

PERFORMANCE EVALUATION OF ELECTROCOAGULATION PROCESS FOR DIAZINON REMOVAL FROM AQUEOUS ENVIRONMENTS BY USING IRON ELECTRODES

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ABSTRACT

The present study investigates the removal of pesticide by electrocoagulation process. A glass tank in 1.56 L volume with four iron plate electrodes was used to perform the experiments. The electrodes connected to a DC power supply (bipolar mode). The tank was filled with synthetic wastewater which contained diazinon pesticide in concentration of 10, 50 and 100 mg/L. The percent of diazinon removal was measured at pH= 3, 7 and 10 and in electric potential range of 20-40V by thin layer chromatography method. The results indicated that initial concentration of diazinon can affect efficiency removal and for higher concentrations of diazinon, higher electrical potential or more reaction time is needed. The results showed that for a given time, the removal efficiency increased significantly with increase of voltage. The highest electrical potential (40V) produced the quickest treatment with >99% diazinon reduction occurring after 60 min. The final pH for iron electrodes was always higher than initial pH. Finally it can be concluded that electrocoagulation process (using iron electrodes) is a reliable, efficient and cost-effective method for removal of diazinon from aqueous environments, especially designed for pH=3 and voltage=40V.

Key words: Pesticide, diazinon, electrocoagulation, aqueous environments

INTRODUCTION

Pesticides comprise a variety of toxic substances and are used in agriculture as well as indoors to kill pests. The health risk of pesticides to humans is worsened by the fact that many of these substances have been shown to be carcinogenic and mutagenic. Organophosphorus pesticides (OPPs) have a higher acute toxicity than organochlorines, but they have the advantage of being rapidly degraded in the environment (Zohair, 2001; Legrouria *et al.*, 2005). Organophosphorus pesticides are widely found in water resources. They are released into the environment from manufacturing, transportation and agriculture applications (Honeycutt and Schabcker., 1994). Several investigators found high levels of pesticide residues after the washing and/or safety period (Kariem *et al.*, 1991; Ramadan *et al.*, 1992; Saleh

et al., 1993). Organophosphorus pesticides are very toxic when absorbed by human organisms because of acetyl-cholinesterase de activation (Berijani *et al.*, 2006). The European Union (EU) allows a maximum concentration of 0.1 µg/L of each individual pesticide and 0.5 µg/L of the sum of pesticides in drinking water (European Union., 1998). Diazinon is one of the most widely used organophosphate insecticides in agriculture (Gokcimen *et al.*, 2007). Chemical formula of diazinon is C₁₂H₂₁N₂O₃PS, molecular weight is 304.3 and density (at 20°C) is 1.117 g/mL (Badawya *et al.*, 2006). It is an organophosphorus insecticide classified by the World Health Organization (WHO) as “moderately hazardous” class II. It was associated with toxicity to aquatic organisms at concentration of 350 ng/L, with an LC₅₀ in killifish (48 h) of 4.4 mg/L. Fetal human doses were found to be in the range from 90 to

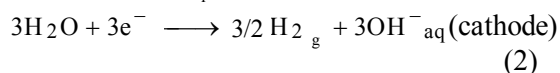
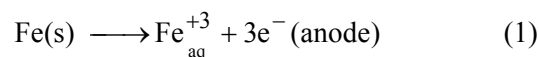
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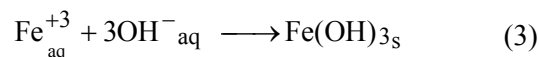
444 mg/kg (Shemer and Linden, 2006). Toxic effects of diazinon are attributed to its inhibition of the enzyme acetyl-cholinesterase. Diazinon is relatively water soluble (40 mg/L at 25 °C), non-polar, moderately mobile and persistent in soil; hence, it is of concern for groundwater and surface derived drinking water (Kidd and James, 1991). Diazinon has a log K_{ow} of 3.3, vapor pressure of 1.4×10^{-4} mm Hg at 20 °C, and Henry's law constant of 1.4×10^{-6} atm m³/mol which would indicate that it would not easily volatilize from soil or water. However, vaporization of diazinon from water of up to 50% of applied mass was reported (Howard, 1991). Diazinon and its metabolites have been detected in aquatic systems worldwide (Shemer and Linden, 2006). Its sediment-water partition coefficient is small indicating minor adsorption of the substance on sediments. Contamination of water by pesticides is mainly due to runoff, usually within a few weeks after application. Once in the environment, its fate depends on volatilization, hydrolysis, and photolysis (Feigenbrugel *et al.*, 2004). Diazinon undergoes fast hydrolysis at acidic and basic conditions, with half lives of 0.5, 171, and 6 days at pH= 3.1, 7.3, and 10.4 (at 20–25°C), respectively (Zhang and Pehkonen, 1999; Mansour *et al.*, 1999).

