

Electrochemical Degradation of some Pesticides in Agricultural Wastewater

Abdel-Gawad S.A.^{*1}, Omran K. A.², Mokhtar M. M.² and Baraka A. M.¹

¹Chemistry Department, Faculty of Science, Cairo University, Egypt

²Central Laboratory for Environmental Quality Monitoring (CLEQM), National Water Research Center (NWRC)

*soha.gawad@yahoo.com

Abstract: This work deals with the possibility of using graphite electrodes for the electro-catalytic oxidation process of some pesticides (malathion, imidacloprid and chlorpyrifos). The graphite electrodes were used in the combined process in the presence of transition metals modified kaolin catalyst. The results of the electrolytic oxidation were expressed in term of chemical oxygen demand (COD) removal, which was determined instrumentally. The highest efficiency of COD removal was obtained in the presence of the transition metals modified kaolin catalyst. The different operating conditions of electro-catalytic oxidation process were studied which include: current density, pH, electrolysis time and initial pesticide concentration. The optimum operating conditions for the above mentioned electrode were determined.

[Abdel-Gawad S. A., Omran K. A., Mokhtar M. M. and Baraka A. M. **Electrochemical Degradation of some Pesticides in Agricultural Wastewater.**] Journal of American Science 2011;7(4):134-145]. (ISSN: 1545-1003).

<http://www.americanscience.org>.

Key words: Graphite electrode, electro-catalytic degradation transition metals modified kaolin catalyst, combined electrochemical oxidation, pesticides.

1. Introduction:

The ambitious plan of the Government of Egypt (GOE) to reclaim 3-4 million feddans as an additional cultivated area up to the year 2017 put further pressure on the existing limited fresh water resources. On the other hand, the vast increase in industrial horizontal and vertical expansions need more water conservation. Furthermore, the increasing population presents another red flag for the available renewable water resources. According to the limited water availability, there is a real need to search for another water sources. These sources can be found within the non-conventional water sources in Egypt. The agricultural wastewater represents one of the major non-conventional water sources in Egypt due to its volume that reaches about 16 billion cubic meters per year (BCM/yr). Most of this volume, about 12 BCM/yr, is disposed in the Mediterranean Sea. Water quality of this major source is threatened due to several pollution causes. So, chemical treatment of this major source before using is very important [Omran, 2009].

Out of the world production of pesticides (3 million tonnes in 2009), 20% (equivalent to 600 000 tonnes) were exported annually to developing countries, and at least 90% were used in agriculture for pest, weed and plant disease control. The remaining 10% were used for public health programmes, particularly for the control of vectors of human diseases (malaria, filariasis, schistosomiasis, leishmaniasis and trypanosomiasis). The amount of pesticides applied actually affecting target pests is often less than 1%, while over 99% moves into the environment to contaminate the land, water and air.

These toxic compounds have been implicated in various disorders and diseases including cancer, adverse reproductive outcomes, peripheral neuropathies, neurobehavioral disorders, impaired immune functions and allergic sensitization reactions, particularly of the skin, cumulative inhibition of cholinesterase activity because of long-term low doses of exposure [Qurainy and Mageed, 2009].

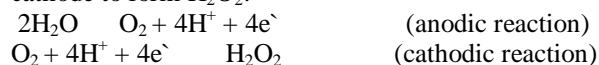
Millions of tons of pesticides applied annually are used in modern agriculture to increase production through controlling harmful effects caused by the targets organisms including insects, fungi, bacteria, viruses as well as grasses grown in between the economical crops [WHO, 1996].

Polluted drainage water from a dump of toxic chemical waste containing organophosphoric pesticides and their natural degradation products was treated with electrochemical oxidation in order to investigate the applicability of the technique in remediation of natural complex polluted water [Muff et al., 2009].

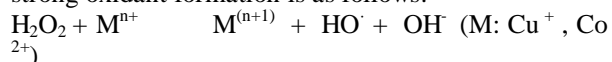
2. Experimental:

In this paper the combined electro-catalytic oxidation of pesticides present in agricultural wastewater in the presence of $\text{Cu}_2\text{O-CoO-PO}_4^{3-}$ modified kaolin was investigated. Two processes are involved in the whole degradation process: catalysts adsorption and synergistic oxidation process. By adsorption process, pollutants can be immediately adsorbed on the catalyst due to its high surface area and porous structure. By combined electrochemical oxidation process, strong oxidants produced through decomposition of electro-generated H_2O_2 can destruct

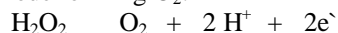
organic pollutants and convert them into CO₂ and H₂O. Near carbon anode, the evolution of O₂ with high yields can immediately reduce on porous graphite cathode to form H₂O₂:



In the presence of transition metal modified kaolin, strong oxidant formation is as follows:



This process is similar to the electro-Fenton process. However, in the Fe²⁺ existed homogeneous aqueous phase, electro-generated H₂O₂ can diffuse onto the anode forming O₂:



Experimental Materials and Methods

1. Preparation of catalyst that is used in an electrolytic batch reactor with graphite electrode:

1.1. Catalyst preparation and analysis

The Cu₂O-CoO-PO₄³⁻ modified kaolin (chemical structure of kaolin is Al₂(OH)₄SiO₅ which is named as aluminosilicate clay) was prepared as follows: adding 66.6gm CuSO₄, 14.2gm CoCl₂ and 70gm K₃PO₄·H₂O into 250mL distilled water (pH 7.1), 10 mL H₃PO₄ was added to dissolve the salts of metal (Cu, Co), then the solution pH was adjusted with NaOH solution to a neutral conditions. Two hundred grams of kaolin powder which was used as support was impregnated into the solution with mechanical stirring in a water bath at 50°C for 4h. After that, the solution was aged at room temperature for 48h and filtrated, washing, the deposit was dried at 100°C for 4h. To immobilize the metals, the prepared dried slurry was sent to calcine at 600°C.

