



Removal of Chlorpyrifos from aqueous solution using Electrocoagulation

إزالة الكلوربيريفوس من المحلول المائي باستخدام الترويب الكهربائي

Mahmoud El Amrety, Mohamed Mossad and Moharram Fouad

KEYWORDS:

Electrocoagulation, Chlorpyrifos, TDS, current, pH, energy consumption.

المخلص العربي:- تشمل هذه الدراسة استخدام تكنولوجيا الترويب الكهربائي لإزالة تراكيز عالية من مبيد الكلوربيريفوس في ظل ظروف تشغيل مختلفة مثل تركيز مبيدات (800 و1200 و1600 و2000 ملليغرام/لتر)، والجهد الكهربائي المستخدم (5 و10 و15 فولت)، وقيم تركيز المواد الصلبة الذائبة (650 و900 و1300 ملليغرام/لتر)، وقيم الأس الهيدروجيني للمركب (5,0، 7,0، 9,0). مع ثبوت قيمة المعاملات الأخرى مثل درجة الحرارة والمسافة بين الأقطاب. وأثبتت تكنولوجيا الترويب الكهربائي فعاليتها للحد من تركيز الكلوربيريفوس بكفاءة إزالة أكبر من 90٪، للجهد العالي المطبق 10 و15 فولت في وقت تشغيل 30 دقيقة. وتم الوصول إلى كفاءة إزالة أكبر من 90٪ لقيم تركيز المواد الصلبة الذائبة العالية 900 و1300 ملليغرام/لتر في وقت تشغيل 40 دقيقة. وتم الوصول إلى الأس الهيدروجيني الأمثل لإزالة مبيد الكلوربيريفوس باستخدام تكنولوجيا الترويب الكهربائي وهو 7±0,5. وقد أثبتت تكنولوجيا الترويب الكهربائي بأنها طريقة فعالة لإزالة مبيد الكلوربيريفوس.

Abstract—The study investigates the use of electrocoagulation method for the removal of high concentrations of Chlorpyrifos pesticide under different operational conditions. The operational conditions such as high pesticides concentration (800, 1200, 1600, and 2000mg/l), applied voltage (5, 10, and 15V), initial feed solution TDS (650, 900, and 1300mg/l), and initial pH (5.0, 7.0, and 9.0) was applied to the system. The other secondary parameters such as temperature and space between electrodes have been kept constant. The removal efficiency was found to be greater than 90%, for high voltage applied 10 and 15V at operational time of 30 minutes. Further, the removal efficiency was found to be greater than 90%, for high TDS solution 900 and 1300mg/l at operational time of 40 minutes. The optimum pH for the removal of Chlorpyrifos pesticide by EC technology was

found to be 7 ± 0.5 . EC technology has proven to be an effective process for the removal of Chlorpyrifos pesticide.

I. INTRODUCTION

SURFACE and ground water runoff may contain pesticides from agriculture, forestry, industrial and domestic activities which are intentionally used for preventing and destroying pests. The presence of high concentrations of pesticides in water and wastewater is considered a major public health concern as it poses threats to human and animal's life. Pesticides continue to be detected in natural water [1, 2], and inland waterways.

Chlorpyrifos is an organophosphorus pesticide that widely used in agriculture. Chlorpyrifos affects biological activity and controls many types of insects such as pests, soil dwelling grubs, rootworms, borers and subterranean termites. Chlorpyrifos concentration between 1 and 10mg/L has been reported to depress growth in blue-green algae and reduce ciliated protozoa in natural microbial community [3]. Exposure to Chlorpyrifos and its metabolites has been related to a variety of nerve disorders in humans. Symptoms of acute poisoning include headache, nausea, muscle twitching and convulsions and in some extreme cases even death. Human birth defect is also related to Chlorpyrifos and its products

Received: 12 December, 2017 - accepted: 21 February, 2018

Mahmoud El Amrety, Demonstrator, Faculty of engineering, MISR Engineering & Technology, Egypt,

(e-mail: Engmahmoudel3amrety@hotmail.com)

Mohamed Mossad, Lecturer, Public Works Dept., Faculty of engineering, Mansoura University, Egypt,

