



ELECTROCHEMICAL DEGRADATION OF CHLORPYRIFOS IN AQUEOUS SOLUTIONS USING G/Nb₂O₅ AND Nb/Nb₂O₅ ELECTRODES

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ABSTRACT

Glass/Nb₂O₅ and Nb/Nb₂O₅ electrodes were prepared by electrodeposition and used as anodes for electrochemical degradation of chlorpyrifos (CPF) in aqueous solution. Different operating conditions and factors affecting the treatment process including current density, temperature, initial concentration of chlorpyrifos, pH, conductive electrolyte and time of electrolysis were studied and optimized. The best degradation occurred in the presence of NaCl (1gL⁻¹) as conductive electrolyte. After 30 min, nearly complete degradation of chlorpyrifos was achieved (94% and 82%) using G/Nb₂O₅ and Nb/Nb₂O₅ electrodes at pH 10.8. Higher degradation efficiency was obtained at room temperature (20-30°C). The optimum current density for the degradation of chlorpyrifos on both electrodes was (25 mAcm⁻²).

KEY WORDS: electrochemical degradation, chlorpyrifos, electrodes, electrocatalytic oxidation.



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1. INTRODUCTION

Chlorpyrifos (O,O-diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate) is a crystalline organophosphate insecticide. It was introduced in 1965 by Dow Chemical Company and is known by many trade names, including Dursban and Lorsban. It acts on the nervous system of insects by inhibiting acetylcholinesterase, moderately toxic to humans and chronic exposure has been linked to neurological effects, developmental disorders, and autoimmune disorders¹. The degradation of chlorpyrifos in water by Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) and solar photo-Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{solar light}$) processes was investigated. A laboratory-scale reactor was designed to evaluate and select the optimal oxidation condition. The degradation rate is strongly dependent on pH, temperature, H_2O_2 dosing rate, and initial concentrations of the insecticide and Fe^{2+} . To achieve 90% of COD removal, the solar photo-Fenton process needs 50% less time than that used in the Fenton process which translates to a 50% gain of H_2O_2 ². Photocatalytic degradation of Chlorpyrifos in aqueous phase by using photocatalyst TiO_2 in the presence of artificial UV-light and sunlight was reported. The degradation of insecticide was investigated in terms of reduction in COD. The effect of catalyst loading, pH, addition of oxidant on the reaction rate was ascertained and optimum conditions for maximum degradation were determined³. A laboratory set-up was designed to compare the effectiveness of UV/ O_3 Advanced Oxidation Process (AOP) with coagulation using Polyaluminum Chloride (PACl) for the removal of three widely used pesticides, Chlorpyrifos, Diazinon and Carbaryl from water resources. Although AOP method showed higher performance for removal of selected pesticides, at similar condition, coagulation by PACl demonstrated acceptable performance without any need to the special equipment and structural requirements⁴. The effect of the operating conditions of the UV photo-Fenton process on COD and TOC removal was examined of combined chlorpyrifos, cypermethrin and

chlorothalonil pesticides in aqueous solution. The study shows that UV photo-Fenton process is effective in pretreatment of combined chlorpyrifos, cypermethrin and chlorothalonil pesticides aqueous solution for biological treatment⁵.

The electrochemical removal of tramadol hydrochloride, herbicidal 2,4-D (albar super) and pure 2,4-dichlorophenoxy acetic acid from aqueous solutions was investigated under several operating conditions using a Pb/PbO₂ electrode^{6, 7}. Pb/PbO₂ and C/PbO₂ electrodes were prepared by electrodeposition and used as anodes for electrochemical degradation of linuron (phenylurea pesticide) in aqueous solution. Different operating conditions and factors affecting the treatment process including current density, temperature, initial concentration of linuron, pH, conductive electrolyte and time of electrolysis were studied and optimized⁸. The electrochemical transformation of the organophosphorous insecticide chlorpyrifos (CPF) was investigated in wastewater. The oxidation of CPF was carried out in a single-compartment electrochemical flow cell working under batch operation mode, using diamond-based material as anode and stainless steel as cathode. In order to evaluate its persistence and degradation pathway, two different concentration levels 1.0 mg L⁻¹ and 0.1 mg L⁻¹ were studied. Liquid chromatography/mass spectrometry was used for evaluation of the initial and electrolyzed solutions⁹. In this study, an electrodegradation method was applied on chlorpyrifos insecticide using G/Nb₂O₅ and Nb/Nb₂O₅ electrodes. Different factors including the pH, concentration of electrolyte, conductive electrolyte type, current density, time of electrolysis, initial concentration of chlorpyrifos solution, and temperature were studied and optimized for its removal from water. Two main parameters were measured to evaluate the electrochemical treatment efficiency, the remaining pollutant concentration and the chemical oxygen demand (COD).