XRD pattern of neat and modified kaolin

The patterns of XRD for the neat kaolin and modified kaolin are shown in Fig.1. Two diffraction peaks that related to kaolinite and muscovite can be clearly observed in Fig.1 (a), the presence of peaks as an attributive indicator of kaolinite and of muscovite is detected. Two common trends can be seen in contrast of Fig.1(a) and (b): first, the intensity of the peaks characteristic of kaolinite decreases at 600 °C, which indicates the stable Al-O octahedron structure in neat kaolin has broken and the losses in crystallinity and the structural deformation. Meanwhile, the characteristic peak for muscovite has been strengthened.

SEM analysis of neat and modified kaolin

The morphology of Cu₂O-CoO-PO₄³⁻ modified kaolin examined by SEM and representative photographs were shown in Fig.2. It can be observed that the previous flaky structure of neat kaolin (see Fig. 2(a)) has changed into granular structure through the

modification process: intercalation of Cu₂O-CoO-PO₄³⁻ into kaolin has resulted in an increase in the stacking disorder of the kaolin. After the modification and calcinations, the layer bonds of neat kaolin are broken, which lead to more micro-sized particles and pored structure (seen in Fig.2 (b)) has formed. This was consistent with the results of that the enlarged BTE surface of modified kaolin (38m²g⁻¹) compared with the neat kaolin (2038m²g⁻¹).

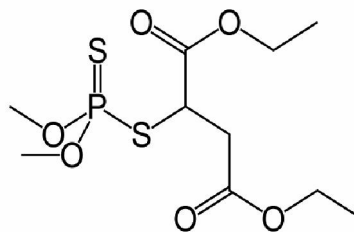
2. Electro-catalytic degradation procedures:

2.1. Electro-catalytic degradation of pesticides using graphite electrodes

The experiments were conducted by batch process using undivided cell of 250 mL capacity under constant temperature conditions. Electrodes were served by porous graphite. The anode and cathode were positioned vertically and parallel to each other with an inner gap of 0.5 cm. The superficial surface of the working electrode (3.5 cm x 1.5 cm) was 5.25 cm². Different quantities of smashed catalyst were added into the system to form an oxidizing electrochemical reactor. The solution was constantly stirred at 200 rpm with a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. The electric power was supplied with regulated DC power supply GW (model: GPR-181 OHD, Taiwan).

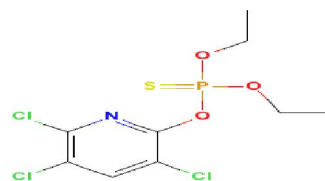
3. Chemicals

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



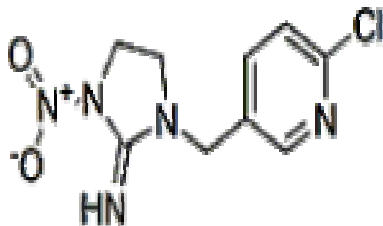
Common name: Malathion

IUPAC name: Diethyl (dimethoxy thio phosphryl thio)succinate



Common name: Chlorpyrifos

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



Common name: Imidacloprid

IUPAC name: 1-(6-chloro-3-pyridylmethyl) -N-nitroimidazolidine-2-ylideneamine

4. Analytical measurements

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

Chemical Oxygen Demand COD ($\text{mg O}_2/\text{L}$), which is a measure of the oxygen equivalent to organic matter content of a sample that is susceptible to the oxidation by strong chemical oxidant. COD during the electrolysis was determined by an open reflux (COD reactor, ECO 6, VELD SCIENTIFICA, Italy), dichromate titrimetric method as described in standard methods [6]. This method for the determination of COD may be used where sample chloride concentration is known to be less than 2000 mg/L . This means that, in the present investigations the interferences of Cl^- ions present in the solution and the electro-generated species may occur. To eliminate the effect of these interferences, two different methods were taken into considerations [7]. The first was carried out by adding sodium bisulphate ($\text{Na}_2\text{S}_2\text{O}_5$) to the organic compound (pesticides) solutions and heating before measurements of COD. The added of sodium bisulphate destroys the hypochlorite with evolution of chlorine gas. The second includes the measurements of COD for blank solutions, which are free from the under test organic compound. These blank solutions were treated under the same operating conditions used in the electro-catalytic oxidation of organic (pesticides) compound solutions. From the measurements of COD values of blank and organic (pesticides) compound solutions after treatment, the value of COD is corresponding to the organic compound present in solution that could be evaluated. The COD values obtained from the two methods were matched with each other. The equation used to calculate the COD removal efficiency in the experiments is:

$$\text{COD Removal \%} = [\text{COD}_0 - \text{COD}_{\text{final}} / \text{COD}_0] \times 100$$

Where, COD_0 (initial) and $\text{COD}_{\text{final}}$ of the pesticide solutions are calculated in mg/L

The average current efficiency (ACE) is calculated by the following equation [8];

$$\text{ACE\%} = (\text{COD}_0 - \text{COD}_t) FV / 8 It$$

Where COD_0 and COD_t are the chemical oxygen demand at initial time and given time t ($\text{g O}_2/\text{L}$), respectively, I the current (A), F the Faraday constant (96487 C/mol), t the treatment time (s), V is the volume of solution (L) and 8 is the oxygen equivalent mass (g/eq).

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

$$\text{EC} = UIt / 3.6 (\text{COD}_0 - \text{COD}_t) V$$

Where U is the voltage applied (V) and other parameters are as defined as before [8].

The optimum operating conditions for the electro-catalytic degradation processes:

Several parameters were studied for investigation the optimum conditions for the degradation synthetic agricultural wastewater (which prepared from pesticides). The studied operating conditions were: current density, initial pesticide concentration, pH and catalyst dose.