(e-mail: Mohamed_a_hakim@hotmail.com)

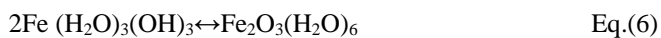
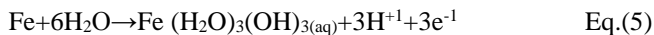
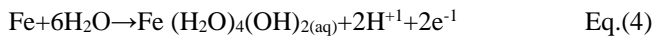
Moharram Fouad, Associate Professor, Public Works Dept., Faculty of engineering, Mansoura University, Egypt,

(e-mail: mf12317@gmail.com)

exposure. Chlorpyrifos also affects male reproductive system. Chlorpyrifos is toxic to a variety of beneficial arthropods, including bees, ladybird beetles and parasitic wasps. It kills fish at concentrations as low as a few parts per trillion [4].

Developing new technologies for the treatment of water and wastewater with high concentrations of pesticides are required to provide better quality effluent at low cost, and solve the problems of pesticides non-biodegradability which cannot be removed by conventional methods. Electrocoagulation (EC) technology is used as an alternative for water and wastewater treatment. It involves the use of voltage to sacrificial electrodes, where an electric current is induced in the reactor tank. Depending on the type of metal used as sacrificial electrodes (such as Al, Fe) destabilizing agents is produced by the process of electrolysis in the EC. Destabilizing agents undergoes the process of neutralization for removing pollutants due to the electric charge, as the pollutants then coagulate with the ions in the water to form flocs, which is similar to chemical coagulation, but does not involve the use of chemicals, then it allows the removal of pollutants by either flotation or sedimentation, as the charged particles bond together like small magnets to form a mass [5]. EC has proved to be successful in the removal of various kinds of contaminants such as oil [6, 7], fluoride [8], arsenic [9], dyes [10–15], suspended particles [16], surfactants [17], chromium ions [18], phosphate [19, 20].

In the EC cell, the reactions at the anode electrode involves the dissolution of iron electrode as shown in Eq.(1,2), and the evolution of oxygen, at the cathode reactions usually involves the evolution of hydrogen as shown in Eq.(3), which dependence on the pH of the solution. At neutral or alkaline pH, hydrogen is produced. Iron ions in the solution then undergoes hydrolysis as shown in Eq.(4), more hydrogen evolution and Fe(III) hydroxide begin to precipitate as flocs with yellowish color as shown in Eq.(5). Hydrogen evolution continues and precipitation of Fe (II) hydroxide also occurs resulting in the presence of a dark green floc. Sludge and rust generation are produced as shown in Eq. (6) [21, 22].



The objectives of this work are to study the effect of different operational parameters, such as initial pesticide concentration, applied voltage, initial TDS concentration, and pH on the removal efficiency of Chlorpyrifos using EC with

iron electrodes and to identify the optimum operational conditions.

II. MATERIALS AND METHODOLOGY

A. Chemicals

The pesticide Chlorpyrifos were obtained from a commercial product PESTBAN from AGROCHEM Fig. (1) shows the chemical structure of the used pesticide. Commercial sodium chloride (NaCl) was used for the EC process. All solutions and reaction mixtures were prepared using distilled water, with the help of a magnetic stirrer.

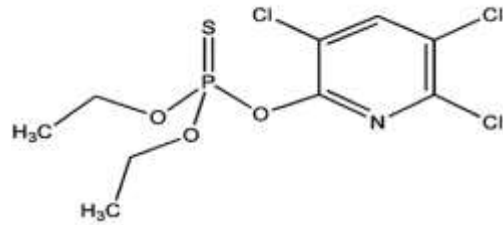


Fig.1. Show the chemical structure of Chlorpyrifos.

B. Batch Reactor Design

Fig. (2) Shows the EC batch reactor used in this study. The EC reactor consists of 2 iron electrodes with a surface area of 99.6 cm² connected to a DC power supply. The distance between electrodes was stated to be 3cm. The volume of solution used for all experiments was 1 liter. The power supply produced a maximum current of 30 ampere (A) and a series of volts ranged from 5 to 25 volts (V). An ammeter and voltmeter were connected to the DC power supply.



