Al-Azhar University of Gaza

Postgraduate Studies and

Research Affairs

Hypochlorite Generation On Some Modified Electrodes For Treatment Of Wastewater Pollutants

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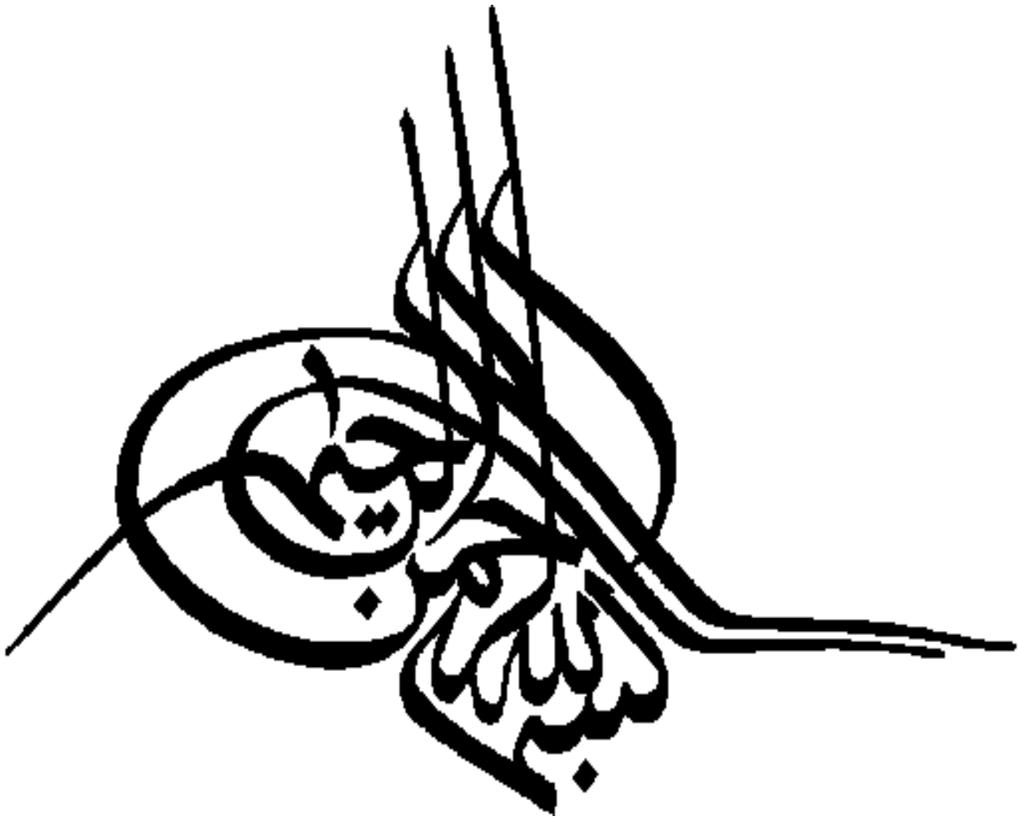
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Abstract

Two modified electrode (Pb/PbO_2 and C/PbO_2) was prepared by electrodeposition of lead oxide layer on lead and carbon substrate. These modified electrodes were used as anodes for generation of sodium hypochlorite (NaOCl) from sodium chloride solution, sea water and brine water. The results of the sodium hypochlorite production expressed in terms of percentage weight of sodium hypochlorite (w/v%). The prepared electrodes were also used as anodes for electrocatalytic oxidation process of picric acid in aqueous solution. The results of the electrocatilytic process of picric acid solutions were expressed in term of the remaining concentration and chemical oxygen demand (COD) values. Different operating conditions and factors affecting the treatment process of sodium hypochlorite generation and electrocatalytic of picric acid including current density, pH, initial concentration of picric acid, conductive electrolyte and time electrolysis were studied. The optimum operating condition for sodium hypochlorite generation and degradation of picric acid were investigated. For both sodium hypochlorite generation and electrodegradation of picric acid C/PbO_2 electrode indicated higher efficient than Pb/PbO_2 electrode.

Key words: hypochlorite generation, electrodegradation, electrode, electrocatalytic, picric acid.

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Abdul- Rahman M. A. El-Agha

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CHAPTER "ONE"

INTRODUCTION

1.1Introduction

Hypochlorite is the term used to denote the sum of hypochlorous acid (HOCl) and the hypochlorite anion (ClO⁻) [1]. NaOCl can be produced by infusing chlorine gas into a cold solution of NaOH or by electrolyzing NaCl solution. Concentrated sodium hypochlorite is hyper-unstable, and the available chlorine in the solution rapidly decreases during storage and transportation [2].

Both hypochlorous acid and hypochlorite ion in water undergo a decay process, whose rate depends on exposure to light (UV), temperature, pH, initial available chlorine concentration and presence of catalysts, atmospheric carbon dioxide organic matter and metal ions [3,4]. Studies indicated that decay rates are increasing at higher concentration and higher temperatures [5,6].

Polishing complete dentures with a common pumice pan and polishing wheel causes cross-contamination from denture to denture [7,8].Autoclaving or replacing the pumice and polishing wheel after each use has been suggested[8-10]. Quaternary ammonium compoundsor diluted sodium hypochlorite [9- 10] added to the pumice has been shown to be ineffective in prevention of crosscontamination. Full-strength sodium hypochlorite has been shown to be effective against microorganisms including spores [11,12]. Senia et al have shown that a l-minute soak in undiluted Clorox (The Clorox Co., Oakland, Calif.) sterilized gutta-percha cones used for filling root canals. Trevelyan [13] has shown that sodium hypochlorite was effective against hepatitis virus. Abbott [14] and Treveno [15] laboratories recommended 2.5% sodium hypochlorite for inactivating liquid wastes containing the infectious agent of viral hepatitis.

There is concern that the use of sodium hypochlorite (NaOCl) may lower the bond strength of resin cements. The objective of this study was to evaluate the effect of 5% NaOCl treatment on the bond strength of a resin cement. The results demonstrated that 5% NaOCl produced significantly large reductions in resin bond strengths, and the reductions could be completely reversed by the application of either 10% ascorbic acid or 10% sodium ascorbate [16].

On-site electrochemical generated hypochlorite is a low-cost, strong disinfectant and oxidizing agent with a broad spectrum of applications, and with minimal associated hazard. This type of generation has been in existence for more than 25 years but only in the last few years it has emerged as a recognized viable method to replace chlorine gas and high strength hypochlorite. That increasing the operating current density by 50%, will increase the production rate of hypochlorite by 50% and have a slight beneficial effect on current efficiency and product concentration. M. Rudy *et al.* that the salt utilization, current efficiency, and product concentrations are all improved by controlling the electrolyzer operating temperature below the conventional operating parameters.[17]

Sodium hypochlorite (NaOCl) is used on a large scale for surface purification, fabric bleaching, odour removal and water disinfection[18-20]. In-situ produced hypochlorite was used for anodic oxidation of dye molecules [21-24] and phenols [25] in the wastewater. It has numerous advantages namely simple dosage, safe storage and transportation and leaves no residual effluent. Electro synthesis of NaOCl is preferred due to the environmental hazard associated with the storage and transportation of liquid chlorine. It is now becoming popular for users to produce their own hypochlorite solutions by means of undivided electrolytic cells by direct electrolysis of weak brine or seawater [26].

1.2 Stability and storage of sodium hypochlorite

The shelf-life or stability of sodium hypochlorite solutions has been investigated previously [27-30].Martin [31]stated, though without any support, that the shelf-life of NaOCl was 3 months. Fabian and Walker[27] found that low concentrations (< 1%) of NaOCl remained stable (90% of initial concentration) for up to 23 months when stored in two-thirds full, amber glass bottles potentially exposed to sunlight. Pappalardo *et al.* [28], comparing two chlorine-containing antiseptics, found that NaOCl solution obtained by an electrolytic process was a chloroxydiser and more stable than Dakin's solution. They found an association between the stability of pH and available chlorine concentration. Johnson and Remeikis [32] tested the shelf-life of different concentrations of NaOCl by determining the 'mean dissolving time' for standard human umbilical cord samples. They found the dissolving time for 5.25%

NaOCl remained relatively consistent over 10 weeks. However, diluted solutions did not retain stability for longer than 1 week. Piskin and Turkun [33] measured the stability of three commercially available sources of NaOCl at different concentrations and temperatures over 200 days. The only significant reduction in available chlorine was caused by storage of 5% NaOCl at 24°C. Cunningham and Balekjian [34] showed warming of NaOCl to 37°Ccaused a 9.5% and 4% reduction in the available chlorine for the 5% and 2.5% solutions, respectively, after 24 hr. Recently the trend for heating NaOCl solutions up to 50°Cor more has become popular [35]. Gambarini *et al.*[30] testedthe stability of heated NaOCl and found the available chlorine in a commercial source declined by less than 1% when heated to 50°C and tested up to 30 days later. [33,34].

G. Gambarini *et al* [30] investigate the effect of heating sodium hypochlorite to 50°C on the stability of the solution. An iodometric titration test was used to evaluate the decomposition rates of heated and nonheated solutions over 30 days. Results showed that all specimens exhibited a minimal, gradual degradation versus time. However, no statistically significant difference was noted between the two groups. After 30 days, both heated and nonheated solutions maintained high available chlorine content and pH values consistent with excellent tissue-dissolving and antibacterial properties.

Although the manufacturers use at least a 2-yr expiration date for sealed undiluted NaOCl solutions chemical stability of NaOCl may be adversely affected by many factors [33].

1.3Advanced electrolytic generators of sodium hypochlorite

An advanced electrolytic generator has been developed for the on-site production of hypochlorite.An electrochemical cell electrolyzes sodium chloride brine to chlorine gas and sodium hydroxide solution, which are reacted immediately outside the cell to produce a 5 to 10 percent sodium hypochlorite solution [36].

A process for producing an alkali metal hypochlorite which comprises electrolyzing an aqueous solution of an alkali metal chloride in an electrolytic cell including a plurality of unit cells, each equipped with at least one anode and at least one cathode, in which the unit cell is arranged in series via partitioning plates, wherein hydrogen gas generated at the cathode in each unit cell is passed out of each

unit cell such that the hydrogen gas does not contact the cathode portion that takes part in electrolysis in the next adjacent unit cell and an electrolytic cell [37,38].

An apparatus and method for producing small quantities of chlorine and sodium hydroxide or sodium hypochlorite was presented by S. Lynn [39].The apparatus of the invention includes the use of an electrolytic cell embodying an anode chamber charged with an acidic, concentrated sodium chloride solution and a cathode chamber charged with a basic aqueous solution and through which an electric current may be passed under controlled condition to initiate and maintain reaction that produces chlorine gas in the anode chamber and hydrogen gas and a solution of sodium hydroxide in the cathode chamber may be combined as separate product to form a solution of sodium hypochlorite.

N. Krstajic and V. Nakic [40] established a model for production of hypochlorite giving the dependence of the cathodic current efficiency on the hypochlorite concentration and the total cathodic current density . Measurements have shown good agreement with the value predicted by the model.

 G . Y. Cheng and G. H. Kelsall [41] developed two models to predict the hypochlorite ($HOCl + OCl^-$) production by electrolysis of near-neutral aqueous sodium chloride solution, in reactors with (a) an anode and cathode in the form of plates, and (b) a lead dioxide-coated graphite felt anode and titanium plate cathode. The model was used to investigate the feasibility of using a porous anode to achieve high single pass conversions in oxidising chloride ions. For the same operating conditions, the overall current efficiency was also predicted to increase from 0.71 to 0.77 by replacing the plate with the porous anode.

Chlorine treatment of the cooling water of coastal power station is required to prevent infestation of the circulating water culverts by mussels and marine organisms. As such enormous quantities of cooling water are required at modern coastal power station, the addition of even a fraction of a ppm of chlorine will result in the consumption of large tonnages of chlorine. The possibility was therefore investigated of producing hypochlorite (which is claimed to be equally effective for controlling mussels) by the direct electrolysis of sea water. [42].

1.4 Generation of sodium hypochlorite from sodium chloride solution

On-site chlorine or sodium hypochlorite generation is a feasible alternative compared to purchased and delivered chlorine. The technology is based on the electrolysis of brine solution to produce either variable concentrations of sodium hypochlorite or pure chlorine gas. Three best available technologies that should be considered for this application include:

1) direct electrolysis, producing 0.8% liquid sodium hypochlorite by weight.

2) membrane cell electrolysis, producing 12.5% liquid sodium hypochlorite by weight.

3) membrane cell electrolysis, producing gaseous chlorine and liquid caustic soda [43].

On-site electrochlorination (OSEC) is a technology for producing sodium hypochlorite as an effective disinfectant from the electrolysis of water and salt solution. S. Esposto [44] evaluated the introduction of this technology in Iraq and compared it with two traditional disinfection systems already present in the country.

1.5 Generation of sodium hypochlorite from sea water

Due to its abundance and its high sodium chloride content, sea water appears to be an ideal medium for the electrogeneration of active chlorine[24]. The main inconvenience of using sea water as a starting material is that it contains magnesium and calcium ions, which in local alkaline conditions, precipitate as hydroxides. This scale is usually produced at the cathode, and tends to passivate the surface. Thermodynamic calculations carried out by Boxall and Kelsall [45] predict the precipitation of $Mg(OH)_2$ and $Ca(OH)_2$ at pH values above 9 and 12.5, respectively. To solve the problem of the formation of calcium carbonate scales on the cathode surface. New type of electrochemical reactor for use in electrochemical water disinfection was tested. A cathode which simultaneously acts as a sonotrode was used. This sonotrode is an efficient means for in situ cleaning the cathode surface from calcareous deposits formed during hydrogen evolution from potable water. The production rate of active chlorine from potable water in the new reactor in

dependence on current, ultrasound intensity, and flow-through velocity was measured. The production of active chlorine is not significantly changed by the effect of ultrasound [46].

The formation of hardness caused deposits on the cathodic surfaces of cells used in the electrolytic production of hypochlorite from impure saline solution is reduced and good current efficiencies are realized by employing flat, continuous cathodes having a surface roughness [47].

For the production of hypochlorite, two cell configurations are used: divided cells, with a cationic or an anionic membrane [48], or undivided cells [49-51]. Divided cells have the ability to produce hypochlorite at very high concentration (8-15%) but require the use of very pure solvent and are therefore not very suitable for sea water. In contrast, in an undivided cell, the hypochlorite concentration is limited due to side reactions [52].

In order to prevent or to limit the oxidation of water, Dimensionally Stable Anodes are often used. DSA electrodes are usually made of ruthenium or iridium dioxides deposited on titanium. Their use favours chloride oxidation. The reduction of the hypochlorite can be limited by the formation of a $Mg(OH)_2$ or $Ca(OH)_2$ film by increasing the anode to cathode ratio. [40]

On site generation of hypochlorite has been largely developed in the last few decades mainly for the disinfection of drinking water [53] or for cooling water in sea side power plants [54]. The use of seawater as a starting material has the advantage to be inexpensive, however the scale deposition at the cathodes is a major drawback. The different reactions occurring in an electrochlorator have been described in a large number of reviews [55].

Various techniques are currently employed for removing the scale from the cathode surface. The main commercial plants advise an acid cleaning during the electrolysis to dissolve the scale. The inversion of the electrode polarity can also be a way to limit scale accumulation. When the polarity is inverted, the scale is dissolved in the acid anodic layer. Goodridge [56] pioneered this technique in a fluidized bed bipolar reactor and the Socrematic's system, Setrelec, employs this polarity inversion. More recently, interdigitated band electrodes have also proved to reduce scale accumulation at cathodes [57]. Scale deposits on the cathodic bands readily detach

and fall of to the bottom of the tank cell. Numerical simulations [58] have shown the existence of a static pH gradient above the electrodes where acid areas close to the anodes are in close proximity to alkaline areas near the cathodes. This modulated pH profile may be responsible for the limitationof the scale growth.

Screen printing technology was employed here for the fabrication of interdigitated electrodes for sea water electrolysis. The anodes consisted of a ruthenium dioxide film printed on top of a thick film of platinum limiting the anodic formation of oxygen, whereas the cathodic bands are made of platinum ink. Despite the low inter-electrode gap (1 mm) and the electrode alignment, the production of hypochlorite from synthetic sea water in an agitated tank cell, could reach a current   efficiency of 80% and conversion up to 30%. [57]

A novel design for interdigitated band electrodes was described by R. Ferriggno et al [59]. The electrode is built by successive printing of conductive and insulating layers on a steel substrate. This geometry exhibits a high performance for the hypochlorite electrogeneration from seawater. The active chlorine concentration reached at the end of the electrolysis varies from 0.5 to 10 gL^{-1}, depending on the number of electrodes, their configuration in batch or single flow mode, the flow rate and the current density. This geometry also limits scale development at the cathode.

R. Holca[60] discussed that the electrolysis of sodium chloride solution, either seawater or a synthetic solution, produce a strong oxidizing and disinfecting solution of hypochlorite and hypochlorous acid. pH is adjusted to regulate the proportion of acid and salt produced. The problem associated with the presence of salt other than sodium chloride, when natural seawater is the electrolyte, and the equipment used to solve them, are described. The application of the process include chlorination of cooling circuit waters, disinfection of treated waste water, sterilization of water injected in to oil wells and removal of obnoxious from industrial effluents. A cost comparison with direct chlorine injection shows that the electrolysis system has economic advantages, particularly those related to operating costs**.**

1.6 Generation of sodium hypochlorite using undivided cell

The oxidation of chloride ion at DSA anodes gives higher yields of hypochlorite than were obtained at Pt or graphite electrodes. It is also shown that the problem of hypochlorite reduction at the cathode in undivided cells can largely be overcomed by use of a " reduced area " cathode. These two improvements have both been included in a new cylindrical hypochlorite cell capable of a 70% conversion of a 0.048 mol. dm^{-3} NaCl solution to NaOCl with a production rate of 50 gh^{-1} active chlorine[61].

T . Bechtold et al [62] investigated theproduction of hypochloritefor denim bleach using undivided unipolar electrolysers. The current efficiency of the electrolysis process was studied at laboratory scale with up to 20 A cell current and at the technical scale using a 1200 A electrolyser. NaCl solutions in the concentration range 0.236–0.944 M NaCl were used. Anodic current densities up to 400 A m^{-2} were used. Hypochlorite solutions with active chlorine concentration c(Cl)=0.10–0.12 M were obtained with current efficiency of 58–70%. The technique overcomes problems of insufficient reproducibility of bleach, chemical costs and released wasted water due to the use of commercial NaOCl solution.

The invention provides method and a device for the production of an alkali metal hypochlorite solution, in particular a sodium hypochlorite solution, having at least one non-divided electrolytic cell,means for supplying a brine solution in to the electrolytic cell at a defined volumetric flow rate and a defined salt concentration , and having an a.c. voltage source for the production of current across the electrolytic cell [63].

1.7 Generation of sodium hypochlorite using divided cells

A hypochlorite cell divided by an anionic membrane was examined by N . Krstaji et al [48]. The results clearly showed that it is possible to suppress cathodic reduction of hypochlorite and to achieve a higher degree of chloride to hypochloriteconversion, at relatively high current efficiencies, than in the case of an undivided cell, using seawater or untreated diluted brine electrolyte.

Electrochemical synthesis of sodium hypochlorite in a membrane electrolyzing cell withan aluminazirconia ceramic membrane and comprising a titanium anode coated with cobalt oxide has been investigated[64]. Effects of the current density, concentration of the NaCl solution, and the rate of supply of solutions into electrode chambers are investigated. Under optimum conditions, the current efficiency for sodium hypochlorite is 77%.[65]

An electrochemical process for the production of sodium hypochlorite is disclosed. The process may potentially be used to produce sodium hypochlorite from seawater or low purity un-softened or NaCl based salt solutions. The process utilizes a sodium ion conductive ceramic membrane. In the process,water is reduced at a cathode to from hydroxyl ion and hydrogen gas, chloride ion from a sodium chloride solution are oxidized in the anolyte compartment to produce chlorine gas which react with water to produce hypochlorous and hypochloric acid.Sodium ion are transported from the anolyte compartment to the catholyte compartment across the sodium ion conductive ceramic membrane. Sodium hydroxide is transported from the catholyte compartment to the anolyte compartment to produce sodium hypochlorite within the anolyte compartment. [66]

1.8 Operating conditions of sodium hypochlorite

L. Petkov et al [67] described the relationship between the quantity of the obtained hypochlorite and the electrical energy consumption from one part and the current value and the concentration of the initial chloride solution, from the other. According to this model, the mass of sodium hypochlorite is obtained maximal for the maximal sodium chloride concentration and the maximal current value.

The electrochemical production of sodium hypochlorite represents the best method to obtain a pure product. To have a good production, it is necessary to optimize the electrochemical process with the optimal of electrocatalytic electrodes (cathode and anode) the gap between electrodes , the temperature of electrochemical cell. It is very important for the product stability during a long peirod, avoid the presence of heavy metal ions and particulate as impurity-like carbon micro-powders in suspension. It is necessary a rigorous control of the pH of final product to have the optimal disinfection power of hypochlorite solution [68].

A. Khelifa et al [69] studied the effects of some parameters on the active chlorine production from aqueous sodium chloride solutions in the hypochlorite electrochemical production cells. These varying parameters included the anodic surface area (S_a), the ratio of anodic and cathodic surface areas (S_a/S_c), the inter-electrode gap, and the type of the cathode used. In addition, a study of the performance of some electrochemical cells that differ in the type of anodes (platinum-coated titanium, ruthenium-coated titanium, and graphite) was made. The optimum conditions, and the formation of optimal concentration of active chlorine were assessed. Under the following conditions: ruthenium-coated titanium anode (S_a = 24 cm^2); titanium cathode, S_a/S_c = 1.33; inter-electrode gap, 0.5 cm; current density, 35 A/dm^2 ; temperature, 20°C; concentration of NaCl aqueous solution, 3 M and time, 2 h 65.67 g/L of active chlorine was gained.

1.9 Types of anodes used in sodium hypochlorite generation

Franks *et al* [70] described a process for the continuous production of hypochlorite solution over long periods of time by electrolysis of aqueous chloride solution with anode having a coating that is a mixture of oxide of tin, antimony, at least one platinum group metal, and a valve metal selected from the group titanium and tantalum, all in certain proportion.

G. H. Kelsall [50] described a parametric study of a parallel plate Ti /PbO$_2$/x mol dm^{-3} NaCl /Ti hypochlorite cell, for which the cell voltage, current efficiency, and energy yield (mol ClO$^-$ kWh^{-1}) were examined as functions of current density, chloride concentration, and electrolyte flow rate, inlet temperature and pH. The cell was found to behave ohmically, with current efficiencies of 85–99% for 0.5 mol dm^{-3} NaCl electrolyte, a typical chloride concentration for sea water. However, the hypochlorite energy decreased substantially with increased current density, reflecting the large contribution of the electrolyte ohmic potential drop to the cell voltage. The behavior of the Ti/PbO$_2$ anode was found to be irreproducible, and low temperature (say $\leq$ 278K)/high current density operation was irreversibly detrimental both in terms of the anode potential/cell voltage and current efficiency. [71].

The electrochemical synthesis of sodium hypochlorite from a solution with a reduced concentration of sodium chloride is efficiently carried out with the use of

ruthenium oxide-titanium anodes (ROTA). For comparison, with a graphite anode under laboratory conditions a flow-type electrolyzer was selected in view of the fact that it most closely satisfies the purposes of gas purification. The current efficiency with respect to sodium hypochlorite was almost two times higher, and the specific consumption of electrical energy was 1.6-1.8 times lower in the case of the ROTA than in the case of the graphite electrode[72].

A method provided for manufacturing hypochlorite efficiency [73-75],using an anode , which has a coating containing palladium oxide by 10 to 45 weight %, ruthenium oxide by 15 to 45 weight % , titanium dioxide by 10 to 40 weight %and platinum by 10 to 20 weight % as well as an oxide of at least one metal selected from cobalt, lanthanum , cerium , or yttrium by 2 to 10 weight% being formed on a conductive base, and a cathode comprising a coating having low hydrogen overvoltage and covered with a reduction preventive film and being formed on a conductive base, and an aqueous solution of a chloride is electrolyzed without a diaphragm[76].

The electrolytic production of hypochlorite from tap water in a through reactor system was investigated using stacked platinum or iridium oxide coated titanium sheet or expanded metal electrodes. The influence of fast chlorine consumption and polarity reversal on the hypochloriteproduction rate was determined along with the dependence of the hypochloriteproduction rate on temperature, flow through velocity and current density. It was found that in most cases, the hypochloriteproduction rate was higher on iridium oxide compared to platinum electrodes. An increase in the flow-through velocity leads to an increased hypochloriteproduction rate while the hypochloriteproduction rate falls with increasing temperature[77,78].

The electrodes widely used in the hypochlorite production by electrolyzing are RuO_2. TiO_2/Ti and Pt/Ti [96,79]. Though traditional $RuO_2.TiO_2$/Ti anode performs the best electrocatalytic activity among all kinds of dimensional stable anodes (DSA) [80] for NaOCl production. Therefore, the accelerated life test (ALT) value of Pt/Ti in NaOCl production is limited and Pt/Ti shows a higher overpotential in NaOCl production and the cost is very high.

Both IrO_2 and MnO_2 have rutile structures and have been widely used in industries. MnO_2 with excellent anti-corrosion properties in several media and low-

price has attracted attention for use as an insoluble anode both for chlorine evolution and oxygen evolution and is regarded as a DSA material with bright future [81]. MnO_2 was obtained by thermal decomposition or by anodic electric deposition [82-84]. The IrO_2 anode was also widely used as the anode for both oxygen evolution and chlorine evolution[85,86] .

Ruthenium-tin binary (RS) oxides [(Ru+Sn)O_2], and Ruthenium Platenium (RP) oxide [(Ru +Pt)O_x] were coated on titanium substrates by thermal decomposition. The effects of electrolysis condition for the current efficiency (CE) of hypochlorite production on binary (Ru+Sn)O_2 and (Ru + Pt) O_2 electrodes and the treatment of a high salt-containing dye wastewater using this hypochlorite were also investigated. The major factors influencing CE for hypochlorite production were the electrolyte flow rate, current density, and chloride (Cl⁻) concentration. Major factors affecting energy yield are current density, Cl⁻ concentration, and electrode distance. For low current density (300 mAcm^{-2}), high Cl⁻ concentration (1 mol.L^{-1}), and 0.45 cm electrode separation, a high specific energy is obtained. The RS and RPelectrodes exhibits the best removal of organics and chromophor groups in the dye wastewater. On this electrode, better removal of organics and chromophor groups is obtained at 300 mAcm^{-2}, while the chemical oxygen demand (COD) of this wastewater is decreased from 10500 mg.L^{-1} to 1250 mgL^{-1} [87,88].

1.10Reactionmechanism of sodium hypochlorite generation

The disinfectant hypochlorous acid/hypochlorite is produced at the anode in a side reaction to oxygen evolution. The following simplified reaction mechanism is proposed. As the following: chlorine is produced electrochemically from chloride ions dissolved in the water:

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (1)$$
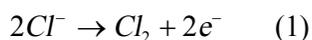
Chlorine hydrolyses in water and hypochlorous acid(HClO) is formed:

$$Cl_2 + H_2O \rightarrow HClO + HCl \quad (2)$$

Hypochlorous acid and the hypochlorite anion forma pH-dependent equilibrium:

$$HClO \leftrightarrow ClO^- + H^+ \quad (3)$$

In the nomenclature of water disinfection, the sum of hypochlorous acid and hypochlorite concentrations is usually termed 'free chlorine' or 'active chlorine'. The

disinfecting effect of free chlorine is based on the release of atomic oxygen according to:

$$HClO \rightarrow O + Cl^- + H^+ \quad (4)$$

$$ClO^- \rightarrow O + Cl^- \qquad (5)$$
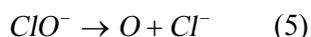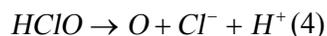
During the disinfection, chloride ions which have been consumed by electrochemical free chlorine production are reformed. Thus there is no overall change in the chemical composition of the water during electrochemical water disinfection.

Where there is a low chloride concentration in the water to be treated (as in drinking water) then the current efficiency of the electrode material for the production of free chlorine is crucial; it should be as high as possible. As reported in [78,89,90] there are very great differences have been found in the efficiency of free chlorine production between different electrode materials at low chloride concentrations.

1.11 Electrochemical oxidation of organic compound using modified electrode

The electrochemical method for wastewater treatment has attracted a great attention recently. The ease of control and the increased efficiencies provided by the use of compact bipolar electrochemical reactors. The large surface area of three dimensional electrodes have been used [91-95]. Detoxification of wastewater containing heavy metals decontamination (while their application to remove the organic pollutants is little used industrially) may occur because of the simultaneous oxidation-reduction process taking place at the electrodes without adding chemicals.

Amadelli *et al* [96] showed the feasibility of bisphenol-A (BPA) degradation by means of electrochemical oxidation in aqueous solutions. This process was carried out by using a platinum mesh or titanium supported lead oxide film as anodes. Synthetic effluents in concentration ranging from 20 to 200 mgdm^{-3} and NaCl 2.8% at PH>10.5 were used. The electrolysis of concentrated solution of BPA (2 mgdm^{-3}) conducted on a mesh or lead oxide anodes with a total current 100 Am^{-2}. When lead oxide film electrode was used instead of a platinum mesh, the rate of BPA disappearance, increases at the same current density. The products of the decomposition are simple short chain aliphatic acids.

Kraft *et al* [78] showed that, the electrolytic production of hypochlorite from tap water in a flow-through reactor system is investigated using stacked platinum or iridium oxide coated titanium sheet or expanded metal electrodes. An increase in the flow-through velocity leads to an increased hypochlorite production rate which falls with increasing temperature.

The electrocatalytic oxidation of 2-chlorophenol on a composite PbO_2/polypyrrole (PPy) electrode was carried out in 0.1 N H_2SO_4 solution [97]. The composite PbO_2/PPy electrode was developed by the codeposition of polypyrrole and PbO_2 microparticles on the Ti /PbO_2-SnO_2 substrate. The PbO_2 microparticles and polypyrrole in the composite electrode were observed by hydrophilic active-sites and hydrophobic inactive-sites, respectively. The results indicated that the conversion of 2-chlorophenol and the efficiency of electrooxidation were improved on the hydrophobic modified PbO_2/PPy electrode. The performance for electrooxidation of 2-chlorophenol on the composite PbO_2/PPy electrode was better than that on Pt or Ti /PbO_2-SnO_2 electrodes. The thicker the composite (PbO_2/PPy) layer, the more active–sites in the composite electrode and the more 2-chlorophenol could be oxidized.

In the case of phenol, oxidation occurs in accordance with a complex mechanism involving both transfer of oxygen atoms and direct transfer of electrons [98]. It is often assumed that the first step of oxygen transfer is the water molecule discharge at one electron leading to the formation of a hydroxyl radical (OH^*) adsorbed on an active site of the anode surface [99-103]. The second step is an electrophilic attack of the hydroxyl radical on the organic compound transported from the bulk of the solution to the electrode interface. Theoretically most organic compounds can be oxidized on classical anode materials such as Au, Pt, C, etc., if the electrode potential value is sufficient to form the hydroxyl radicals. However, on these anode materials, the oxygen transfer reactions are slow and characterized by low Faradic yields; in fact, a loss of current occurs with formation of molecular oxygen [104, 105].

Thus, to oxidize an organic compound in an aqueous solution, an anode material with a high oxygen overpotentail should be used. Among the materials which have this criteria are tin (IV) dioxide, synthetic diamond, and lead (IV) dioxide [106, 107].

Electrochemical oxidation of 2-chlorophenol was studied at Ti/PbO_2 and Ti/SnO_2 anodes [108]. The performance of the electrodes was evaluated in term of Faradic yield and fraction of toxic intermediates removed during the electrolysis. The results showed that, although similar average Faradic yields were obtained using Ti/PbO_2 or Ti/SnO_2 anodes, the latter material is preferred because of its ability to oxidize toxic compounds.

The initial stage of oxidation of aqueous solutions of p-chlorophenol (PCP) on Bi-doped PbO_2 electrodes have been studied. Form deconvolution and analysis of UV-Vis spectra of the solutions obtained during electrochemical oxidation, benzoquinone and aliphatic acids were identified as the primary oxidation intermediates; oxidation of benzoquinone was found to be the slowest step during the early stages of the electrochemical combustion process. The effect of competing adsorption of PCP and p-nitrophenol (PNP) on $Bi-PbO_2$ was also examined, and the presence of PNP in solution was found to inhibit the rate of addition of PCP during concurrent oxidation of both phenols [109].

Dimensionally stable anodes (DSA), discovered by Beer [110, 111] in the seventies, are the natural candidates. This designation denotes a class of thermally prepared oxide electrodes, where a titanium substrate is covered by metallic oxides. Coatings on titanium include TiO_2 , IrO_2 , RuO_2 and Ta_2O_5. Combinations such as $x(TiO_2)/y(RuO_2)$ and $x(IrO_2)/y(Ta_2O_5)$ are currently marketed and used as electrodes, in a flow-cell reactor for the electrooxidation of phenol [111] and also for the chlor-alkali industry. On the other hand, some DSA type oxide electrodes may receive additions of SnO_2 and Sb_2O_5 in concentrations ranging from minor to main components.

