



Electrochemical Process for Diazinon Removal from Aqueous Media: Design of Experiments, Optimization, and DLLME-GC-FID Method for Diazinon Determination

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Abstract In the present study, electrochemical process was studied via removal of diazinon (O,O-diethyl O-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate) as an insecticide/acaricide organic case study. Influences of three operational parameters including initial ferrous ion concentration, initial hydrogen peroxide concentration, and initial diazinon concentration were measured and optimized in diazinon removal process. Response surface methodology (RSM) was used to design the experiments. The experimental data collected in a laboratory-scaled batch reactor equipped with four graphite bar electrodes as cathode and an aluminum sheet electrode as an anode. Quantitative analysis of diazinon was done with gas chromatography equipped with flame photometric detector. Disperse liquid–liquid microextraction was used prior to gas chromatography in order to extraction and preconcentration of diazinon from aqueous media to extraction phase. Acetone and chlorobenzene were used as disperser and extraction solvent, respectively. Maximum diazinon removal efficiency of 87 % (0.85 mg mass removal) in C_0 of 2 mg/L and 80 % (120 mg mass removal) in C_0 of 300 mg/L was achieved under different experimental conditions. The obtained experimental data were used for model building by RSM approach. Finally, optimization process was carried out using RSM algorithm.

Keywords Diazinon removal · Electrochemical process · Electro-Fenton · Electro-coagulation · Response surface methodology · Disperse liquid–liquid microextraction

1 Introduction

The environment widespread occurrence of pesticides especially in water is a recognized concern [1–3]. Agricultural and pesticide industries' wastewaters were reported to have pesticides contamination levels as high as 500 mg/L which pose a threat to the quality of surface water, groundwater, and drinking water. Pesticides are generally toxic to nontarget receptors including humans [4,5]. Pesticides reach humans through food chain. Different pesticides cause to different types of risks and disease [6].

Organophosphorus insecticides (OPPs) have been widely used in agriculture. The acetylcholinesterase enzyme inhibiting is toxic action of OPPs. Diazinon is an insecticide and acaricide OPP [7,8]. Diazinon is used to control a wide range of agricultural soil-dwelling insects, sucking and chewing insects, mites, sheep dip, and ectoparasites. However, diazinon is a contact, stomach, and respiratory poison. Also, diazinon has been identified as a potential chemical mutagens [9–11].

Since most of the pesticides are nonbiodegradable, various novel technologies such as membrane technology, photocatalytic oxidation, and ultrasonic radiation have been proposed as the novel treatment approaches. However, the proposed approaches have some disadvantages such as not cost-effective, not ecofriendly, and not involving low concentrations [1, 12–16]. In recent years, the studies of electrochemical method application including electro-oxidation process (EOP), electro-coagulation process (ECP), electrofloatation process (EAP), and electro-Fenton process (EFP)

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for pesticides removal are of interest [17–20]. These methods are environmentally friendly, and they do not often form new toxic wastes. The previous reports revealed that the efficiencies of these processes are drastically dependent on the operational parameters [5, 6, 8, 21].

The electro-based process consist of electro-coagulation (ECP) [17, 18] technique, and electro-Fenton (EFP) [8, 22, 23] and Electro-flotation (EAP) are considered to be potentially effective approaches to treat several wastewaters [24]. ECP is a process consisting metallic hydroxide flocs generation within the wastewater by electro-dissolution of soluble anodes, usually made of iron and aluminum. The produced gas of ECP could create and float the flocs. Several publication of ECP/EFP approves the compatibility of this combined method. EFP consists of electro-generation of H_2O_2 and Fe^{2+} that cause to avoid of the high cost of H_2O_2 and to maintain constant H_2O_2 and Fe^{2+} concentration [8, 19].

Therefore, the objectives of this study are diazinon removal through the synthetic aqueous solution, investigation of three more important operational parameters, and application of response surface methodology (RSM) for modeling and optimization of the process [25, 26].

2 Materials and Methods

The desired concentrations of diazinon were prepared by serial diluting of the 500 mg/L stock solution of diazinon in acetone HPLC grade. Graphite electrodes were prepared from KIG-Co., Iran. Aluminum sheet electrodes were purchased from local seller and prepared by cutting in desired size. Ferrous ammonium sulfate (Merck, Germany) was used to prepare standard ferrous (Fe^{2+}) solutions. Hydrogen peroxide 30% (Merck, Germany) was used to prepare the stock solutions by serial dilution. The hydrogen peroxide stock solution was standardized using manganometry method. Whole other reagents were purchased from Merck, Germany.