2. EXPERIMENTS

2.1. Chemicals and Instrumentation

Sodium chloride, sodium fluoride, sodium carbonate, sodium sulphate, calcium chloride, potassium chloride, sodium hydroxide, sulphuric acid, potassium dichromate, silver sulfate, sodium thiosulphate were of analytical grade and purchased from Merck. Chlorpyrifos insecticide was purchased from Dow AgroSciences 480g/L. Other reagents were of the analytical grade. Distilled water was used for the preparation of solutions. Standard solutions of potassium dichromate ($K_2Cr_2O_7$), sulfuric acid (H_2SO_4) reagent with silver sulfate (Ag_2SO_4) were prepared to measure the COD. Different standard solutions of chlorpyrifos with concentration from 10 – 70 mg/L were prepared to measure its degradation at different conditions. The double-beam UV-visible spectrophotometer is from Shimadzu, the DC power supply is model GP4303D, LG Precision CO. Ltd. (Korea), a pH meter model AC28, TOA electronics Ltd., (Japan) to adjust pH of the solutions and a digital multi-meter is kyoritsu model 1008, (Japan) for reading out the current and potential values. A closed reflux titrimetric unit was used for the COD determination.

2.2. Electrodeposition of Nb_2O_5 at different substrates

2.2.1. Electrodeposition of Nb_2O_5 at Nb metal (Nb/ Nb_2O_5 electrode)

The Nb– Nb_2O_5 electrode was prepared from a cylindrical rod of spectroscopically pure niobium metal (6.0 cm length and 0.5 cm diameter). A stout copper wire lead was affixed at one end by mechanical jamming. The electrode surface was mechanically polished using 2/0 and 3/0 emery papers and was then rubbed against soft cloth to acquire a silvery bright appearance. After polishing, the electrode was immersed in molten KNO_3 for a few hours at 625 K whereby a thick layer of Nb_2O_5 was formed on its surface¹⁰.

2.2.2. Electrodeposition of Nb_2O_5 at glass substrate (G/ Nb_2O_5 electrode)

2.2.2.1. Preparation of the sol

The starting solution to produce Nb_2O_5 films was prepared by dissolving $NbCl_5$ powder (1.3 g, 0.005 mol) in butanol (15 mL, 0.16 mol), acetic acid (3 mL, 0.05 mol) and $LiCF_3SO_3$ salt, (10 %mol). The solution mixture was submitted for ~5 min to the action of a 95 W, 20 kHz ultrasonic irradiation from a sonicator resulting in a transparent and viscous solution¹¹.

2.2.2.2. Preparation of the films

The coatings were deposited by dip-coating method on ITO coated glass substrates (Asahi Glass 14 Ω) previously cleaned and rinsed with bi-distilled water, ethanol and then dried at room temperature. The ITO glasses were immersed into the solution in ambient atmosphere (RH 60%) and withdrew at rate of 10 cm/min, dried at room temperature for 5 min and then sintered at 450 °C during 5 min. The process was repeated to obtain 3 layer films. The final heat treatment was performed at 560 °C in air atmosphere for 15 min. The resulting coatings were transparent and homogeneous without any visual cracking¹¹.

2.3. Electrolysis for chlorpyrifos degradation

Galvanostatic electrolysis were carried out at G/ Nb_2O_5 and Nb/ Nb_2O_5 electrodes, with current density ranging from 0 to 400 $mAcm^{-2}$ and electrical potential ranging from 1-12 volts. Runs were performed at 5 - 40°C. Solutions of 50 mgL^{-1} of pure chlorpyrifos solution were used. Electrolysis done with 1 gL^{-1} of different types of electrolytes NaCl, $CaCl_2$, KCl, Na_2CO_3 , NaF, and Na_2SO_4 , at sodium chloride concentration from 0.5-10 gL^{-1} with pH around 1.5-12. The electrolysis of time ranges from 0-180 min. The electrolysis of the aqueous solution containing the chlorpyrifos to be treated electrochemically was carried out in one compartment Pyrex glass cell of 50 ml volume with the prepared G/ Nb_2O_5 and Nb/ Nb_2O_5 as anode and austenitic stainless steel as cathode. DC power supply was used for the degradation of chlorpyrifos insecticide. The current and potential measurements were carried out using digital multi-meter.

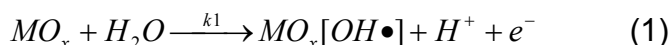
2.4. Analysis

Two main parameters were measured to evaluate the electrochemical treatment efficiency, the remaining pollutant concentration and the chemical oxygen demand (COD). Remaining pollutants (chlorpyrifos) concentration was measured using a double-beam UV-visible spectrophotometer from Shimadzu at $\lambda_{\text{max}} = 220$ nm using calibration curve with standard error $\pm 0.2\%$. While the COD was determined using a closed reflux titrimetric method¹².

3. RESULTS AND DISCUSSIONS

3.1. Mechanism of electrochemical oxidation of organic pollutants

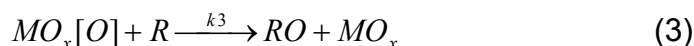
The electrochemical oxidation of many organic pollutants in aqueous solutions on anode could



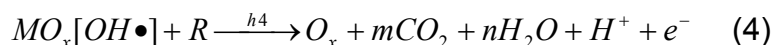
The hydroxyl radicals produced can be oxidized to higher oxide:



The higher oxide formed participate the formation of selective oxidation of the organic pollutants (R) without complete incineration:



The above route can take place only if the transition of the underlying oxide to a higher oxidation state occurred. The electrodes of this class are called "active electrodes". However, if the product of equation (3) is not obtained the electrogenerated hydroxyl radicals could directly oxidize the organic compound to carbon dioxide and water, predominantly cause the combustion of the organic compound through hydroxylation of these compounds:



And this class of electrodes are called " non-active electrodes "

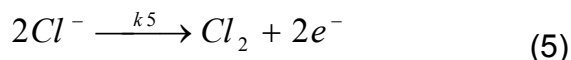
On the basis of the above mentioned mechanism, the lead dioxide anode employed in this investigation is characterized by high oxygen overvoltage on which (OH•) are generated from the oxidation of water. Hydroxyl radicals (OH•) are electrosynthesized in aqueous solutions and can react rapidly with aromatic pesticides, leading to a polyhydroxylation reaction, followed

take place by direct electron transfer or oxygen atom transfer. In addition to direct oxidation, organic pollutants can also be treated by an indirect electrolysis generating chemical reactant to convert them into less deleterious products. Oxidation of these pollutants might go further to carbon dioxide and water via successive reactions. Each of them could proceed through several steps such as mass transport, adsorption and direct or indirect reaction at the anode surface of the chlorpyrifos by using G/Nb₂O₅ and Nb/Nb₂O₅ electrodes The direct electrochemical oxidation of organic compounds could generally occur through the following mechanism in which the first step is the oxidation of water molecules on the electrode surface (MO_x). This process may give rise to the formation of hydroxyl radicals according to:

by complete mineralization of the initial pollutants¹³. However, Nb₂O₅ does not have a higher oxidation state; consequently it is classified as a "non-active electrode". It was reported that lead dioxide electrode is hydrated one and the electrogenerated hydroxyl radicals are expected to be more strongly adsorbed on its surface. This behavior, makes lead dioxide anode very

reactive towards organic oxidation. The degradation of the organic pollutants is completed by reaction with adsorbed hydroxyl radicals forming carbon dioxide and water. Indirect electrochemical oxidation of organic pollutants occurs through the "in situ" electro generation of catalytic species with powerful oxidizing property. This process is capable of eliminating the detrimental pollutants from their solutions by converting them into harmless

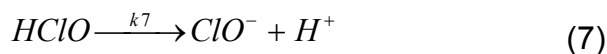
compound. Although a large number of electrogenerated oxidants can be used such as Fenton's reagent and ozone, the hypochlorite ion is the most widely employed oxidant in wastewater treatment. The mechanism of electrogeneration, from a solution, containing chloride ions involves two steps. The first one is primary oxidation of chloride ions to chlorine at the electrode surface according to¹⁴



The second step is formation of hypochlorous acid:



The HClO undergoes dissociation into hypochlorite and hydrogen ions:



3.2. The effect of different operating factors on degradation of chlorpyrifos and COD removal using G/Nb₂O₅ and Nb/Nb₂O₅ electrodes.

The effect of different operating conditions such as: type of conductive electrolyte, current density, pH of simulated solution, temperature, time interval of treatment, initial concentration, and NaCl concentration were studied. The remaining concentration (mgL⁻¹) and COD removal (mgO₂L⁻¹) were illustrated in Figures. (1-8).

3.2.1. Effect of pH value

The pH of the solution was varied while the other conditions were kept constant. As shown in Figure 1, maximum removal of chlorpyrifos was achieved at pH 10.8 for G/Nb₂O₅ and Nb/Nb₂O₅. The pH values of the solutions were adjusted by adding drops of H₂SO₄ and NaOH. The reactions were carried out for 30 min under the following conditions: the initial concentration of 100 mgL⁻¹, a current density of 25 mAcm⁻², a temperature of 20-30 °C and NaCl concentration of 1 gL⁻¹. The distance between the two electrodes was adjusted to 1cm. In this study, it was found that

the of electrocatalytic oxidation of chlorpyrifos was depending on pH value of solution as shown in Figure 1. It was shown that the maximum rate of degradation using both G/Nb₂O₅ and Nb/Nb₂O₅ electrode was in the basic medium. In this medium, the Nb₂O₅ anode employed in this investigation is characterized by high oxygen overvoltage on which (OH•) are generated from the oxidation of water. Hydroxyl radicals (OH•) are electro synthesized in aqueous solutions and can react rapidly with aromatic pesticides, leading to a polyhydroxylation reaction, followed by complete mineralization of the initial pollutants¹³. Also the rate of hypochlorite generated increase in basic medium.

3.2.2. Effect of the electrolysis time

To assess the effect of electrolysis time, experiments were conducted with operating treatment conditions that were consistent with those described for both G/Nb₂O₅ and Nb/Nb₂O₅ electrodes. As shown in Figure 2, the maximum removal of chlorpyrifos was achieved using G/Nb₂O₅ and Nb/Nb₂O₅ electrodes after at least 30 min. Therefore, this was taken as optimal degradation time for the removal of chlorpyrifos.

This can be explained by the overall oxidizing agent in solution was generated in the first half hour. However, the degradation of most chlorpyrifos pesticide in all process was reached after 30 minutes.