1.12 Degradation of picric acid by electrochemical oxidation and other methods.

Picric acid (2, 4, 6-trinitrophenol) is one of the toxic nitroaromatic compounds present in over 1000 munition sites in the United States, and this constitutes a major environmental and human health hazard. In a laboratory study, 250 mg/l of picric acid was degraded in an aqueous medium with Fenton's reagent [acidified ferrous (Fe^{2+}) solution and hydrogen peroxide (H_2O_2)]. Approximately 90% of the picric acid was mineralized within 60 min of reaction. Analyses revealed that the picric acid ring structure was destroyed after treatment with Fenton's reagent and the reaction byproducts include nitrates, CO_2, NH_4^+ and carboxylic acids.[112]

Picric acid (2,4,6 tri-nitro-phenol) was taken as the model pollutant under investigation since it is one of the most oxidation persistent organic pollutants.[113,114]

Picric acid (2, 4, 6, tri-nitro-phenol), which is a hardly-oxidized aromatic compound, was studied as a water pollutant. Different supported catalysts were tested in the presence of hydrogen peroxide as a method for elimination of the organic pollutant from waste water. Among some transition metal ions, Cobalt (II) nitrate immobilized in silica gel was selected for detailed study. The effect of pH, initial concentration of hydrogen peroxide, amount of catalyst, and temperature were studied to find the optimum conditions for the wet oxidation of this organic pollutant. Experimental kinetic study was conducted using visible spectrophotometric techniques and chemical oxygen demand (COD). Supported catalysts demonstrated experimentally some reusability. The present data show that the rate of oxidation is a first order with respect topollutant concentration, hydrogen peroxide concentration and the amount of catalyst used. The dependence of the reaction rate on the nature of the immobilized transition metal, temperature, and pH of reaction media has also been discussed.[115]

Photoelectrocatalytic degradation of picric acid was experimentally investigated using a two electrode system. The decomposition of substrate was observed to be affected by photo-catalytic characteristics. Kinetics of reaction were found to be affected by parameters like concentration of substrate, pH, amount of semiconductor, light intensity, cell voltage, radical quencher and band gap, etc.

Probable mechanism for the photoelectro catalytic degradation of picric acid is proposed. [116]

D. James *et al*[117] studied the electrolysis of nitrotoluene congeners, which are persistent pollutants that enter the environment as a consequence of their manufacture and use as explosives. Reduction to aminotoluenes occurred with high current efficiency at a variety of cathodes, at potentials −0.5 to −1 V vs SCE. The products were formed in high chemical yield and with excellent mass balance. Preliminary experiments were also carried out to find methods of removing the electrolysis products from solution by oxidative oligomerization. The most satisfactory method was partial reoxidation at a Ti/IrO$_2$ anode, suggesting an overall remediation technology in which reduction is followed by reoxidation of the spent catholyte in the anode compartment of the same electrolytic cell.

Theelectrochemical oxidation of 2,4,6-trinitrophenol (TNP) has been studied on boron-dopeddiamond electrodes. Galvanostatic electrolyses causecomplex oxidation reactions that lead to incineration of TNP. Phenol,benzoquinone, maleic, and oxalic acid have been detected as solubleproducts during the electrolysis of TNP. These results suggest thatthe electro-oxidation of TNP begin by the release of nitrogroups from the aromatic ring to form non-nitrogenated phenolic compounds.These compounds are transformed into carboxylic acids which end tobe oxidized to CO$_2$. The complete removal of organic compoundscontained in the waste has been obtained in sulfuric medium.[118]

A series of catalytic degradation of nitro aromatic explosives, namely picric acid (PA) and ammonium picrate (AP) have been investigated by M. J. Liou [119] using the FeOOH/H$_2$O$_2$ process. The controlling factors, such as adsorption of goethite dosage, hydrogen peroxide concentration and UV-light exposure on the oxidation of nitro aromatic explosives were investigated. The results showed that target compounds were adsorbed on the surface of goethite while the oxidation was proceeding.

CHAPTER "TWO"

EXPERIMENTAL PART

2. Experiment

2.1. Electrodeposition of doped lead dioxide at different substrates

2.1.1. Preparation ofPb/PbO$_2$modified Electrode

1) Lead surface treatment

Pretreatments of the lead substrate were carried out before anodization to ensure good adhesion lead dioxide film. Lead was first roughened to increase the adhesion of PbO$_2$ deposit via subjecting its surface to mechanical abrasion by sand papers of different grades, down to 40/0. Then, it was cleaned by acetone to remove sand particles or any other particles lodged in the metal surface. This process has a great application and good penetrating power. Then it was treated with an alkali solution [a mixture of sodium hydroxide (50g/L) and sodium carbonate (20g/L)], Tri-sodium orthophosphate (20g/L) and sulphuric acid (2g/L). Uniform and well adhesive deposit necessitates a smooth surface with no oxide or scales. To confirm our preparation , the lead substrate was soaked for 2 min. in a pickling solution consisting of nitric acid (400g/L) and hydrofluoric acid (5g/L) and then chemically polished in boiled oxalic acid solution (100g/L) for 5 min. [120].

2) Electrochemical deposition of PbO$_2$

PbO$_2$ was deposited galvanostatically on the pretreated lead substrate by electrochemical anodization of lead in oxalic acid solution (100g/L). This acid solution was electrolyzed galvanostatically for 30 min. at ambient temperature using an anodic current density of 100 mAcm^{-2}. The cathode was stainless steel (austenitic type), the two electrodes were concentric with the lead electrode was axial. This arrangement gave the formation of a regular and uniform deposit [120].

2.1.2. Preparation of modified C/PbO$_2$Electrode

1) Carbon surface treatment

Pretreatment of Carbon rod (8mm × 25cm) was carried out following the procedure applied by Narasimham and Udupa [121]. The carbon rod was soaked in 5% NaOH solution, washed with distilled water, dried in furnace at 105°C, cooked

with linseed oil to reduce the porosity of rod. The electrode after the previous treatment is ready to receive doped PbO_2 .

2) Electrochemical deposition of PbO_2

The electrodeposition of PbO_2 was performed at constant anodic current of 20 $mAcm^{-2}$ from 12% w/v $Pb(NO_3)_2$ solution. Containing 5% w/v $CuSO_4.5H_2O$ and 3% surfactant. The role of the surfactant is minimizing the surface tension of the solution. Electrodeposition was carried out for 60 min. at 80^oC with continuous stirring [121].

2.2. Chemicals

All chemicals and reagents used in this study were used as received without further purification. Sodium chloride, sodium fluoride, sodium carbonate, sodium phosphate, sodium sulphate, calcium chloride, potassium chloride, sodium hydroxide , sulphuric acid, potassium iodied, sodium thiosulphate and picric acid were of analytical grade and purchased from Merck. Other reagents were of the analytical grade. Distilled water , sea water 0.5 M of sodium chloride [57] (in Gaza city) and brine water 0.3 M of sodium chlorides (Disalination plant in Khanyonis – Gaza strep) were used in this work.

2.3. Electrolysis

2.3.1 Electrolysis for generation of sodium hypochlorite

The experiment were carried out in an electrolysis pyrex glass cell with volume of 100 ml with the prepared (C/PbO_2 and Pb/PbO_2) electrode as anodes and titanium as cathode .

The operating condition were ranging under the following condition: 0.5-2.5A current density, 1-13 pH value with potential ranging from 2-12 volts, $5-40^0C$ of temperature, 5-60 g/L of NaCl solution and 20%-100%(v/v) sea and brine water solution. The time of electrolysis was ranging from 5-800 min. The distances between the two electrode (anode & cathode)varying from 1-4cm and the area of cathode different from 1-6cm.^{2} The investigation of this study were carried in the presences of15 g/L sodium chloride and 5 g/L of different type of electrolyte (NaCl, $CaCl_2$, KCl, Na_2CO_3, NaF, Na_3PO_4, and Na_2SO_4)

2.3.2 Electrolysis for degradation of picric acid

Galvanostatic electrolyses were carried out at Pb/PbO_2 and C/PbO_2 electrodes, with current density ranging from 0 to 60 $mAcm^{-2}$ with potential ranging from 1-10 volts. Runs were performed at 5-40°C. Solutions of 50 mg/ L of pure picric acid were used. Electrolysis done with 4 g/L of different types of electrolytes NaCl, $CaCl_2$, KCl, Na_2CO_3, NaF, Na_3PO_4, and Na_2SO_4, at sodium chloride concentration from 1-12 g/L with pH around 1.3-11. The electrolysis oftime ranges from 0-60 min.

The electrolysis of the aqueous solution containing the picric acid to be treated electrochemically was carried out in one compartment Pyrex glass cell of 50 ml volume with the prepared Pb/PbO_2 and C/PbO_2 as anode and austenitic stainless steel as cathode.

DC power supply (model GP4303D, LG Precision CO. Ltd, Korea) was used for the Electrolysis for generation of sodium hypochlorite and Electrolysis for degradation of picric acid. The current and potential measurementswere carried out using digital multimeter (kyoritsu model 1008, Japan).

2.4. Analysis

The hypochlorite content was determined by two methods, the first one was by reacting liquid bleach with iodide and treating the iodine produced with a measured excess of thiosulfate solution previously standardized coulometrically [122]. The second method was bymeasuring with spectrophotometer from Shimadzu double-beam UV-visible λ_{max} = 292 nm using calibration curve with standard error ± 0.1%.

Two main parameters were measured to evaluate the electrochemical treatment efficiency, remaining pollutant concentration and COD (chemical oxygen demand). Remaining pollutants (picric acid) concentration was measured with the spectrophotometer at λ_{max} =355nm using calibration curve with standard error ± 0.2%. While the COD was determined using a closed reflux titrimetric method [115].

2.5 Data treatment

1- The percent yield of the hypochlorite is calculated as:

percent yield $=$ <u>Experimental yiled of hypochlorite</u> $\times 100$

Theoretical yield of hypochlorite

2- The cost of hypochlorite generation and degradation of picric acid as:

Cost = Electrical energy consumption $\times$ price in Dollars

Electrical energy consumption = I t v/ 1000$\times$3600

Price in Dollar = 0.12$

CHAPTER "THREE"

RESULTS

Results

3.1 Effect of operating condition on the sodium hypochlorite generation from Sodium chloride solution using Pb/PbO$_2$ and C/PbO$_2$ electrodes

3.1.1 Effect of conductive electrolyte type

The effect of conductive electrolyte type was performed on the hypochlrite generation by using (NaCl, CaCl$_2$, KCl, Na$_2$CO$_3$, NaF, Na$_3$PO$_4$, and Na$_2$SO$_4$) on both Pb/PbO$_2$ and C/PbO$_2$electrodes. The operation conditions of the treatment process were : current density of 1Acm^{-2} , temperature of 10^{0}C, the time of electrolysis was 90 and 60 min for Pb/PbO$_2$ and C/PbO$_2$ electrodes respectively, pH of 12, and the distance between the two electrodes of 1cm.As shown in Figs. (1 and 2) it is clear that sodium chloride is the most effective conductive electrolyte for the generation of sodium hypochlorite. For this reason sodium chloride was chosen as conductive electrolyte in the following series of experiments.

3.1.2 Effect of current density

In electrochemical reactions, production of sodium hypochlorite is based on quantity of current passed, as per Faraday's first law of electrolysis. In industry, current passed is usually reported in terms of current density which denotes the current passed per unit electrode area. As current density increases, hypochlorite production also increases. However, the cell temperature also increases with increase in current density. Figs. (3 and 4) show that the concentration of NaClO increases up to 1A.cm^{-2} by using Pb/PbO$_2$ and C/PbO$_2$ electrodes, while at higher current densities the concentration decreases due to increase in temperature. In other words, rate of decomposition of hypochlorite increases with increase in current density. Optimum current density is 1 Acm^{-2}, at which the maximum concentration of hypochlorite is obtained. The treatment processes were carried out at pH of 12, temperature of 10^{0}C and NaCl concentration 20g/L for the time of electrolysis was 90 and 60 min for Pb/PbO$_2$ and C/PbO$_2$ electrodes respectively. Different current densities were applied to investigate the optimum current density for generation of sodium hypochlorite at a fixed distance of 1 cm between the two electrodes.

3.1.3 Effect of temperature

Temperature plays a vital role in the electrogeneration of hypochlorite using Pb/PbO_2 and C/PbO_2 electrodes. Figs. (5 and 6). Illustrate that byincrease of temperature up to 10^oC decreases the NaClO concentration as well as current efficiency of the reaction. Low temperature favors the higher NaClO generation. Higher temperature leads to chemical decomposition of the hypochlorite formed as mentioned already. The electrolyser has to be maintained at the ambient temperature (10^oC) at which maximum NaClO concentration of about 2 % has been obtained for Pb/PbO_2 and C/PbO_2 electrodes respectively. These experiments were carried out under the following condition: current density of $1Acm^{-2}$, pH of 12, the concentration of NaCl 20g/L and the time of electrolysis was 90 and 60 min for Pb/PbO_2 and C/PbO_2 electrodes respectively and a distance of 1 cm between the two electrodes.

3.1.4 Effect of the electrolysis time.

Figs. (7 and 8) represent the effect of time on hypochlorite generation by using both Pb/PbO_2 and C/PbO_2 electrodes. Experiments were carried out at different time electrolysis ranging from 10 min to 300 min with a fixed distance of 1cm between the two electrodes under the following conditions : current density of $1Acm^2$, pH of 12 and NaCl concentration of 20g/L. A general trend was observed, an increasing of time leads to increase in hypochlorite generation up to 90 and 60 min for Pb/PbO_2 and C/PbO_2 electrodes respectively. Further increase in time did not show any effect .

3.1.5 Effect of NaCl concentration

Figs. (9 and 10) represent the effect of variable NaCl concentration on the sodium hypochlorite generation. The results indicate that an increase of sodium chloride concentration leads to increase in hypochlorite production up to 20 g/L. A further increaseof sodium chloride concentration has no effect on the hypochlorite generation. For this reason 20 g/L of NaCl was considered as optimum concentration. These processes were carried out at pH of 12, temperature of 10^0C, current density $1Acm^{-2}$ and a distance of 1 cm between cell electrodes. The time of electrolysis was 90 and 60 min for Pb/PbO_2 and C/PbO_2 electrodes respectively**.

3.1.6 Effect of pH

The pH has an important effect on sodium hypochlorite generation. As clearly shown in Figs. (11 and 12) the increase of pH leads to increase in hypochlorite production up to pH 12. Therefore, pH 12 was taken as optimum for sodium hypochlorite generation using Pb/PbO_2 and C/PbO_2 electrodes. The electrolysis was carried out under the following conditions: initial concentration of NaCl 20g/L, temperature of 10^0C, current density of $1Acm^{-2}$ and a distance of 1 cm between the two electrode for the time of electrolysiswas 90 and 60 min for Pb/PbO_2 and C/PbO_2 electrodes respectively.

3.1.7 Effect of distance between the cathode and anode

The effect of distance between the two electrodes of the cell was studied. It was found from Figs. (13 and 14) that there was an increase of hypochlorite generation by decreasing the distance between the two electrodes up to 1cm for both Pb/PbO_2 and C/PbO_2 electrodes.Therefore 1 cm was chosen as optimum distance between electrodes for sodium hypochlorite generation.The experiments were carried out under the following conditions: current density $1Acm^{-2}$, pH of 12, temperature of 10^0C and the concentration of NaCl 20g/L. The time of electrolysis was 90 and 60 min for Pb/PbO_2 and C/PbO_2 electrodes respectively.

3.2.Effect of operating conditions of hypochlorite generation from sea water using Pb/PbO_2 and C/PbO_2 electrodes

3.2.1 Effect of the current density

Figs. (15 and 16) show that the concentration of NaClO increases with increasing the current density up to $1A.cm^{-2}$ by using Pb/PbO_2 and C/PbO_2 electrodes. Further increasing of current density had brought no effect. The operating conditions of these experiments were as following: temperature of 10^oC, pH of 10.3, the time of electrolysis was 600 and 240 min for Pb/PbO_2 and C/PbO_2 electrodes respectively, the distance between the cell electrodes of 1 cm and the initial concentration of 100 % (v/v).

3.2.2 Effect of temperature

Figs. (17 and 18) illustrates the effect of temperature on the hypochlorite generation from sea water using Pb/PbO_2 and C/PbO_2 electrodes. The conditions of the experiments were as follows: current density of $1Acm^{-2}$, pH of 10.3, the time of electrolysis was 600 and 240 min for Pb/PbO_2 and C/PbO_2 electrodes respectively,the distance between the cell electrodes of 1 cm and the initial concentration of 100 % (v/v). It is clear that the change of temperature from 10 to 40^oC lead to decrease in rate of sodium hypochlorite generation. For this reason 10^oC was taken as the optimum temperature. A further decrease in temperature down to 10^oC did not bring any effect**.**

3.2.3 Effect of the time electrolysis

The effect of time electrolysis on the hypochlorite generation from sea water using Pb/PbO_2 and C/PbO_2 electrodes was investigated. Figs. (19 and 20) show that the sodium hypochlorite generation increases with time increasing up to 600 and 240 min for for Pb/PbO_2 and C/PbO_2 electrodes respectively. Further increasing of the time for both electrodes has no effect. Therefore, 600 and 240 min were considered as the optimum time. The experiment were carried out under the following conditions: temperature of 10^oC, pH of 10.3, current density of $1Acm^{-2}$, the distance between the cell electrodes of 1 cm and the initial concentration of 100 % (v/v).

3.2.4 Effect of initial concentration

Figs. (21 and 22) display the effect of different initial concentration on the hypochlorite generation from sea water. The treatments were carried out under the following conditions: temperature of 10^oC, pH of 10.3, current density of $1Acm^{-2}$, distance between the cell electrodes of 1 cm, the times of electrolysis was 600 and 240 min for Pb/PbO_2 and C/PbO_2 electrodes respectively and the initial concentration of 100 % (v/v). It is pervious that the rate of hypochlorite generation increases by increasing the initial concentration load of sea water by using both Pb/PbO_2 and C/PbO_2 electrodes .

3.2.5 Effect of pH

Figs. (23 and 24) display the effect of pH variation value on the hypochlorite generation from sea water by using both Pb/PbO_2 and C/PbO_2 electrodes. The operating conditions were: current density of $1Acm^{-2}$, temperature of 10^oC, the time of electrolysis of 600 and 240 min for Pb/PbO_2 and C/PbO_2 electrodes respectively, distance between the cell electrodes of 1 cm and the initial concentration of 100 % (v/v). It is clear from these results that the efficiency of hypochlorite generation increases gradually with increasing pH value uo to 10.3 and then fall down. Therefore the optimum maximum values of the hypochlorite generation were obtained at pH 10.3.

3.2.6 Effect of distance between the cathode and anode

Figs. (25 and 26) illustrate the effect of distance between the cathode and anode on the hypochlorite generation from sea water. The experiments were carried out under the following conditions: temperature of 10^oC, pH of 10.3, current density of $1Acm^{-2}$, the time of electrolysis was 600 and 240 min for Pb/PbO_2 and C/PbO_2 electrodes respectively and the initial concentration of 100% (v/v). It is clearly that there is a decrease of hypochlorite generation by increasing distance up to 1 cm by using both Pb/PbO_2 and C/PbO_2 electrodes respectively. Therefore 1 cm was taken as the optimum distances between the two electrodes.

3.3 Effect of operating condition of hypochlorite generation from brine water usingPb/PbO_2 and C/PbO_2 electrodes

3.3.1 Effect of current density

The effect of current density on the hypochlorite generation from brine water using Pb/PbO_2 and C/PbO_2 electrodes was investigated. Figs. (27 and 28) show that the rate of hypochlorite generation increases by increasing current density up to $1Acm^{-2}$. Further increase of current density did not bring any effect. The experiments conditions were: temperature of 10^oC, pH of 10.73, distance between the two electrodes of 1 cm, the time of electrolysis was 300 and 120 min for Pb/PbO_2 and C/PbO_2 electrodes respectively and the initial concentration of 100 % (v/v).

3.3.2 Effect of temperature

Fig 29 show that the hypochlorite generation efficiency remain constant at 1.37% by increasing temperature up to $30^{\circ}C$ for Pb/PbO_2 electrode by increasing temperature higher than $10^{\circ}C$ the hypochlorite production decreases and up to $20^{\circ}C$ remain constant by 0.8%

3.3.3 Effect of the time electrolysis

Figs. (31 and 32) represent the effect of time electrolysis on the hypochlorite generation from brine water using Pb/PbO_2 and C/PbO_2 electrodes. The treatment conditions were: pH of 10.73, current density of 1 Acm^{-2}, temperature of $10^{\circ}C$, distance between the two electrodes of 1 cm and the initial concentration of 100 % (v/v). From the obtained results, it is found that the highest efficiency of hypochlorite production was reached with increasing the time up to 300 and 120 min for Pb/PbO_2 and C/PbO_2 electrodes respectively. For this reason 300 and 120 min was take as the optimum time for Pb/PbO_2 and C/PbO_2 electrodes respectively.

3.3.4 Effect of initial concentration

Figs. (33 and 34) show that the effect of initial concentration on the hypochlorite generation from brine water using Pb/PbO_2 and C/PbO_2 electrodes was investigated. The hypochlorite generation increases by increasing the initial concentration of brine water up to 100 % (v/v). As a result of that 100%(v/v) was taken as the optimum concentrations. The experiments were carried out under the following conditions: pH of 10.73, current density of 1 Acm^{-2}, temperature of $10^{\circ}C$, distance between the two electrodes of 1 cm, and the time of electrolysis was 300 and 120 min for Pb/PbO_2 and C/PbO_2 electrodes respectively.

3.3.5 Effect of pH value

Figs. (35 and 36) display the effect of variation of pH on the hypochlorite generation from brine water using Pb/PbO_2 and C/PbO_2 electrodes. The results indicate that the pH value of 10.73 can be taken as the optimum pH value. The treatment conditions were: temperature of $10^{o}C$, current density of 1 Acm^{-2}, distance between the two electrodes of 1 cm, the time of electrolysis was 300 and 120 min for Pb/PbO_2 and C/PbO_2 electrodes respectively and the initial concentration of 100 % (v/v).

3.3.6 Effect of distance between the cathode and anode

Figs. (37 and 38) represent the distance between the two electrodes on the hypochlorite generation from brine water using Pb/PbO_2 and C/PbO_2 electrodes. It is previous that the efficiency of hypochlorite generation increased by reducing the distance between the cell electrodes up to 1 cm. For this reason 1 cm was taken as the optimum distance. The experiments were carried out under the following conditions: pH of 10.73, current density of 1 Acm^{-2}, temperature of $10^{o}C$, the time of electrolysis was 300 and 120 min for Pb/PbO_2 and C/PbO_2 electrodes respectively and the initial concentration of 100 ml(%v/v).

3.4 Effect of different conditions for degradation of picric acid and COD removal using Pb/PbO_2 and C/PbO_2 electrodes

3.4.1 Effect of conductive electrolyte type

The effect of the type of conductive electrolyte was performed by using a concentration of 4g/L of the following salts: $NaCl$, $CaCl_2$, KCl, Na_2CO_3, NaF, Na_3PO_4, and Na_2SO_4 by using Pb/PbO_2 and C/PbO_2 electrodes to study the degradation of picric acid and COD removal . As shown in Figs. (39 - 42), it appears that the NaCl was the most effective conductive electrolyte. NaCl best for C/PbO_2 but for Pb/PbO_2 NaCl and $CaCl_2$ are also good.

As clearly seen in Figs. (39 - 42), the electrocatalytic rate of degradation of the investigated picric acid and COD removal was poor in the (Na_2SO_4, Na_3PO_4) electrolyte. The operating conditions of the treatment process were: current density of 20 $mAcm^{-2}$, pH of 2.6, temperature of $10^{o}C$, initial concentration 50 mg/L, and the distance between the two electrode was 1cm. The reaction were allowed to proceed for 30 and 20 min using Pb/PbO_2 and C/PbO_2 electrodes respectively.

3.4.2 Effect of current density

As shown in Figs. (43-46) both picric acid degradation and COD removal increase with increasing the applied current density up to 20 mAcm^{-2}using Pb/PbO$_2$ and C/PbO$_2$ electrodes. Furtherincrease of thecurrent density was followed by gradual decrease in acid degradation and COD removal. The treatment processes were carried out for 30 and 20 min using Pb/PbO$_2$ and C/PbO$_2$ electrodes respectively under the following condition : pH 2.6, temperature of 10^{0}C, initial concentration of 50 mg/L and NaCl concentration 4g/L. The distance between the two electrodes was adjusted of 1cm.

3.4.3 Effect of temperature

The experiments were used to test the effect of temperature on picric acid degradation and COD removal efficiency. As indicated from the results, at low temperature, below 10^0 C, the picric acid degradation and COD removal were high by using both Pb/PbO$_2$ and C/PbO$_2$ electrodes. This is displayed in Figs. (47-50)which presents correlation between the concentration of the remaining picric acid and COD residual as a function of the solution temperature. The rate of the picric acid degradation and COD removal decreasesignificantly with increasing the solution temperature. And further decrease inthe temperature below 10^{0}C did not bring any effect. Similar conditions were applied asin the previous experiments (3.4.2).

3.4.4 Effect of time electrolysis

As shown in Figs. (51 and 53), the maximum removal of picric acid were achieved using Pb/PbO$_2$ and C/PbO$_2$ electrodes by reaction that proceeds for at least 30 and 20 min respectively. Therefore, the electrolysis of 20 and 30 min for both Pb/PbO$_2$ and C/PbO$_2$ electrodes respectively were taken as optimum for the removal of picric acid and COD respectively .

It is clearly shown from Figs. (52 and 54) that the optimum time for COD removal for both Pb/PbO$_2$ and C/PbO$_2$ were 5 and 4 hr respectively. To assess the effect of electrolysis time, experiments were conducted with operating treatment conditions that were consistent with those described for both Pb/PbO$_2$ and C/PbO$_2$ electrodes : current density of 20mAcm^{-2}, pH 2.6, temperature of 10^{0}C, NaCl 4g/L,

initial concentration of 50 mg/L and the distance between the two electrode was 1cm. The electrolysis time ranges from 0-40 min

3.4.5 Effect of picric acid concentration

The effect of picric acid concentration on the rate of acid degradation and COD removal using Pb/PbO_2 and C/PbO_2 electrodes was investigated. This investigation was carried out under the optimum operating conditions mentioned above (3.4.4). Figs. (55-58) show the effect of different initial picric acid concentrations (10–100 mg/L) on the rate of picric acid degradation and corresponding COD removal. Total removal of the picric acid and COD can be achieved in the presence of initial picric acid load up to 50 mg/L. However, increasing the picric acid concentration above this level resulted in a decrease in the electrocatalytic rate of degradation. The removal efficiency of the picric acid by using Pb/PbO_2 electrode at 100, 75 and 50 mg/L initial concentrations were 94.4, 97.4 and 99.65% respectively. The results of this investigation indicated that 50 mg/L was the optimum concentration for the initial load concentration of picric acid. Theses experiments were carried out under the following operating conditions: current density of $20mAcm^{-2}$, pH 2.6, temperature 10^0C, NaCl 4g/L, the distance between the two electrodes of 1cm . The time of electrolysis was 30 and 20 min using Pb/PbO_2 and C/PbO_2 electrodes respectively.

3.4.6 Effect of pH

The pH of the solution was varied while the other conditions mentioned in 3.4.4 where kept constant. As shown in Figs. (59-62) maximum removal of picric acid and COD were achieved in the pH 2.6 using Pb/PbO_2 and C/PbO_2. The pH of the solution was changed by adding drops H_2SO_4 and NaOH solutions using a pH meter. The reactions were carried out for 30 and 20 min using Pb/PbO_2 and C/PbO_2 electrodes respectively under the following condition: The initial concentration of 50 mg/L, a current density of $20mAcm^{-2}$, a temperature of 10^0C and NaCl concentration of 4g/L. The distance between the two electrodes was adjusted to 1cm.

3.4.7 Effect of the distance between the cathode and anode

Different distance between the two electrodes were applied to investigate the effect of distance under the operating conditions: current density of 20 mAcm^{-2}, pH 2.6, temperature of 10^{0}C, NaCl 4g/L, time of 30 and 20 min for Pb/PbO$_2$ and C/PbO$_2$ electrodes respectively andthe initial concentration of 50mg/L. Figs. (63-66) show the effect of changing distance between the two electrodes of the cell on the degradation rate of picric acid and the corresponding COD removal. It was found that there is increase in picric acid and COD removal by decreasing the distance down to 1cm by using both Pb/PbO$_2$ and C/PbO$_2$ electrodes. Therefore the distance of 1cm was considered to be the optimum condition for removal of picric acid and COD.

3.4.8 Effect of NaCl concentration

Variation of NaCl concentration were applied to investigate the removal of picric acid under the following conditions: 20mAcm^{-2} of current density, temperature of 10^{0}C, pH 2.6, initial concentration 50 mg/L, distance between the two electrodes of 1cm and time of electrolysis 30 and 20 min using Pb/PbO$_2$ and C/PbO$_2$ electrodes respectively.Figs. (67-70) represents the effect of different NaCl concentrations on the degradation rate of picric acid and the corresponding COD elimination. A general trend was observed: an increase of the picric acid degradation rate and COD removal with decreasing the electrolyte concentration up to 4 g/L using both Pb/PbO$_2$ and C/PbO$_2$ electrodes. Further decreasing the NaCl concentration leads to decreasing in the rate of picric acid degradation and COD removal.
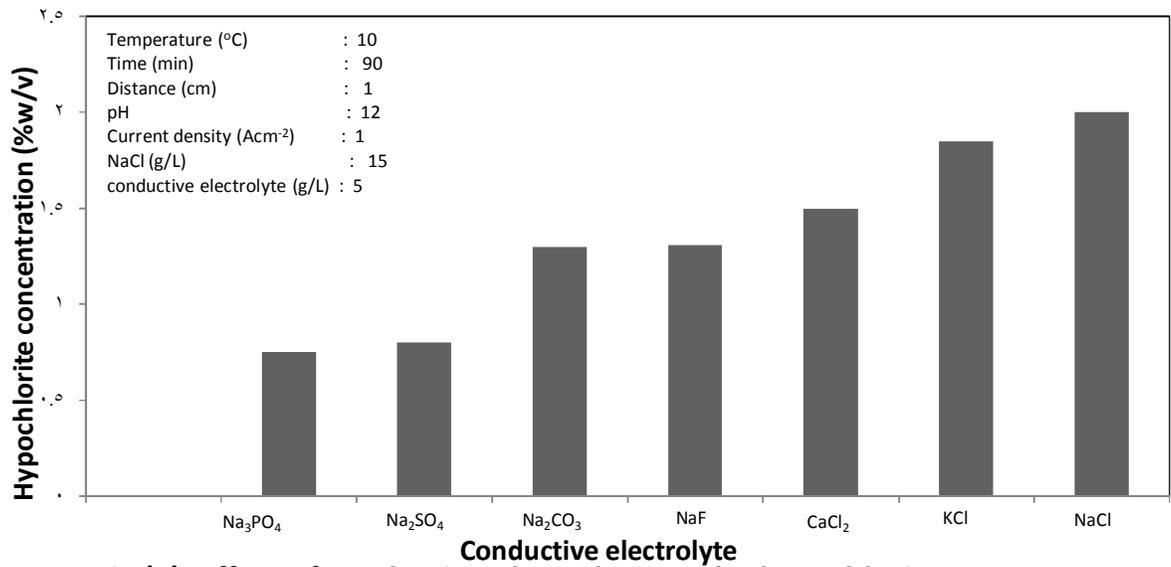
Fig (1): Effect of conductive electrolyte on the hypochlorite generation from sodium chloride solution using Pb/PbO$_2$ electrode .
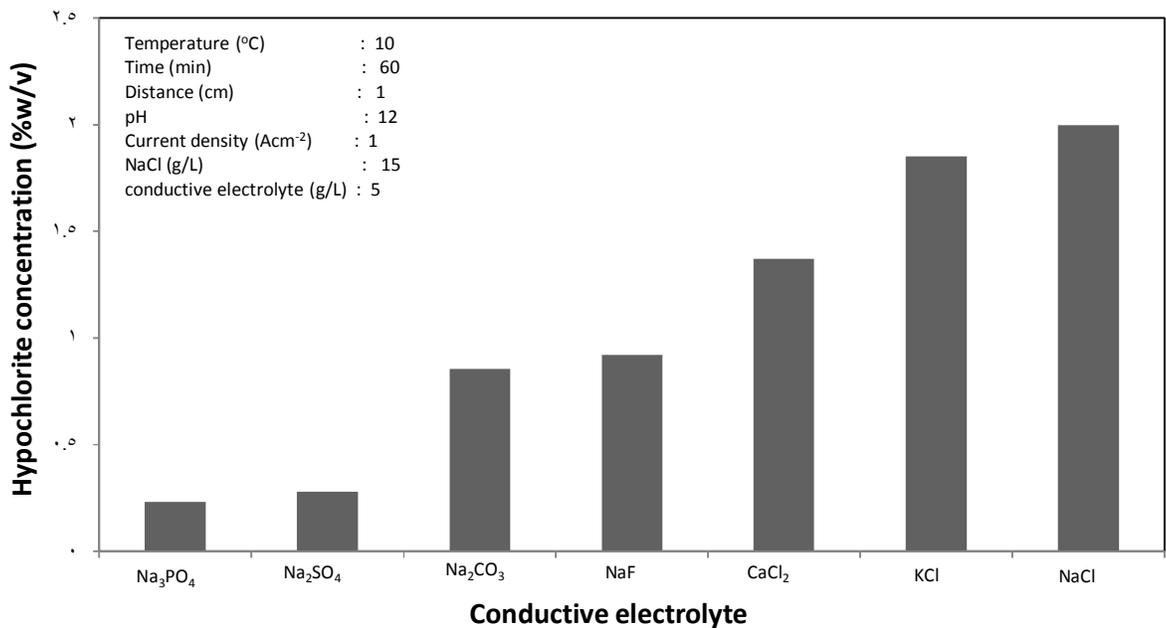