Fig. 2 show the EC batch reactor.

C. Experimental procedure

A digital magnetic stirrer was used for all the mixing purposes. A digital weight balance was used for weighting NaCl. Alignet 1200 series HPLC system was used for the analysis of Chlorpyrifos concentration. The wavelength of the maximum absorbance for Chlorpyrifos was found to be 230 nm. The solvent used for eluting the compound through the HPLC column was acetonitrile and water in the ratio of 80:20, respectively. These results were used in quantification of unknown concentrations of Chlorpyrifos. Samples were taken for every 10 minutes in each run, and passed through Whatman filter paper before analysis. A 1.5ml of this filtered sample was then taken in a syringe and placed in the HPLC for analysis. A digital multimeter is connected externally to measure the voltage and current induced on the plates. A digital pH, conductivity, TDS meter was also used for sample analysis.

To investigate the effects of operational conditions (pesticides concentration, voltage applied, TDS, and pH) on the percentage removal rate of Chlorpyrifos by EC technology, a series of laboratory experiments were conducted. These experiments were conducted as follows: first, the initial pesticide concentration was increased from 800 to 2000mg/l, at pH of 7, initial TDS 650mg/l and applied voltage of 5V. Second, voltage applied to the EC process was studied at (5, 10, and 15V), at pesticide concentration 1600mg/l, initial TDS concentration of 650mg/l, and pH of 7. Third, various initial TDS was studied at (650, 900, and 1300mg/l), at pesticide concentration 1600mg/l, pH of 7, and applied voltage 5V. Finally, pH of the feed solution was studied at (5.0, 7.0, and 9.0), at pesticide concentration 1600mg/l, initial TDS 650mg/l and applied voltage 5V. In these experiments, the pesticides removal efficiency was calculated as follows as shown in Eq. (7):

$$\text{Removal efficiency (\%)} = \frac{(T_0 - T)}{T_0} * 100 \quad \text{Eq. (7)}$$

Where, T_0 and T (mg/l) represent the influent and treated effluent, respectively.

Energy consumption was calculated in (KWh/m³) as follows as shown in Eq. (8):

$$\text{Energy consumption} = \frac{\text{Voltage (V)} * \text{Current (A)} * 1000}{1000} \quad \text{Eq. (8)}$$

III. RESULTS AND DISSCUSION

A. Effect of initial concentration of pesticides

Fig. (3, 4) show the pesticides concentration and removal efficiency with EC operational time under various initial pesticides concentration of 800, 1200, 1600, and 2000 mg/l, using initial TDS concentration 650mg/l, pH 7 and applied voltage of 5V.

It was clear that the pesticides concentration decreased with time. This decrease is related to the formation of iron hydroxides during the system operation. The pesticides concentration decreased by 99.9%, 99.3%, 49.9% and 33.4%, when using initial pesticides concentration of 800, 1200, 1600, and 2000mg/l, respectively. This indicates that the increase in

initial pesticides concentration is inversely proportional to the removal efficiency of EC process due to less adsorption sites are available to capture organic pesticide molecules in excess [23, 24]. The removal was found to be maximum (greater than 90%), for low initial pesticide concentration less than 1200 mg/l at operational time of 50 minutes. At high initial pesticide concentration at operational time of 60 minutes, the removal is observed to be low (less than 50%). The efficiency of EC process decreased rapidly when increasing pesticide concentration to 1600mg/l.

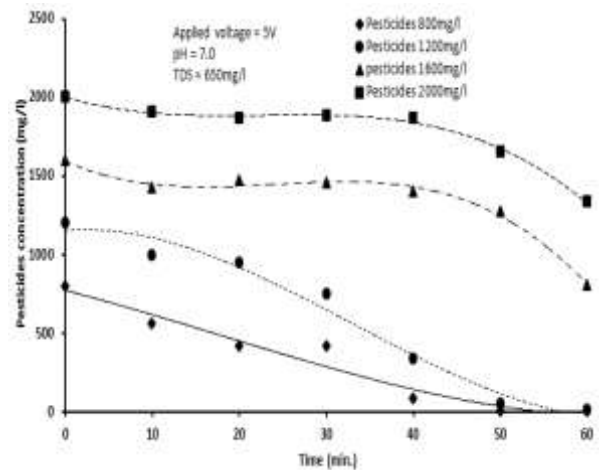


Fig. 3. pesticides concentration with operational time using various initial pesticides concentrations.