The pesticide and chemical industries are considered to generate wastewaters containing toxic and non-biodegradable compounds that remain in the environment even after their wastewaters have been subjected to conventional processing (Badawy, 1998; Jannsens *et al.*, 1997). Therefore, the human population is exposed to pesticides and other organic micropollutants either through drinking water or via the food supply. In addition, there is a formation of mutagenic compounds during conventional oxidation processes (Jannsens *et al.*, 1997; Bertanza *et al.*, 2001). Therefore, it is very important to develop water and wastewater treatment technologies for the removal of toxic and refractory organic compounds from water and wastewater. A way for diazinon removal from aqueous environments is electrocoagulation process which is without any chemical material using and only uses transferring iron ion's electron to solution in the form of metal. In this method, diazinon precipitates and remove.

In fact, in electrocoagulation process, the flocculating agent is generated by electro oxidation of a sacrificial anode, generally made of iron or aluminum. In this process, the treatment is done without adding any chemical coagulant or flocculants, thus reducing the amount of sludge which must be disposed (Cenkin and Belevstev, 1985). An examination of the chemical reactions occurring in the electrocoagulation process shows that the main reactions occurring at the electrodes are:



In addition, Fe^{3+} and OH^{-} ions generated at electrode surfaces react in the bulk wastewater to form ferric hydroxide:



The iron hydroxide flocs act as adsorbents and/or traps for pollutants and so eliminate them from the solution (Cenkin and Belevstev, 1985; Ogutveren *et al.*, 1994).

The objective of this research was to survey efficiency of electrocoagulation process removal of diazinon from aqueous environments with iron electrodes and determination of the effects of voltage, pH and reaction time on the removal efficiency.

MATERIALS AND METHODS

This study has been conducted in the environmental chemistry laboratory of School of Public Health at Tehran University of Medical Sciences, in late 2006. All chemicals including diazinon, acetone, hexane, sodium hydroxide pellets, concentrated sulfuric acid and potassium chloride were provided from Merck Company. Desired concentrations of diazinon solution were prepared by mixing proper amount of diazinon (60%) with deionized water. In order to increase the conductivity of the solution to 1.6 mS/cm, potassium chloride (1 N) was added to the solution before injecting it into the apparatus. The chloride salt added to the solution can also prevent the formation of the oxide layer on the anode and therefore reduce the passivation problem of the electrodes. The pH of the initial solution was

adjusted by using sulfuric acid solution and sodium hydroxide (0.1 M). Experiments were performed in a bipolar batch reactor, with four iron electrodes connected in parallel (bipolar mode). Only the outer electrodes were connected to the power source, and anodic and cathodic reactions occurred on each surface of the inner electrode when the current passed through the electrodes. The internal size of the cell was 10 cm×13cm×12cm (width×length×depth) with an effective volume of 1000 cm³. The volume (V) of the solution of each batch was 1 l. The active area of each electrode was 10×10 cm. The distance between the electrodes was 1.5 cm. A power supply pack having an input of 220V and variable output of 0–40V with maximum current of 5 am was used as a direct current source. The pH values in influent and reactor unit were measured using a pH meter model E520 (Metrohm Herisau, Switzerland). A Jenway conductivity meter (Model 4200) was employed to determine the conductivity of the solution. Samples were extracted after 10, 20, 40 and 60 minutes. Diazinon concentration was determined with mobile phase of hexane-acetone (10:40) in water and absorbance detection at 254 nm. Finally diazinon concentration was determined by high performance thin layer chromatography method (TLC scanner 3, program cats 4, Camay, Swiss). In order to study the effect of turbidity on diazinon pesticide removal by electrocoagulation process, a set of experiments with different initial concentrations of turbidity (10, 50 and 200 NTU) were performed under optimum conditions (pH=3, time=60 min, voltage= 40 V). Standard solution of turbidity was prepared by dissolving 5 g of hydrazine sulfate and 50 g of hexamethylenetetramine in one liter of distilled water (this solution is equal to 4000 NTU). Also, in order to study the effect of organic matter presence (such as COD) on diazinon removal by electrocoagulation process, a set of experiments with different initial concentrations of COD (100, 500 and 1000 mg/L) were performed under optimum conditions (pH=3, time=60 min, voltage= 40V). Standard solution of COD was prepared by dissolving 8.502 g of potassium hydrogen phthalate (KC₈H₅O₄) in distilled water and diluted to 1,000 mL. The prepared solution had a theoretical COD value of 10,000 mg/L.

