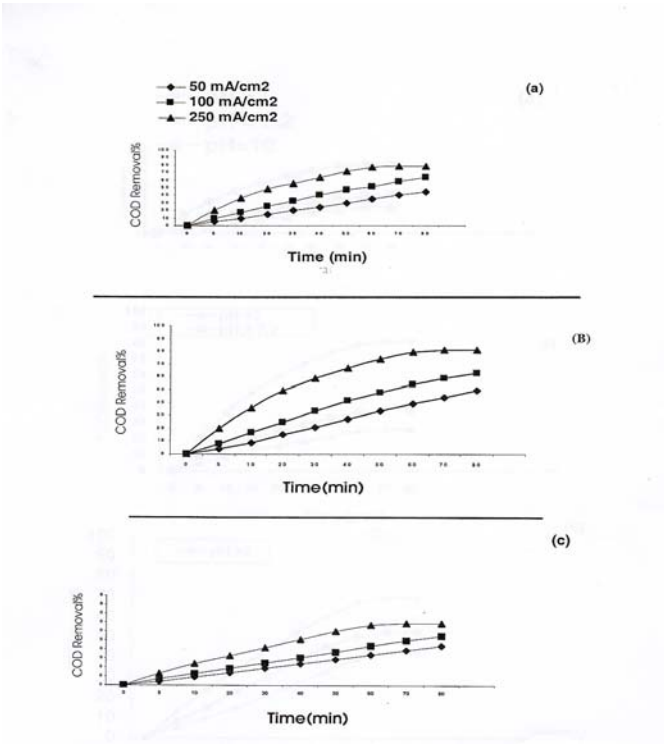

Fig. (1): Removal of COD with electrolysis time for 1% concentration of (a): imidacloprid, (b): malathion and (c): chlorpyrifos pesticides, supporting electrolyte 2 g/L NaCl, pH 3, and Ti/Rh modified electrode.

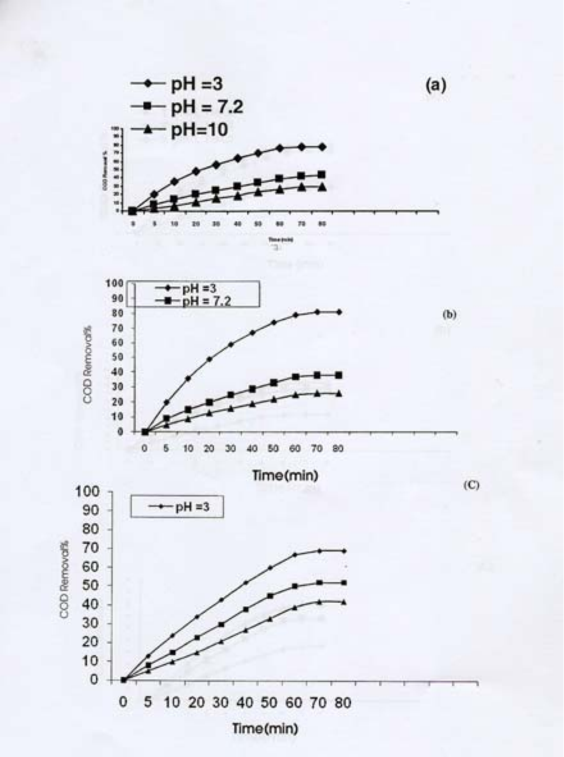

Fig. (2): Removal of COD with electrolysis time for 1% concentration of (a): imidacloprid, (b): malathion and (c): chlorpyrifos pesticides, supporting electrolyte 2 g/l NaCl, pH (3, 7.2, 10) and Ti/Rh modified electrode.

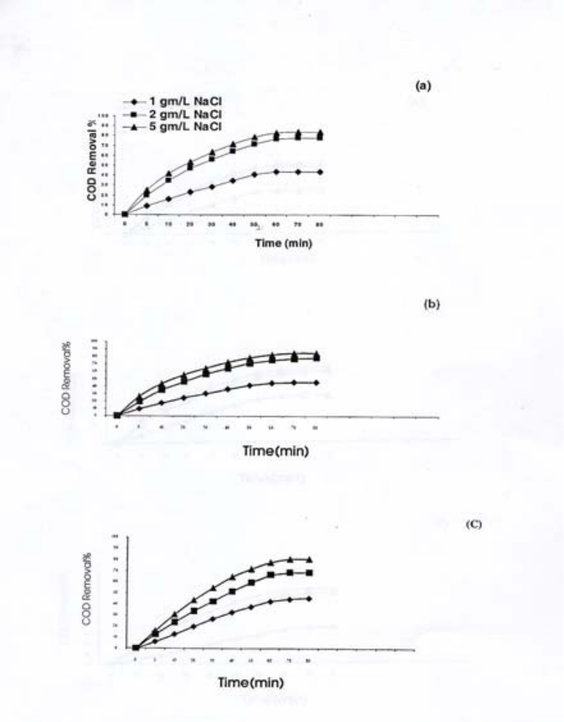

Fig. (3): Removal of COD with electrolysis time for 1% concentration of (a): imidacloprid, (b): malathion and (c): chlorpyrifos pesticides in different supporting electrolyte (1, 2, 5) g/L NaCl, pH (3) and Ti/Rh modified electrode.

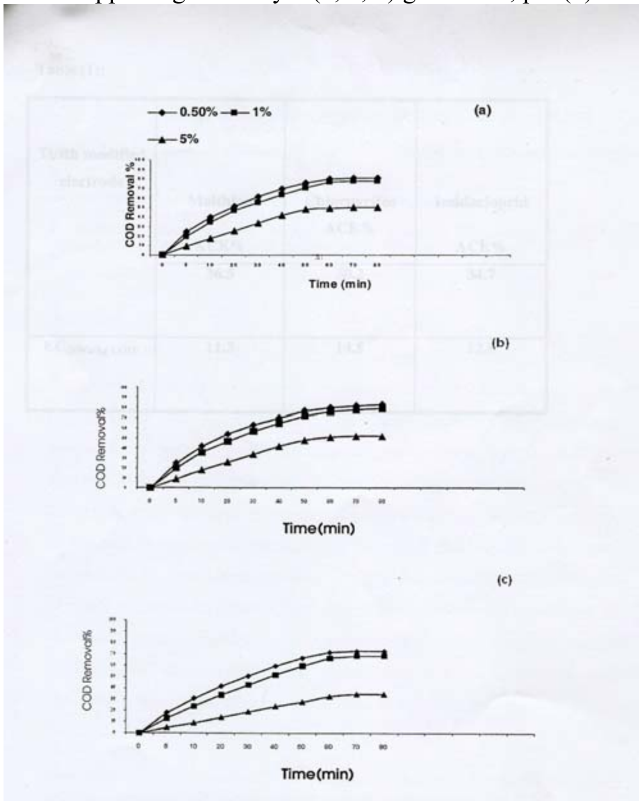

Fig. (4): Removal of COD with electrolysis time for 0.5%, 1% and 5% concentration of (a): imidacloprid, (b): malathion and (c): chlorpyrifos pesticides, supporting electrolyte 2 g/L NaCl, pH 3 and Ti/Rh modified electrode.