Fig (2): Effect of conductive electrolyte on the hypochlorite generation from sodium chloride solution using C/PbO$_2$ electrode .
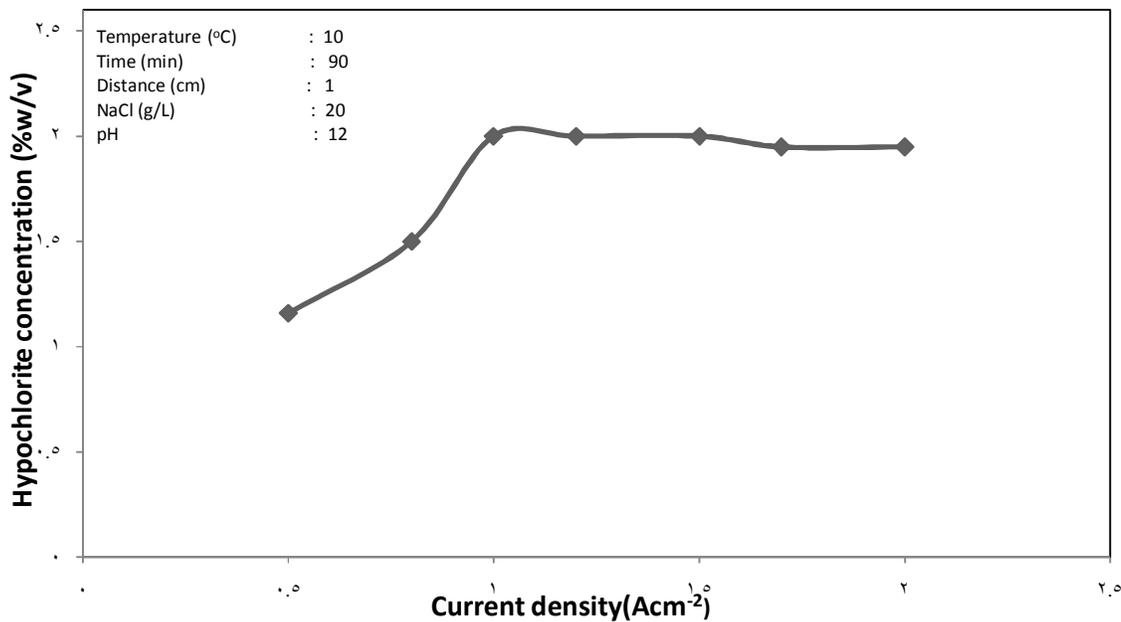
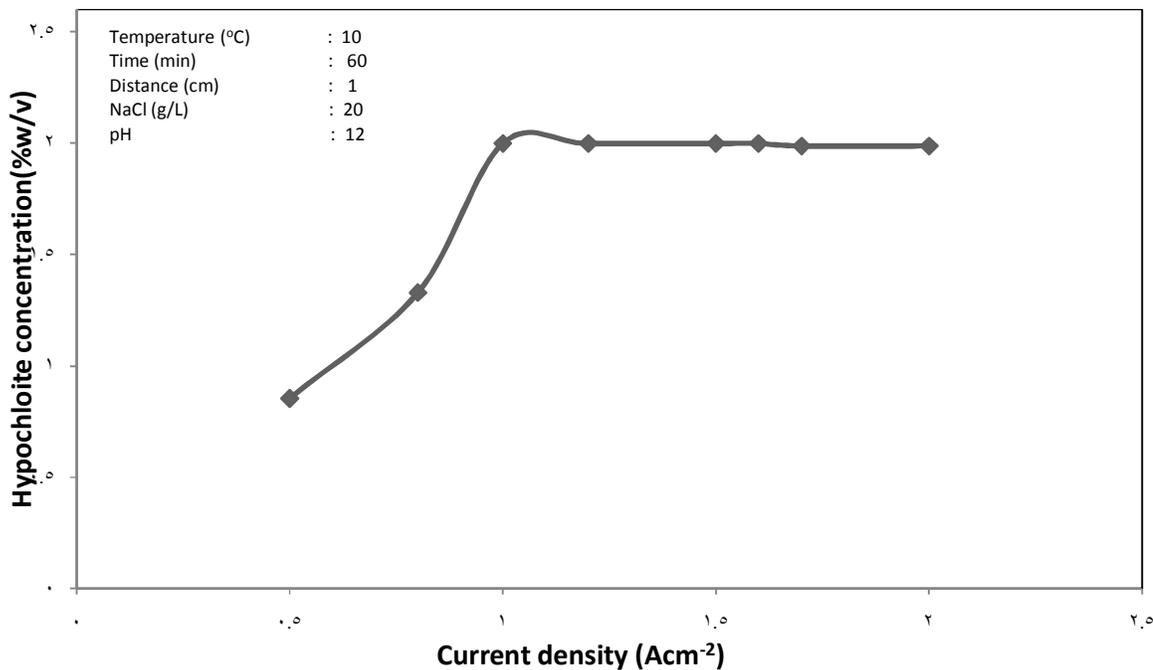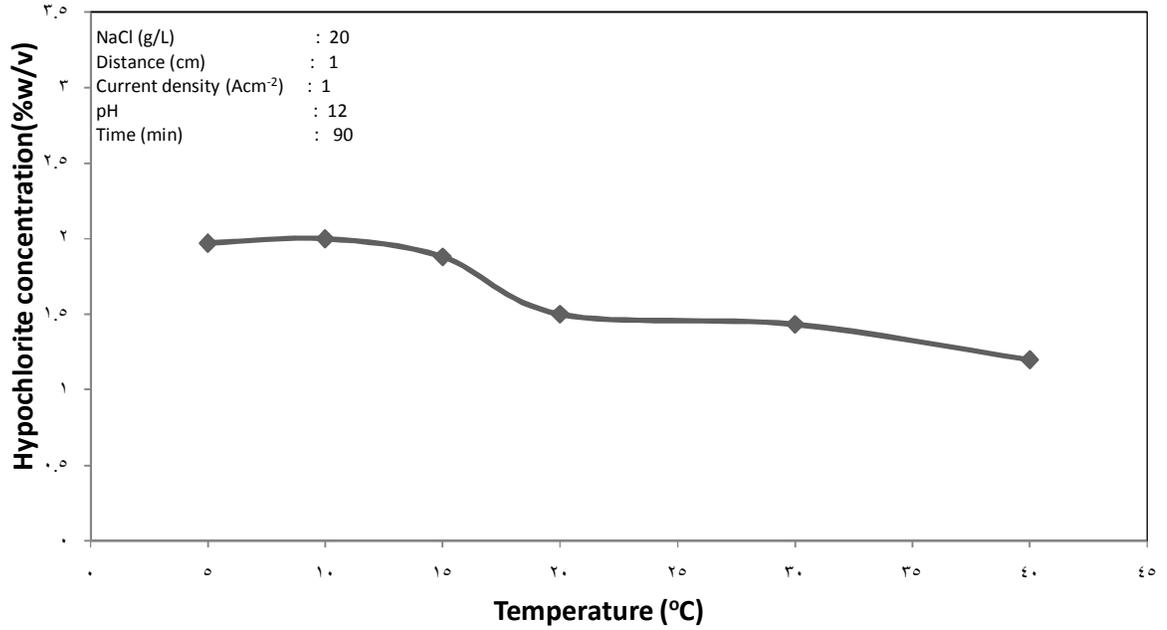**Fig (3): Effect of current density on the hypochlorite generation from sodium chloride solution using Pb/PbO$_2$ electrode**
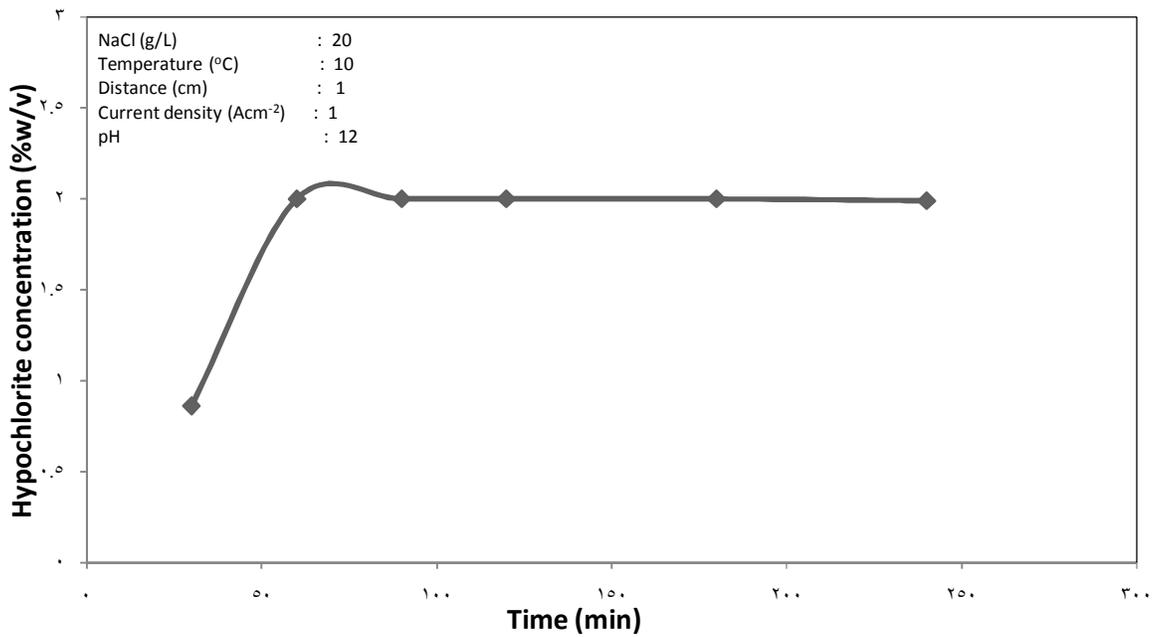

Fig (4): Effect of current density on the hypochlorite generation from sodium chloride solution using C/PbO$_2$ electrode.

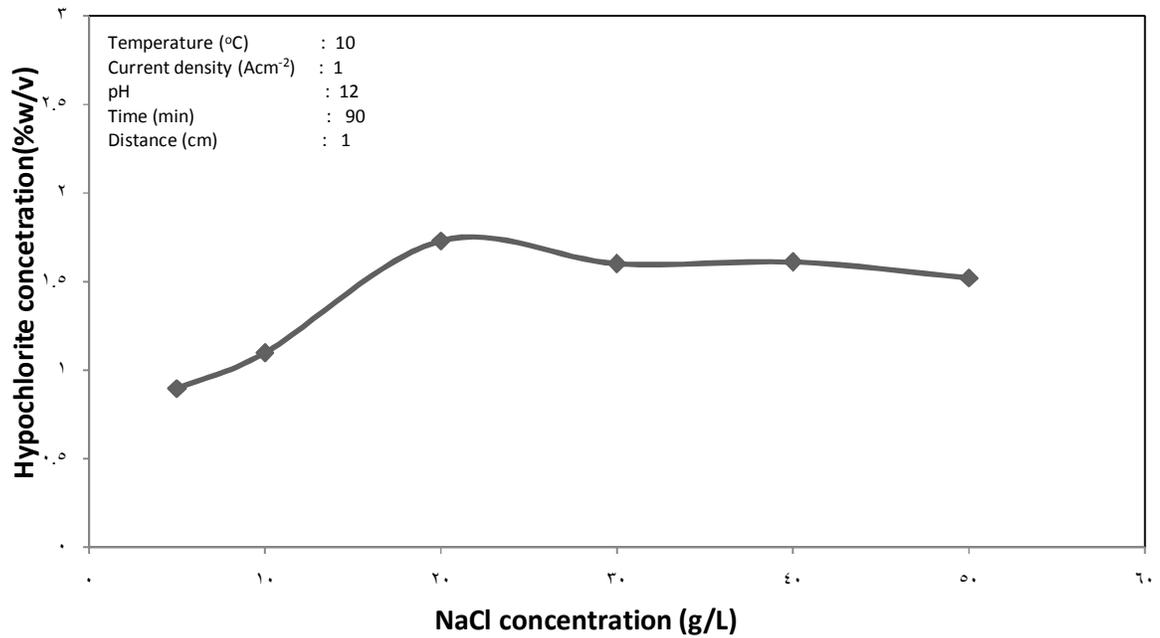**Fig (5): Effect of tempreture on the hypochlorite generation from sodium chloride solution using Pb/PbO₂ electrode .**
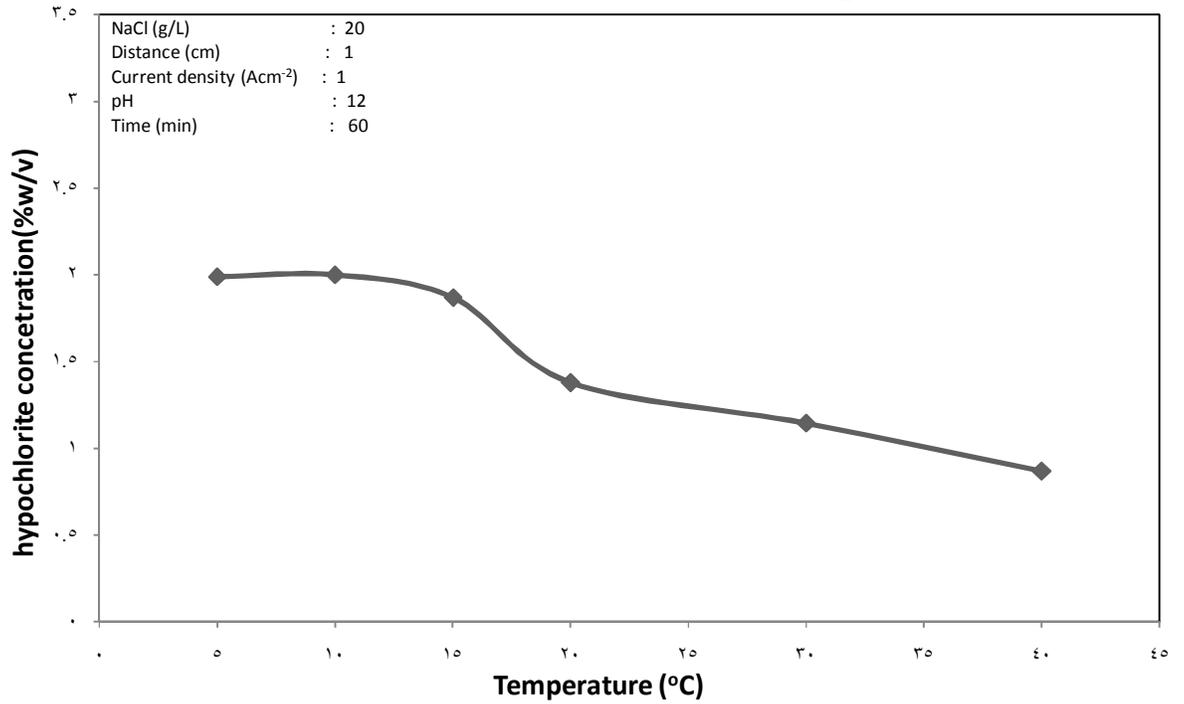
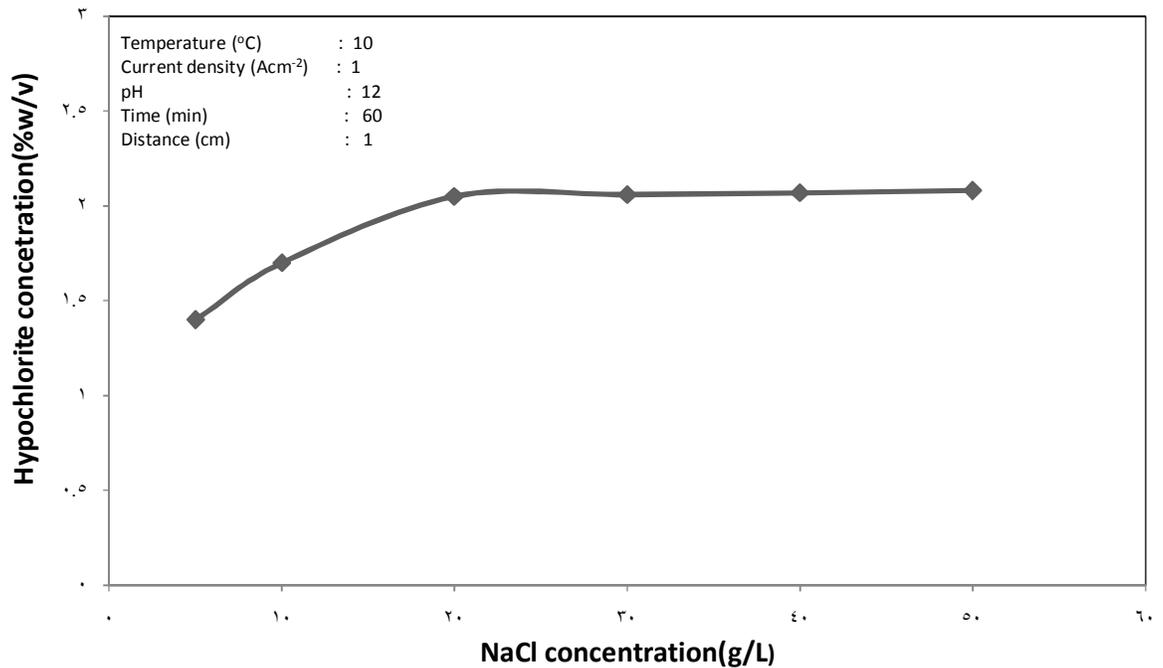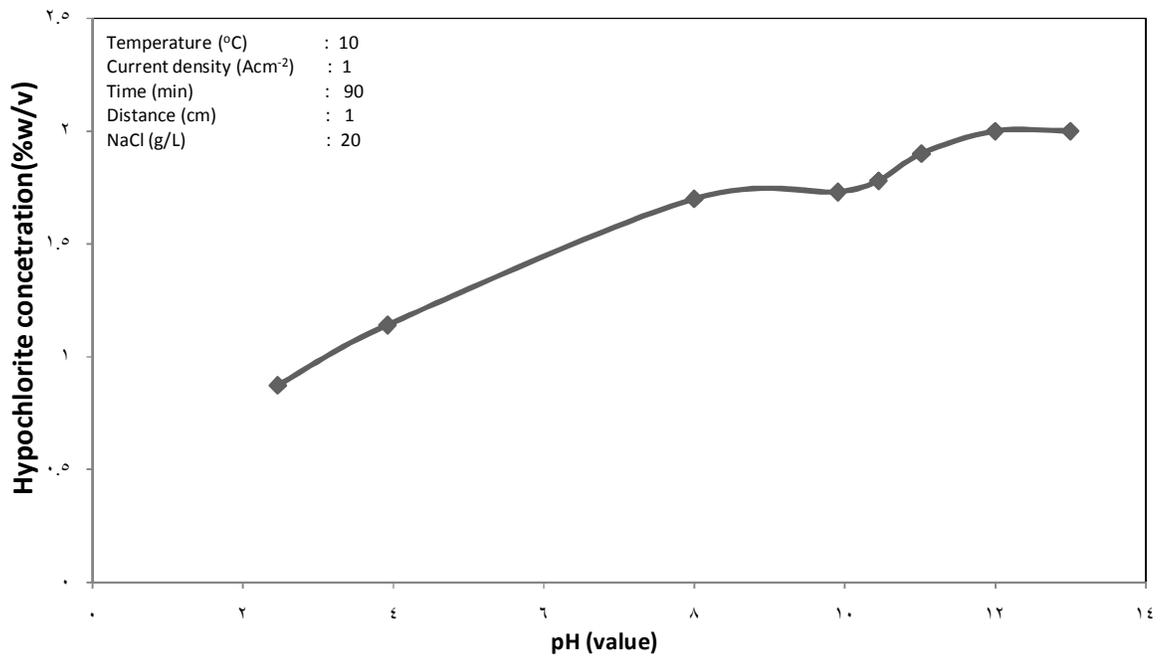**Fig (6): Effect of temperature on the hypochlorite generation from sodium chloride solution using C/PbO₂ electrode .**
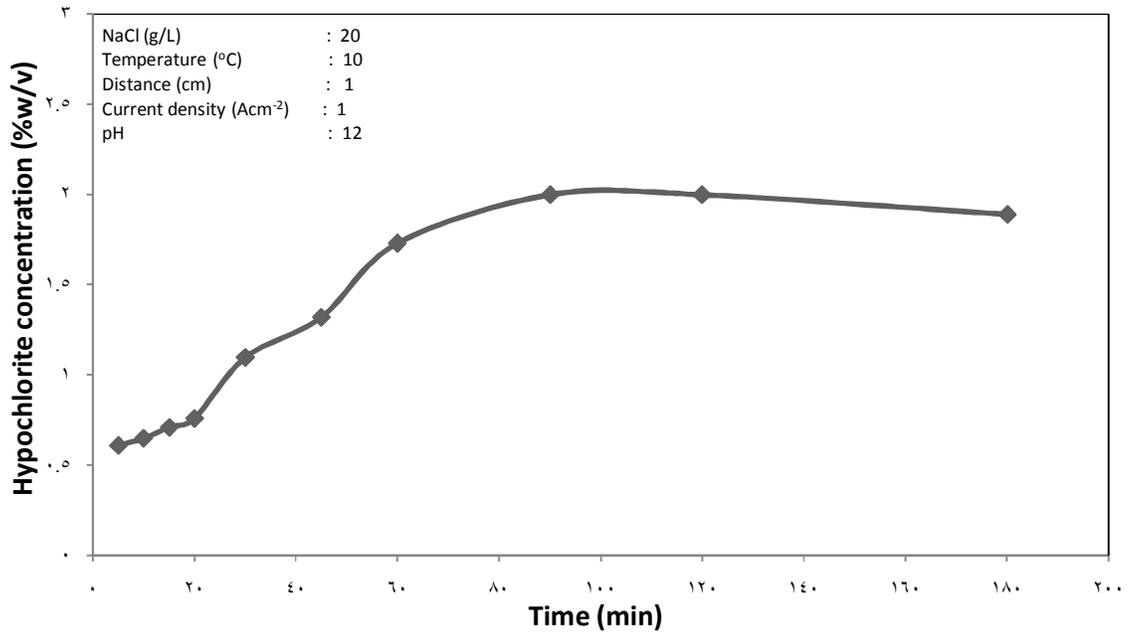
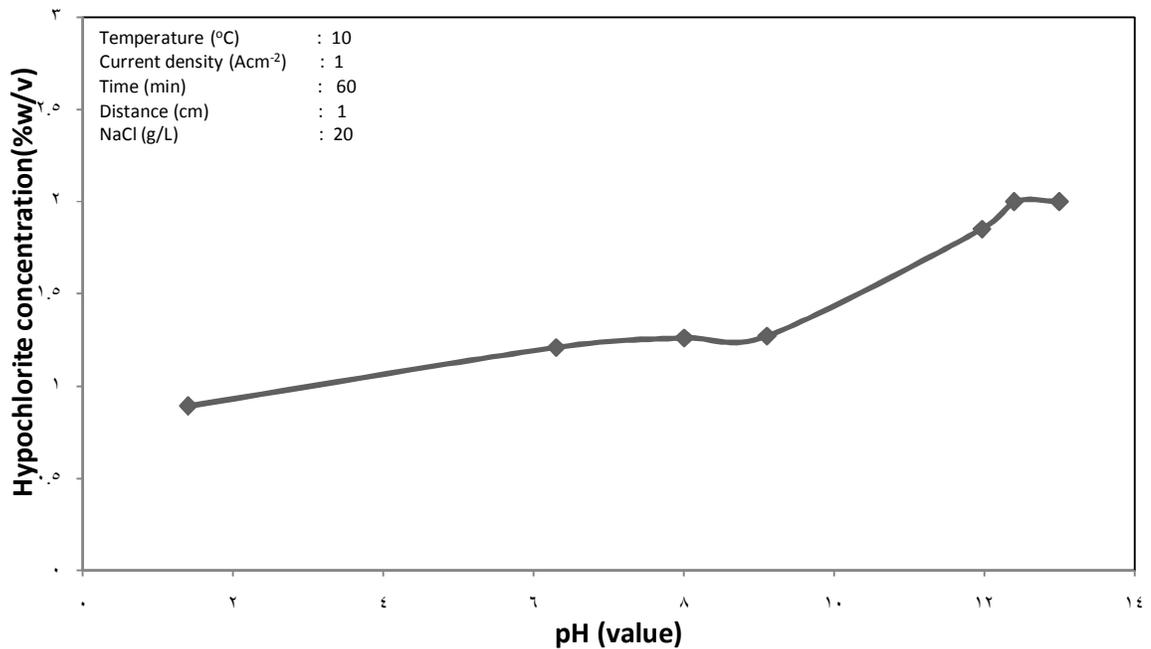**Fig (7): Effect of time on the hypochlorite generation from sodium chloride solutioin using Pb/PbO$_2$ electrode** .

Fig (8): Effect of time on the hypochlorite generation from sodium chloride solution using C/PbO$_2$ electrode .

Fig (9): Effect of NaCl concentration on the hypochlorite generation from sodium chloride solution using Pb/PbO$_2$ electrode .

Fig (10) : Effect of NaCl concentration on the hypochlorite generation from sodium chloride solution using C/PbO$_2$ electrode .

Fig (11): Effect of pH on the hypochlorite generation from sodium chloride solution using Pb/PbO$_2$ electrode .

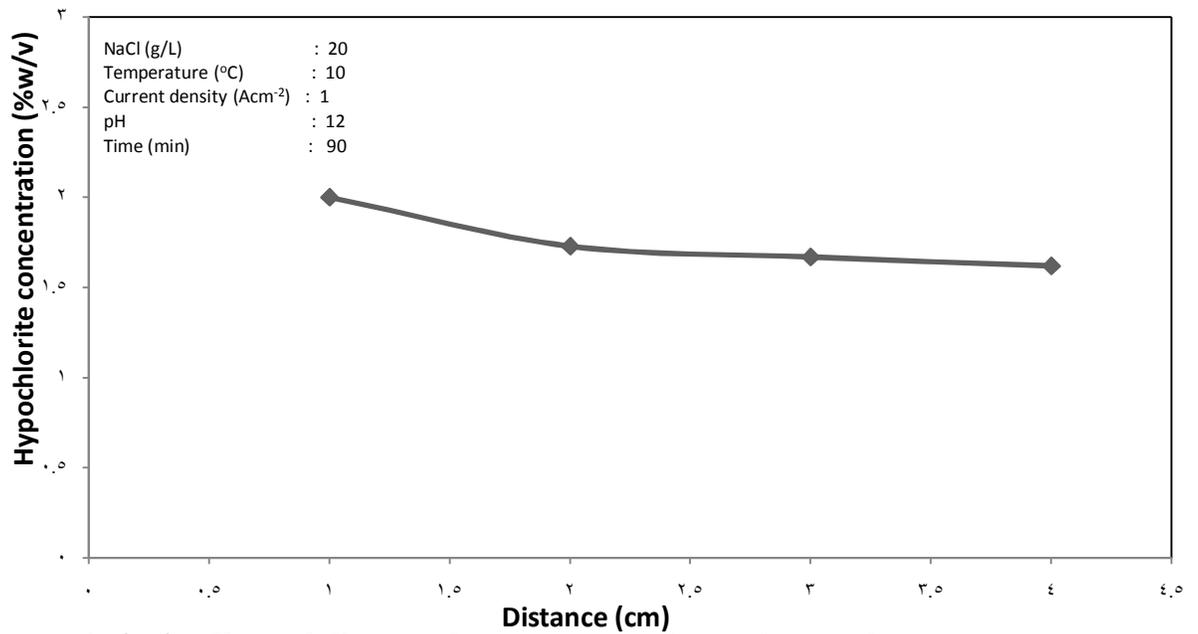**Fig (12): Effect of pH on the hypochlorite generation from sodium chloride solution using C/PbO$_2$ electrode .**

NaCl (g/L)   : 20
Temperature (°C)   : 10
Current density (Acm^{-2}) : 1
pH   : 12
Time (min)   : 90

Hypochlorite concentration (%w/v)

Distance (cm)

Fig (13): Effect of distance between two electrodes on the
hypochlorite generation from sodium chloride solution
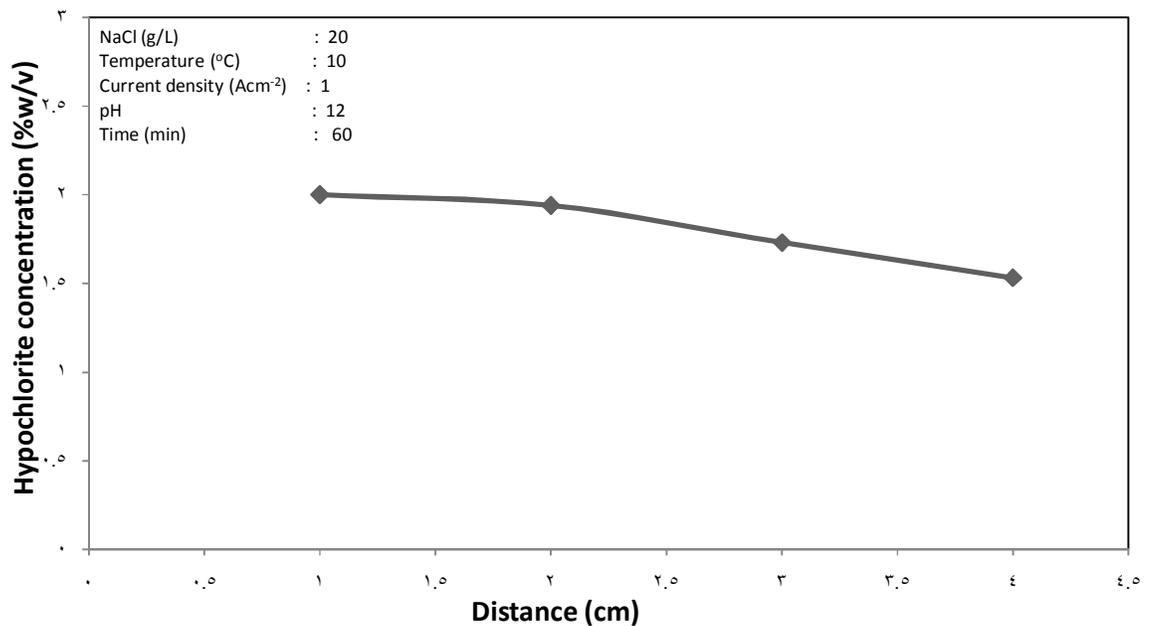**using Pb/PbO$_2$ electrode .**

NaCl (g/L)   : 20
Temperature (°C)   : 10
Current density (Acm^{-2}) : 1
pH   : 12
Time (min)   : 60

Hypochlorite concentration (%w/v)

Distance (cm)

Fig (14): Effect of distance between two electrodes on the
hypochlorite generation from sodium chloride solution
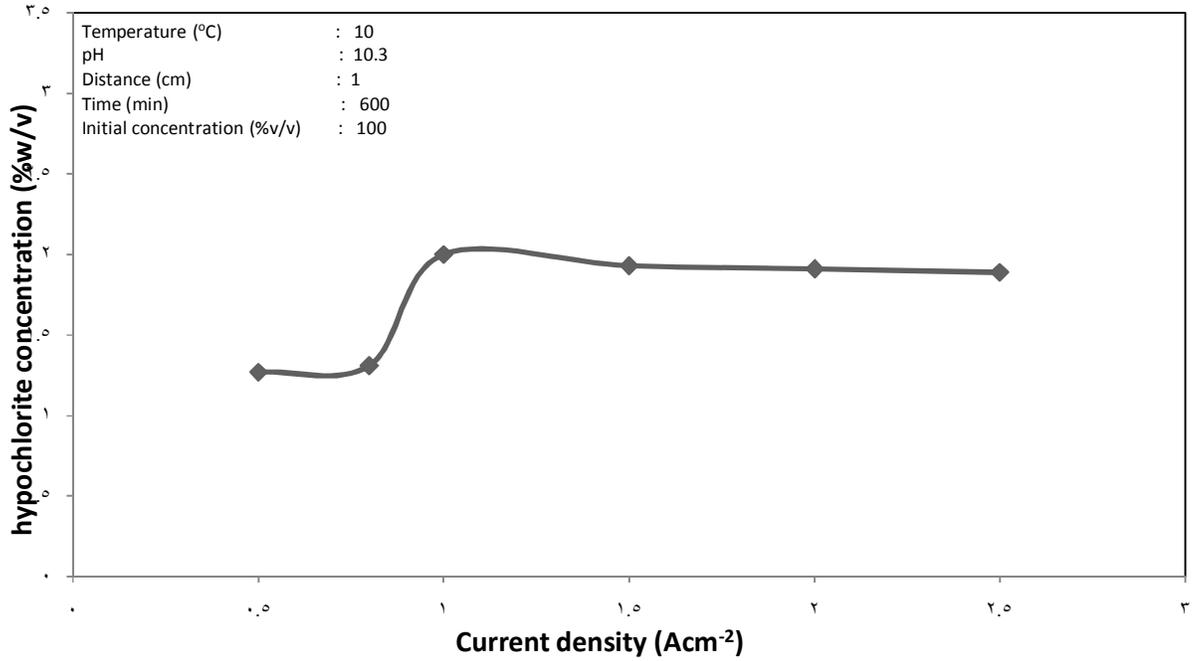**using C/PbO$_2$ electrode .**

Fig (15): Effect of current density on the hypochlorite generation
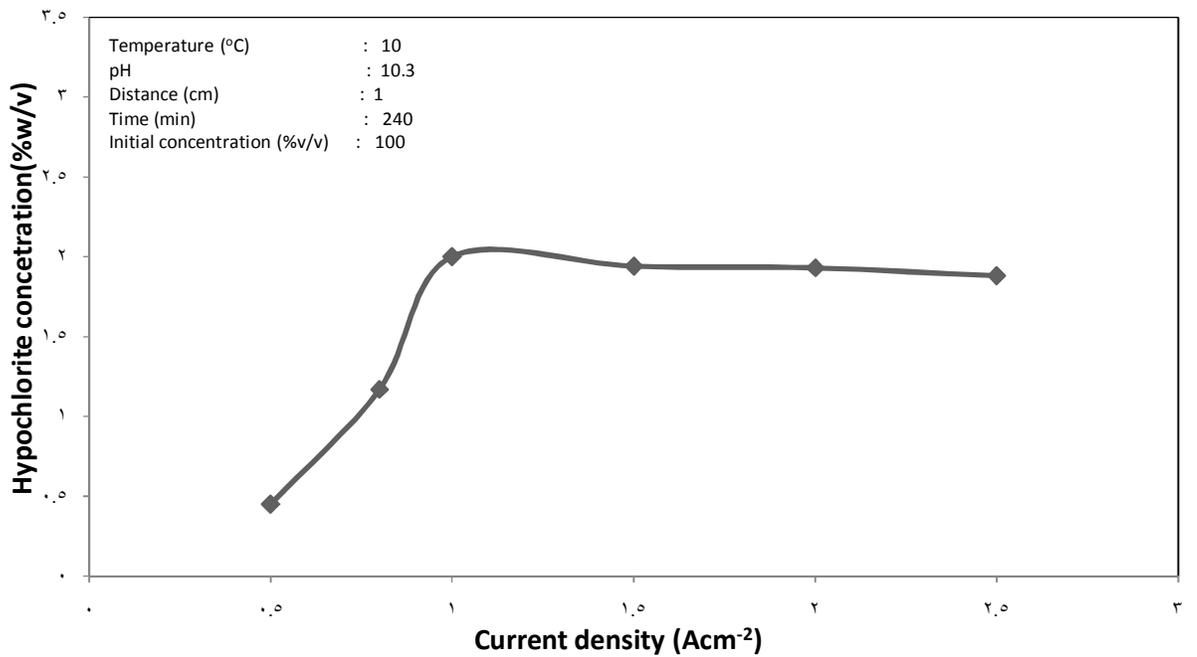from sea water using Pb/PbO$_2$ electrode.