3.2.3. Effect of type of electrolyte

Electrolytes of 1 g L^{-1} of the following salts: NaCl, CaCl_2 , KCl, Na_2CO_3 , NaF, and Na_2SO_4 were studied by both electrodes. As appears in Figure 3, the KCl and NaCl were the most effective conductive electrolytes for the electrocatalytic degradation of the investigated chlorpyrifos while Na_2SO_4 and Na_2CO_3 electrolytes show poor results. The operating conditions of the treatment process were: current density of 25 mAcm^{-2} , pH 10.8 using both G/ Nb_2O_5 and Nb/ Nb_2O_5 , temperature of $20\text{-}30\text{ }^\circ\text{C}$, initial concentration 100 mgL^{-1} , and the distance between the two electrodes was 1cm. The reaction was allowed to proceed for 30 min. From figure 3 it is clear that the less value of remaining concentration was obtained in the presence of KCl and NaCl. Addition of KCl or NaCl provides the effective Cl^- ion. In addition, NaCl is the cheapest electrolyte containing chloride ions. This observed behavior may be due to the small ion size of K^+ and Na^+ which increases the ability of loss Cl^- ion. From Fig. 3, it is clearly that the less effective electrolytes in the degradation of pollutant are Na_2SO_4 and Na_3CO_3 . This behavior may be attributed for the formation of an adherent film (PbO_2 [O]) on the anode surface which poisoned the electrode process surface. Also these electrolytes does not contain chloride ion (Cl^-). Also those electrolytes may form stable intermediate species that could not be oxidized by direct electrolysis. These observations were confirmed in other studies¹⁵. Also, it was shown that CaCl_2 and NaF have an intermediate effect on the rate of degradation of pollutants because CaCl_2 contains effective ion (Cl^-), while the electrodegradation of pollutants may be occurred

through electrocatalytic oxidation in the presence of NaF electrolyte.

3.2.4. Effect of the NaCl concentration

Different concentrations of NaCl were applied to study their effect on the removal of chlorpyrifos as indicated in Figure 4. The results indicate that an increase of the electrolyte concentration up to 1 gL^{-1} lead to increase in the chlorpyrifos degradation rate for both G/ Nb_2O_5 and Nb/ Nb_2O_5 electrodes. Further increase of the NaCl concentration reflected negatively on the degradation rate of chlorpyrifos. The operating conditions of the treatment process were: current density of 25 mAcm^{-2} , pH 10.8 using both G/ Nb_2O_5 and Nb/ Nb_2O_5 , temperature of $20\text{-}30\text{ }^\circ\text{C}$, initial concentration 100 mgL^{-1} , and the distance between the two electrodes was 1cm. The reaction was allowed to proceed for 30 min.

3.2.5. Effect of current density

As shown in Figure 5 chlorpyrifos degradation increase with increasing the applied current density up to 25 mAcm^{-2} by using both G/ Nb_2O_5 and Nb/ Nb_2O_5 electrodes. Further increase of the current density was followed by gradual decrease in chlorpyrifos degradation due to increase in temperature. Theses experiments were carried out under the following operating conditions: initial concentration 100 mgL^{-1} , pH 10.8 using both G/ Nb_2O_5 and Nb/ Nb_2O_5 , temperature $20\text{-}30\text{ }^\circ\text{C}$, NaCl 1 gL^{-1} , and the distance between the two electrodes of 1cm. The time of electrolysis was 30 min using G/ Nb_2O_5 and Nb/ Nb_2O_5 electrodes. As shown in Figure 5 chlorpyrifos degradation increase with increasing the applied current density up to 25 mAcm^{-2} by using G/ Nb_2O_5 and Nb/ Nb_2O_5 electrodes. Further increase of the current density was followed by gradual decrease in chlorpyrifos degradation due to increase in temperature. Above a temperature $35\text{ }^\circ\text{C}$, sodium hypochlorite tends to chemically decompose to sodium chlorate.



(8)

So when temperature rises higher than 35 °C, production of NaClO falls.

3.2.6. Effect of initial chlorpyrifos concentration

Figure 6 shows the effect of different initial chlorpyrifos concentrations on the rate of chlorpyrifos degradation. Total removal of the chlorpyrifos can be achieved in the presence of initial chlorpyrifos load up to 100 mgL⁻¹. However, increasing the chlorpyrifos concentration above this level result in a decrease in the electrocatalytic rate of degradation. The removal efficiency of the chlorpyrifos by using G/Nb₂O₅ and Nb/Nb₂O₅ electrodes at 100 mgL⁻¹ was the optimum concentration for the initial load concentration of chlorpyrifos. Figure 6 shows the effect of different initial chlorpyrifos concentrations on the rate of chlorpyrifos degradation. As the initial chlorpyrifos concentration increase, the degradation efficiency decrease. This evidence that the generation of the powerful oxidizing agent Cl⁻ ions on electrode surface was not increased in constant current density.

3.2.7. Effect of temperature

Figure 7 represents the correlation between the concentration of the remaining chlorpyrifos as a function of the solution temperature. The rate of the chlorpyrifos degradation increase significantly with increasing the solution temperature up 20-30 °C. Further increase of the temperature up 35°C reflected negatively on the degradation rate of chlorpyrifos. It is clear from Figure 7 that the optimum temperature of sodium hypochlorite production was 20-30 °C for G/Nb₂O₅ and Nb/Nb₂O₅ electrodes. At moderate temperature, the losses of chlorine gas decrease, which lead to increase the sodium hypochlorite formation. Asokan and Kraft found that at 35 °C, the sodium hypochlorite tends to chemically decompose to sodium chlorate^{16, 17}. In addition, increasing of remaining

concentration above 40 °C may be attributed to decomposition of adsorbed film on anodic side. The electrodes are unstable at high temperature above 40 °C.