3- Results and Discussion

3.1. Synergetic effect

In the presence of catalyst (modified kaolin), organic pollutants can be degraded by electrolysis and removed by adsorption. To evaluate the feasibility of adding catalyst into the electro-catalysis process, the efficiencies of COD removal by only modified kaolin, electro-catalysis and their combined process were compared in the same reactor, respectively for the three pesticides. Effect of kaolin's adsorption was performed at the same conditions except the absence of current. The tendency of COD value variation during the whole electrolysis, adsorption process and combined processes in the first 75 min. was shown in Fig. (3) for imidacloprid, malathion and chlorpyrifos pesticides. It can be seen that COD was removed by catalyst adsorption more rapidly than that of by electro-catalysis. Such a combined process obtained a 90%, 95% and 84% COD removal for the three pesticides, respectively compared with 57%, 58.5 and 55 removal in catalyst adsorption process and 31%, 33% and 25% COD removal in electrochemical process, respectively. However, the two processes were environmentally equivalent due to the accumulation of unconverted contaminants on the solid phase by adsorption. Moreover, the whole combined process is a mass transfer process and its COD removal rate may depend on the stirring speed, particle size and also the solution conditions.

3.2. Effect of catalyst concentration

This investigation was carried out in the presence of 1% initial concentration of each pesticide under the following operating conditions: 100 mA/cm^2 , pH of 3, and electrolysis time of 75 min. Figure (4) show the variation of COD removal % as a function of

modified kaolin catalyst dose for the pesticides. The plots of figure (4) indicated that the COD removal % of pesticides was greatly increased with the increase of kaolin catalyst from 20 to 40 g/L and then slightly increased with increase of kaolin catalyst from 40 to 80 g/L. For this reason the optimum amount of kaolin catalyst ranged from 40 to 60 g/L. A series of experiments was carried out in the presence of presence of 40 g/L kaolin catalyst to investigate the effect of different operating conditions on the rate of the electrochemical degradation of the investigated pesticides. These operating conditions were: current density and pH of solution.

3.3. Effect of applied current density

Different current densities of values 50,100, and 250 mA/ cm² were applied on graphite electrode to investigate the electro-catalytic degradation of the investigated pesticides in the presence of 40 g/L kaolin catalyst and pH of 3. Figure (5) show that the variation of COD removal % of pesticides as a function of electrolysis time at different current densities for the investigated pesticides.

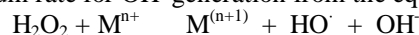
The plots of figure (5) indicated that:

- i) At a given current density, the COD removal % increased with the increase of electrolysis time reaching a limiting value (especially at 100 and 250 mA/ cm²).
- ii) At a given time of electrolysis, the COD removal % increased with the increase of applied current density up to 100 mA/ cm² and further increase in the current density did not bring any effect. For this reason, the optimum value of the applied current density was taken as 100 mA/ cm². The values of the COD removal % at the optimum current density were: 90%, 95% and 84% for the pesticides imidacloprid, malathion and chlorpyrifos respectively. These COD removal % indicated a good electro-catalytic degradation on graphite electrode occurred for the investigated pesticides. As shown from figures (9-11) at a current density of 100 mA/ cm², the time required for the degradation of 50% of the initial concentration of the pesticide ($t_{1/2}$) is greatly depended on nature of the investigated pesticide. The deduced values of $t_{1/2}$ were: 11.6, 12.5 and 20.0 minutes for pesticides imidacloprid, malathion and chlorpyrifos, respectively.

3.4. Effect of pH of solution

The obtained results shown in Figure (6) for the pesticides imidacloprid, malathion and chlorpyrifos, respectively indicate that the maximum COD removal was achieved at initial pH of 3, while the removal efficiency decreases with the increase of pH. The better

effectiveness at pH of 3 agrees with the fact that the maximum rate for OH⁻ generation from the equation:



Inferred that the optimal operating conditions should be in acid solution, while the diffused oxygen may get electrons easily in this pH region. In alkaline solution, hydroxide can scavenge hydroxyl radicals [9]:



Which influence the oxidizing property of the free radicals (HO[·]) to degrade the organics. These results are similar to the previously obtained [10, 11] which reported that the catalyst displays higher catalytic activity in the acid or moderate acid solutions.

3.5. Comparison with homogeneous Co and Cu combined system

To evaluate the effect of Cu₂O-CoO-PO₄³⁻ modified kaolin in electrochemical system concerning the ability to degrade organic pollutants (pesticides malathion, chlorpyrifos and imidacloprid), the homogeneous electro-Co-Cu combined system was applied. 40 g/L CoSO₄ or CuSO₄ (Merck) was added into the solution instead of the modified kaolin. The operating conditions were: 1% initial pesticide concentration, pH of 3 and current density of 100 mA/cm². Figure (7) show the variation of COD removals % as a function of electrolysis time in different electrochemical systems (homogeneous electro-Co-Cu system and the modified kaolin system) for the pesticides (malathion, imidacloprid and chlorpyrifos), respectively. The plots of these figures indicated that:

- i) The maximum COD removals obtained in the modified kaolin system were higher than those obtained in homogeneous electro-Co-Cu system.
- ii) The COD removal rate was faster in electro-Co-Cu modified kaolin combined heterogeneous system than that of electro-Co-Cu catalyzed homogeneous electrochemical system. This as indicated from the value of $t_{1/2}$ in each of the both systems, where $t_{1/2}$ values in modified kaolin system were: 11.6, 12.5 and 20.0 minutes for the pesticides imidacloprid, malathion and chlorpyrifos, respectively. While, the values of $t_{1/2}$ in electro-Co-Cu catalyzed homogeneous system were: 35.0, 34.4 and 31.2 minutes for the pesticides imidacloprid, malathion and chlorpyrifos, respectively.

The multi-transition metals modified kaolin gains more advantages than Co-Cu electrochemical system when treating organic pollutants in aqueous phase. This probable due to its ability to condense pollutants and electro-generated H₂O₂ onto its big surface and make the degradation reactions more easily to occur. Moreover, because modified kaolin existed electrochemical system is heterogeneous; the adsorbed

multi-metal compounds were stable and friendly environmental pollution [11].