Fig (16): Effect of current density on the hypochlorite generation
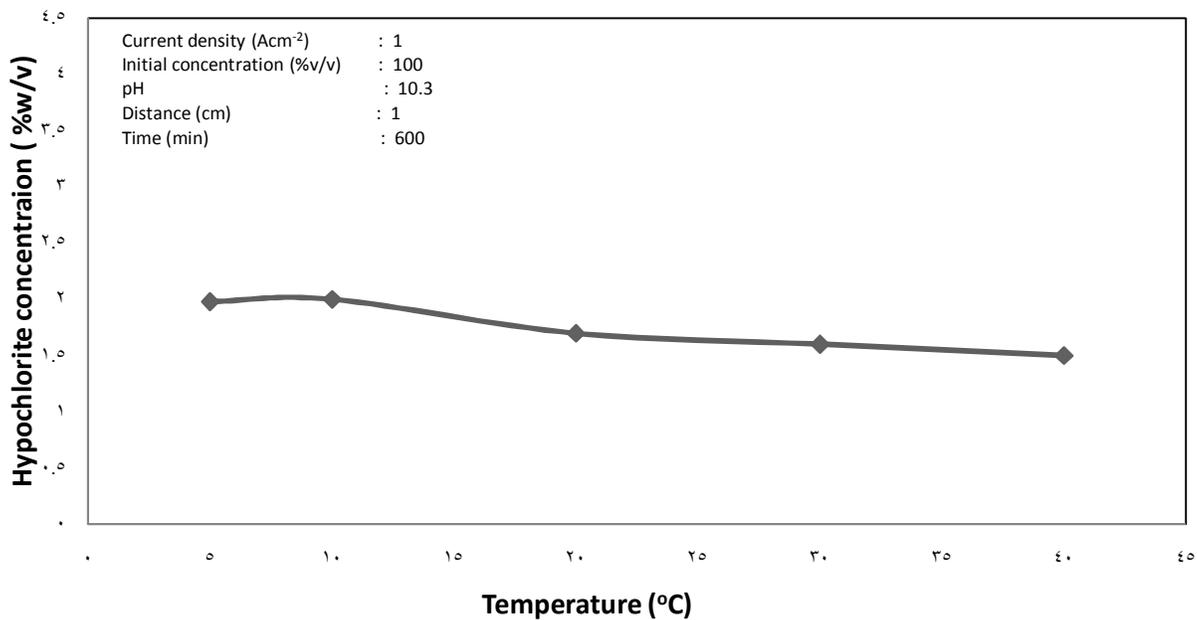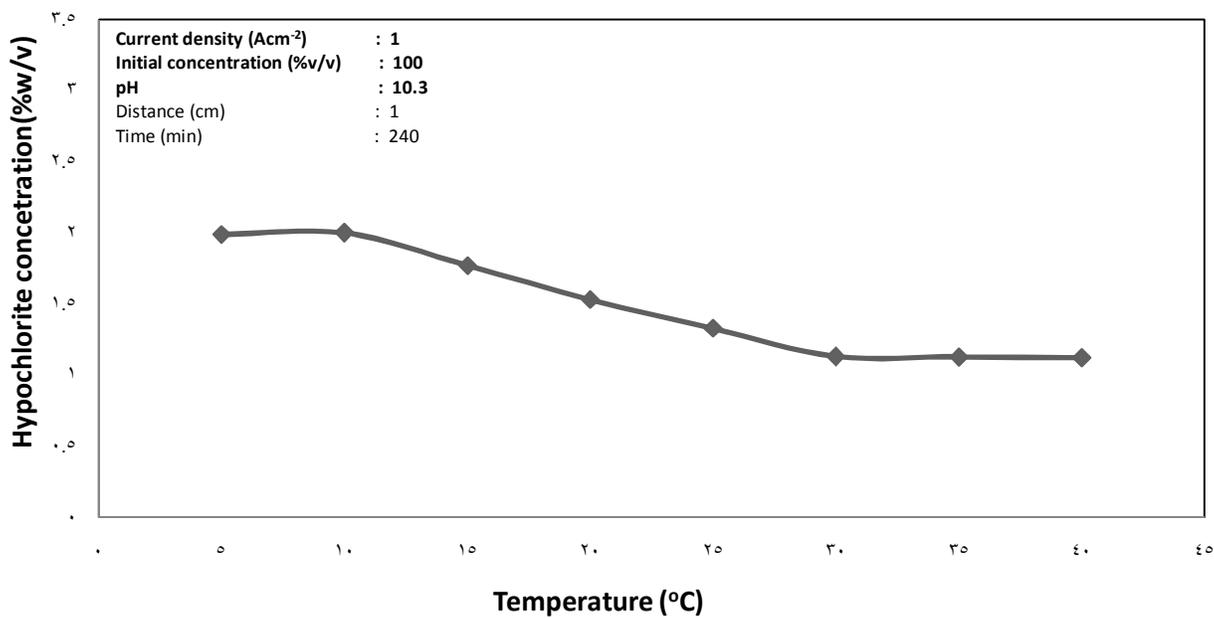from sea water using C/PbO$_2$ electrode.

Fig (17): Effect of temperature on the hypochlorite generation from sea water using Pb/PbO₂ electrode.

Fig(18): Effect of temperature on the hypochlorite generation from sea water using C/PbO₂ electrode.
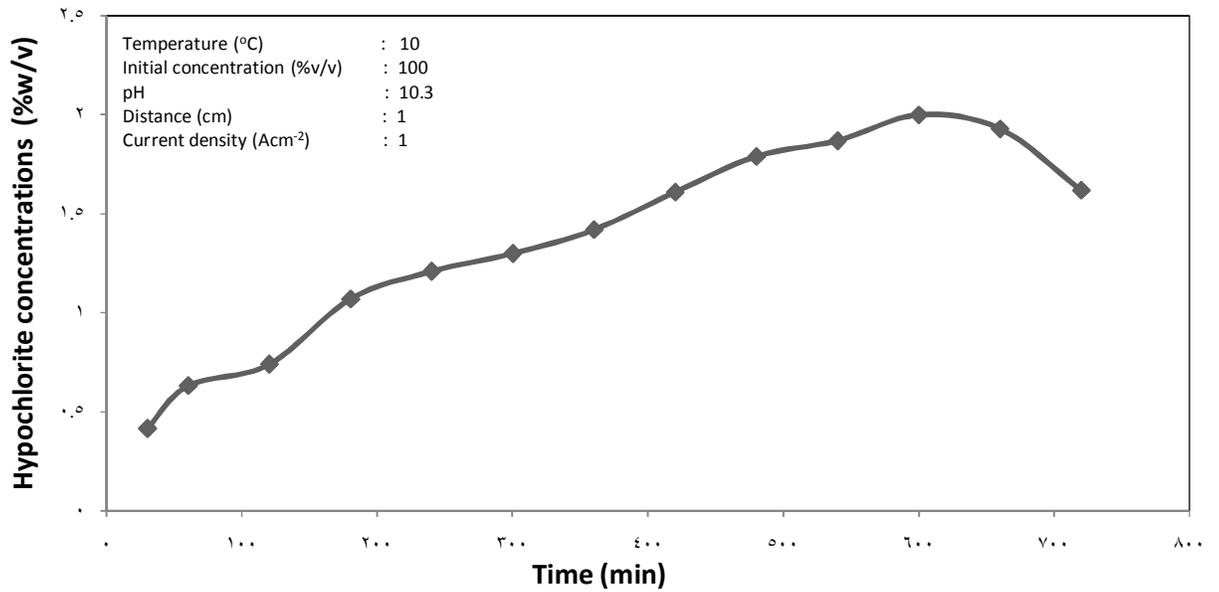
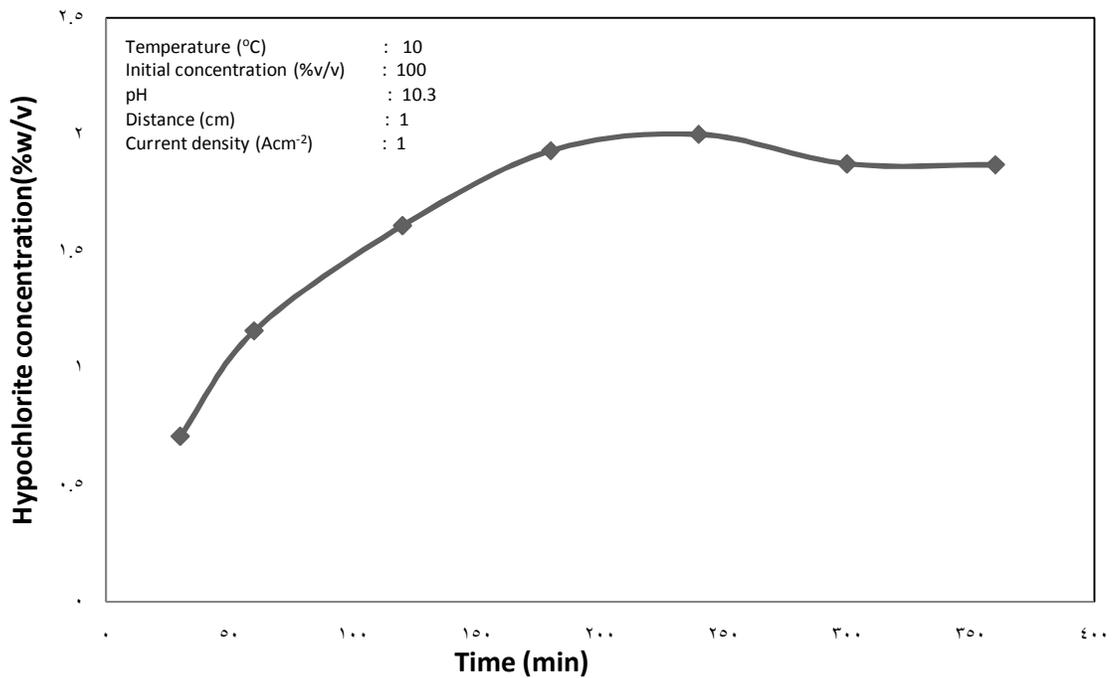**Fig (19): Effect of time on the hypochlorite generation from sea water using Pb/PbO$_2$ electrode.**

Fig (20): Effect of time on the hypochlorite generation from sea water using C/PbO$_2$ electrode.
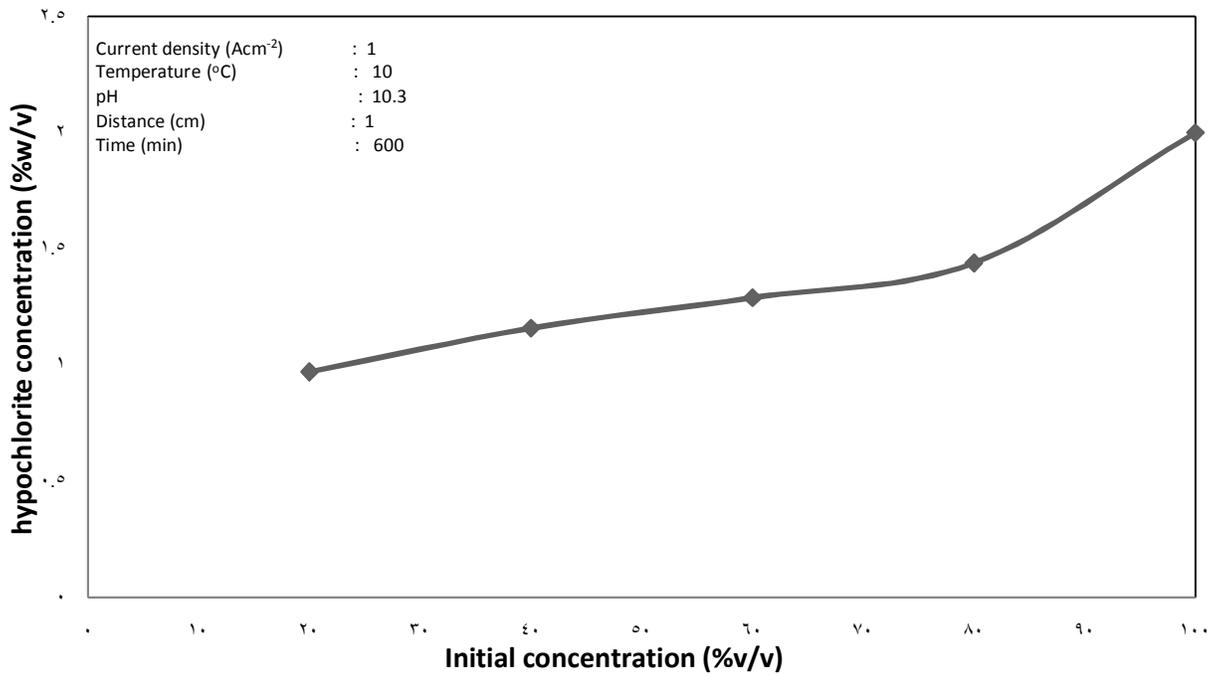
Fig (21): Effect of initial chloride concentration on the hypochlorite generation from sea water using Pb/Pbo₂ electrode .
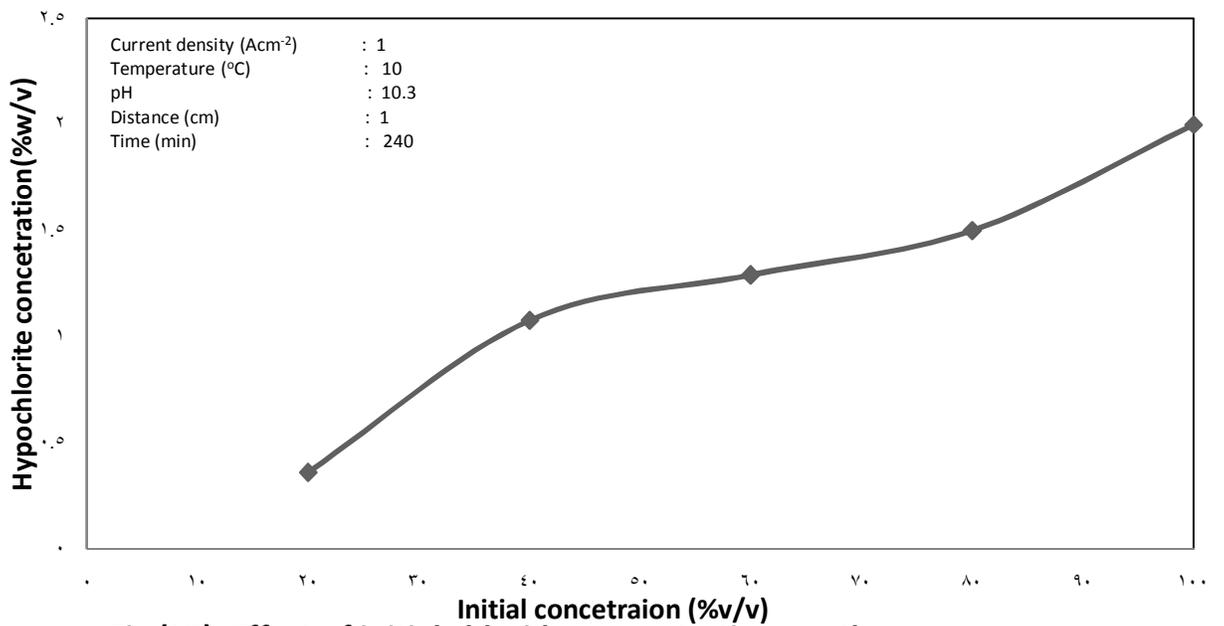

Fig (22): Effect of initial chloride concentration on the hypochlorite generation from sea water using C/PbO₂ electrode.
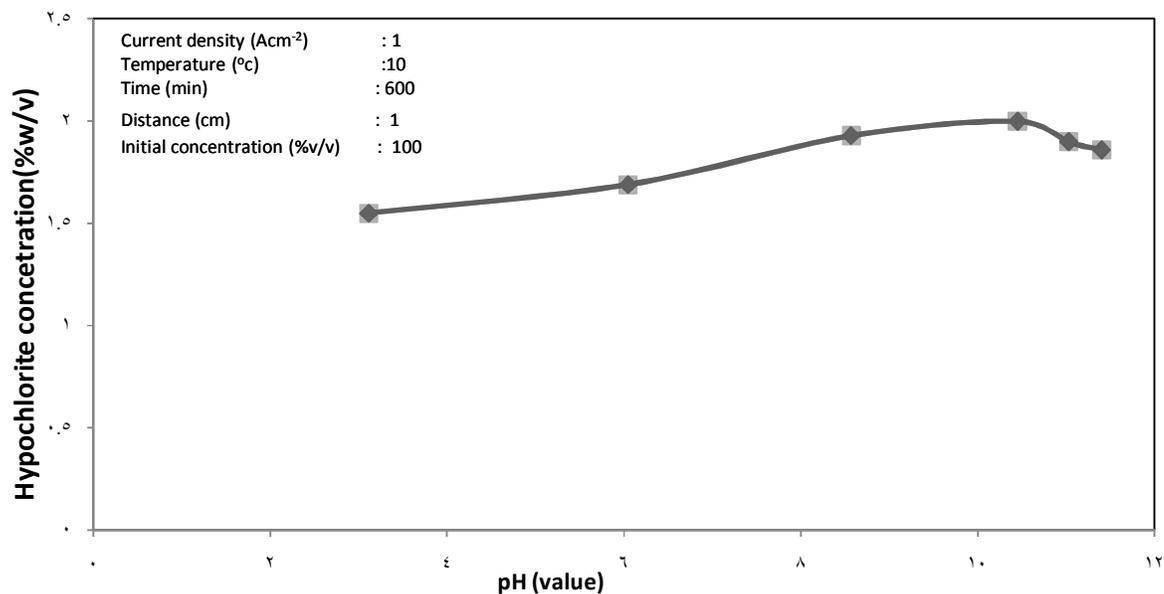
…

Fig (23): Effect of pH on the hypochlorite generation from sea water using Pb/PbO$_2$ electrode.
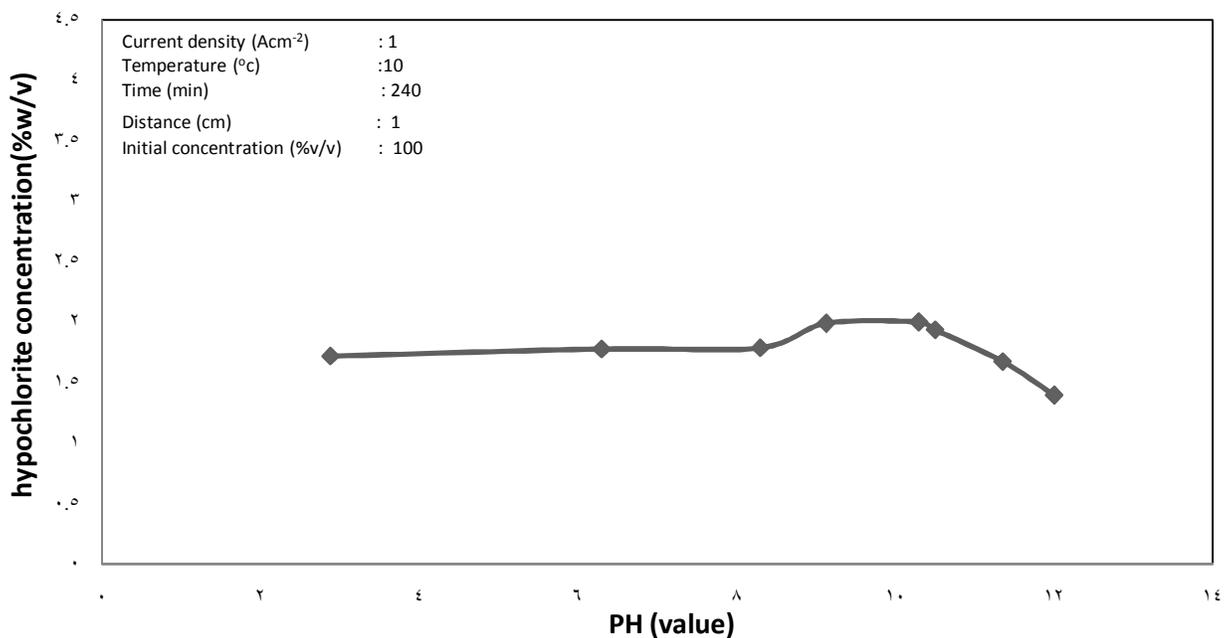

Fig (24): Effect of PH on the hypochlorite generation from sea water using C/PbO$_2$ electrode.
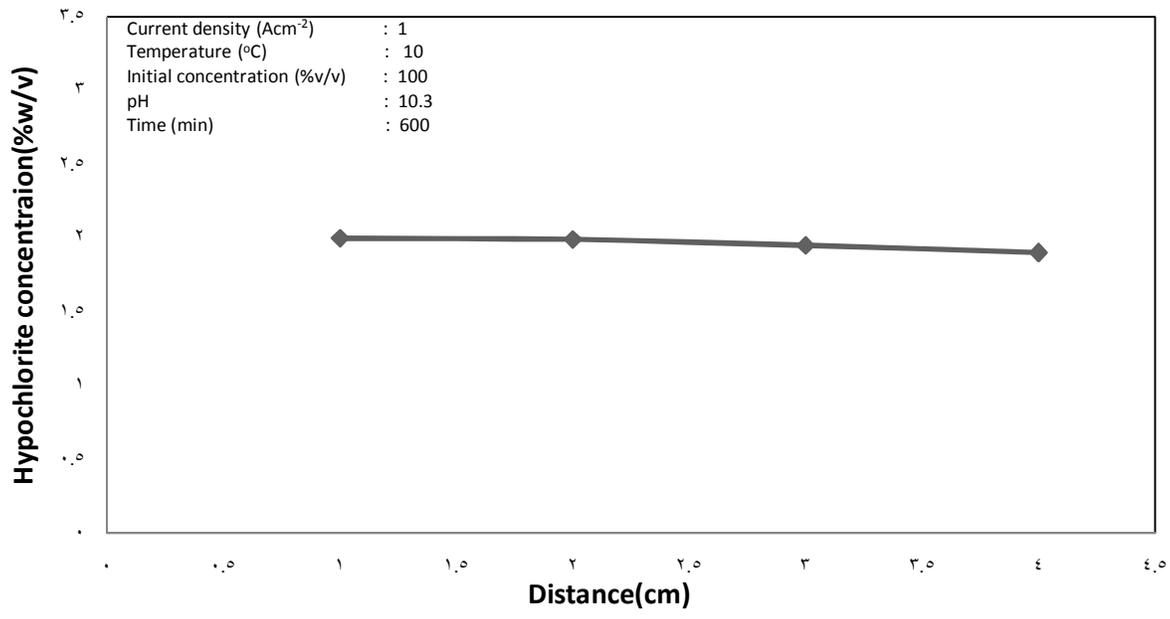
Fig (25): Effect of distance between the two electrodes on the hypochlorite generation from sea water using Pb/PbO$_2$ electrode.

Fig (26): Effect of distance between the two electrodes on the hypochlorite generation from sea water using C/PbO$_2$ electrode.

Distance (cm)   : 1
Time (min)   : 300
Temperature (°C)   : 10
pH   : 10.73
Initial concentration (%v/vl) : 100
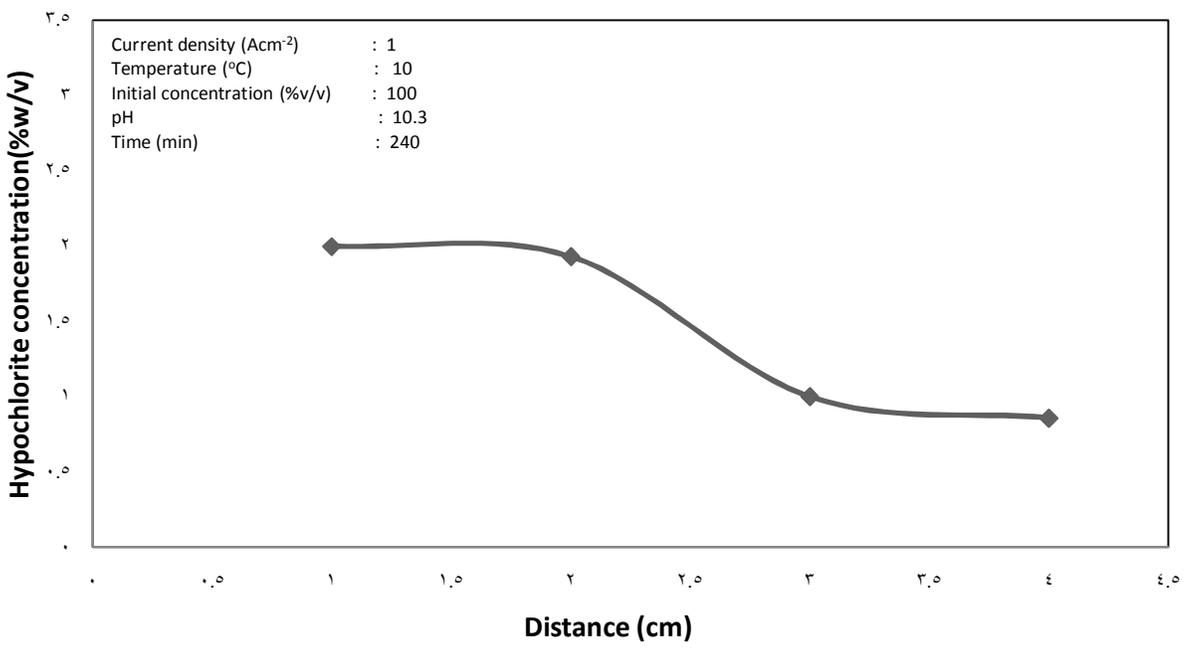
Fig (27): Effect of current density on the hypochlorite generation from brine water using Pb/PbO$_2$ electode.

Distance (cm)   : 1
Time (min)   : 120
Temperature (°C)   : 10
PH   : 10.73
Initial cancentration (%v/v) : 100

Fig (28): Effect of current density on the hypochlorite generation from brine water using C/PbO$_2$ electrode.

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Fig (29): Effect of temperature on the hypochlorite generation from brine water using Pb/PbO$_2$ electrode.

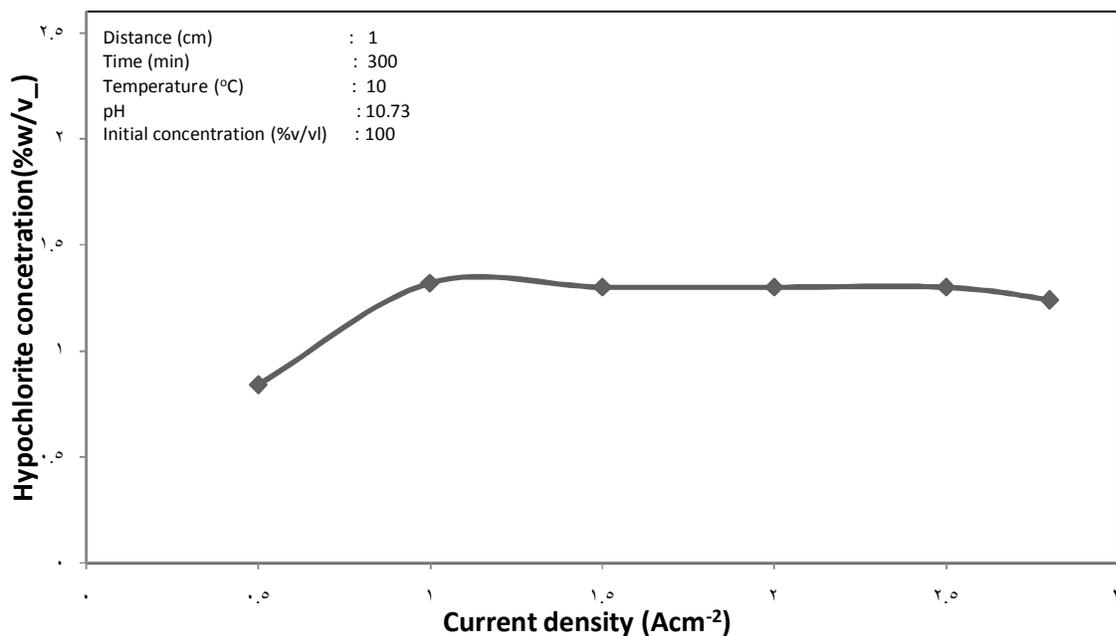**Fig (30): Effect of temperature on the hypochlorite generation from brine water using C/PbO$_2$ electrode**.