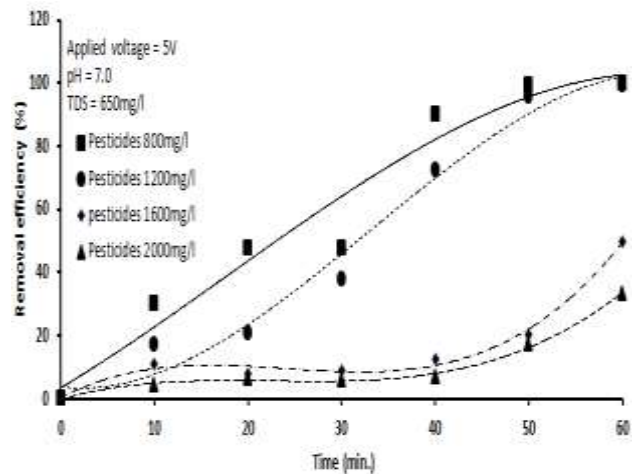


Fig. 4. pesticides removal efficiency with operational time using various initial pesticides concentrations

B. Effect of applied voltage

Fig. (5,6) show the pesticides concentration and removal efficiency with EC operational time using various applied voltage of 5, 10 and 15V, initial pesticides concentration of 1600mg/l, initial TDS concentration 650mg/l and pH 7.

The pesticides removal efficiency increases with time depending on the voltage applied to EC process. This increase is due to the amount of iron ions release from the respective

electrodes which allows the formation of more iron hydroxides. The removal efficiency was found to be maximum (greater than 90%), for high voltage applied 10 and 15V at operational time of 30 minutes, using low applied voltage of 5V at operational time of 60 minutes, the removal is observed to be low (less than 50%). This study has proven that 5V corresponds to the lowest pesticides removal, while 15v achieved the highest removal efficiency. It was noticed that the efficiency for pesticides removal increased gradually from 50% to 99.9%, when increasing the voltage applied from 5 to 15V. This result proves that pesticides removal efficiency is directly proportional to the voltage applied to EC process.

Fig. (7) Shows the effect of voltage applied on the EC unit for current produced (A) and energy consumption (KWh/m³). The EC unit current increased gradually from 0.10 to 0.36A, when increasing the voltage applied from 5 to 15V. Similarly, EC energy consumption increased gradually from 0.5 to 5.4 KWh/m³, when the applied voltage increased from 5 to 15V. This result indicates that the removal efficiency of EC process is higher at high applied voltage but the energy consumed for the treatment process also increases.

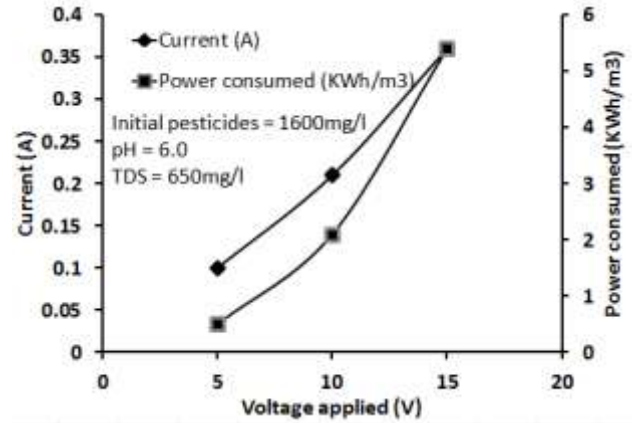


Fig. 7. The effect of voltage applied on used current and power consumed

C. Effect of initial TDS concentration

Fig. (8,9) show the pesticides concentration and removal efficiency with EC operational time using various TDS feed solution 650, 900, and 1300mg/l, initial pesticides concentration of 1600mg/l, voltage applied 5V and pH 7.