The results of the influence of modified kaolin catalyst on the COD removals% indicated that the optimum amount of the catalyst ranged from 40 to 60 mg/L. The reasons may be lie in that, when the catalyst reaches a certain amount, it will reach equilibrium with electro-generated H_2O_2 , so the generation of HO^\bullet radicals was mainly determined by the concentration of H_2O_2 . Moreover, because the whole degradation process is mass transfer controlled, its COD removal rate may depend on stirring speed, particle size and also solution conditions. When the catalyst reaches a certain amount, the COD removal may be further influenced by other factors.

3.6. Effect of initial pesticide dosage

The results so far have indicated that the maximum electrochemical degradation of the investigated pesticides was obtained at 100 mA/cm², 40g/L kaolin catalyst and pH of 3. Figure (8) shows the effect of different initial pesticides of concentrations 0.5%, 1% and 5% on the variation of COD removal % as a function of electrolysis time under the optimum

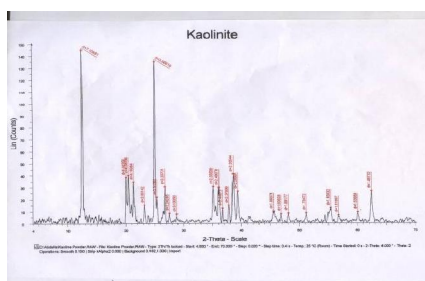
operating conditions mentioned above. Inspection of plots of figure (8), revealed that:

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

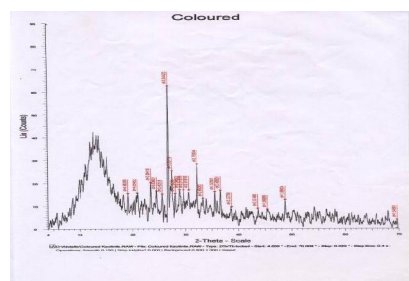
At a given initial loaded concentrations, the COD removal % increased with increase of the electrolysis time with a rate depending on both of nature of each pesticide and its initial concentration. Increasing the pesticides concentration resulted in a decrease in the electrochemical degradation rate of the investigated pesticides.

3.7. Calculation of electrical yield (Current Efficiency)

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

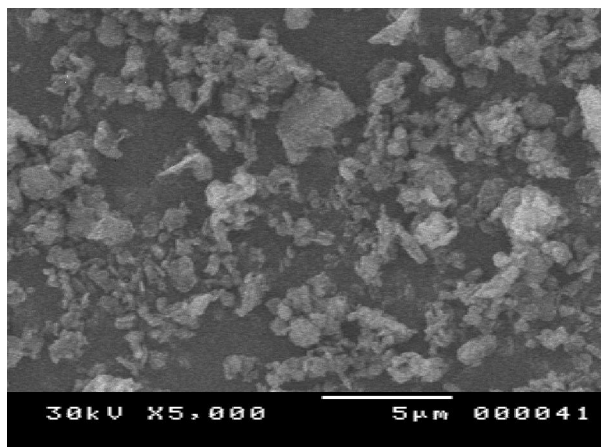


(a) Kaolin

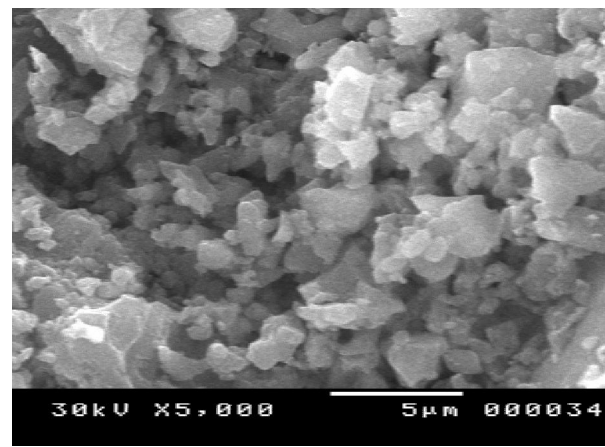


(b) modified kaolin

Fig. (1): XRD patterns of neat kaolin (a) and modified kaolin (b)



(a)



(b)

Fig. (2): Morphologies of neat (a) and modified kaolin (b) by SEM (Magnification 1500x)