Fig (31): Effect of time on the hypochlorite generation from brine water using Pb/PbO₂ electrode.
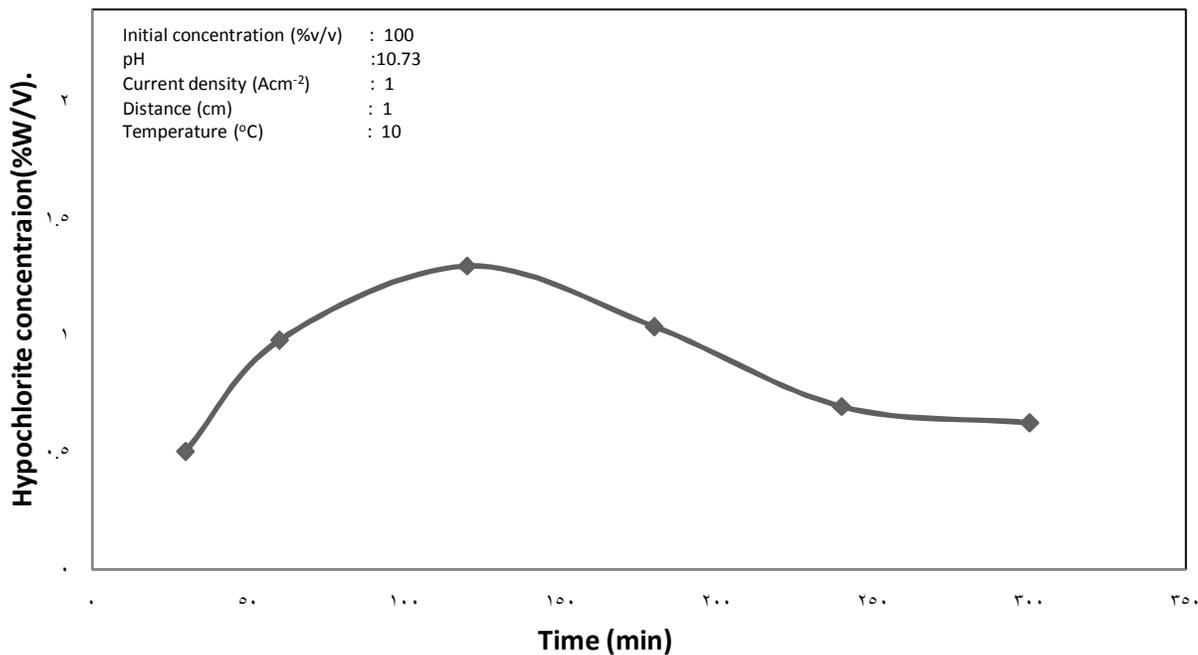
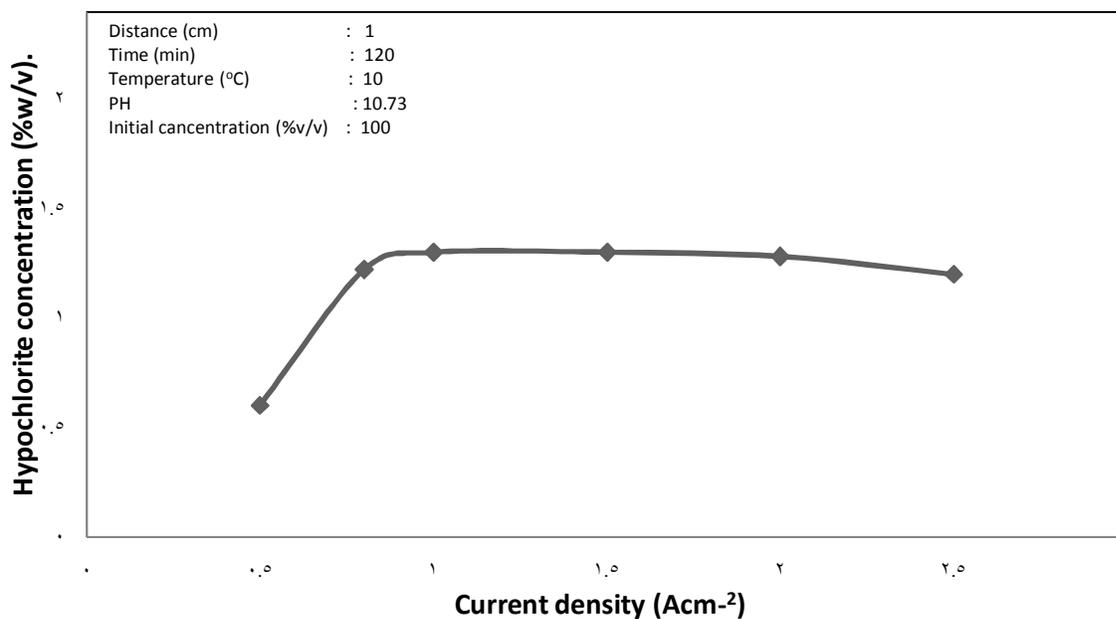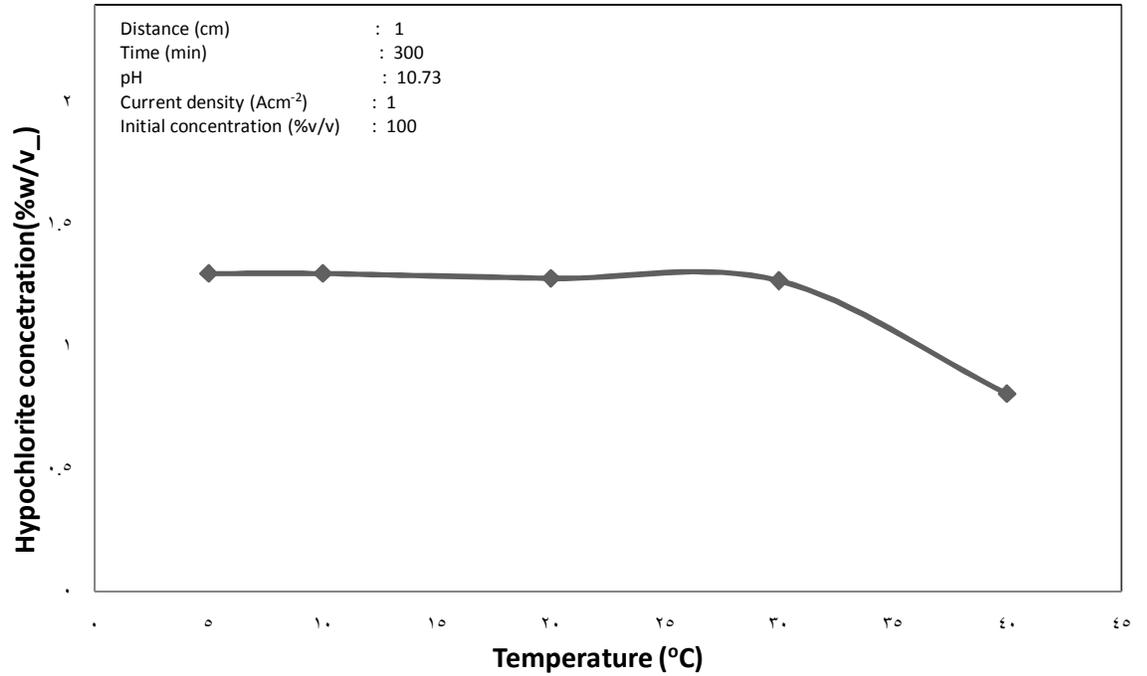**Fig (32): Effect of time on the hypochlorite generation from brine water using C/PbO₂ electrode.**
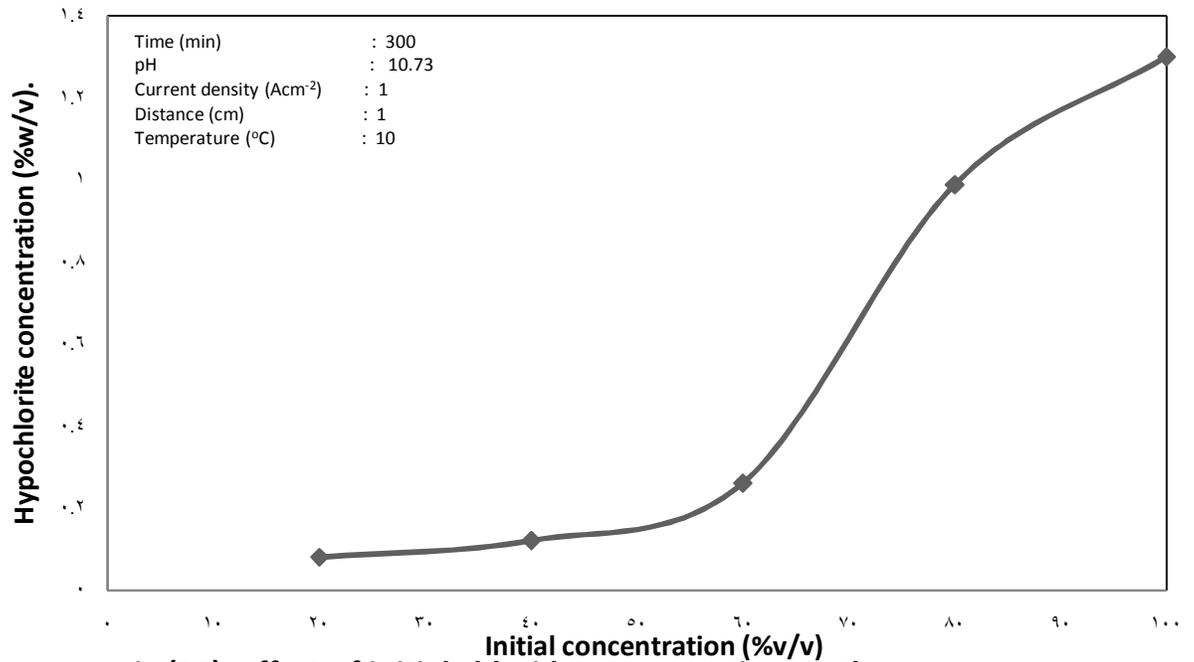
50

Time (min)	: 300
pH	: 10.73
Current density (Acm^{-2})	: 1
Distance (cm)	: 1
Temperature (^{o}C)	: 10

Fig (33): Effect of initial chloride concentration on the hypochlorite generation from brine water using Pb/PbO$_2$ electrode.…

Time (min)	: 120
pH	: 10.73
Current density (Acm^{-2})	: 1
Distance (cm)	: 1
Temperature (^{o}C)	: 10
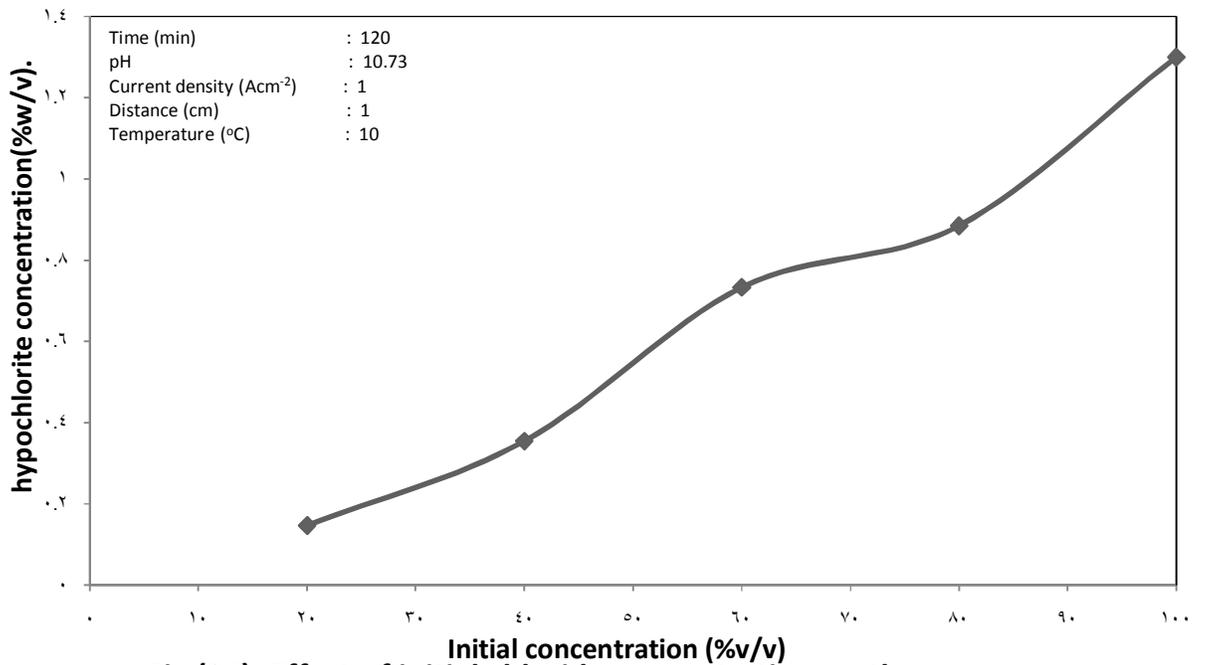
Fig (34): Effect of initial chloride concentration on the hypochlorite generation from brine water using C/PbO$_2$ electrode.…

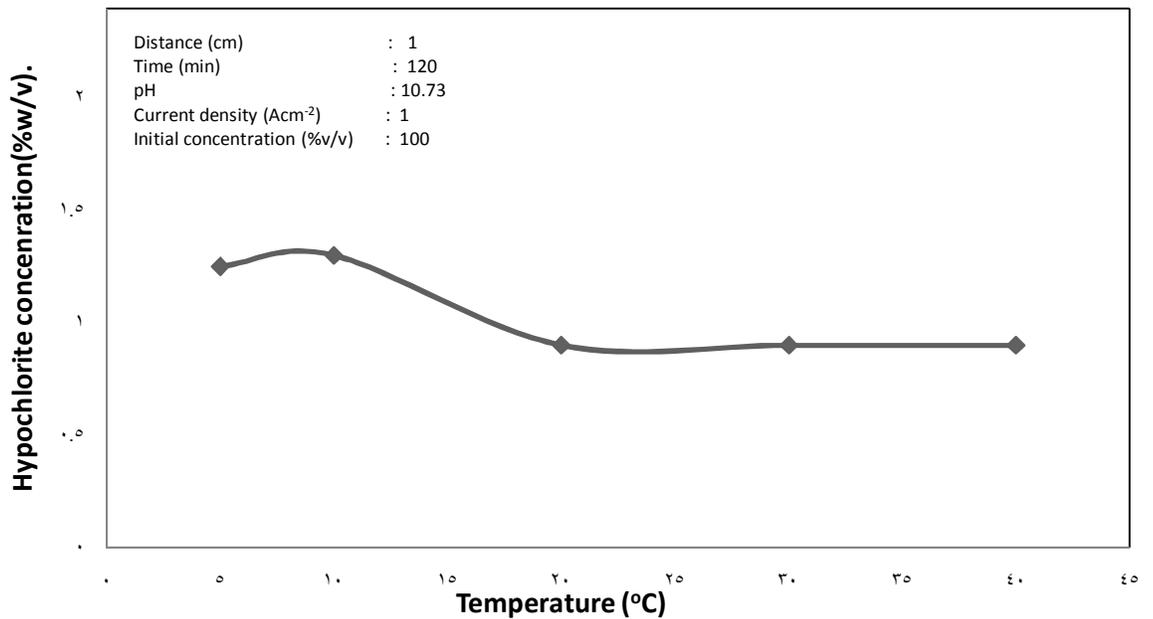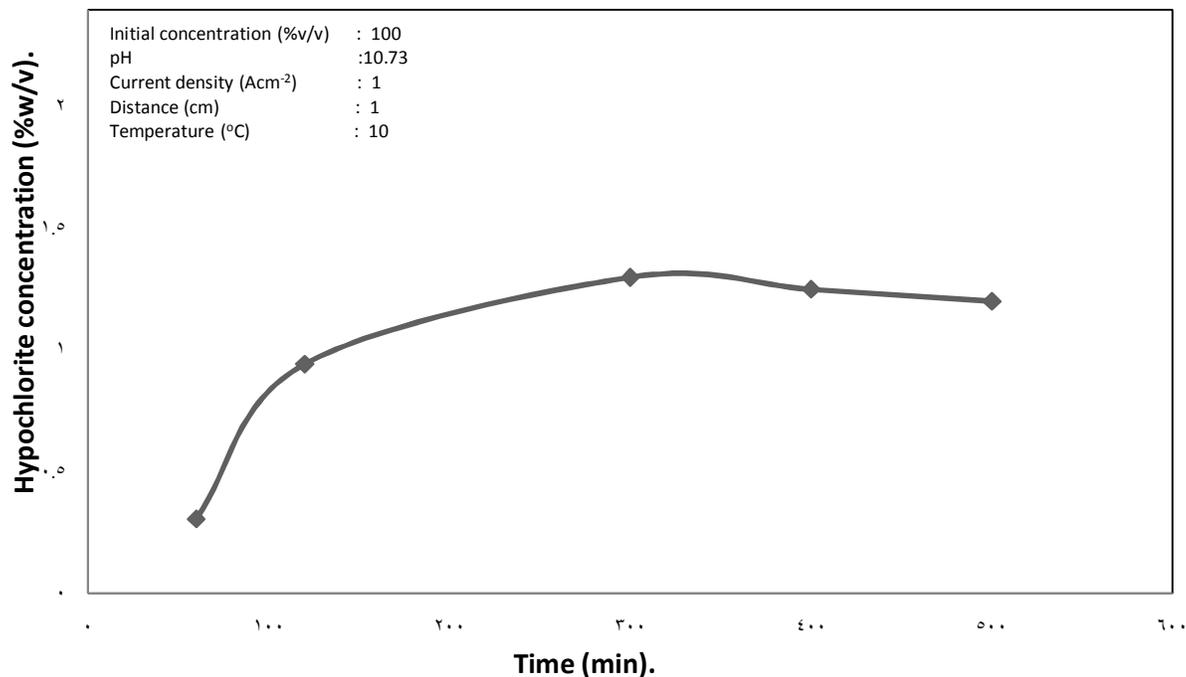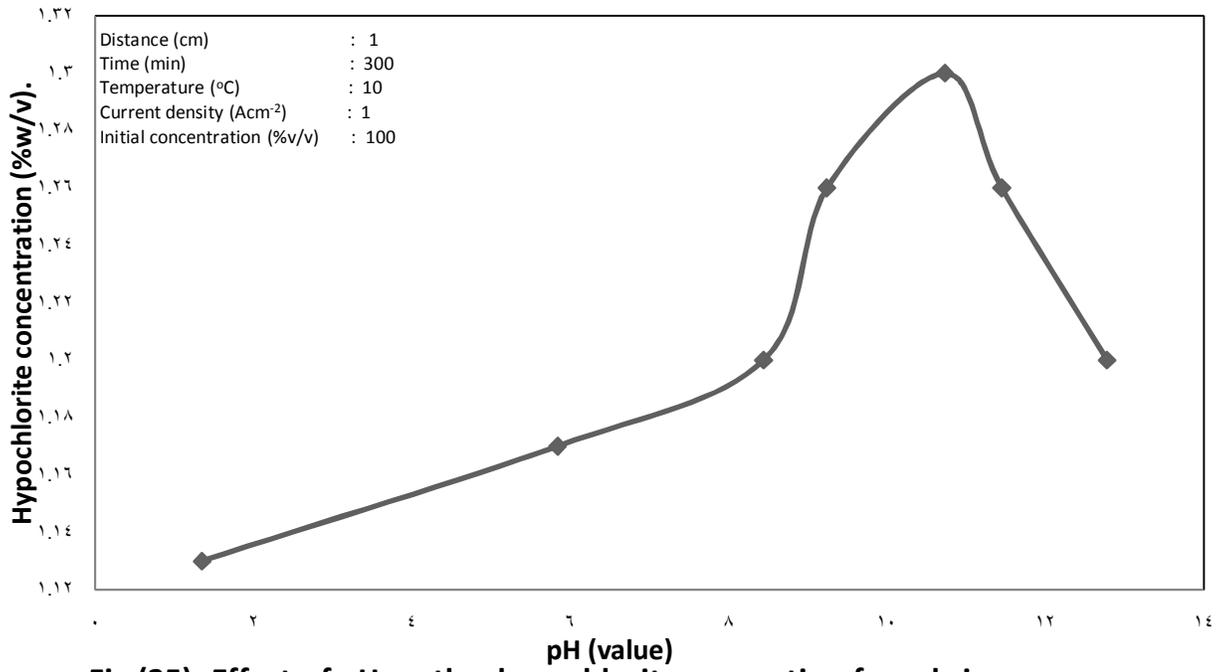**Fig (35): Effect of pH on the hypochlorite generation from brine water using Pb/PbO$_2$ electrode.**
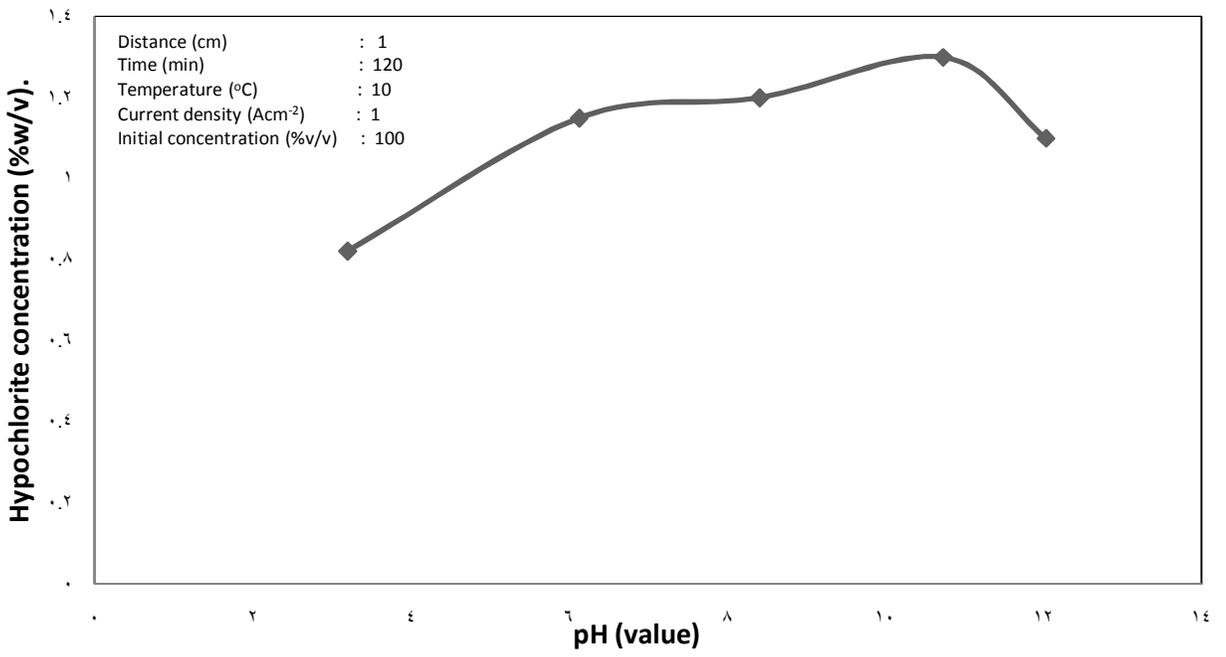
Fig (36): Effect of pH on the hypochlorite generation from brine water using C/PbO$_2$ electrode.

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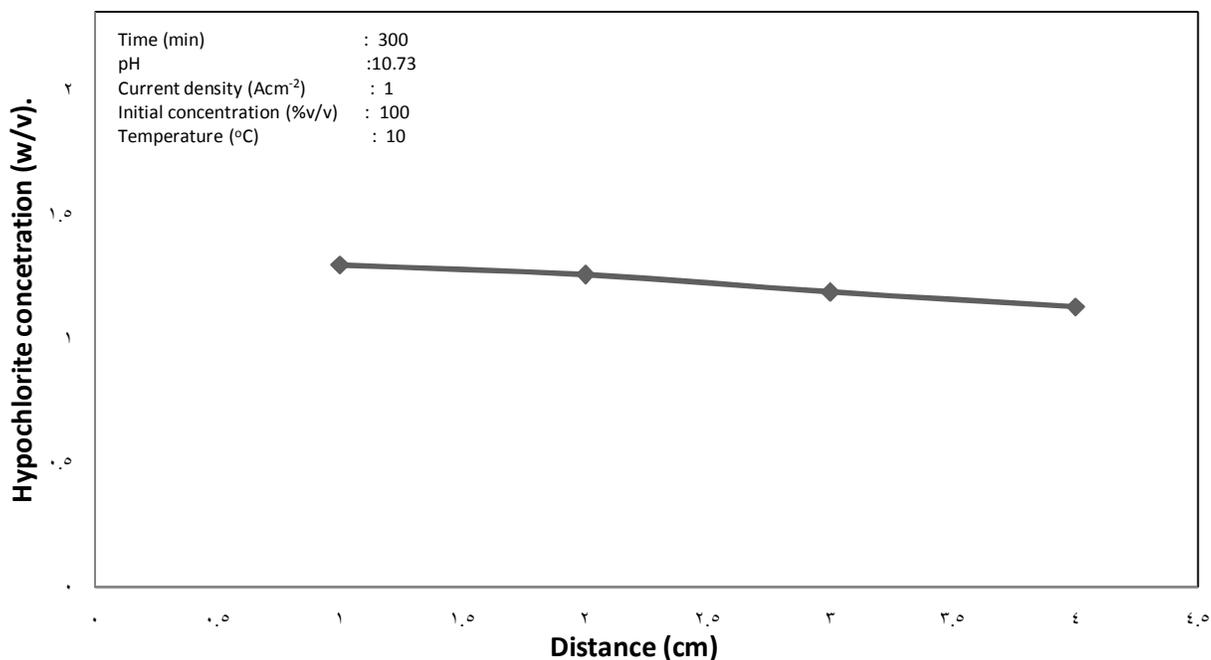
Fig (37): Effect of distance between two the electrodes on the hypochlorite generation from brine water using Pb/PbO$_2$ electrode.
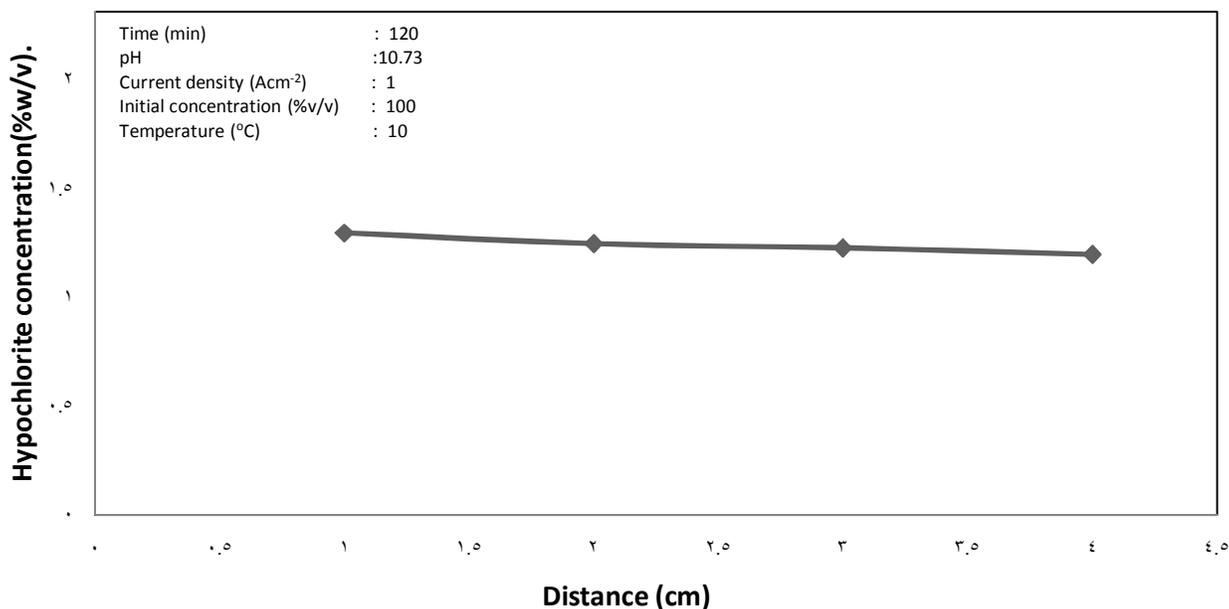
Fig (38): Effect of distance between two the electrodes on the hypochlorite generation from brine water using C/PbO$_2$ electrode.
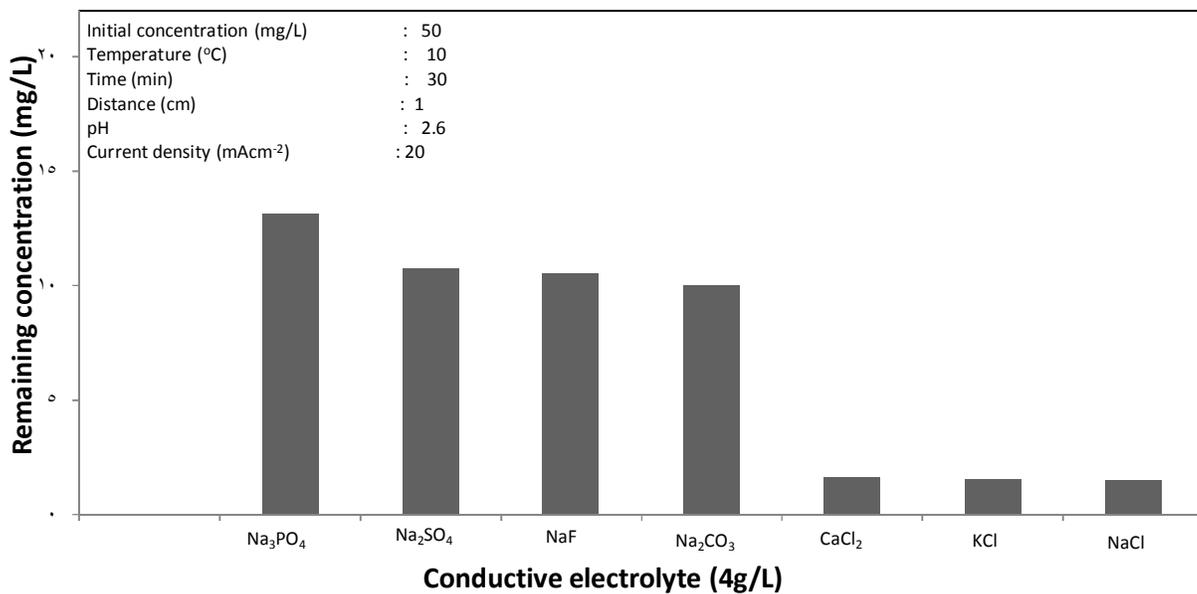
Fig (39): Effect of conductive electrolyte on the removal of picric acid using Pb/PbO₂ electrode.
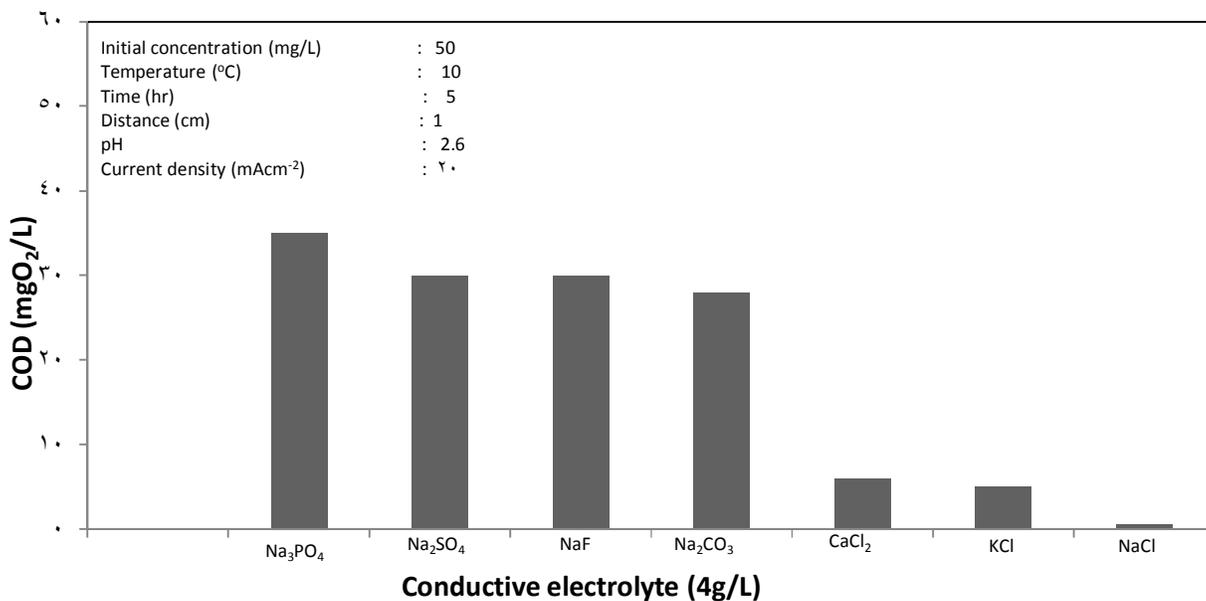
Fig (40): Effect of conductive electrolyte on the COD removal of picric acid using Pb/PbO₂ electrode.

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Fig (41): Effect of conductive eclecrolyte on the removal of picric acid using C/PbO$_2$ electrode.

Fig (42) : Effect of conductive electrolyte on the COD removal of picric acid using C/PbO$_2$ electrode.
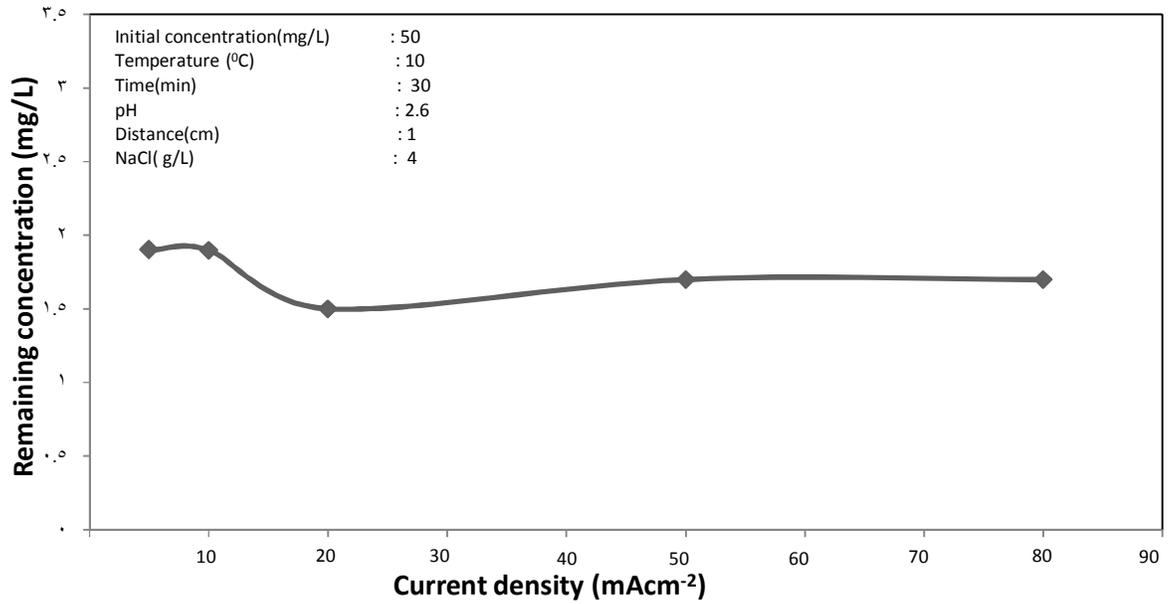
Fig (43): Effect of current density on the removal of picric acid using Pb/PbO₂ electrode.
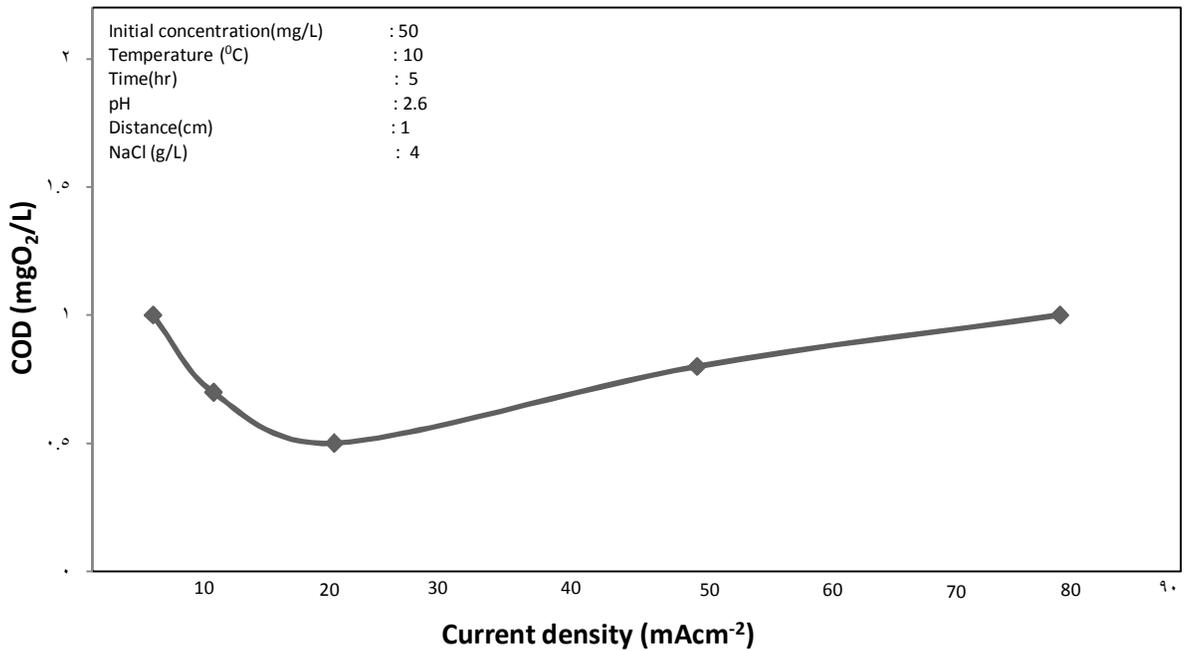
Fig (44): Effect of current density on the COD removal of picric acid using Pb/PbO₂ electrode.