NaCl is used to adjust the TDS and conductivity of the feed solution in EC process. The pesticides removal efficiency increases with time depending on the TDS of the feed solution in EC process. This increase is due to the increase in conductivity of the solution and the formation of Cl₂ and OCl⁻ at the anode, when chlorides are present in the solution. So, added NaCl not only increases the conductivity but also contributes strong oxidizing agents [25]. The removal efficiency was found to be maximum (greater than 90%), for high TDS solution 900 and 1300mg/l at operational time of 40 minutes, using low TDS solution 650mg/l at operational time of 60 minutes, the removal is observed to be low (less than 50%). This study has proven that initial TDS solution of 650mg/l corresponds to the lowest pesticides removal, while initial TDS solution of 900 and 1300 mg/l achieved the highest removal efficiency. This result proves that increase in pesticides removal efficiency is directly proportional to the TDS of the feed solution in EC process. It was noticed that the efficiency for pesticides removal increased gradually from 50% to 99.9%, when increasing the initial TDS of the feed solution from 650 to 1300mg/l.

Fig. (10) shows the effect of initial feed solution TDS on the EC unit for current produced (A) and energy consumption (KWh/m³). The EC unit current increased gradually from 0.10 to 0.28A, when increasing the TDS of the solution from 650 to 1300mg/l. Similarly, EC energy consumption increased gradually from 0.5 to 1.4 KWh/m³, when the initial TDS increased from 650 to 1300mg/l. This increase in current produced and energy consumed by EC unit is due to the increase in concentration of NaCl salt, which increases the conductivity of the solution. So, the higher ionic strength will generally cause an increase in current at the same cell voltage. Consequently, the necessary voltage for attaining certain current and electrical energy consumption will be diminished

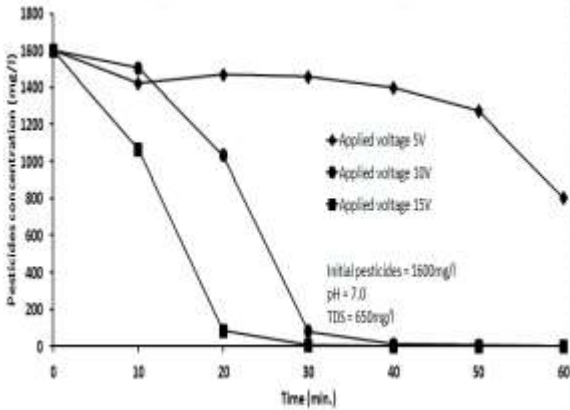


Fig. 5. pesticides concentration with operational time at various applied voltage

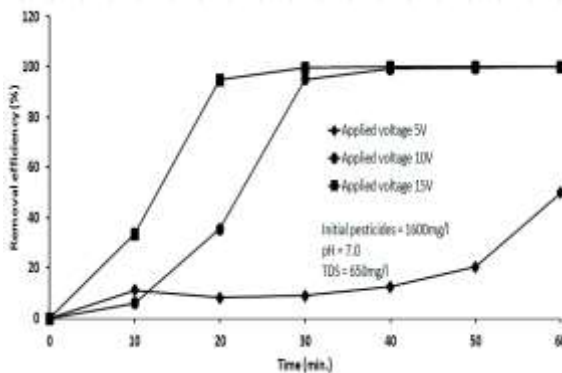


Fig. 6. pesticides removal efficiency with operational time at various applied voltage.

and the increase in TDS will cause an increase in electrical energy consumption.

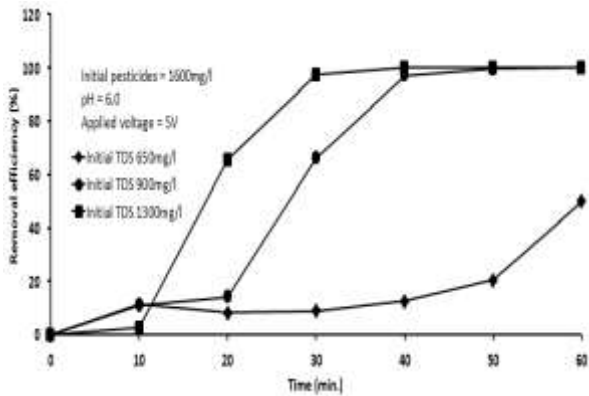


Fig. 8. pesticides removal efficiency with operational time at various initial TDS concentrations.