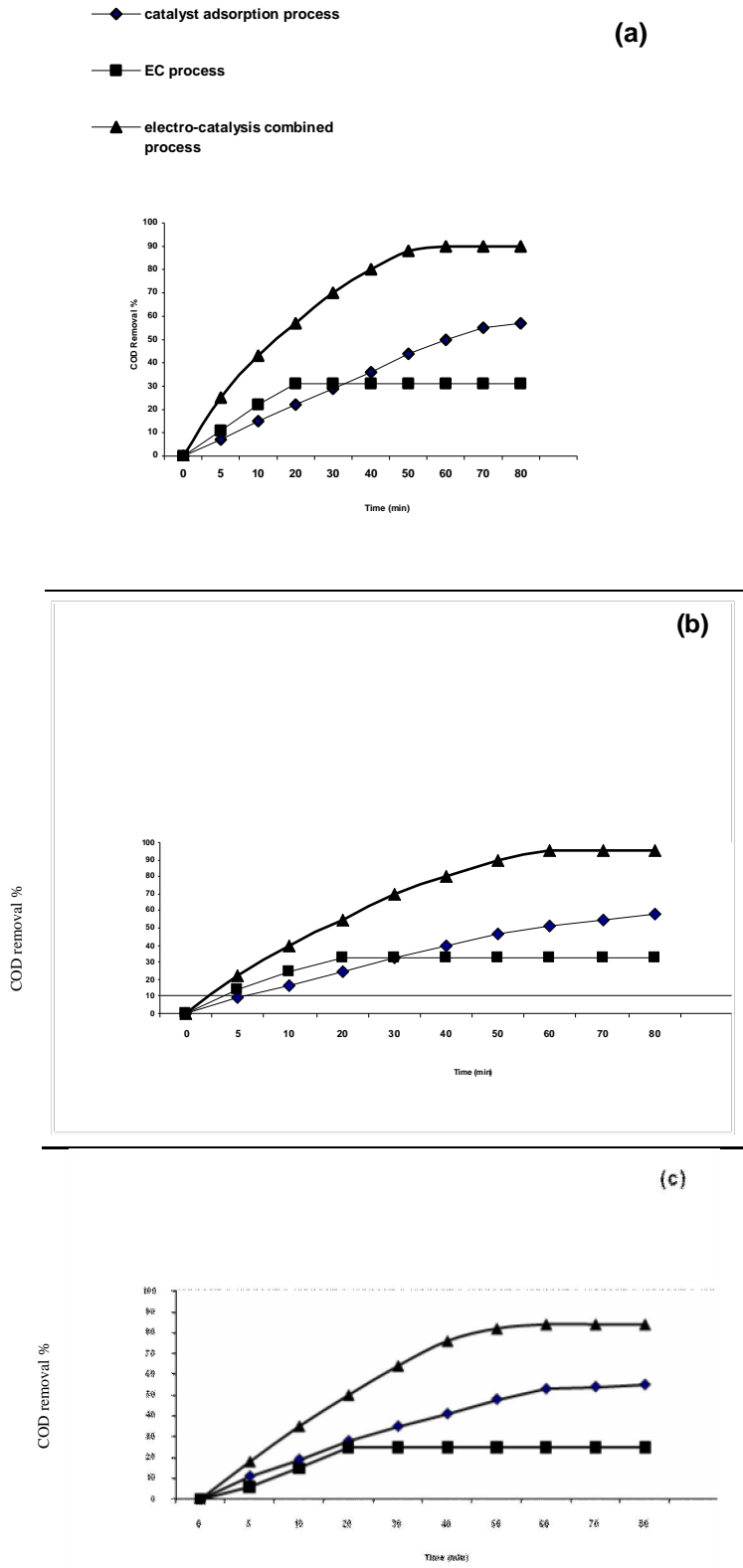
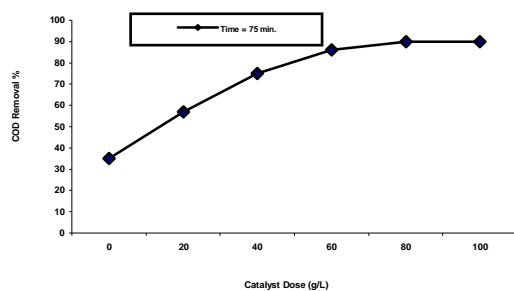
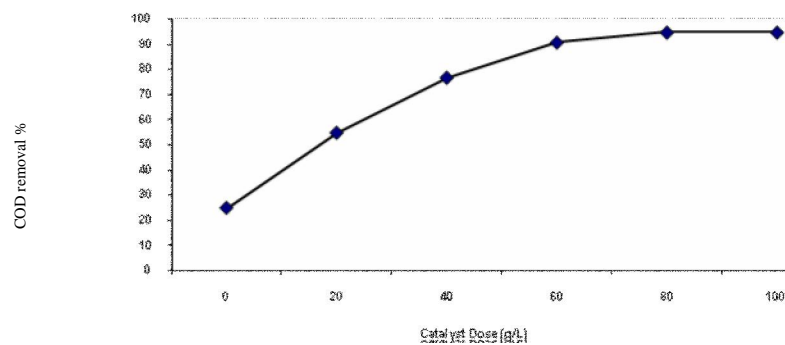


Fig. (3): Synergetic effects on COD removal for 1% concentration of (a): imidacloprid, (b): malathion and (c): chlorpyrifos pesticides (100 mA/cm², pH 3, 40 g/L of kaolin and graphite electrodes).

(a)



(b)



(c)

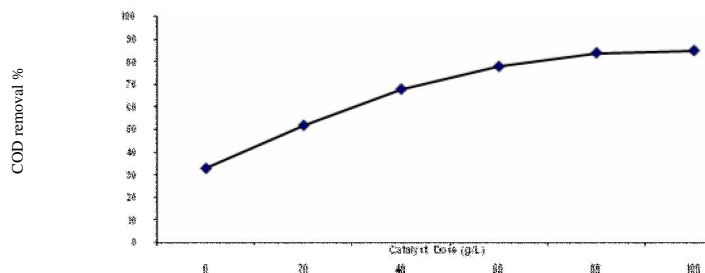


Fig.(4): Removal of COD with electrolysis time for 1% concentration of (a): imidacloprid ,(b): malathion and (c): chlorpyrifos pesticides with different doses of kaolin catalyst, 100 mA/cm², pH 3 and graphite electrodes.