Fig (45): Effect of current density on the removal of picric acid using C/PbO₂ electrode.
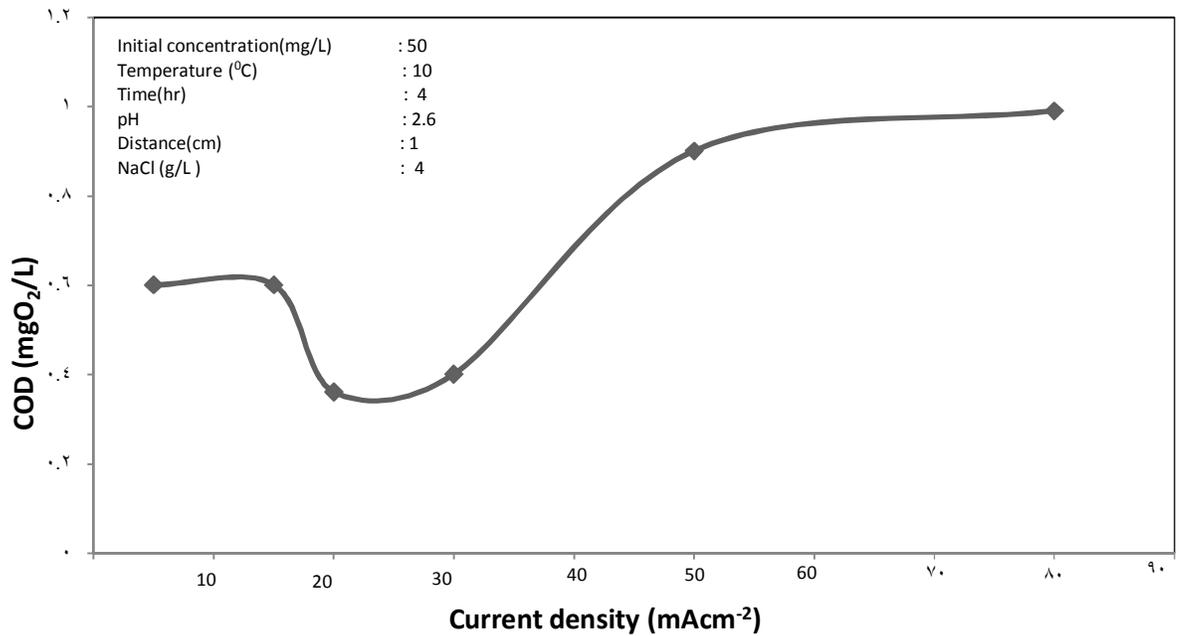
Fig (46): Effect of current density on the COD removal of picric acid using C/PbO₂ electrode.
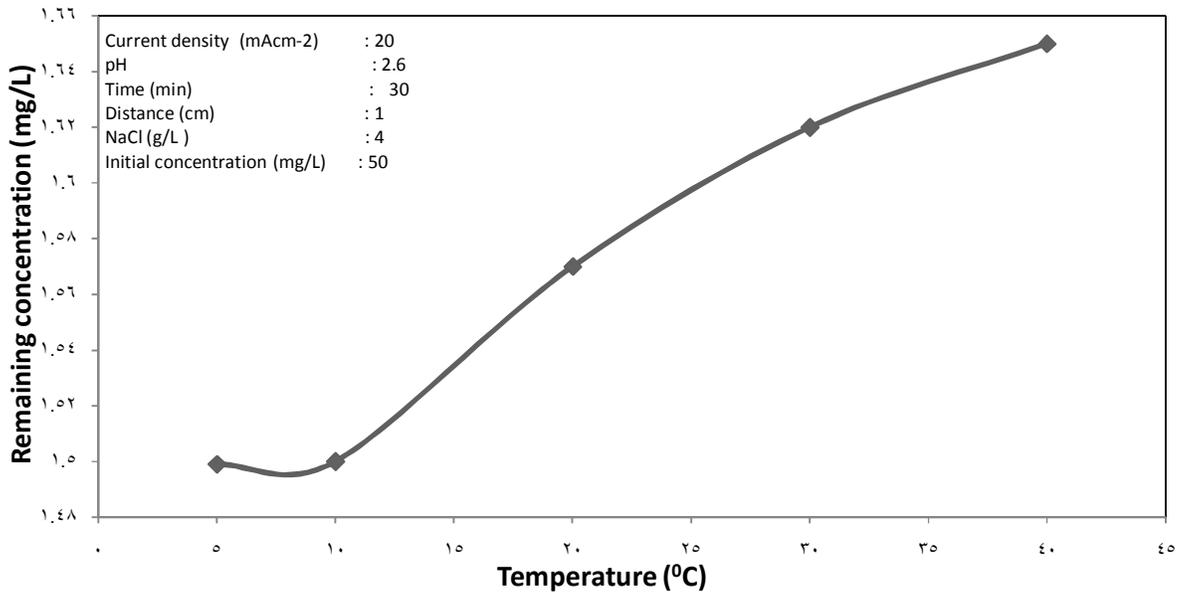
Fig (47): Effect of temperature on the removal of picric acid using Pb/PbO$_2$ electrode.
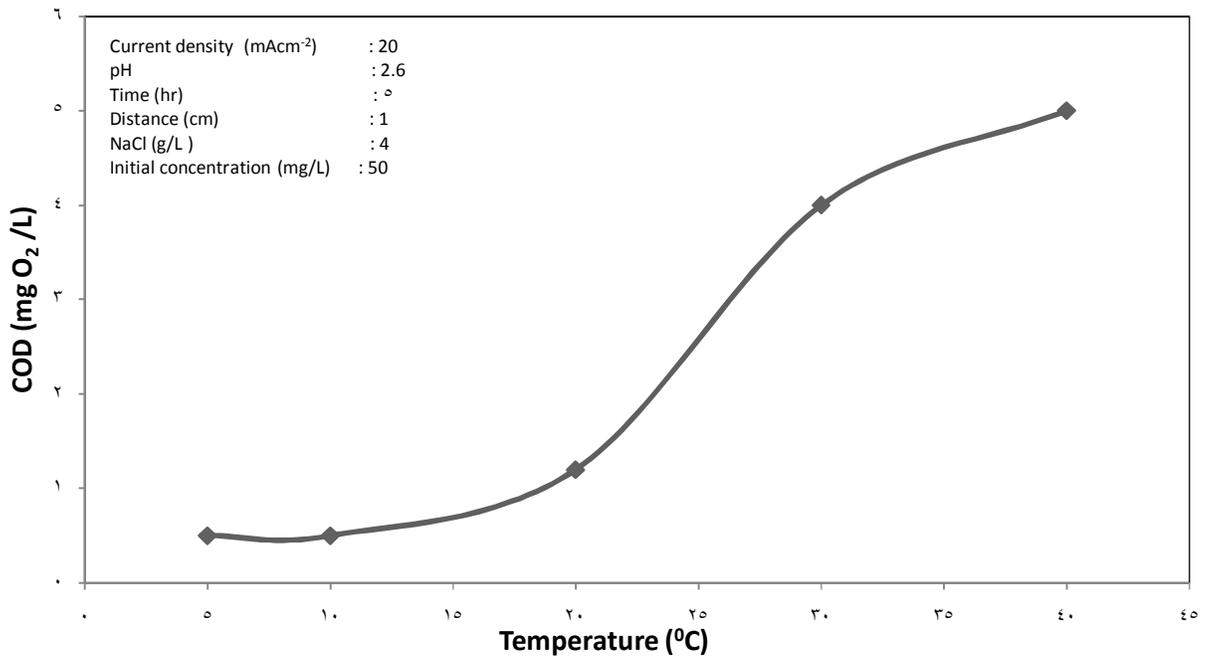
Fig (48): Effect of temperature on the COD removal of picric acid using Pb/PbO$_2$ electrode.

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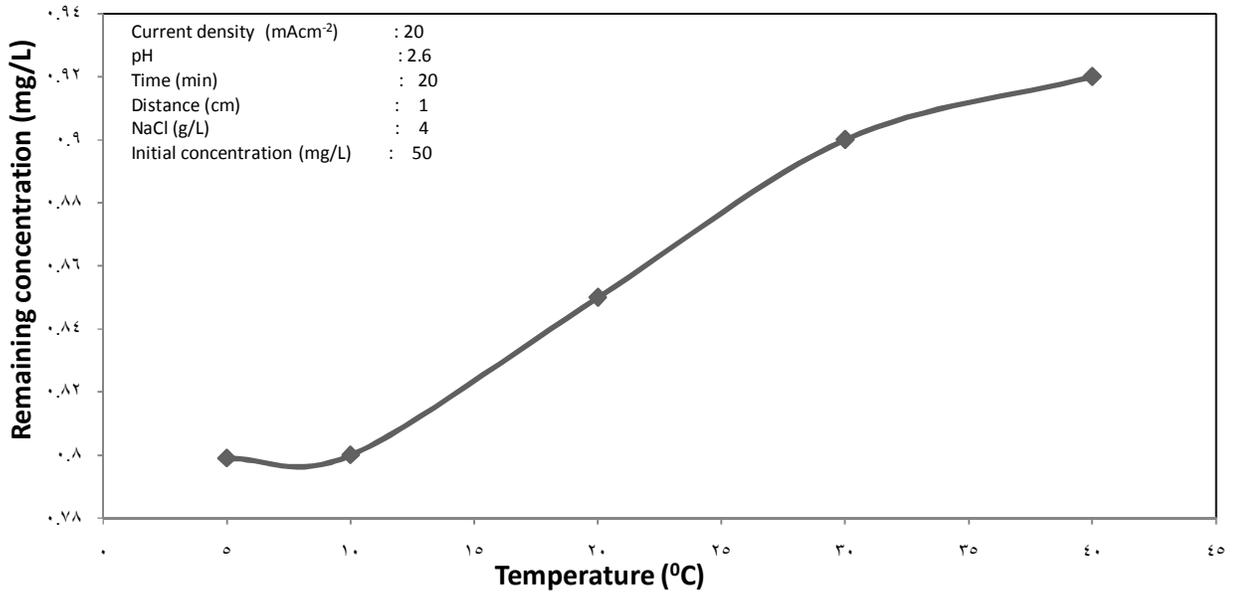
Fig (49): Effect of temperature on the removal of picric acid using C/PbO₂ electrode.
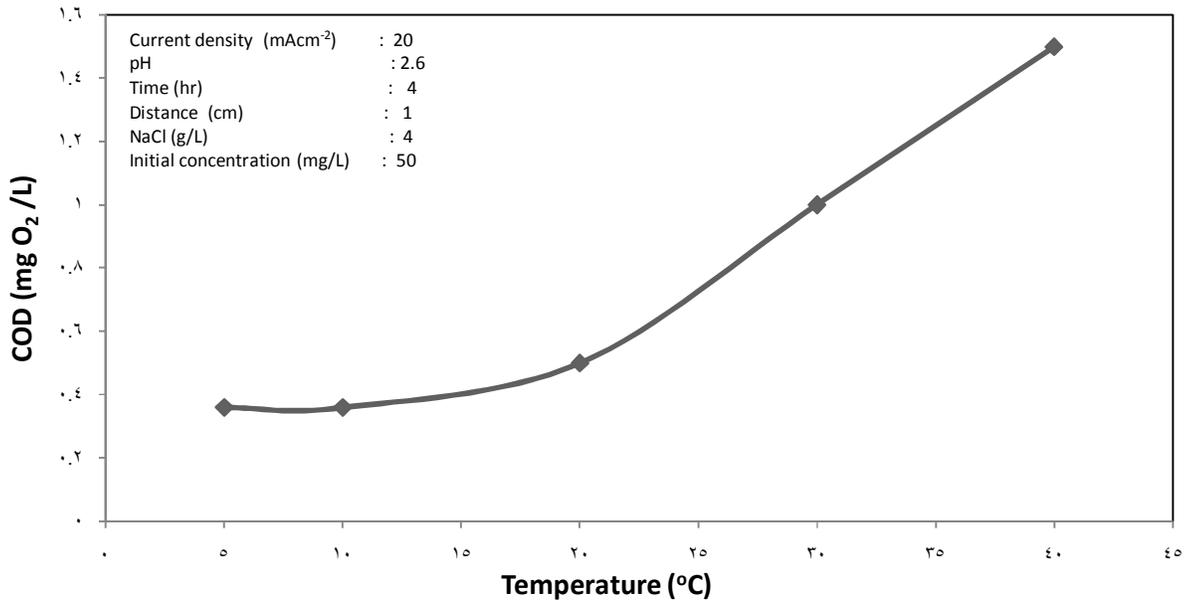
Fig (50): Effect of temperature on the COD removal of picric acid using C/PbO₂ electrode.
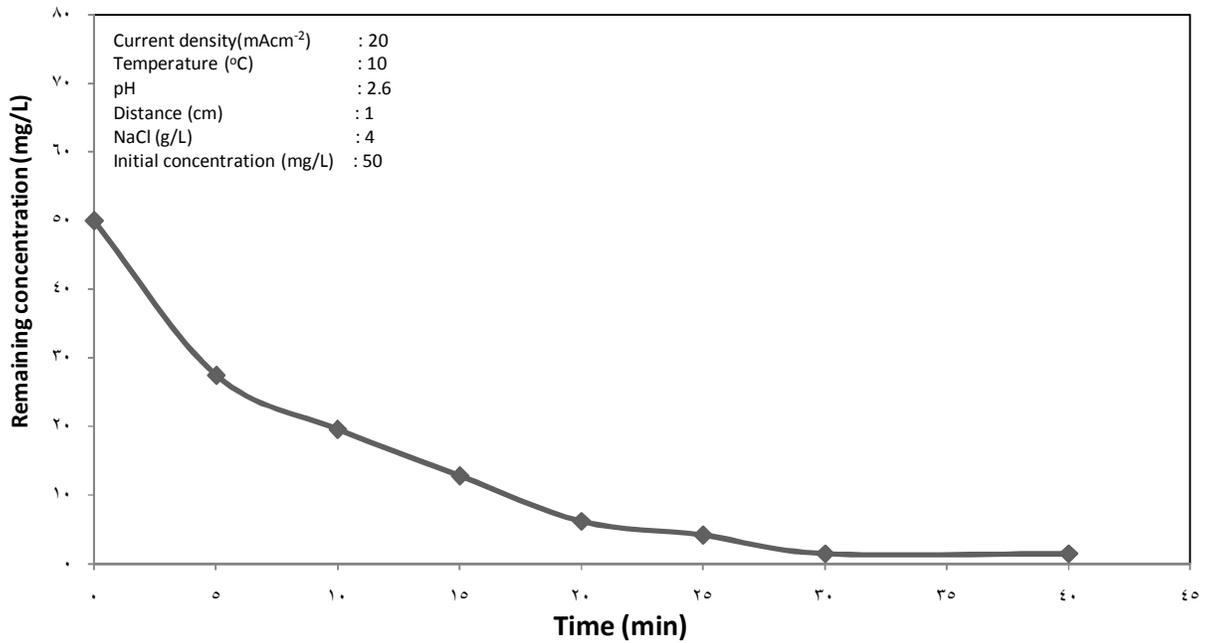
**Fig (51): Effect of electrolysis time on the removal of picric acid
using Pb/PbO₂ electrode.**
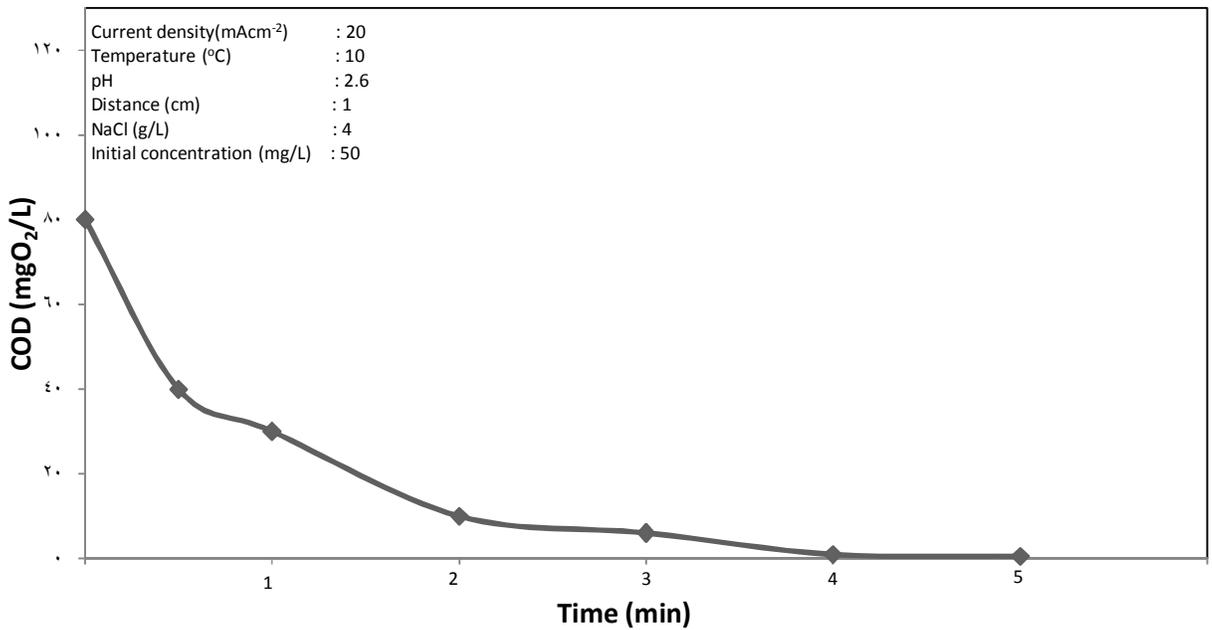
**Fig (52): Effect of electrolysis time on the COD removal of picric
acid using Pb/PbO₂ electrode.**
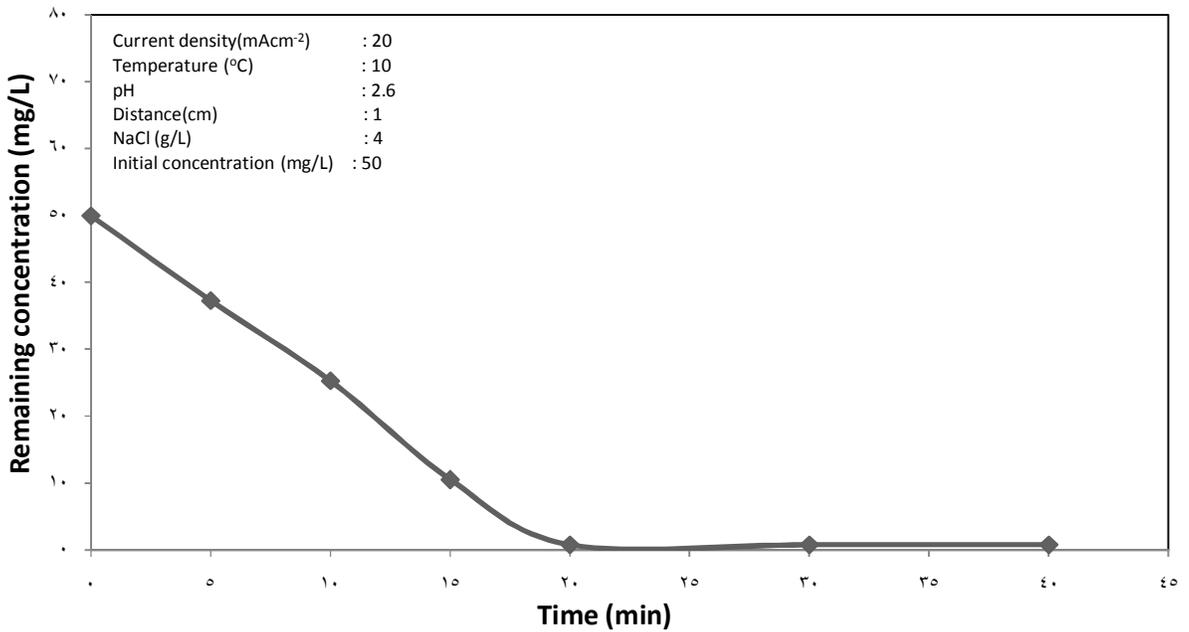
Fig (53): Effect of electrolysis time on the removal of picric acid using C/PbO₂ electrode.
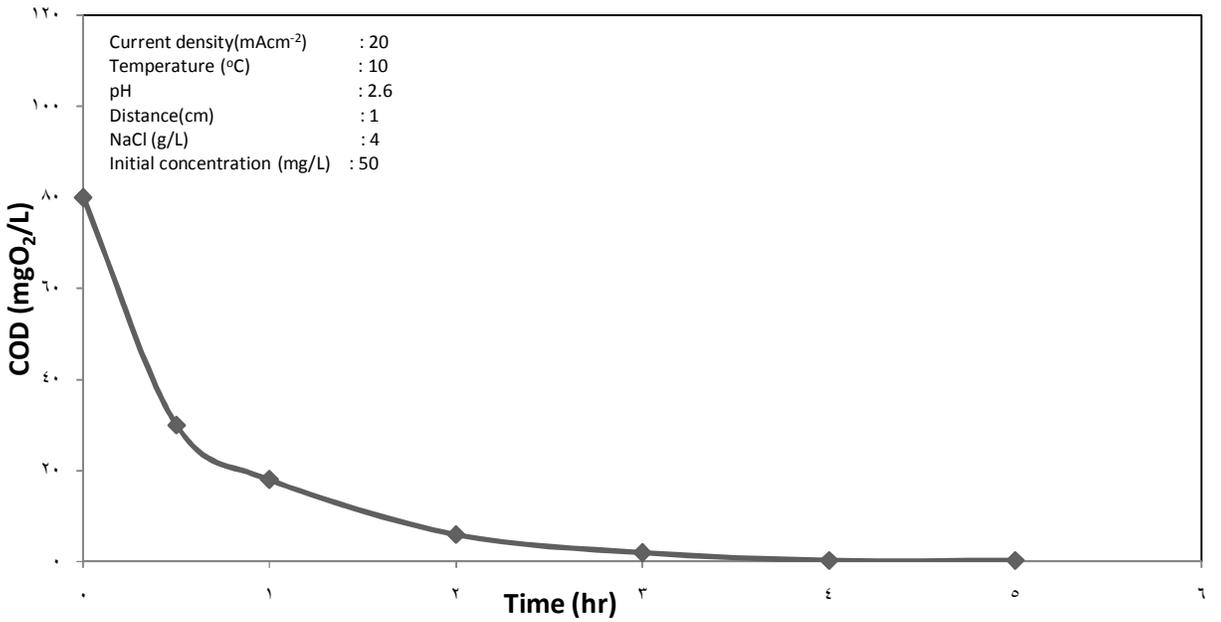
Fig (54): Effect of electrolysis time on the COD removal of picric acid using C/PbO₂ electrode.
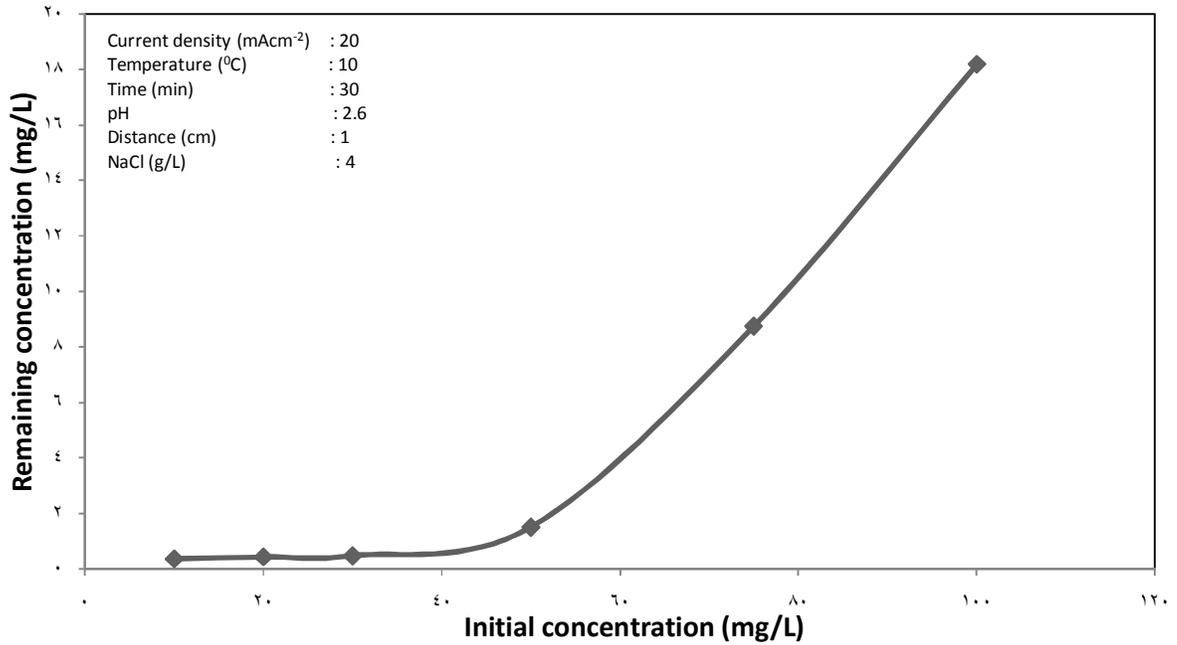
Current density (mAcm⁻²) : 20
Temperature (⁰C) : 10
Time (min) : 30
pH : 2.6
Distance (cm) : 1
NaCl (g/L) : 4

Fig (55): Effect of initial concentration on the removal of picric acid using Pb/PbO₂ electrode.