RESULTS

The electrocoagulation process is quite complex and may be affected by several operating parameters such as pollutant concentration, initial pH, electric potential (voltage), presence of organic matter (such as COD), electrical conductivity and turbidity. The results of diazinon pesticide removal for various initial concentrations of 10, 50 and 100 mg/L by electrocoagulation process using iron electrodes are shown in Tables 1, 2 and 3.

Table 1: Percent of diazinon removal
Initial concentration = 10 mg/L

pH	voltage (V)	Time (min)			
		10	20	40	60
3	20	23.0	38.0	52.0	72.0
	30	31.0	39.0	57.0	79.0
	40	39.0	51.0	69.0	>99.9
7	20	31.0	37.0	41.0	49.0
	30	30.0	37.0	55.0	69.0
	40	34.0	49.0	58.0	86.0
10	20	29.0	35.0	47.0	49.0
	30	32.0	35.0	56.0	76.0
	40	38.0	51.0	59.0	87.0

Table 2: Percent of diazinon removal
Initial concentration = 50 mg/L

pH	voltage (V)	Time (min)			
		10	20	40	60
3	20	23.2	31.6	71.4	83.2
	30	30.2	39.2	71.8	86.6
	40	41.4	51.8	73.6	>99.98
7	20	19.6	27.8	57.6	65.2
	30	23.8	37.6	47.2	69.2
	40	27.8	43.2	55.4	84.8
10	20	23.2	27.8	65.4	73.6
	30	29.8	42.2	67.8	85.4
	40	39.2	49.8	69.6	95.4

Table 3: Percent of diazinon removal
Initial concentration = 100 mg/L

pH	voltage (V)	Time (min)			
		10	20	40	60
3	20	55.4	60.9	81.7	90.8
	30	58.8	66.1	85.9	92.6
	40	66.9	71.6	87.7	>99.99
7	20	53.3	58.1	78.7	85.9
	30	56.2	62.6	81.9	88.7
	40	61.9	70.2	82.6	92.4
10	20	52.9	59.2	79.6	89.7
	30	56.9	63.6	84.3	91.9
	40	63.8	69.2	84.9	>99.99

Results illustrate that diazinon removal efficiency for different conditions such as initial pH and electrical potential is significant (>90%). Table 4

illustrates the results of consumed iron electrode during electrocoagulation process for various pH and diazinon initial concentrations. With increase in electrical potential, the amount of electrode consumption increased, too. So, the highest electrode consumption was observed at electrical potential of 40V. Table 5 shows the amount of consumed energy during electrocoagulation process at voltage 40V and for different initial concentrations of diazinon. These results illustrated that consumed energy decreased with increase in diazinon initial concentration.