3.2.8. Effect of time on COD removal

The optimal time for COD removal of the chlorpyrifos using G/Nb₂O₅ and Nb/Nb₂O₅ electrodes were 9 and 7 hr respectively as shown in Fig.8. These experiments were carried out under the following operating conditions: current density of 25 mAcm⁻², pH 10.8, temperature 20-30 °C, NaCl 1g/L⁻¹, initial concentration 100 mgL⁻¹, and the distance between the two electrodes was 1cm. From Figures (1-8) and Table 1, it was found that the G/Nb₂O₅ electrode was more effective than Nb/Nb₂O₅ electrode in the degradation of chlorpyrifos. The degradation of chlorpyrifos was nearly completed and reached 92 % and 84 % using G/Nb₂O₅ and Nb/Nb₂O₅ electrodes in 30 min. The COD removal was completed using these electrodes in 7 and 9 hours respectively, while degradation using chlorpyrifos degradation was enhanced probably due to high growth on easily metabolizable compounds which in turn increased degradation. The strain C2A1 showed 90% degradation within 8 days of incubation¹⁸. It is clear that the sodium hypochlorite production increase with decreasing distance down to 1cm. This is due to drop of electrolyte ohmic potential, and hence the cell voltage¹⁹. The highest hypochlorite production was achieved with narrow distance between the cell electrodes of 1cm.

3.3. Comparison with other method of treatment

The percentages of degradation for each method using in literature and the electrochemical method in this work were represented in table 1. It is clear that the electrochemical degradation is the best.

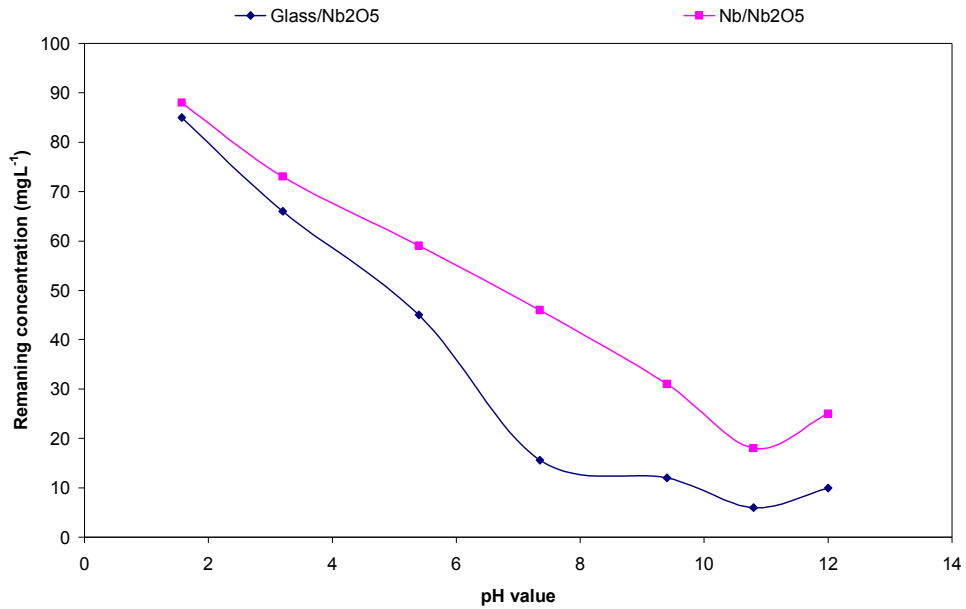


Figure 1
Effect of pH value on chlorpyrifos removal using Glass/Nb₂O₅ and Nb/Nb₂O₅ electrodes.