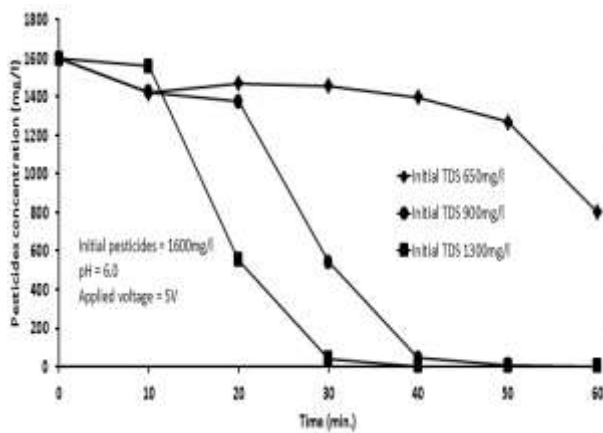


Fig. 9. pesticides treated concentration with operational time at various initial TDS concentrations.

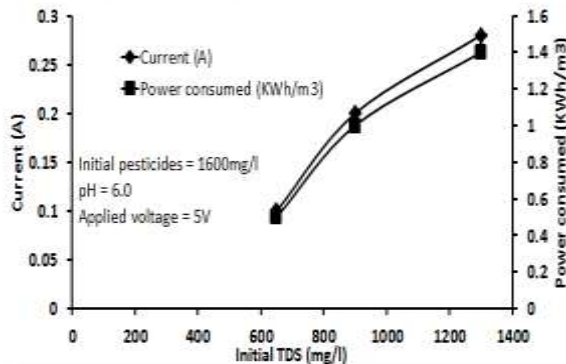


Fig. 10. The effect of initial TDS on the used current and power consumed.

D. Effect of feed solution pH

Fig.(11,12,13) show the pesticides concentration and removal efficiency with EC operational time using various pH feed solution 5, 7, and 9, initial pesticides concentration of 1600mg/l, voltage applied 5V and TDS 650mg/l.

The pesticides removal efficiency increases with time depending on the pH of the feed solution in EC process. This increase depends on the initial pH of the solution and the formation of iron hydroxides which changes the pH of the solution. The highest increase in pesticides removal efficiency was found at initial feed solution pH 5, which corresponds to a removal efficiency of about 81.3% after operational time of 60 minutes, at which the pH of the solution was 7 ± 0.5 . While initial feed solution pH 7 and 9, corresponds to removal efficiency 50 and 62%. It seemed that the optimal pH value was 7 ± 0.5 .

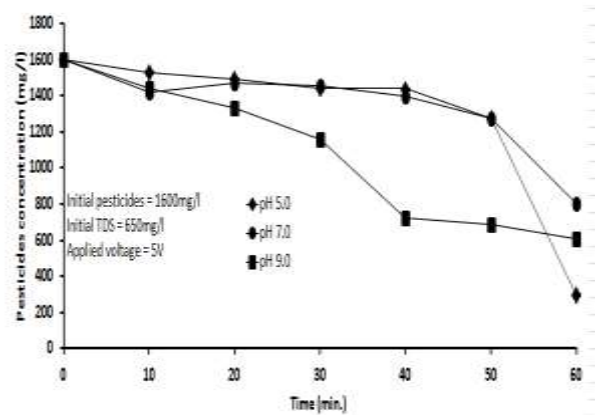


Fig. 11. Pesticides Concentration With Operational Time At Various Initial Ph.

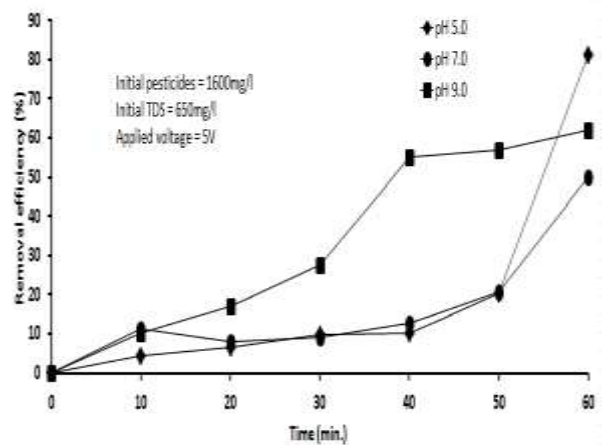


Fig. 12. pesticides removal efficiency with operational time at various initial pH.