Table 4: Iron electrode consumption (g/L)

Voltage (V)	Initial diazinon concentration (mg/L)		
	10.0	50.0	100.0
20	2.7	3.83	4.1
30	4.83	9.2	8.87
40	12.6	12.0	8.43

Table 5: Energy consumption (kwh/g), using iron electrodes at voltage = 40 V

Initial pH	Initial diazinon concentration (mg/L)		
	10	50	100
20	11.48	3.51	1.39
30	14.28	3.56	1.43
40	14.0	2.83	1.41

DISCUSSION

In the present study, electrocoagulation process has been evaluated as a treatment technology for diazinon removal from industrial effluents. Diazinon removal efficiency at different condition (pH, electrical potential) in various times was evaluated. It has been established in previous studies (Vik *et al.*, 1984; Chen *et al.*, 2000) that pH has a considerable effect on the efficiency of the electrocoagulation process. Also, as observed by other investigators the pH of the medium changed during the process. This change depends on the type of electrode material and initial pH. In this study, the pH was varied in the range 3–10 in an attempt to investigate the influence of this parameter on the removal of diazinon. Removal efficiencies of diazinon as a function of initial pH with iron electrodes are presented in Tables 1 and 3. As observed by other investigators (Vik *et al.*, 1984), a pH increase occurs when the initial pH is low (< 7). Vik ascribed this increase to hydrogen evolution at cathodes. In addition, if the initial pH is acidic, reactions would shift towards which

causes a pH increase. In alkaline medium (pH > 8), the final pH does not vary very much and a slight drop was recorded. This result is in accord with previously published works and suggests that electrocoagulation can act as pH buffer. In this research, the initial pH did not affect the removal efficiencies significantly over a wide range. Therefore, pH adjustment before treatment is not required in practical applications. The highest efficiency of diazinon removal observed in acidic medium (pH=3). The pH variation of solution after electrocoagulation process in various voltages showed that the final pH for all of experiments with iron electrodes is higher than initial pH, which is in agreement with other studing (Kobya *et al.*, 2003).

Preliminary laboratory testing of the electrolysis cell involved determining the effect of applied voltage on the efficiency of diazinon removal. It is well-known that electrical potential not only determines the coagulant dosage rate but also the bubble production rate and size and the flocs growth (Letterman *et al.*, 1999; Holt *et al.*, 2002), which can influence the treatment efficiency of the electrocoagulation. Therefore, the effect of electrical potential on the pollutants removal was investigated. As expected, it appears that for a given time, the removal efficiency increased significantly with increase of electrical potential. The highest electrical potential (40V) produced the quickest treatment with >90% diazinon reduction occurring after 60 min and the lowest diazinon removal efficiency occurred in the lowest electrical potential (20V). This is ascribed to the fact that at high voltage, the amount of iron oxidized increased, resulting in a greater amount of precipitate for the removal of pollutants. In addition, it was demonstrated that bubbles density increases and their size decreases with increasing current density (Khosla *et al.*, 1991), resulting in a greater upwards flux and a faster removal of pollutants and sludge flotation. As the current decreased, the time needed to achieve similar efficiencies increased and the results of this research confirm this fact. This expected behavior is explained by the fact that the treatment efficiency was mainly affected by charge loading ($Q=It$), as reported by Chen (Chen *et al.*, 2000).

However, the cost of the process is determined by the consumption of the sacrificial electrode and the electrical energy which economically are the advantages of this method. These results suggest 40V as an optimal electrical potential for the treatment of effluents containing diazinon, since it ensures the quickest removal rate with the lowest cost.

A set of experiments was performed with different initial concentrations of diazinon to determine the time required for removal under various conditions of electrocoagulation process. The results obtained at different electrical potential showed that initial concentration of diazinon can effect on efficiency removal and for higher concentration of diazinon, higher electrical potential or more reaction time is needed. On the other hand, if the initial concentration increases, the time required of process should increase too. And, also it is clear from Tables 1 and 3 that for higher concentrations, greater time was needed for removal of diazinon, but that higher initial concentrations of diazinon were reduced significantly in relatively less time than lower concentrations. The time taken for reduction thus increased slowly with increase in concentration. This can be explained by the theory of dilute solution. In dilute solution, formation of the diffusion layer at the vicinity of the electrode causes a slower reaction rate, but in concentrated solution the diffusion layer has no effect on the rate of diffusion or migration of metal ions to the electrode surface (Chaudhary *et al.*, 2003).