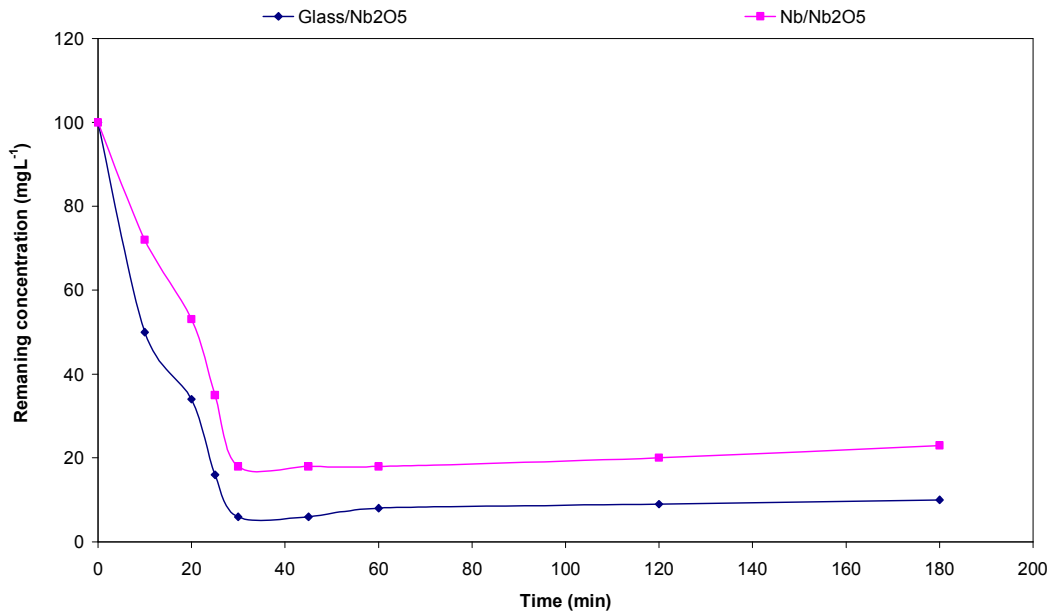


Figure 2
Effect of time electrolysis on chlorpyrifos removal using Glass/Nb₂O₅ and Nb/Nb₂O₅ electrodes.

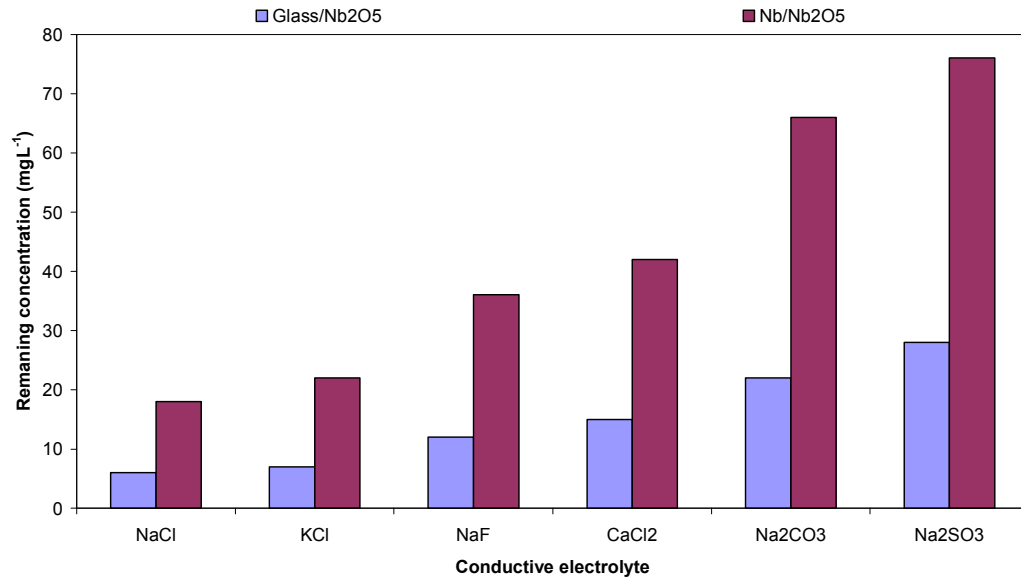


Figure 3
Effect of conductive electrolyte type on chlorpyrifos removal using Glass/Nb₂O₅ and Nb/Nb₂O₅ electrodes.

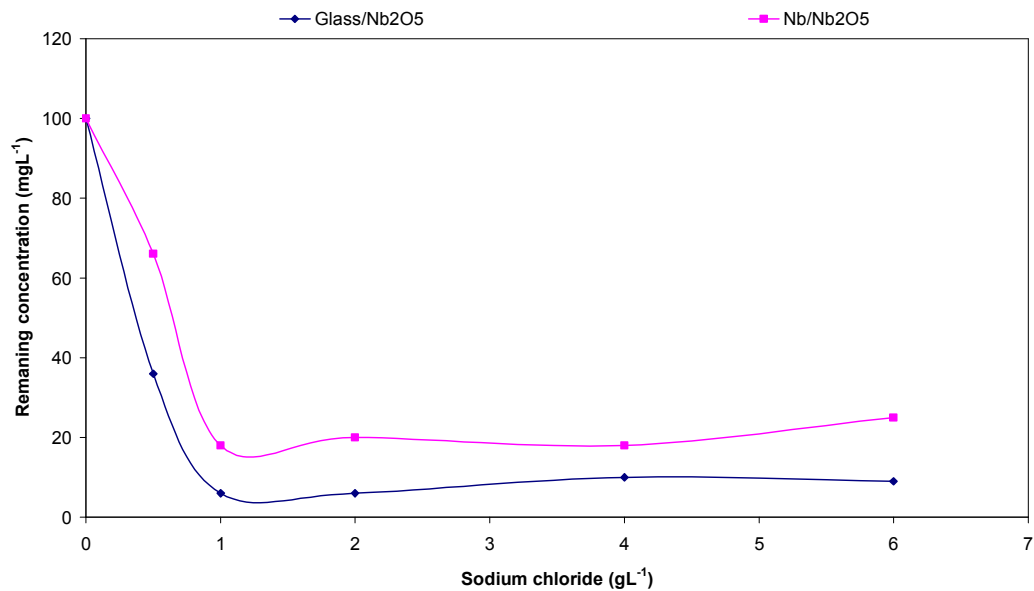


Figure 4
Effect of Sodium chloride concentration on chlorpyrifos removal using Glass/Nb₂O₅ and Nb/Nb₂O₅ electrodes.