Current density (mAcm⁻²) : 20
Temperature (⁰C) : 10
Time (hr) : 5
pH : 2.6
Distance (cm) : 1
NaCl (g/L) : 4
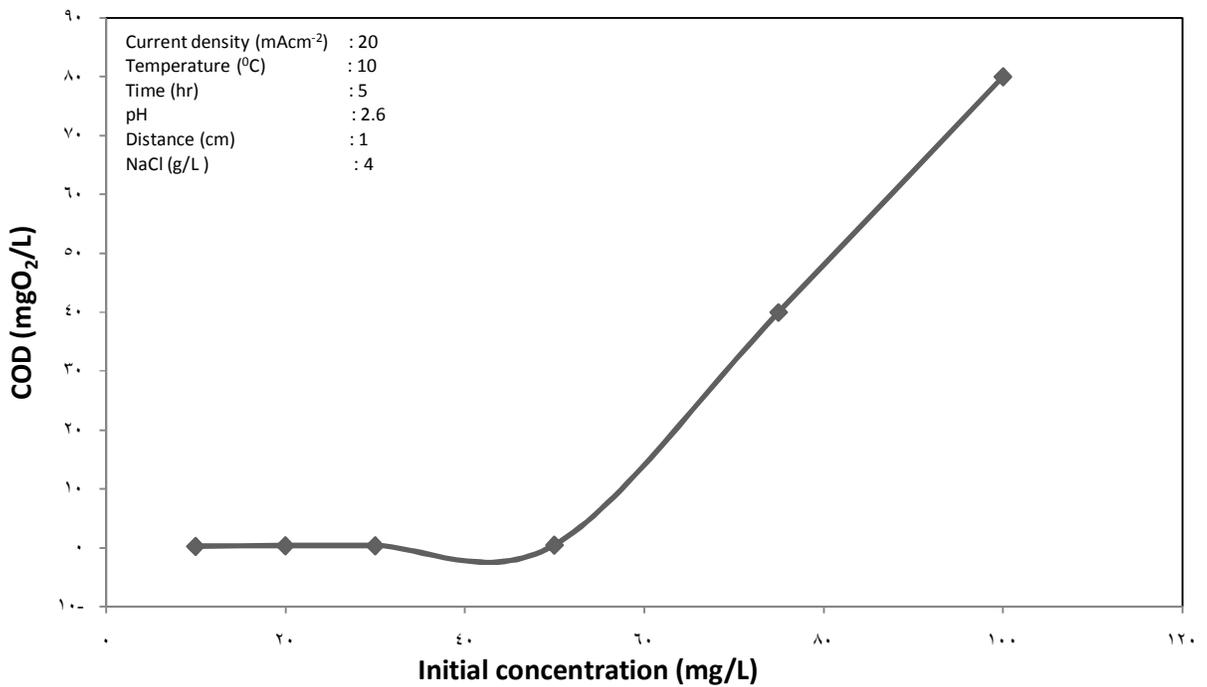
Fig (56): Effect of initial concentration on the COD removal of picric acid using Pb/PbO₂ electrode .
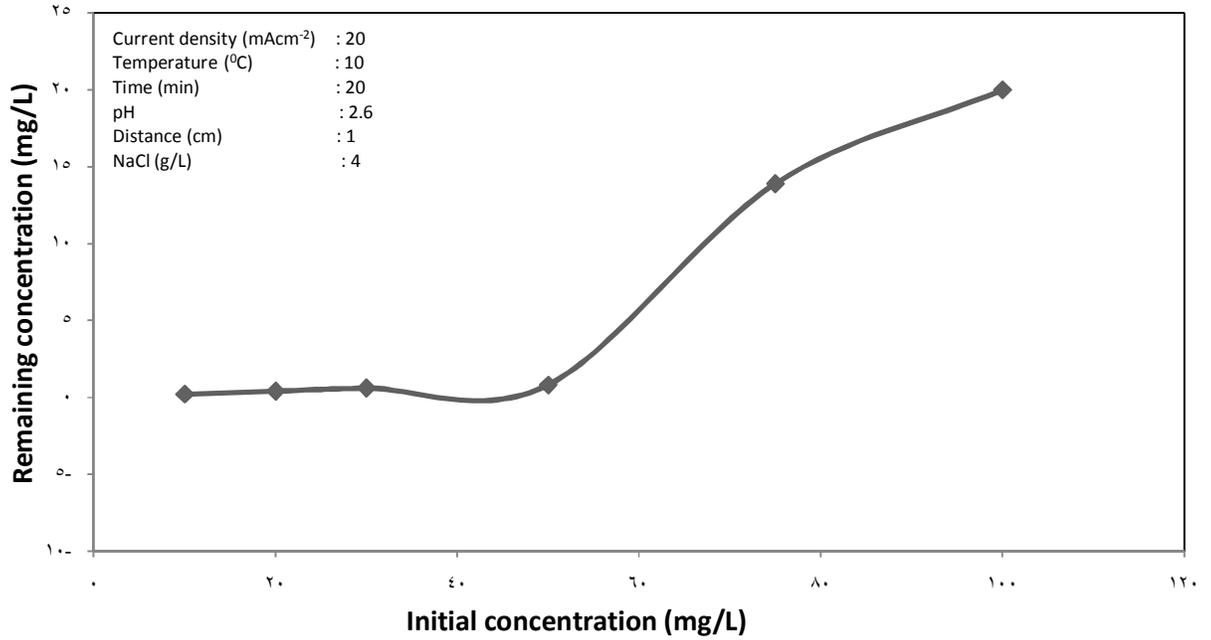
Fig (57): Effect of initial concentration on the removal of picric acid using C/PbO2 electrode.
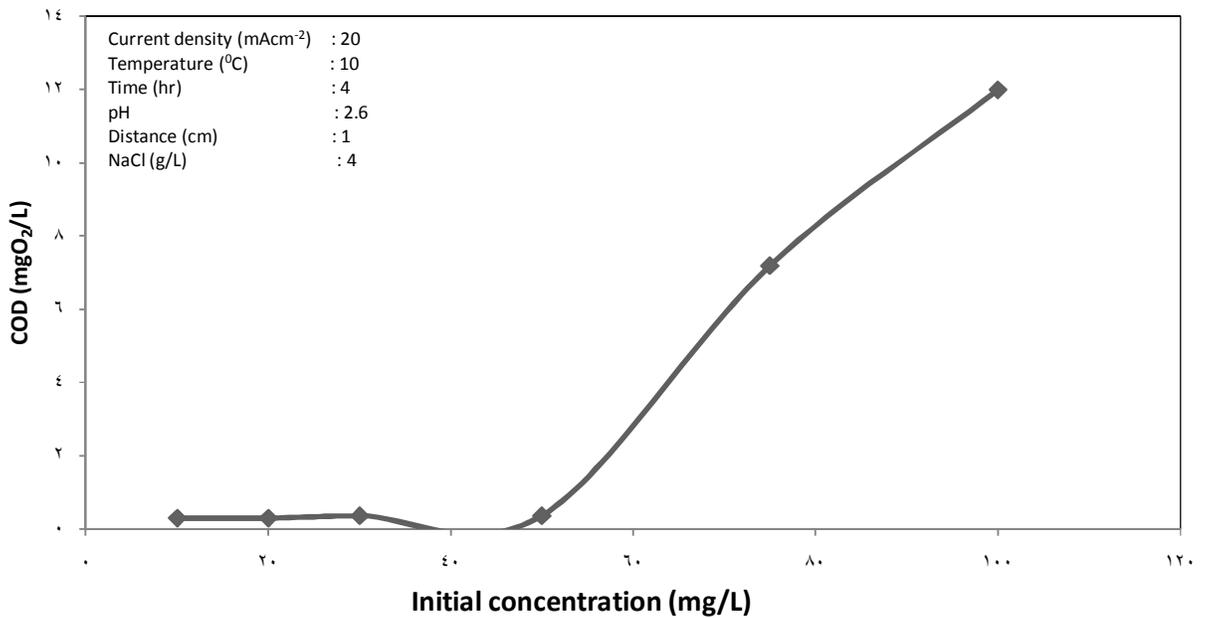
Fig (58): Effect of initial concentration on the COD removal of picric acid using C/PbO$_2$ electrode .
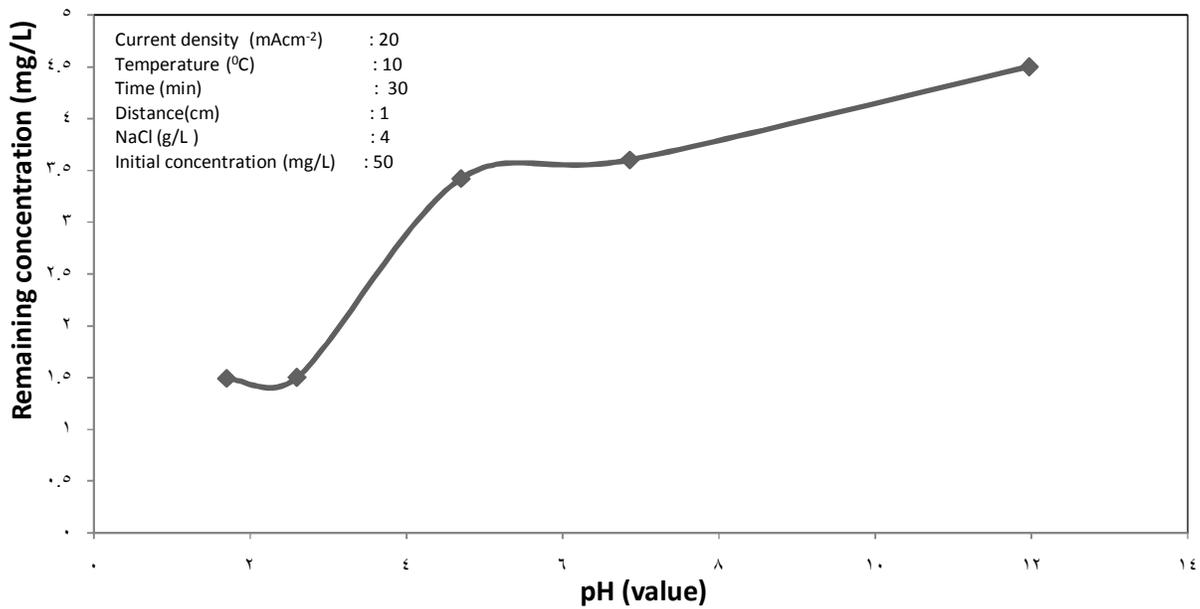
Fig (59): **Effect of pH on the removal of picric acid using Pb/PbO$_2$ electrode.**
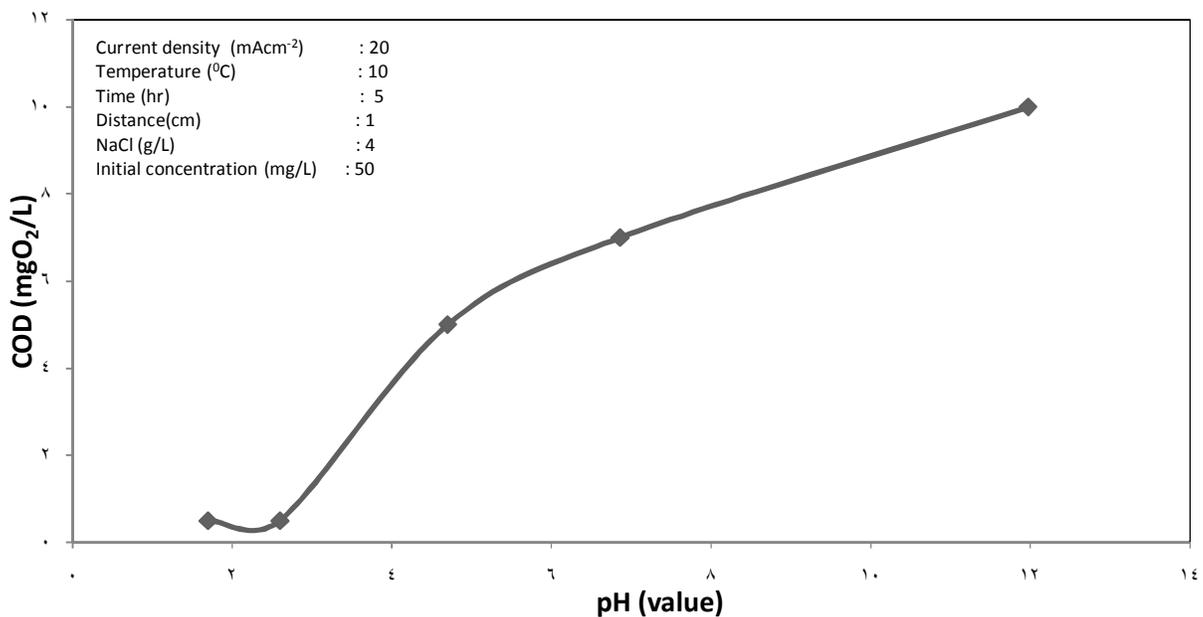
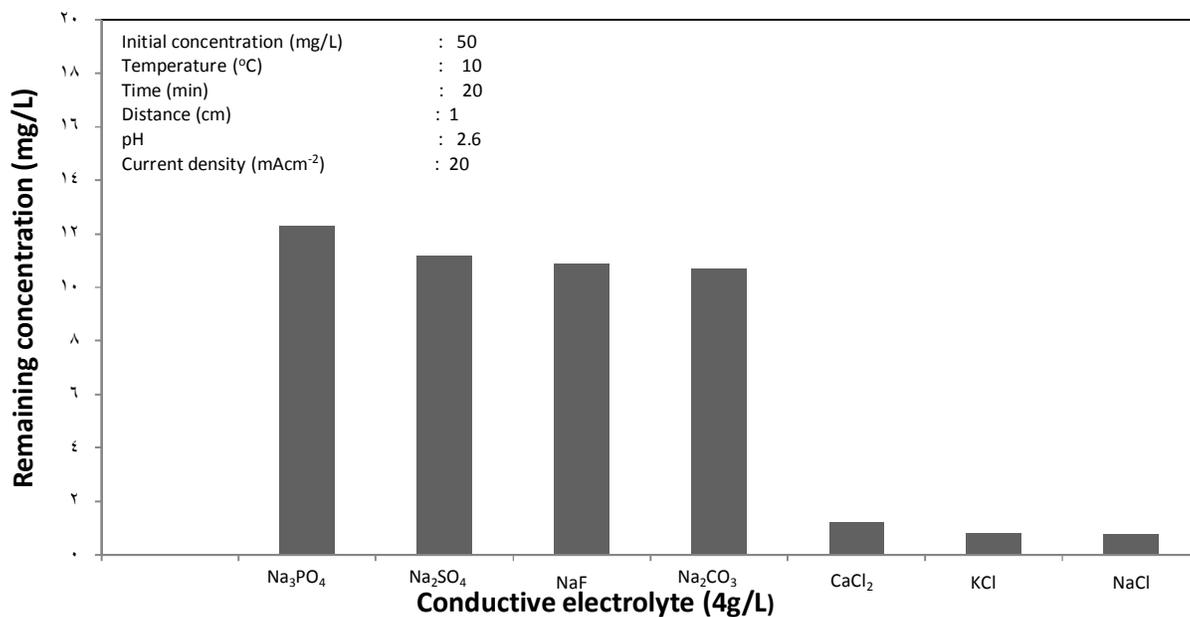**Fig (60): Effect of pH on the COD removal of picric acid using Pb/PbO$_2$ electrode.**
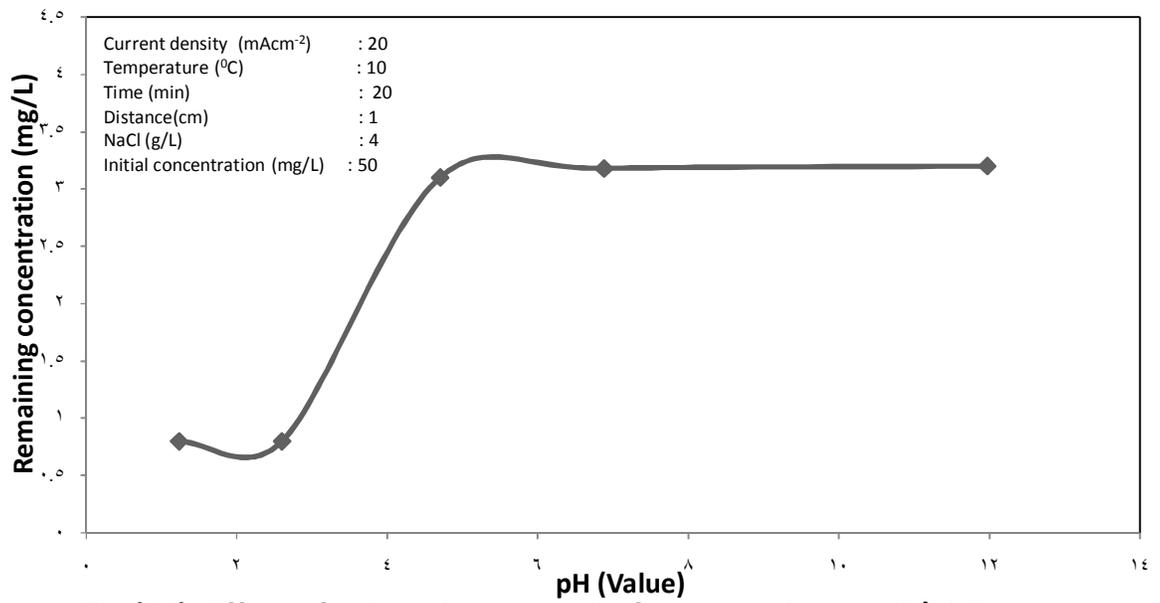
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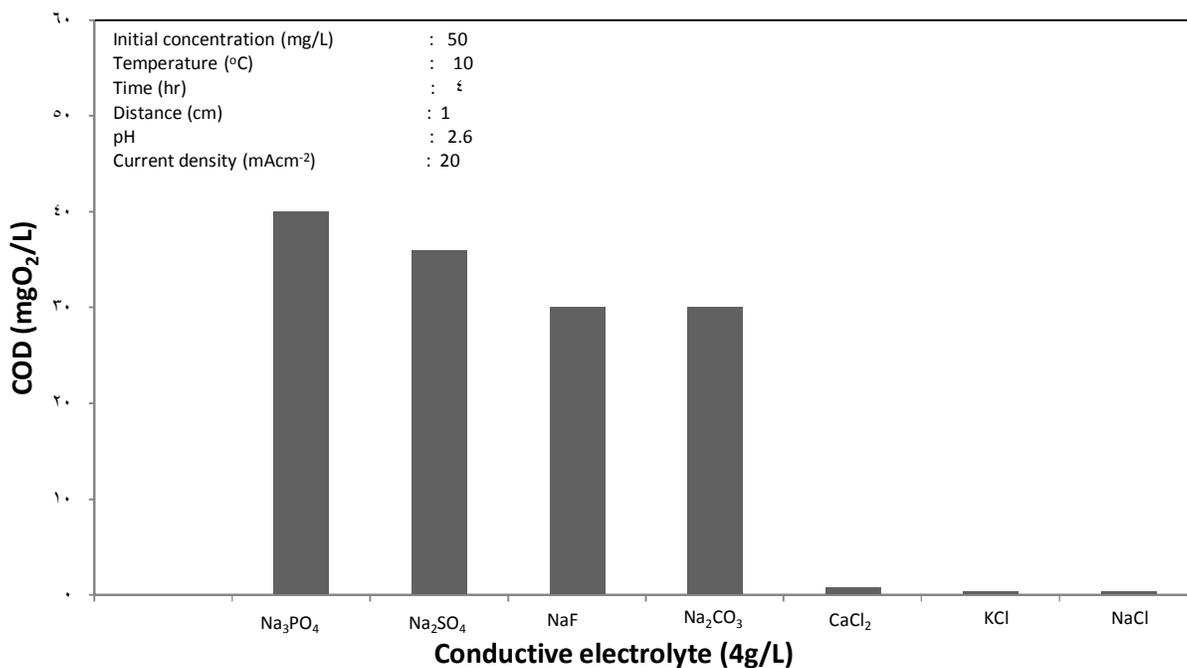**Fig (61): Effect of pH on the removal of picric acid using C/PbO$_2$ electrode.**
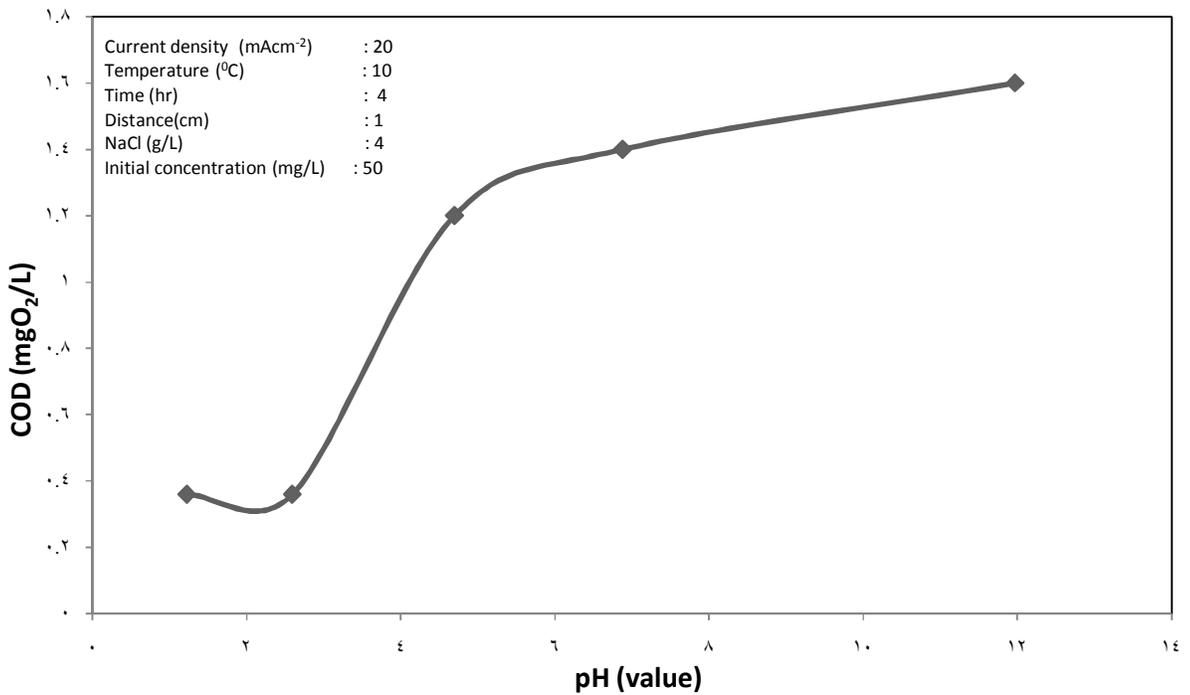
Current density (mAcm^{-2}) : 20
Temperature (^{0}C) : 10
Time (min) : 20
Distance(cm) : 1
NaCl (g/L) : 4
Initial concentration (mg/L) : 50

Fig (62): Effect of pH on the COD removal of picric acid using C/PbO$_2$ electrode.

Current density (mAcm^{-2}) : 20
Temperature (^{0}C) : 10
Time (hr) : 4
Distance(cm) : 1
NaCl (g/L) : 4
Initial concentration (mg/L) : 50

65
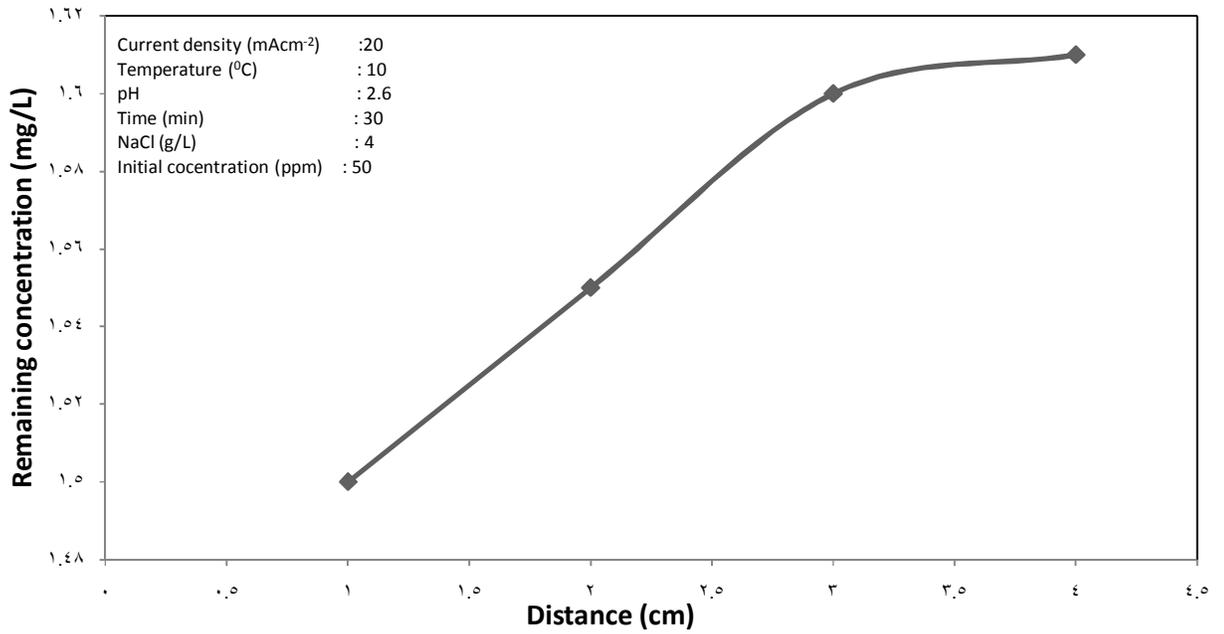
Fig (63): Effect of distance between the two electrodes on the removal of picric acid using Pb/PbO₂ electrode.
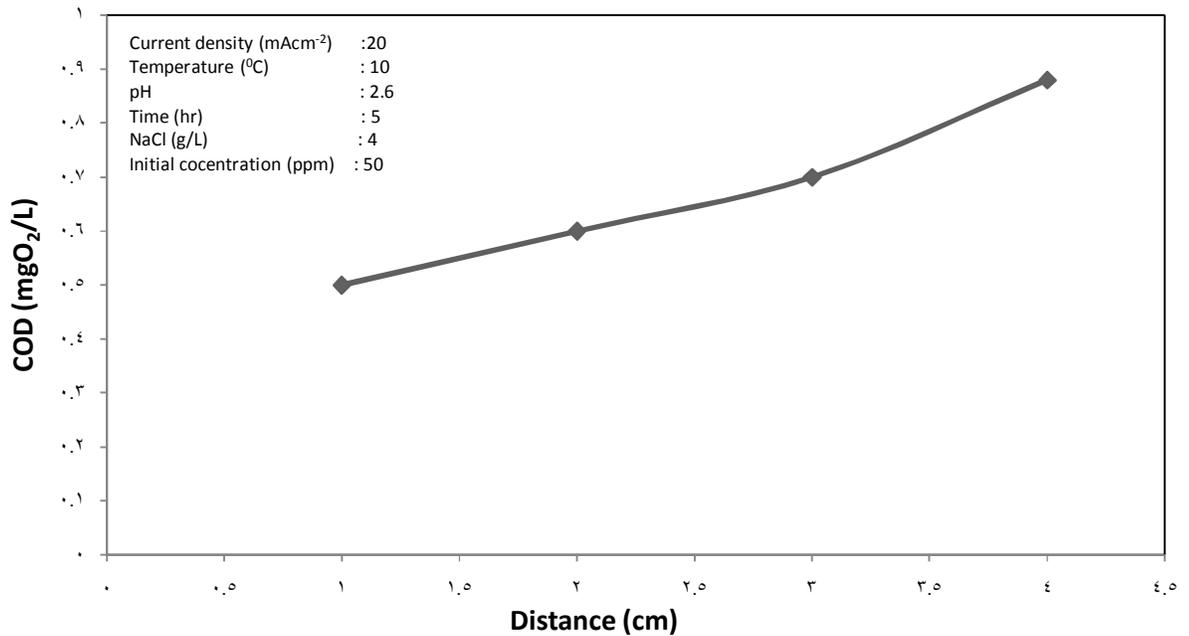
Fig (64): Effect of the distance between the two electrodes on the COD removal of picric acid using Pb/PbO₂ electrode.
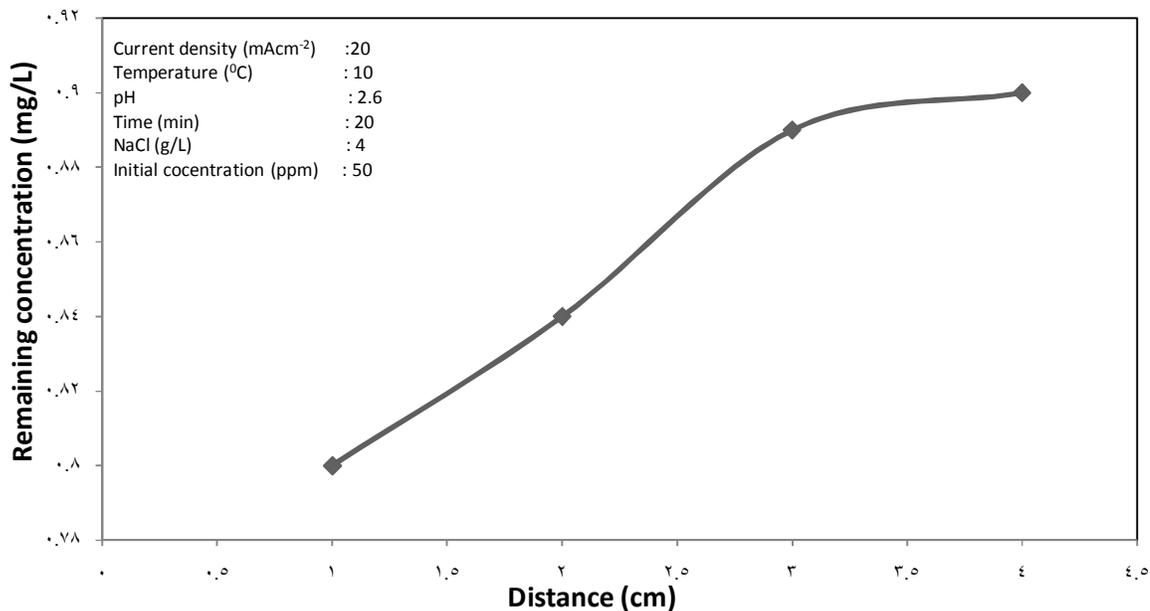
Fig (65): Effect of distance between the two electrodes on the
removal of picric acid using C/PbO$_2$ electrode.
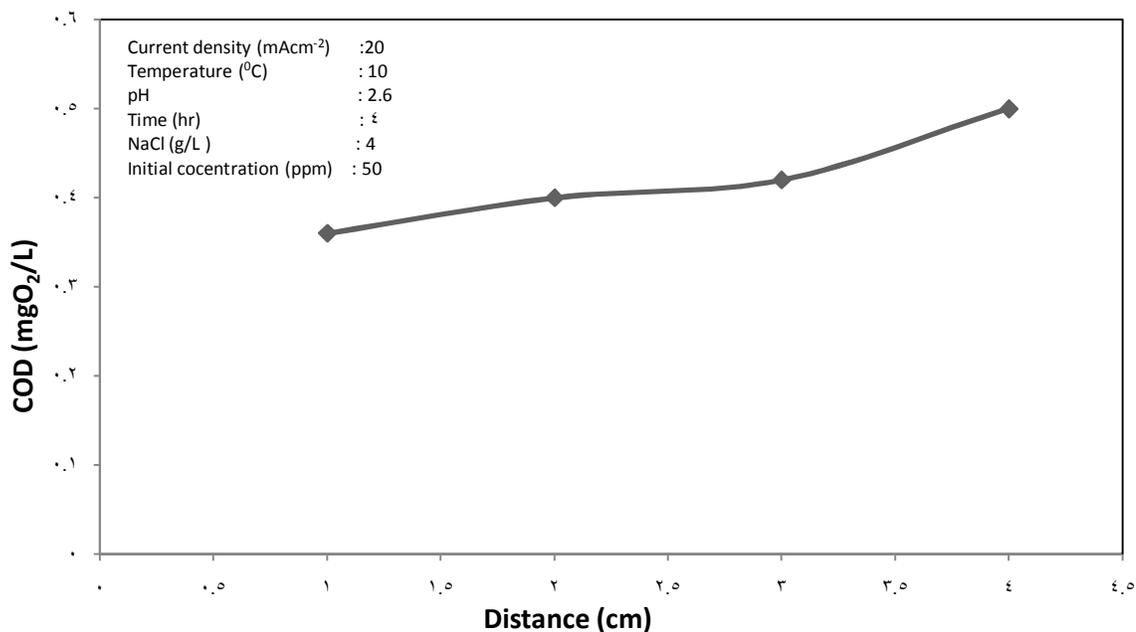
Fig (66): Effect of the distance between the two electrodes on
the COD removal of picric acid using C/PbO$_2$ electrode.
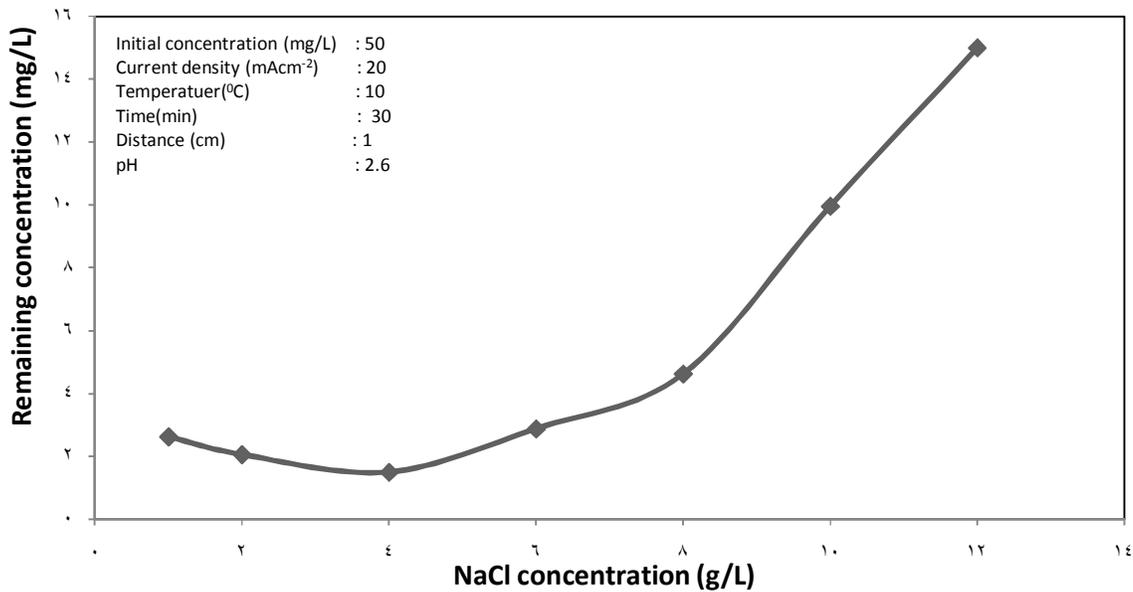
Fig (67): Effect of NaCl concentration on the removal of picric acid using Pb/PbO₂ electrode.
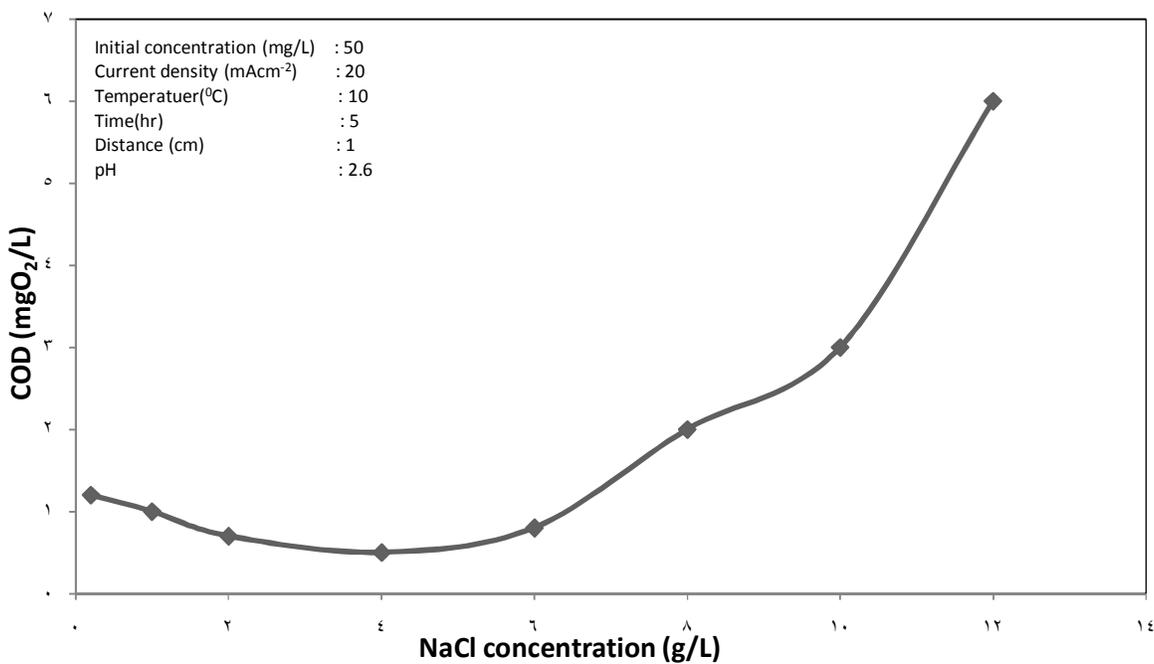
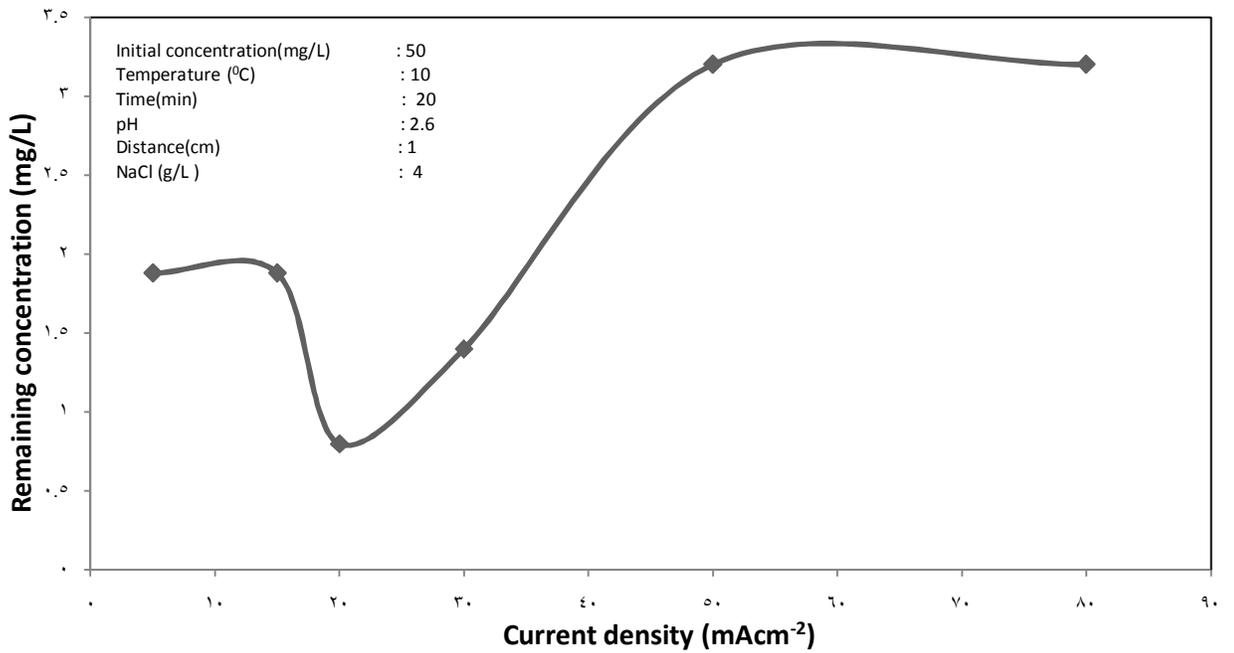**Fig (68): Effect of NaCl concentration on the COD removal of picric acid using Pb/PbO₂ electrode.**