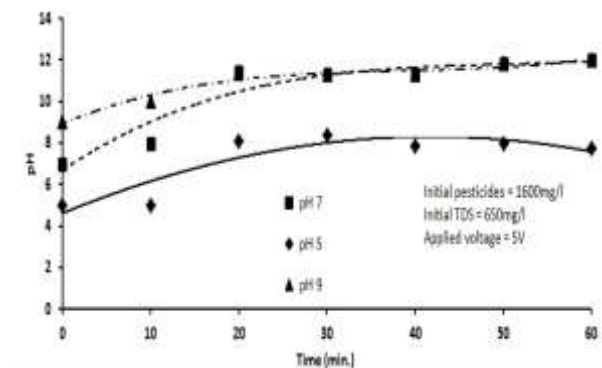


Fig. 13. pH of the solution with operational time using various initial pH.

IV. CONCLUSION

A series of laboratory experiments have been conducted on EC bench scale reactor using iron plates as sacrificial electrodes for the removal of Chlorpyrifos pesticide. It has been found that EC technology is effective to reduce Chlorpyrifos pesticide concentration with removal efficiency of 99% for high pesticide depending on the voltage applied, initial TDS of the feed solution and pH. The increase in initial pesticides concentration is inversely proportional to the removal efficiency of EC process, while the removal efficiency is directly proportional to the voltage applied and initial TDS concentration. The removal efficiency was found to be greater than 90%, for high voltage applied 10 and 15V at operational time of 30 minutes. Further, the removal efficiency was found to be greater than 90%, for high TDS solution 900 and 1300mg/l at operational time of 40 minutes. Although the increase in voltage applied and TDS achieves higher removal efficiencies, it causes an increase in energy consumption. The optimum pH for the removal of Chlorpyrifos pesticide by EC technology was found 7 ± 0.5 . EC technology has proven to be an effective process for the removal of Chlorpyrifos pesticide.

References

- [1] J.D. Mattice, B.W. Skulman, R.J. Norman, and E.E. Gbur, "Analysis of river water for rice pesticides in eastern Arkansas from 2002 to 2008," *J. Soil Wat. Conserv.*, vol. 65, pp. 130-140, 2010.
- [2] A. Navarro, R. Tauler, S. Lacorte, and D. Barcelo, "Occurrence and transport of pesticides and alkylphenols in water samples along the Ebro river basin," *J. Hydrol.*, vol. 383, pp. 18-29, 2010.
- [3] M. E. DeLorenzo, G. I. Scott, P. E. Ross, "Toxicity of pesticides to aquatic microorganisms: a review," *Environ. Toxicol. Chem.*, vol. 20, pp. 84-98, 2001.
- [4] M. S. Hossain, A. N. M. Fakhrudin, M. A. Z. Chowdhury, and M. K. Alam, "Degradation of chlorpyrifos, an organophosphorus insecticide in aqueous solution with gamma irradiation and natural sunlight," *J. Environ. Chem. Eng.*, vol. 1, pp. 270-274, 2013.