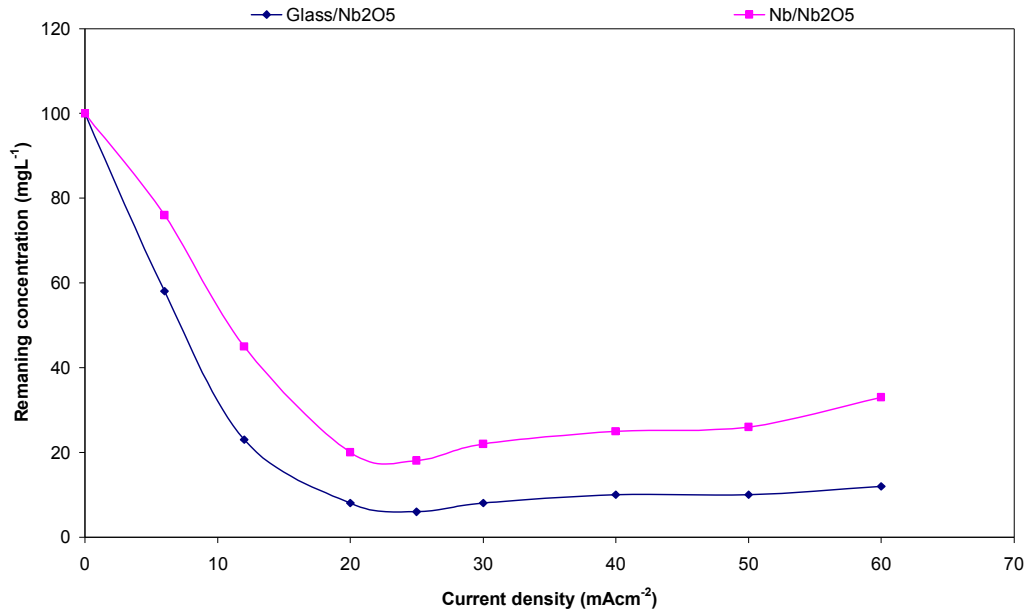


Figure 5
Effect of current density on chlorpyrifos removal using Glass/Nb₂O₅ and Nb/Nb₂O₅ electrodes.

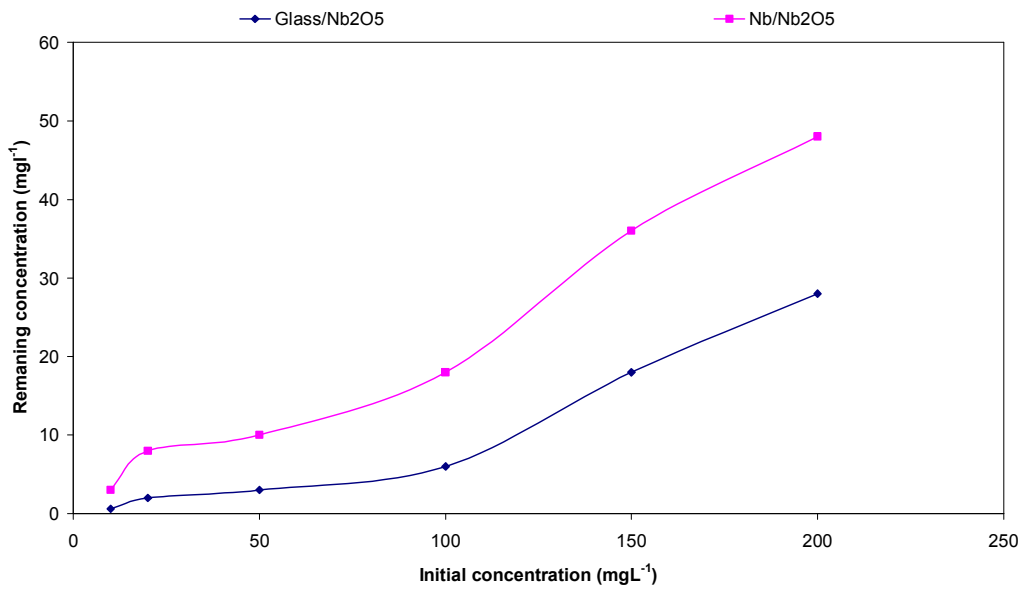


Figure 6
Effect of the initial concentration of chlorpyrifos on its removal using Glass/Nb₂O₅ and Nb/Nb₂O₅ electrodes.