68
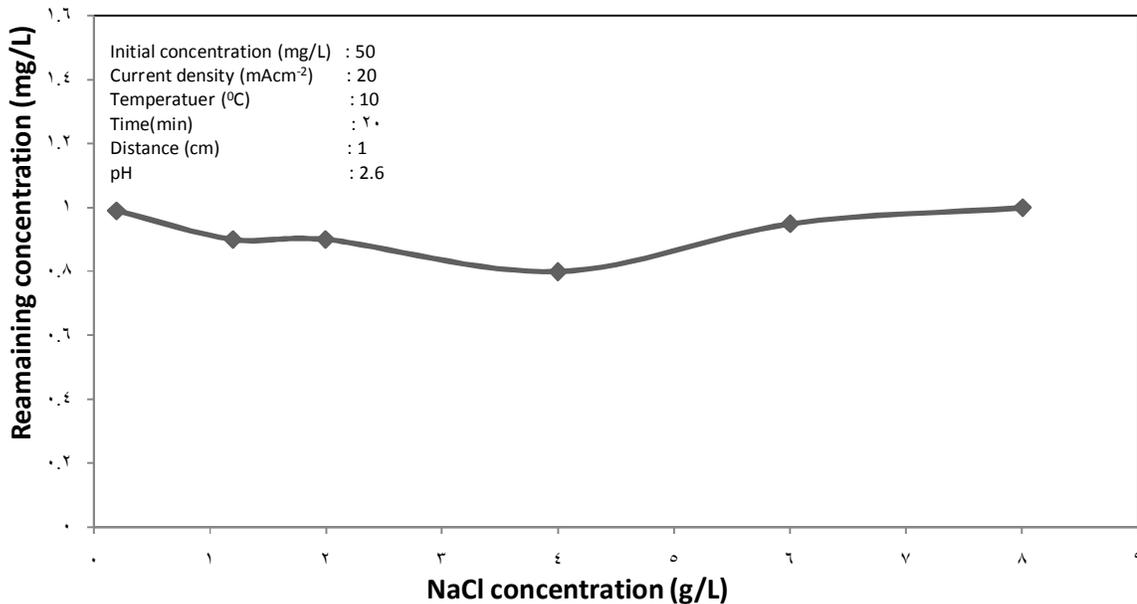
Fig (69): Effect of NaCl concentration on the removal of picric acid using C/PbO₂ electrode.
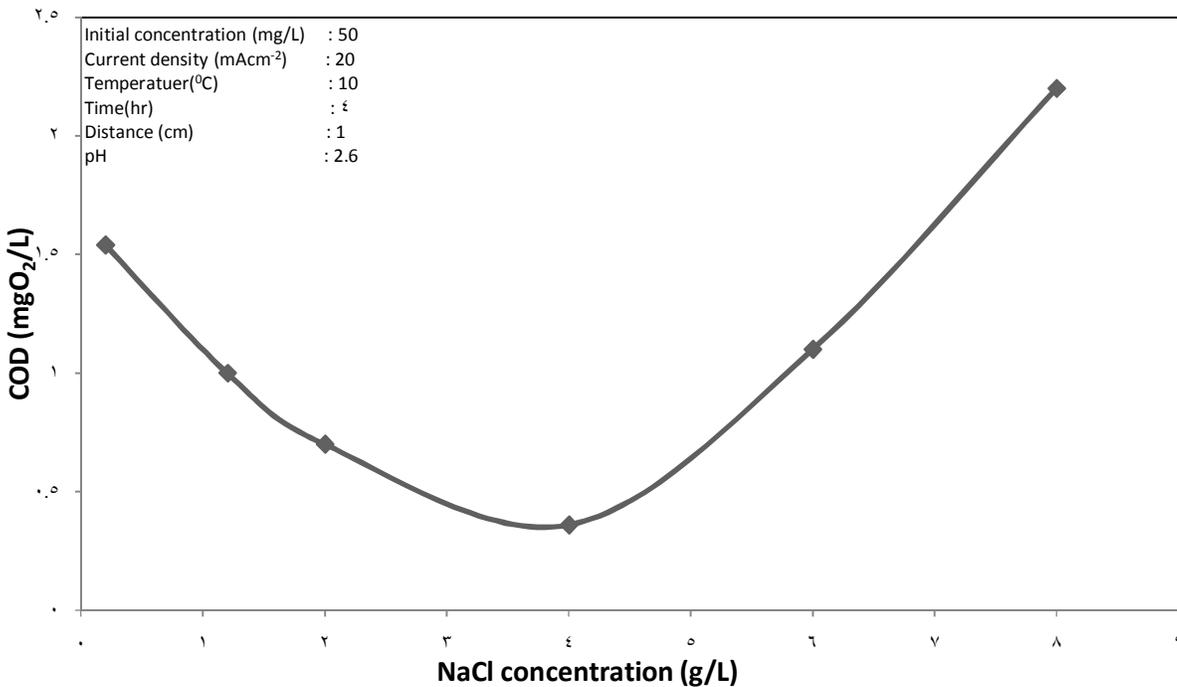

**Fig (70): Effect of NaCl concentration on the COD removal of picric acid using C/PbO₂ electrode.**

CHAPTER "FOUR"

DISCUSSION

4. Discussion

The different reactions of sodium hypochlorite production occurring at the electrodes and in the bulk solution are described in various reviews [123,124].

Primary reactions

$$\text{at the anode}: 2Cl^- - 2e^- \rightarrow Cl_2 \ (1)$$

$$\text{at the cathode}: 2H_2O + 2e^- \rightarrow 2OH^- + H_2 \ (2)$$

$$\text{In the bulk}: Cl_2 + 2H_2O \leftrightarrow HClO + Cl^- + H_3O^+ \ (3)$$

$$HClO + H_2O \leftrightarrow ClO^- + H_3O^+ \ (4)$$
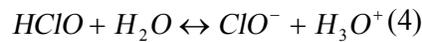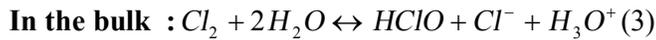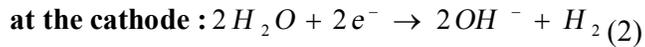
The equilibrium constants for the two reversible reaction are 4×10^{-4} mol^2 L^{-2} and 3×10^{-8} mol^{-1}, respectively, at 25^0C [125].

Side reaction

$$\text{at the anode}: 6ClO^- + 3H_2O - 6e^- \leftrightarrow ClO_3^- + 4Cl^- + H^+ + \frac{3}{2}O_2 \ (5)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (6)$$

$$\text{At the cathode}: \quad ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \qquad (7)$$

$$\text{In the bulk}: 2HOCl + ClO^- \rightarrow ClO_3^- + 2Cl^- + 2H^+ \qquad (8)$$

$$2ClO^- \rightarrow 2Cl^- + O_2 \qquad (9)$$
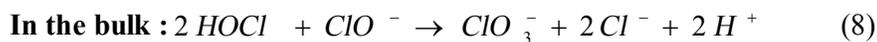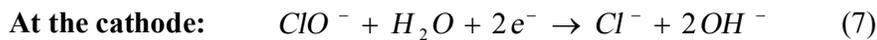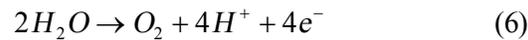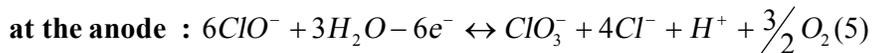
Figs. (1 and 2)show that the effect of conductive electrolyte on the production of sodium hypochlorite production on Pb/PbO$_2$ and C/PbO$_2$ electrodes. It

is clear from the above Figs that the highest sodium hypochlorite was obtained in the presence of NaCl. This indicated that the NaCl is the most effective electrolyte on sodium hypochlorite generation. Theobserved behavior may be due to the small ion size of Na^+ which increase the ion mobilities. From the above Figs, it is clear that the (Na_2CO_3, NaF, Na_3PO_4, and Na_2SO_4) reduce the sodium hypochlorite production.This behavior may be related to the formation of an adherent film on the anode surface which poisoned the electrode process. Also the a forementioned electrolytes do contain chloride ions which is the main source of OCl^-. $CaCl_2$ is less effective electrolyte than NaCL in sodium hypochlorite production. This may be duo to formation of insoluble calcium hypochlorite $Ca(OCl)_2$.

In electrochemical reactions, production is based on quantity of current passed, as per Faraday's first law of electrolysis. In Industry, the passed current passed is usually reported in terms of current density which denotes the current passed per unit electrode area. As current density is increased, hypochlorite production also increases. However cell temperature increases with increasing current density. Above a temperature 35^oC, sodium hypochlorite tends to chemically decompose to sodium chlorate.

$$3\,NaClO \rightarrow NaClO_3 + 2\,NaCl \qquad\qquad (10)$$

So when temperature raise higher than 35^oC, production of NaClO falls. Figs. 3 and 4, 15 and 16, 27 and 28 show that the concentration of NaClO increases up to $1Acm^{-2}$, but at higher current densities the concentration decreases due to increase in temperature. In other words, the rate of hypochlorite decomposition increases with increase in current density. Optimum current density is1 $A.cm^{-2}$, at which maximum concentration of hypochlorite is obtained. That maximal quantities of hypochlorite can be obtained for the corresponding maximal concentration of the initial NaCl and for current values in the studies range of these parameter as shown in Figs. (9 and 10). The analysis of the model shows that the influence of the chloride concentration is stronger than that of the current density. This can be explained taking into consideration that with the increase of both the chloride concentration and the current, the first parameter acts in higher degree on the current efficiency of the process of hypochlorite generation. In this case the influence of the sodium chloride concentration is much stronger too. The concentration increase provokes a decrease of the solution resistance. The current efficiency for the product increases, too. The

current influence is a result of the applied factors. From one side, the current efficiency increases, as well as the voltage of the electrolysis cell increases and the energy consumption. It is evident that the decrease of the energy consumption due to the increased current efficiency [26]

So when temperature goes above 35°C, production of NaClO falls. The current efficiency of hypochlorite production as a function of current density, the current efficiency initially increases with increasing current density and thereafter decreases. The maximum current efficiency occurs at about 1 A cm^{-2}. The current efficiency of C/PbO$_2$ electrode is much higher than that of a Pb/PbO$_2$ electrode. It is important to note that the C/PbO$_2$ electrode possesses the highest current efficiency.

The sodium hypochlorite production rate depends on temperature [77].There was reduction in the sodium hypochlorite production rate between 23 and 30 °C. Over this small temperature range, the sodium hypochlorite production rate was lowered and sodium hypochlorite tends to chemically decompose to sodium chlorate at 35°C[26]. It is clear from the above Figs. (5 and 6, 17 and 18, 29 and 30) that the optimum temperature of sodium hypochlorite production was 10 °C for Pb/PbO$_2$ and C/PbO$_2$ electrodes. At low temperature, the losses of chlorine gas decreases, so the sodium hypochlorite is increased.

Figs. (9 and 10, 21 and 22, 33 and 34) show the generation of sodium hypochlorite from sodium chloride solution, sea water and brine water on Pb/PbO$_2$ and C/PbO$_2$ electrodes. It is clear from the above Figs. that the sodium chloride solution was more sufficient than sea water and brine water for production of sodium hypochlorite due to the presence of Ca^{+2} and Mg^{+2} ions in sea and brine water. The reduction of hypochlorite can be limited by the formation of scale made of magnesium and calcium hydroxides [Mg(OH)$_2$ and Ca(OH)$_2$] [47]. The accumulation of scale in undivided cells may have two effects: on the positive side it can reduce or inhibit hypochlorite reduction at the cathode, but on the negative side, it can also increase the energy consumption of the cell and passivates the electrode. While a thin film of scale can be an advantage for the current efficiency, an excessive growth can be a drawback.

The dependence of the sodium hypochlorite production rate on the chloride ion concentration for chloride concentrations up to 20g/L at 10 °C and with a current density of 1 Acm^{-2} is shown in Figs. (9 and 10). It can be seen that the sodium

hypochlorite production rate on Pb/PbO$_2$ and C/PbO$_2$ increases with increasing NaCl concentration. [77]

By further increasing of the chloride concentration, even the absolute difference in the sodium hypochlorite production rate between the two materials cannot be changed for both Pb/PbO$_2$ and C/PbO$_2$ electrodes as present in the above Figs. [77]

Figs. (11 and 12, 23 and 24, 35 and 36) show that the efficiency rate of sodium hypochlorite generation increased as the pH value increasing in both Pb/PbO$_2$ and C/PbO$_2$ electrodes. The basic medium initiated the absorption of chlorine which produced on the anode, and then the percentage of hypochlorite will be increased because the reaction between chlorine and NaOH will produce sodium hypochlorite (NaOCl) according to the following reaction:

$$NaOH + Cl_2 \rightarrow NaOCl + Cl^- + H^+ \quad (11)$$

Further, basic medium decreases the losses of chlorine gas which is produced on the anode and this also increases the percentage of sodium hypochlorite. The most stable sodium hypochlorite solutions are those at pH between 11.5 and 13; [68]

Figs. (13 and 14, 25 and 26, 37 and 38) show the effect of distance between the cathode and anode on the sodium hypochlorite production in Pb/PbO$_2$ and C/PbO$_2$ electrodes. It is clear that the sodium hypochlorite production increase with decreasing distance down to 1cm. An increase in distance between cathode and anode was to increase the electrolyte ohmic potential drop, and hence the cell voltage [50]. The highest hypochlorite production was achieved with narrow distance between the cell electrodes of 1cm.

Allsodium hypochloritesolution showed degradation versus time.However, this degradation occurred very slowly in dark at 25°C and in dark at 4°C for both hypochlorite solution using Pb/PbO$_2$ and C/PbO$_2$ electrodes. They solutions stored at 4°C and 25°C in dark showed satisfactory stability at 60 days as show in table (1)

Time	Concentration of NaOCl production on C/PbO$_2$(%)			Concentration of NaOCl production on Pb/PbO$_2$(%)		
	4°c in dark	25°c in light	At 25°C dark	4°c in dark	25°c in light	At 25°C dark
0 Day	100	100	100	100	100	100
1 Day	100	96.6	99.9	100	81.5	99.9
5 Days	100	80.1	97.79	100	75.8	97.7
8 Days	100	79.92	97.4	99.7	47.67	95.3
16 Days	99.5	68.19	95.4	99.5	35	95
26 Days	99.5	27.5	94.2	97.3	15	94.6
36 Days	99.6	12.8	94.2	96.9	10.3	94
50 Days	97.4	5.14	94.1	95.3	4.2	93.8
60 Days	96.8	1.8	94	94.8	1.5	93.1

Table 1. Stability of sodium hypochlorite prepared on Pb/PbO$_2$ and C/PbO$_2$ at different condition (temperature and light).

odium hypochlorite solutions at 25°C in light showed nearly complete degradation reaching to 1.8% for sodium hypochlorite prepared using C/PbO$_2$ electrode and 1.5% for sodium hypochlorite prepared using Pb/PbO$_2$ electrode.

The results of studying the possibility of using different electrodes in the treatment of picric acid and COD removal were presented in Figs (39-70). These include: Pb/PbO$_2$ and C/ PbO$_2$ modified electrodes, which prepared in the present work. These electrodes were used as anodes in the electrocatalytic oxidation process. The remaining concentration (mgL^{-1}) and COD removal (mgO$_2$L^{-1}) were determined. 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. From the results of these studies the optimum operating conditions for each electrode were determined. At these conditions, the electrodes are more efficient at the optimum results for the

removal of both picric acid and COD. The percentages of degradation for each electrode were represented in the table (2).

Type of electrode	Remaining concentration of picric acid at 20 min	COD removal at 4 hr
Pb/PbO$_2$	87.54	80
C/PbO$_2$	98.4	99.4

.

Table 2. Percentage of COD and concentration removal of picric acid on Pb/PbO$_2$ and C/PbO$_2$ electrodes

Electrochemical oxidation of many organic pollutants in aqueous solutions on anode could 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[126].

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 formation of hydroxyl radicals according to [127]:

$$MO_x + H_2O \xrightarrow{\ k1\ } MO_x[OH^*] + H^+ + e^- \qquad (12)$$

The produced hydroxyl radicals can, be oxidized to a higher state forming the so-called higher oxide:

$$MO_x[OH^*] \xrightarrow{\ k2\ } MO_x[O] + H^+ + e^- \qquad (13)$$
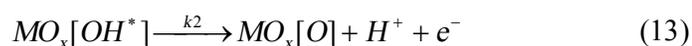
The role of the formed higher oxide is the participation in the formation of selective oxidation of the organic pollutants (R) without complete incineration:

$$MO_x[O] + R \xrightarrow{k3} RO + MO_x \qquad\qquad (14)$$
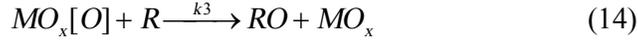
The above route can take place only if the transition of the underlying oxide to a higher oxidation state occurred. The electrodes of this class arecalled "active electrodes". However, if the product of equation (14) is not obtained the electrogenerated hydroxyl radicals could directly oxidize the organic compound to carbon dioxide and water, redominantly cause the combustion of the organic compound through hydroxylation of these compounds:

$$MO_x[OH^*] + R \xrightarrow{h4} O_x + mCO_2 + nH_2O + H^+ + e^- \qquad\qquad (15)$$
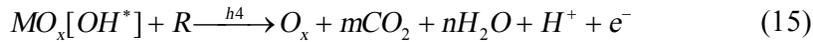
And this class of electrodes are called "non-active electrodes"

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 according to equation (1) [128]. However, PbO_2 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 [129]. While unhydrated electrodes such as boron doped diamond, which iswell-known to have weak adsorption properties due to its inert surface. In this type of electrodes, the hydroxyl radicals are very weakly 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" electrogeneration 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 beused such as Fenton's reagent [129] and ozone [130], the hypochlorite ion is the most widely employed oxidant in wastewater treatment [129]. 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 a node surface according to the following [131] :

$$2Cl^- \xrightarrow{\ k5\ } Cl_2 + 2e^- \qquad\qquad (16)$$
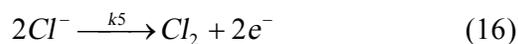
The second step is formation of hypochlorous acid:

$$Cl_2 + H_2O \xrightarrow{\ k6\ } HClO + Cl^- + H^+ \qquad\qquad (17)$$

The HClO undergoes dissociation into hypochlorite and hydrogen ions:

$$HClO \xrightarrow{\ k7\ } ClO^- + H^+ \qquad\qquad (18)$$
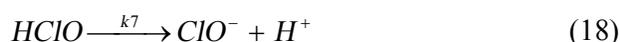
It was reported [118] that the reaction between the hydroxyl radical (OH^*) and picric acid gives the following products: Phenol,benzoquinone, maleic, and oxalic acid. Also the product is converted   to water and CO_2 .

Figs (39-42)   show the effect of conductive electrolyte on degradation of picric acid using Pb/PbO_2 and C/PbO_2 electrodes . From these Figures it is clear that the less value of remaining concentration and COD was obtained in presence of NaCl. This indicate   that NaCl is the most effective electrolyte in electrodegradation of wastewater. The OCl^- anion is a powerful oxidizing agent. It enhances the degradation of pollutants. Therefore, addition of NaCl provide the effective Cl^- ion which intern the main source for formation of OCl^- ion. From the above Figs. NaCl is considered as the most preferential electrolyte. This observed behavior may be due to the small ion size of Na^+ which increases the ion mobilities.

From the above Figs. it is clear that the less effective electrolytes in the degradation of pollutant are Na_2SO_4 and Na_3PO_4. this behavior may be attributed to formation of an adherent film on the anode surface which poisoned the electrode process surface. Also these electrolytes does not contain chloride ion which is the main source of OCl^-. Also those electrolytes may form stable intermediate species that

could not be oxidized by direct electrolysis. These observations were confirm in other studies [132].

Also from those Figs. it is clear that NaF and Na_2CO_3 have an intermediate effect on the rate of degradation of pollutantsbecause contain effective ion (Cl^-), While the electrodegradation of pollutants may be occurred through electrocatalytic oxidation in the presence of these electrolytes.

It is well known that the rate of diffusion of ions increases with increasing temperature. In the present work, it was found that the remaining concentrations have the smallest value at 5 and 10^oC for picric acid as shown in Figs (47- 50). From these figures, it is clear that the increasing of remaining concentration and COD above 35^oC may be attributed to decomposition of adsorbed film on anodic side. Also, the electrode is unstable at high temperature above 40^oC.

In this study, it was found that the of electrocatalytic oxidation of picric acid increased with decreasing pH value of solution as shown in Figs (59-62). In acidic medium the hypochlorite will liberate Cl_2 gas which is considered as the active species for the degradation of organic compound as in eq(19).

$$HClO + H^+ + Cl^- \rightarrow Cl_2 + H_2O \qquad (19)$$

In the present work the electrodegradation were carried out at low current densities (20-40mAcm^{-2}). At these values there are great possibility of electrogeneration of Cl_2 and OCl^- in solution [133]. Also it was reported that any increases in current densities (above 40 mAcm^{-2}) will promote formation of oxygen as shown in equation (8).

$$MO_x[OH^*] \xrightarrow{\ k8\ } MO_x + \tfrac{1}{2}O_2 + H^+ + 2e^- \qquad (20)$$
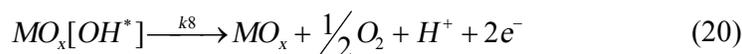
All these observations were depicted in figures (43- 46).

The electrical properties of PbO_2 (resistivity as low as 40 to 50×10^{-10} ohm cm) show that it is a better electrical conductor than many metals and a much better conductor than carbon or graphite and this make the efficiency for doped PbO_2 is not complete in case of C/PbO_2 modified electrode [134].

From Figs (39-70). It is found that the C/PbO_2 electrode was more than Pb/PbO_2 effective modified electrode in the degradation of picric acid.

These behavior may be attributed to the color and structure of electrodes. C/PbO_2 modified electrodes have a black color, while Pb/PbO_2 modified electrode has a brown color. It was reported that PbO_2 film has two structures, α-structure (brown

color) and β-one (black color) [135]. The black one has a tetrahedral crystal structure which is a close-packed structure more disorder by comparing with the close-packed structure of the brown α-form (orthorhombic). Therefore, the surface area in case of tetrahedral structure is more than orthorhombic one, then the β- PbO_2 form will be more effective than α- PbO_2 form. This is established by the ability of perchlorate production through doped β- PbO_2 electrodes while this hindered in case of doped α-PbO_2 electrodes [136]. That because the overpotential for oxygen evolution of β-PbO_2 is more than that of α-PbO_2. We can expect that the electrocatalytic properties for C/PbO_2 modified electrodes more efficient than Pb/PbO_2 modified electrode [137].

The energy by kWh that consumed in the electrodegradation by using the modified electrodes (C/PbO_2 and Pb/PbO_2) was calculated using equation

Table 3. represent the efficiency of $Pb/PbO_2$and C/PbO_2electrodes on sodium hypochlorite generation and electrical energy consumption from sodium chloride solution, sea water and brine water. It is clear that the C/PbO_2has more efficientthan Pb/PbO_2 in the generation of sodium hypochlorite and the less in energy consumption.

The electrical energy that consumed for sodium hypochlorite and picric acid degradation using Pb/PbO_2 and C/PbO_2 electrodes was calculated by the following equation :

Electrical Energy consumed=IEt/1000×3600

Where I is the applied current (A), E is the voltage (V) of electrolytic cell, t is the electrolytic time (min.), and V is the volume (L) of electrolytic solution [21].

Electrode	Percent yield in NaCl solution	Cost	Percent yield in sea water	Cost	Percent yield in brine water	Cost
C/PbO$_2$	80	4.8×10^{-4}	31.35	1.8×10^{-2}	29.7	2.4×10^{-4}
Pb/PbO$_2$	69.2	7.2×10^{-3}	17.1	0.48	9.2	7.9×10^{-3}

Table 3. Percent yield of Pb/PbO$_2$ and C/PbO$_2$ electrodes on sodium hypochlorite generation and cost in Dollar from sodium chloride solution, sea water and brine water.

The yield of sodium hypochlorite using Pb/PbO$_2$ and C/PbO$_2$ electrodes was 2% compared with 0.8% of sodium hypochlorite generated using dimensional stable anode (ruthenium and iridium oxide on titanium substrate) so, the Pb/PbO$_2$ and C/PbO$_2$ electrodes is more efficient in generation of sodium hypochlorite than dimensional stable anode.The C/PbO$_2$ electrode is cheaper than dimensional stable anode ,ruthenium electrode.The C/PbO$_2$ electrode is higher anti corrison than platinum electrode [43].

The electrodes of C/PbO$_2$and Pb/PbO$_2$ were preparation by electroplating and anodization respectively , but dimensional stable anode preparation was thermal decomposition.

The degradation of picric acid was nearly completed (99% and 87.5%) using C/PbO$_2$ and Pb/PO$_2$ electrodes on 20-30 min respectively, while the degradation completed (90%) using Fentons reagent and H$_2$O$_2$ in 60 min [113].

5- Conclusion

In this study a modified Pb/PbO_2 and C/PbO_2 electrodes were prepared by the electro deposition of lead oxide layer on lead and carbon substrate.

These modified electrodes were used as anodes for generation of sodium hypochlorite (NaOCl) from sodium chloride solution, sea water and brine water. The results of this study revealed the following :

- C/PbO_2 electrode is more efficient in generation of sodium hypochlorite than Pb/PbO_2 electrode in sodium chloride solution, sea water and brine water.

- The yield of sodium hypochlorite using Pb/PbO_2 and C/PbO_2 electrodes was 2% compared with 0.8% of sodium hypochlorite generated using dimensional stable anode (ruthenium and iridium oxide on titanium substrate) so, the Pb/PbO_2 and C/PbO_2 electrodes is more efficient in generation of sodium hypochlorite than dimensional stable anode.

- C/PbO_2 is cheaper than dimensional stable anode ,ruthenium electrode.

- C/PbO_2 is higher anti corrison than platinum electrode.

- The generation of sodium hypochlorite depends on the conductive electrolyte.

- The highest activity for production of sodium hypochlorite was achieved in the presence of NaCl (20g/L).

- In basic media (pH>10), the generation efficiency of sodium hypochlorite production increased on both Pb/PbO_2 and C/PbO_2.

- As the current density increased, the hypochlorite production increased up to a maximum (1A cm^{-2}).

- The efficiency of sodium hypochlorite production increased on low temperature (5-10°C).

- The percent yield of sodium hypochlorite generation increased as the distance between the cathode and anode decreased (1cm).

- The sodium chloride solution was more effeicient than sea water and brine water for production of sodium hypochlorite on both electrodes due to the presence of Ca^{+2} and Mg^{+2}ions in sea and brine water.

In this work, the modified Pb/PbO_2 and C/PbO_2 electrodeswere used as anodes for electrocatalytic oxidation of picric acid in aqueous solution.

The results of this study revealed the following :

- The electrocatalytic activity of Pb/PbO_2 and C/PbO_2 electrodes depend on the conductive electrolyte.

- The highest electrocatalytic activity was achieved in the presence of NaCl (4g/L) in which degradation of the investigated picric acid occurs by both direct as well as indirect oxidation.

- The degradation of picric acid was nearly completed (99% and 87.5%) using C/PbO_2 and Pb/PO_2 electrodes on 20-30 min respectively, while the degradation completed (90%) using Fentons reagent and H_2O_2in 60 min.

- In acidic media the electrocatalytic was more efficient(pH of 2.6).

- The electrode showed higher degradation efficiency at low temperature (5-10°C).

- The optimum current density for the degradation of picric acid on Pb/PbO_2 and C/PbO_2 electrodes was (20mAcm^{-2}).

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Appendix (1)
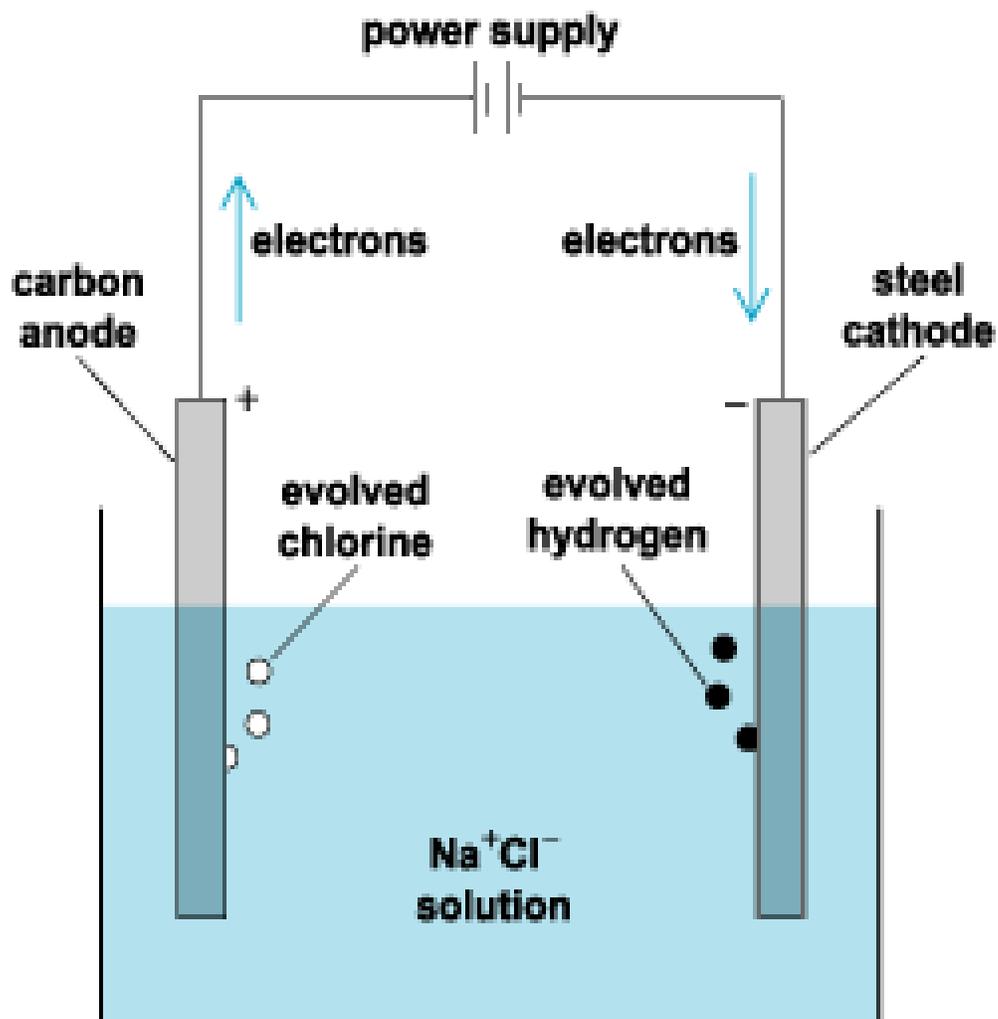
Arabic Summary

الملخص العربي للرسالة تحت عنوان" توليد الهيبوكلورايت بإستخدام الأقطاب المحورة لمعالجة المياه الصناعية الملوثة

يهدف موضوع البحث إلى تحضير الأقطاب المحورة والمحضرة بالترسيب الكهربي كترسيب طبقة من أكسيد الرصاص على قطعة من الكربون و الرصاص والتي استخدمت كآنودات في خلية كهربائية و ذلك في الأغراض التالية :

أولاً : تحضير الهيبوكلورايت باستخدام محلول كلوريد الصوديوم و مياه البحر و المياه المالحة الناتجة من تحليه المياه .

ثانياً : تكسير الملوثات العضوية الملوثة كحمض البكريك باستخدام الأكسدة الحفزية و مثلت النتائج بالكمبية المتبقية من حامض البكريك ، كمية الأكسجين المتبقية (COD) .

تم دراسة بعض التأثيرات المختلفة للحصول على الظروف المثالية لكلتا العمليتين (تحضير الهيبوكلورايت ، الأكسدة الحفزيةلحمض البكريك) ، ومن هذه التأثيرات التيار الكهربي ، الرقم الهيدروجيني ، التركيز الابتدائي لحمض البكريك ، الالكتروليت الموصلة ، الوقت المستغرق ودرجة الحرارة).

أثبتت النتائج أن كفاءة قطب C/PbO_2 أفضل من Pb/PbO_2 في تحضير الهيبوكلورايت و الأكسدة الكهروكيميائية لحمض البكريك .

تم حساب الطاقة اللازمة لتحضير الهيبو كلوريت على كلا القطبين المستخدمين وكذلك على التكسير لمادة حمض البكريك.

توليد الهيبوكلورايت باستخدام الأقطاب المحورة
لمعالجة المياه الصناعية الملوثة

رسالة مقدمة من /

عبد الرحمن محمد علي الأغا

المشرفون

د.حسن مصطفى طموس   د.ناصر محمد أبو غلوة

أستاذ الكيمياء الفيزيائية المساعد   أستاذ الكيمياء الفيزيائية المشارك

جامعة الأزهر –غزة   جامعة الأزهر –غزة