- [5] K. Rajeshwar, and J. Ibanez, "Fundamentals and applications in pollution sensors and abatement," *Environmental Electrochemistry*, 1997.
- [6] L. M. Balmer, and A. W. Foulds, "Separation oil from oil-in water emulsions by electroflocculation/electroflotation," *Filtr.*, vol. 23, pp. 366-369, 1986.
- [7] X. Chen, G. Chen, and P.L. Yue, "Separation of pollutants from restaurant wastewater by electrocoagulation," *Purif. Technol.*, vol. 19, pp. 65-76, 2000.
- [8] C. Y. Hu, S. L. Lo, and W. H. Kuan, "Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes," *Water Res.*, vol. 37, pp. 4513-4523, 2003.
- [9] P. R. Kumar, S. Chaudhari, K. C. Khilar, and S. P. Mahajan, "Removal of arsenic from water by electrocoagulation," *Chemosphere*, vol. 55, pp. 1245-1252, 2004.
- [10] J. S. Do, and M. L. Chen, "Decolorization of dye-containing solutions by electrocoagulation," *J. Appl. Electrochem.*, vol. 24, pp. 785-790, 1994.
- [11] T. H. Kim, C. Park, E. B. Shin, and S. Kim, "Decolorization of disperse and reactive dyes by continuous electrocoagulation process," *Desalination*, vol. 150, pp. 165-175, 2002.
- [12] M. Kobya, O. T. Can, and M. Bayramoglu, "Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes," *J. Hazard. Mater.*, vol. B 100, pp. 163-178, 2003.
- [13] N. Daneshvar, H. Ashassi-Sorkhabi, and A. Tizpar, "Decolorization of orange II by electrocoagulation method," *Purif. Technol.*, vol. 31, pp. 153-162, 2003.
- [14] N. Daneshvar, H. Ashassi-Sorkhabi, and M.B. Kasiri, "Decolorization of dye solution containing Acid Red 14 by electrocoagulation with a comparative investigation of different electrode connections," *J. Hazard. Mater.*, vol. B 112, pp. 55-62, 2004.
- [15] Z. Zaroual, M. Azzi, N. Saib, and E. Chainet, "Contribution to the study of electrocoagulation mechanism in basic textile effluent," *J. Hazard. Mater.*, vol. B 131, pp. 73-78, 2006.
- [16] O. Larue, E. Vorobiev, and C. V. B. Durand, "Electrocoagulation and coagulation by iron of latex particles in aqueous suspensions," *Purif. Technol.*, vol. 31, pp. 177-192, 2003.
- [17] J. Ge, J. Qu, P. Lei, and H. Liu, "New bipolar electrocoagulation-electroflotation process for the treatment of laundry wastewater," *Purif. Technol.*, vol. 36, pp. 33-39, 2004.
- [18] P. Gao, X. Chen, F. Shen, and G. Chen, "Removal of chromium(VI) from wastewater by combined electrocoagulation-electroflotation without a filter," *Purif. Technol.*, vol. 43, pp. 117-123, 2005.
- [19] S. Irdemez, N. Demircioglu, Y. S. Yildiz, and Z. Bingul, "The effects of current density and phosphate concentration on phosphate removal from wastewater by electrocoagulation using aluminum and iron plate electrodes," *Purif. Technol.*, vol. 52, pp. 218-223, 2006.
- [20] S. Irdemez, Y. S. Yildiz, and V. Tosunoglu, "Optimization of phosphate removal from wastewater by electrocoagulation with aluminum plate electrodes," *Purif. Technol.*, vol. 52, pp. 394-401, 2006.
- [21] I. n. Ukiwe, S. I. Ibeneme, C. E. Duru, B. N. Okolue, G. O. Onyedika, and C. A. Nweze, "Chemical and electrocoagulation techniques in coagulation-flocculation in water and wastewater treatment," vol. 18, 2014.
- [22] N. Mameri, et al, "De fluoridation of septentrional sahara water of north africa by electro coagulation process using bipolar aluminum electrodes," *Water Research*, vol. 32, pp. 1604-1612, 1998.
- [23] S. Song, Z. He, J. Qiu, and X. L. Chen, "Ozone Assisted Electrocoagulation for Decolorization of C.I Reactive Black 5 in Aqueous Solution: An Investigation of the Effect of Operational Parameters," *Sep Purif Technol.*, vol. 55, pp. 238-245, 2007.
- [24] A. Vlyssides, P. Karlis, M. Loizidou, A. Zorpas, and D. Arapoglou, "Treatment of leachate from a domestic solid waste sanitary landfill by an electrolysis system," *J. Environ. Technol.*, vol. 22, pp. 1467-1476, 2001.
- [25] A. G. Vlyssides, and C. j. Israilides, "Detoxification of tannery waste liquors with an electrolysis system," *Environ. Pollut.*, vol. 97, pp. 147, 1997.