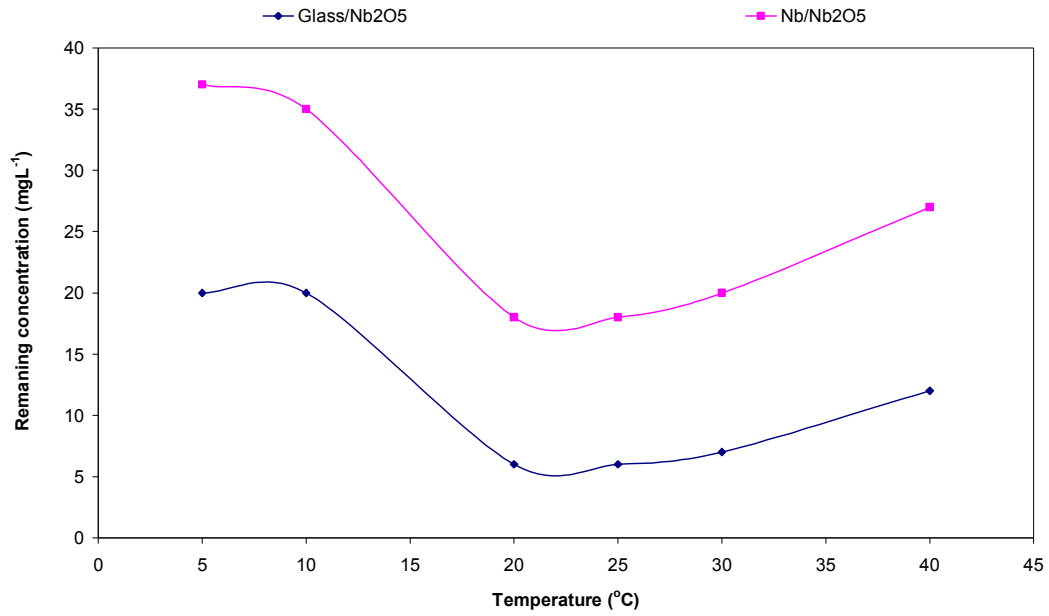


Figure 7
Effect of temperature on chlorpyrifos removal using Glass/Nb₂O₅ and Nb/Nb₂O₅ electrodes.

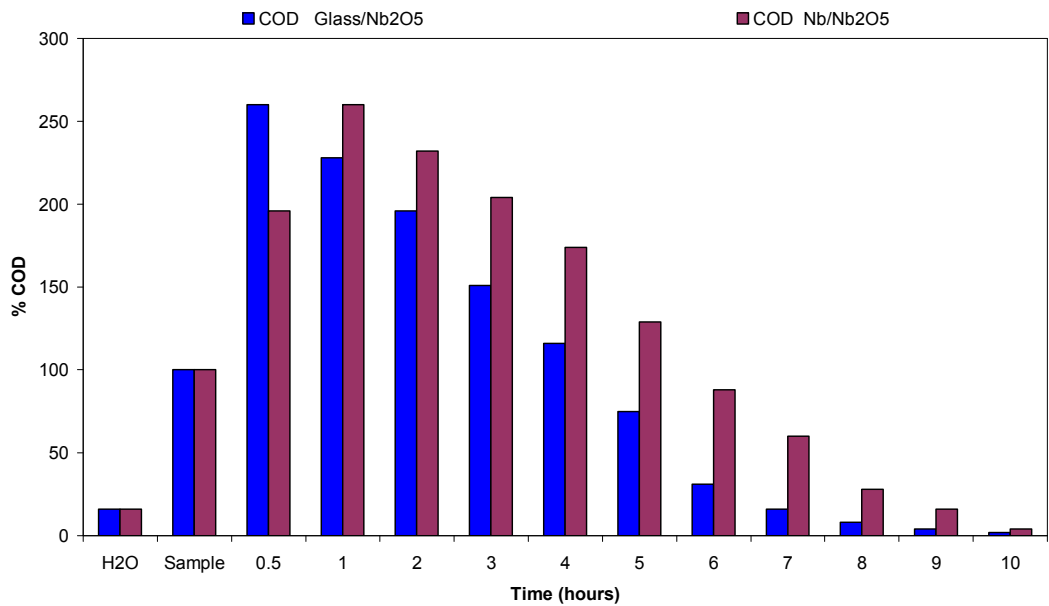


Figure 8
Effect of time in COD removal of chlorpyrifos using Glass/Nb₂O₅ and Nb/Nb₂O₅ electrodes.

Table 1
Comparison of proposed electrodes and some decolonization technologies for chlorpyrifos (CF).

Method of treatment	Initial chlorpyrifos concentration (mg L ⁻¹)	chlorpyrifos removal efficiency (%)	Time	Literature
<i>P. desmolyticum</i> NCIM 2112	100	58.7%	2 day	20
<i>P. desmolyticum</i> NCIM 2112	100	63.52%	4 day	20
<i>P. desmolyticum</i> NCIM 2112	100	98%	6 day	20
Photocatalytic degradation of using photocatalyst TiO ₂	80	90%	8 h	3
Degradation Chlorpyrifos by Noble Metal Nanoparticles	2 ppm (10 mL)	Complete degradation	3 h	21
Electro-enzymatic processes	100	98%	1.5 h	22
Degradation of Chlorpyrifos by Phanerochaete chrysosporium	200	90%	15 day	23
Glass/Nb ₂ O ₅	100	94	1/2 h	This work
Nb/Nb ₂ O ₅	100	82	1/2 h	

CONCLUSION

In this work two modified electrodes G/Nb₂O₅ and Nb/Nb₂O₅ were prepared by electrodeposition and used as anodes for electrodegradation of chlorpyrifos (dursban) in aqueous solution at different parameters including conductive electrolyte, current density, temperature, initial concentration of chlorpyrifos, pH and time. The optimum condition for both electrodes are: NaCl (1g L⁻¹), temperature at (20-30°C), degradation time of 30 min, initial concentration of 100 mg L⁻¹, and current density (25 mA cm⁻²). The degradation of chlorpyrifos was nearly completed (94% and 82%) using C/PbO₂ and Pb/PO₂ electrodes at pH 10.8.

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