The time dependence of diazinon removal by electrocoagulation process at different pH shown in Tables 1 and 3. describe that up to 30-70 % of the initial concentration decreased within 20 min of the process at different concentrations and the residual diazinon concentration in effluent were less 0.01 mg/L and finally at the end of reaction time (60 min) reached to zero mg/L so we could discharge treated effluents to environment, in safety. At the beginning of process the diazinon removal was rapid and later it decreased gradually over almost the entire process examined.

Diazinon was more abundant at the beginning of the electrocoagulation process, and the generated iron hydroxides due to corrosion of the anode at that time will form complexes with diazinon and

therefore rapid removal of diazinon was observed. A set of experiments was performed with different initial concentrations of diazinon (10, 50 and 100 mg/L) to examine the effect of the presence of organic matter (such as COD with concentration 100, 500 and 1000 mg/L O₂) and various levels of turbidity (10, 50 and 200 NTU) in wastewater on the removal efficiency of diazinon. The results obtained at optimum conditions (pH=3, reaction time=60 min and voltage=40V) showed that the removal efficiency for various concentrations of diazinon decreased, but it was not significant. Hence the electrocoagulation process can be efficiently applied for diazinon removal in presence of organic matter and turbidity.

A series of tests were conducted with different concentrations of diazinon in the solution and the weight of the electrode consumed with respect to different voltage levels (given in Table 4) show that the higher the applied voltage, the higher the weight of the electrode consumed. Also, higher initial diazinon concentrations in the solution result in higher electrode consumption weights. As the Table illustrates, the weight of electrode consumed at 40 volts was much higher than that at 20 volts. Also, an increase in initial diazinon concentration to 500 mg/L, did not result in a significant increase in electrode consumption. However, at this concentration, coagulation has taken place and the high formation of the flocs has helped the complexation of diazinon and there was no need for much consumption of the electrode as at low initial diazinon concentrations.

Table 5 shows energy consumption results for the removal of one gram of diazinon at 40V, initial diazinon concentrations of 5, 50 and 500 mg/L, and pH 3, 7 and 10. It can be concluded that the consumed energy decreased with increase in initial diazinon concentration, because the flocs formation will help the adsorption of the diazinon from the solution. Finally, it can be concluded that electrocoagulation method is a reliable, safety, efficient and cost-effective method for removal of diazinon from aqueous environments, especially designed for pH=3 and voltage=40V. On the other hand, in this study it was shown that electrocoagulation process using iron electrodes achieves a fast and effective reduction of diazinon

(more than 99%) present in industrial effluents. Indeed, the reported results show that electrocoagulation is faster and more effective process as compared to other methods alone. Nevertheless, further studies should be carried out to confirm the practical feasibility of this method for treating various wastewaters and with different condition.