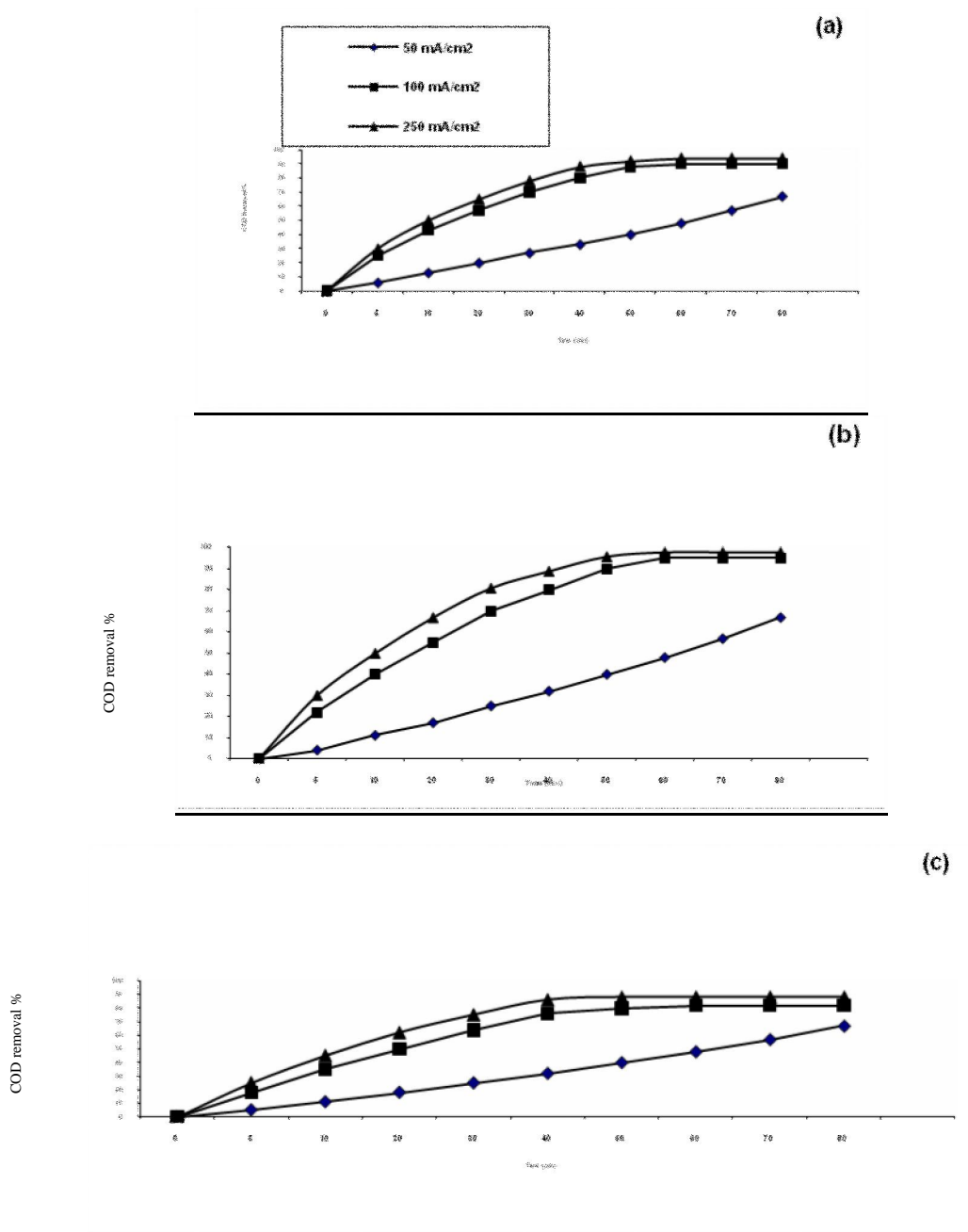


Fig. (5): Removal of COD with electrolysis time for 1% concentration of (a): imidacloprid, (b): malathion and (c): chlorpyrifos pesticides with 40 g/L kaolin catalyst, pH 3 and graphite electrodes.

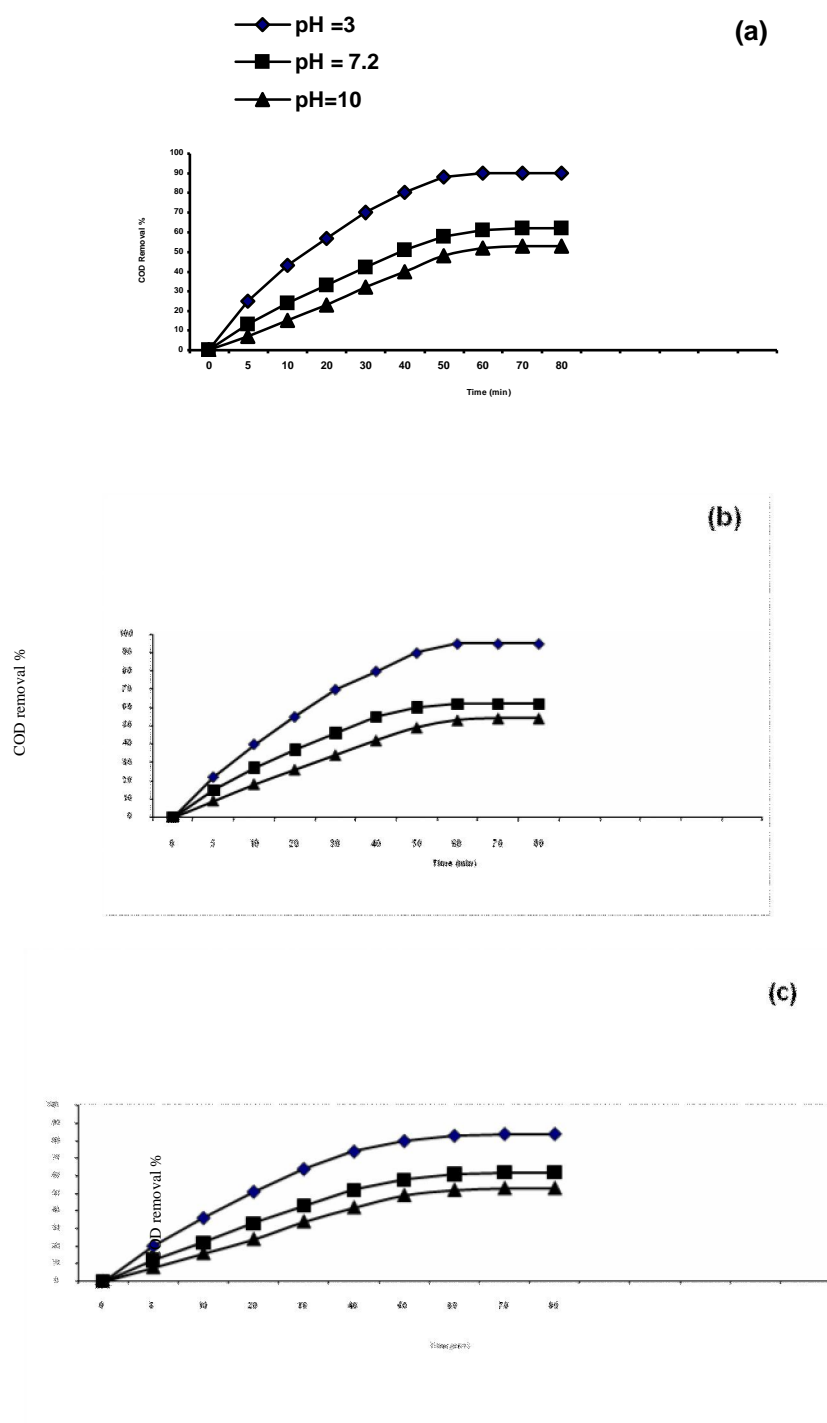


Fig. (6): Removal of COD with electrolysis time for 1% concentration of (a): imidacloprid, (b): malathion and (c): chlorpyrifos pesticide with 40 g/L kaolin catalyst, pH (3, 7.2 and 10) and graphite electrodes.