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REFERENCES

- Badawy, M. I., (1998). Use and impact of pesticides in Egypt. *Int. Environ. Health Res.*, **8**: 223–240.
- Berijani, S., Assadi, Y., Anbia, M., Milani Hosseini, M. R., Aghaee, E., (2006). Dispersive liquid–liquid microextraction combined with gas chromatography–flame photometric detection Very simple, rapid and sensitive method for the determination of organophosphorus pesticides in water. *J. Chromatography.*, **1123**: 1–9.
- Bertanza, G., Collivignarell, C., Pedrazzen, I. R., (2001). The role of chemical oxidation in combined chemical-physical and biological processes: experience of industrial wastewater treatment. *Water. Sci. Technol.*, **44**: 109–116.
- Cenkin, V. E., Belevstev, A. N., (1985). Electrochemical treatment of industrial wastewater, *Eff. Water. Treat. J.*, **25** (7): 243–249.
- Cenkin, V. E., Belevstev, A. N., (1985). Electrochemical treatment of industrial wastewater, *Eff. Water. Treat. J.*, **25** (7): 243–249.
- Chaudhary, A. J., Goswami, N. C., and Grimes, S. M., (2003). Electrolytic removal of hexavalent chromium from aqueous solutions. *J. Chem. Technol. Biot.*, **78**: 877–883.
- Chen, X., Chen, G., Po, L. Y., (2000). Separation of pollutants from restaurant wastewater by electrocoagulation. *Sep. Purif. Technol.*, **19**: 65–76.
- Drinking Water Guideline, 98/83/EEC, European Union, Brussels, 1998.
- Feigenbrugel, V., Le Calve, S., Mirabel, P., (2004). Temperature dependence of Henry's law constants of metolachlor and diazinon, *Chemosphere*. **57**, 319–327.
- Gokcimen, A., Gulle, K., Demirin, H., Bayram, D., Kocak, A., Altuntas, I., (2007). Effects of diazinon at different doses on rat liver and pancreas tissues. *Pestic. Biochem. Phys.*, **87**: 103–108.
- Holt, P. H., Barton, G. W., Wark, M., Mitchell, A. A., (2002). A quantitative comparison between chemical dosing and electrocoagulation, *Colloids Surf. A: Physicochem. Eng. Aspects.*, **211**: 233–248.
- Honeycutt, R. C., Schabcker, D. J., (1994). *Mechanisms of Pesticides Movement into Ground Water*, CRC Press, Boca Raton, FL.
- Howard, P., (1991). *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*, Lewis Publishers, Inc., Chelsea, MI. 209–221.
- Janssens, I., Tanghe, T., Verstraate, W., (1997). Micropollutants: A Bottleneck in sustainable wastewater treatment. *Water. Sci. Technol.*, **35**: 13–26.
- Kariem, A. M., Ramadan, R. A., Mostafa, A. M., (1991). Fungicides in controlling strawberry fruit and their residues in fruits. *Egyptian. J. Appl. Sci.* **6**: 710–719.
- Khosla, N. K., Venkachalam, S., Sonrasundaram, P., (1991). Pulsed electrogeneration of bubbles for electroflotation. *J. Appl. Electrochem.*, **21**: 986–990.
- Kidd, H., James, D. R., (1991). *The Agrochemicals Handbook*, 3rd Ed. Royal Society of Chemistry Information Services, Cambridge, UK., 5–14.
- Kobyas, M., Taner-Can, O., and Bayramoglu, M., (2003). Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. *Journal of Hazardous Materials* **B100.**, **163**–178.
- Legrouria, A., Lakraimib, M., Barroug, A., De Royc, A., Bessec, J. P., (2005). Removal of the herbicide 2, 4-dichlorophenoxyacetate from water to zinc–aluminium–chloride layered double hydroxides, *Water. Res.*, **39**: 3441–3448.
- Letterman, R. D., Amirtharajah, A., and O'Melia, C. R., (1999). *A Handbook of Community Water Supplies*. 5th Ed. AWWA, Mc Graw-Hill, N. Y. USA.
- Mansour, M., Feicht, E. A., Behechti, A., Schramm, K.W., Kettrup, A., (1999). Determination photostability of selected agrochemicals in water and soil, *Chemosphere* **39**: 575–585.
- Ogutveren, U. B., Gonen, N., Koparal, A. S. (1994). Removal of chromium from aqueous solutions and plating bath rinse by an electrochemical method, *Int. J. Environ. Stud.*, **45**: 81–87.
- Ramadan, R. A., Saleh, M. A., El-Shemy, M. K., (1992). Residues of some pesticides on cucumber, green pepper and eggplant fruits under plastic green house conditions., *Egyptian. J. Appl. Sci.*, **7**: 861–870.
- Saleh, M. A., El-Shemy, M. K., Flaifel, M. A., (1993). Determination of benomyl, dichlorfluanid and proclonazole residues in strawberry fruits. *Egyptian. J. Appl. Sci.*, **8**: 15–20.
- Shemer, H., Linden, K. G., (2006). Degradation and by-product formation of diazinon in water during UV and UV/H₂O₂ treatment. *J. Hazardous. Mater.* **B136**, 553–559.
- Vik, E. A., Carlson, D. A., Eikum, A. S., Gjessing, E. T., (1984). Electrocoagulation of potable water. *Water. Res.*, **18**: 1355–1360.
- Zhang, Q., Pehkonen, S. O., (1999). Oxidation of diazinon by aqueous chlorine: kinetics, mechanisms, and product studies, *J. Agric. Food. Chem.*, **47**: 1760–1766.
- Zohair, A., (2001). Behaviour of some organophosphorus and organochlorine pesticides in potatoes during soaking in different solutions. *Food. Chemical. Toxicol.*, **39**: 751–755. 441–3448.