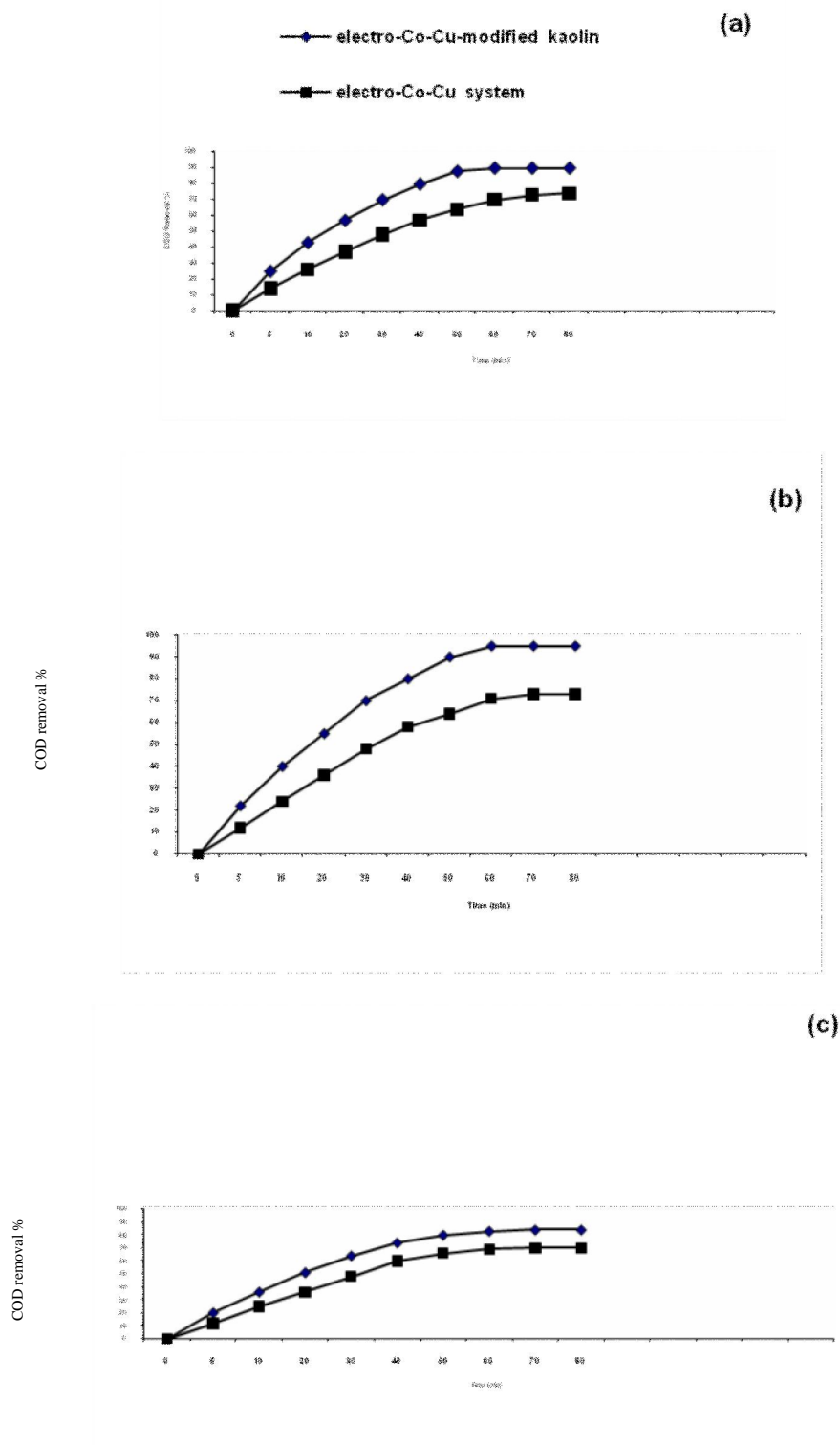


Fig. (7): Comparison of electro-Co-Cu-modified kaolin heterogeneous system and electro-Co-Cu homogenous system on COD removal for 1% concentration of (a): imidacloprid, (b): malathion and (c): chlorpyrifos pesticides at 100 mA/cm², pH 3 and graphite electrodes.

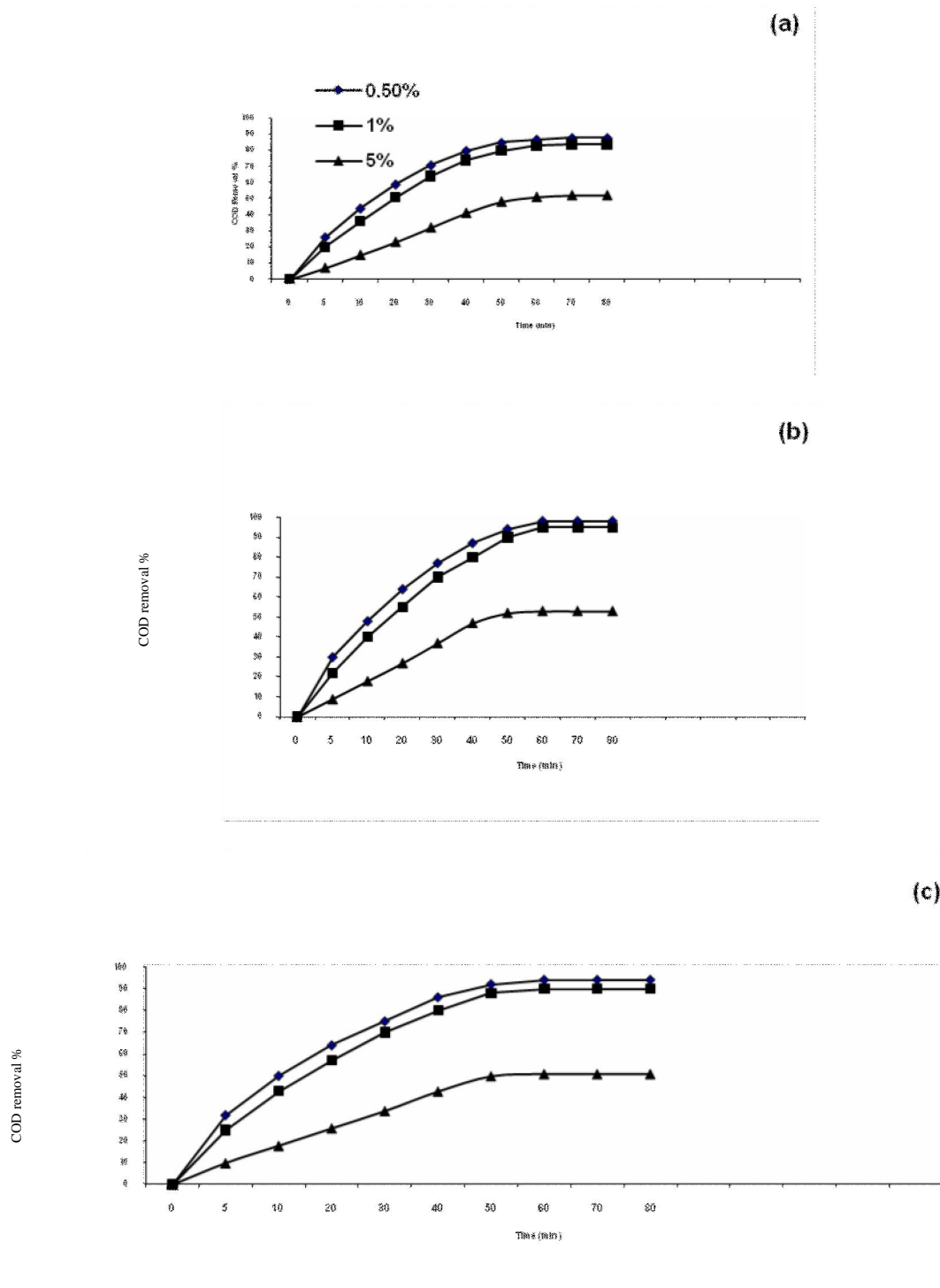


Fig. (8): Removal of COD with electrolysis time for 0.5%, 1% and 5% concentration of (a): chlorpyrifos, (b): malathion and (c): imidacloprid pesticides, 40 g/L kaolin catalyst, pH 3 and graphite electrodes.

Table (1): The current efficiency values and the energy consumption values

Graphite electrodes	Malthion ACE%	Chlorpyrifos ACE%	Imidacloprid ACE%
	88.8	75.4	76.5
EC _(kWh/kg COD) without addition of catalyst	23.54	26.41	25.12
EC _(kWh/kg COD) with catalyst	4.75	6.80	5.24

4. Conclusion:

The combined electro-catalysis of pesticides present in agricultural wastewater assisted with Cu₂O-CoO-PO₄³⁻ modified kaolin catalyst was performed in single undivided cell. The morphology and phase structure of kaolin before and after modification were studied. Optimal operating conditions such as initial pH, current density were also studied. It was found that when the initial pH was 3, current density was 100 mA/cm² and the catalyst dose was 40 g/L, the COD removal rate can reach 95%, 90% and 84% for malathion, imidacloprid and chlorpyrifos, respectively. No significant increase in the COD removal was observed as the current density exceeded 100 mA/cm². The removal of pesticides from agricultural wastewater might be attributed to strong oxidant that produced from the synergistic effect of between modified kaolin and electrochemical system.

Corresponding author

Abdel-Gawad
Chemistry Department, Faculty of Science, Cairo University, Egypt
soha.gawad@yahoo.com

6. References:

1. Omran K.A., "Chemistry of irrigation water and its impacts on environment in Egypt". M.Sc. Thesis Fac. Sci. Cairo Univ. Egypt. (2009).

- Al-Qurainy F. and Megeed A.; J.W.Appl.Sci;6(7),1818-4952 (2009).
- WHO-EM/CEHA/77-E; Cairo, Egypt, 1-4 September 1996.
- Muff J., Andersena D., Erichsena R. and Soegaard E.; J.Sci.Dri.; 54(7),2062-2068 (2009).
- Standard Methods for Examination Water and Wastewater, 19th; "Closed Reflux, Titrimetric Method"; 5220C., 5-14 (1995).
- USEPA; Federal Register, April 21, 45, 26811 (1980).
- Zhou M. and He J.; Hazard J. Mater.; 153, 357-363 (2008).
- Suresh K.B., James T., Jaidev P., Karl F., B. A., Deepak C.G. Stephen. Wet oxidation and catalytic wet oxidation. Ind. Eng. Chem. Res. 45, 1221-1258 (2006).
- Ma H.Z., Wang B.; Electrochemical Pilot-scale plant for oil field produced wastewater by M/C/Fe electrodes for injection, J. Hazard. Mater. 132, 237-243 (2006).
- Wang B., Gu L. and Ma H.; Hazard J. Mater.; 143, 198 (2007).
- Fockedey E. and Lierde A. V.; Water Res.; 36, 4169-4175 (2002).

3/2/2011