2.1 DLLME-GC-FID Approach for Diazinon Deamination

Aqueous samples (5 mL portions) were filtered with 0.21 μm syringe filter. The filtered samples were poured in a 10 mL screw-cap glass test tubes with conical bottoms. Acetone (1 mL) as disperser solvent and 50.0 μL chlorobenzene as extraction solvent were injected rapidly into the sample solution by using a 1 mL Hamilton syringe. The mixture was gently shaken that cause to cloudy solution was formed in the test tube. The test tube was shaken using test tube shaker for 2 min. In this step, diazinon in aqueous sample was extracted into the fine droplets of chlorobenzene. The mixture was then centrifuged for 5 min at 4000 rpm. The dispersed fine

droplet of chlorobenzene that was sedimented in the bottom of the test tube was withdrawn using 1 μL microsyringe and injected into GC-FID. Quantitative analysis of diazinon was done with GC model cp-3800 (Varian Inc., Palo Alto, USA) equipped with flame photometric detector at 280 °C. A CP-Sil 8 CB (CP7721) capillary column for pesticides (50 m, 0.25 mm, 0.12 μm Varian Inc., Palo Alto, USA) was employed for GC separation. Nitrogen carrier gas was set at constant flow rate mode with 1 mL/min flow rate. The GC oven temperature program was as follows: initial temperature of 50 °C held 2 min, then from 50 to 150 °C at 20 °C/min, from 150 to 175 °C at 5 °C/min, from 175 to 195 °C at 2 °C/min, from 195 to 275 °C at 10 °C/min and held 5 min at 275 °C. The injector and detector temperatures were set at 250 and 270 °C, respectively. Sample solution (1 μL) was injected in split-less mode.

2.2 Design of Experiments, Reactor and Experiments Procedures

Design of experiments was used to reduce a number of experiments. In this study, 15 experiment runs were designed based on response surface methodology (RSM). It was applied for investigation of $C_{\text{Fe}^{2+}}$, $C_{\text{H}_2\text{O}_2}$, and C_0 in five levels for each parameter. The details of the RSM design are presented in Table 1.

A cylindrical glass reactor was constructed that was equipped with 120 rpm magnetic stirrer, DC power supply (RXN-303D-II, Zhaoxin Electronic Tech. Co.), an aluminum electrode as anode, and four-connected graphite electrode as cathode. The anode was made of aluminum sheets [40 × 100 × 1 (mm)] with 40 cm² effective immersed surface area. Each cathode electrode made of graphite bar [10 × 120 (mm)] with 3 cm² effective immersed surface area. The cubic arrangement of four electrodes was used to increase effective current intensity. The electrodes were placed vertically and dipped in 500 mL synthetic waste solutions. The distance between electrodes was fixed at 1 cm (Fig. 1). The reactor was opened to the atmosphere in the room temperature and potentiostat condition at 10 V.

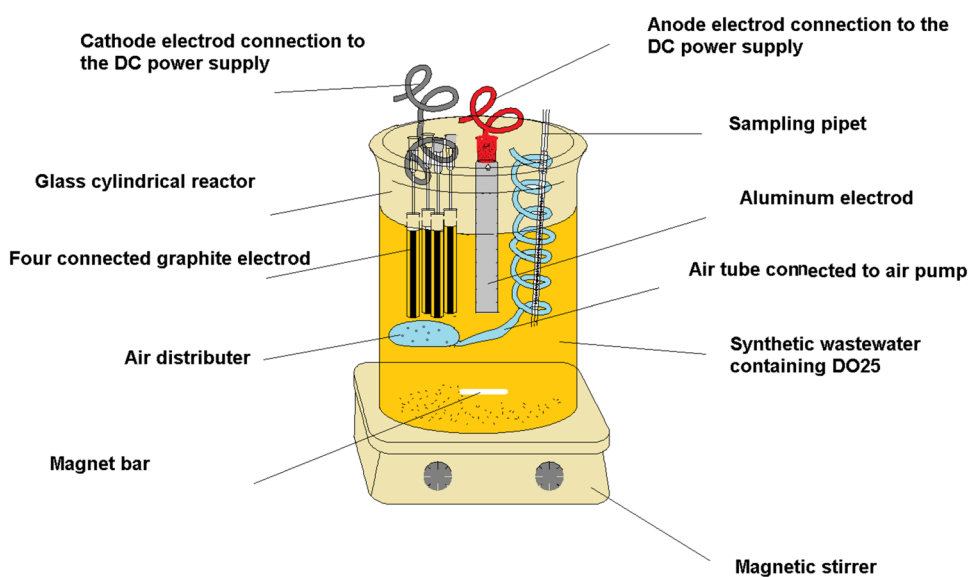
In each run, 500 mL diazinon solution was decanted into the reactor. Because of real-state simulation, no additional buffer was added to the solution. Therefore, pH was natural with small variation between 6.5–7. To increase solution conductivity, the electrolyte KCl salt (0.1 M) was added to the whole samples. The empirical parameters including $C_{\text{Fe}^{2+}}$, $C_{\text{H}_2\text{O}_2}$, and C_0 were adjusted to the desired value according to design of experiments by pouring the determined amount of stock solution of ferrous cations, hydrogen peroxide, and diazinon. In each experiment, the concentration of diazinon in samples was determined by mentioned DLLME-GC-FID method. Finally, the diazinon removal was calculated for samples using Eq. 1:

Table 1 The 15 run details of RSM design of experiments

Run	C _{Fe2+} (mg/L)	C _{H2O2} (mg/L)	C ₀ (mg/L)	DR (mg)	Run	C _{Fe2+} (mg/L)	C _{H2O2} (mg/L)	C ₀ (mg/L)	DR (mg)
1	5	5	2	0.87	9	7.5	2.5	10	3.66
2	5	5	50	14.4	10	2.5	7.5	10	2.54
3	0	5	50	14.7	11	5	0	50	13.7
4	2.5	2.5	10	2.37	12	7.5	7.5	10	2.96
5	7.5	7.5	100	13.7	13	2.5	2.5	100	23.0
6	2.5	7.5	100	32.8	14	7.5	2.5	100	33.7
7	5	10	50	11.9	15	5	5	300	120
8	10	5	50	15.0					

Where voltage = 10(V), pH = natural (6.5–7), and time of reaction = 45 (min)

Fig. 1 The laboratory-scale batch reactor



$$\text{Diazinon removal (mg)} = (1 - C/C_0) \times V \times C_0 \quad (1)$$

where *V* is the solution volume (L), *C*₀ and *C* are diazinon concentration (mg/L) before and after process, respectively.

3 Results and Discussions

The diazinon retention time was almost 11.6 min in the chromatograms. A few variation in diazinon was observed during the 15 runs. It may be because of alteration of chemical environment (matrix effect) during serial dilution of samples. There is no oxidation peak in chromatograms that is logical when the anode is aluminum sacrificial electrode as an active electrode for electrocoagulation process. In electrocoagulation, sacrificial electrode is oxidized and produces the electro-coagulants. It is an advantage of electro-coagulants that prevents production of secondary toxic materials by oxidation of contaminants.

The experimentally obtained diazinon removal values (mg) are presented in Table 1. High diazinon removal values (mg) demonstrate good efficiency of electrochemical process in diazinon removal. Also, the glance of Table 1 can illustrate the influences of three studied operational parameters on electrochemical efficiency in diazinon removal. The maximum diazinon removal was 80 % (120 mg) in *C*₀ of 300 mg/L, *C*_{H2O2} of 5 mg/L, and *C*_{Fe2+} of 5 mg/l. Also, diazinon removal was 87 % (0.87 mg) in *C*₀ of 2 mg/L, *C*_{H2O2} of 5 mg/L, and *C*_{Fe2+} of 5 mg/L. The high efficiency of low concentration Fenton reagents confirms the influences of electrochemical process to generate/regenerate the Fenton reagents during the process.

Since this study was done in potentiostat condition at 10 V, the electric current intensity will be dependent to conductivity of the solution and also electrode lifetime. The initial and final electric current intensities and initial and final electric current densities were determined during the process and are presented in Table 2. Based on Table 2, electric current intensity declines during the process. This phenomenon may

Table 2 Initial and final electric current intensity and electric current density in whole 15 runs

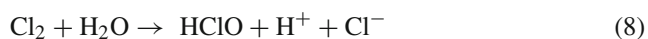
Run number	Initial electric current intensity	Final electric current intensity	Initial electric current density of anode	Final electric current density of anode	Initial electric current density of cathode	Final electric current density of anode
1	0.49	0.16	123	40	408	133
2	0.44	0.17	110	43	367	142
3	0.06	0.05	15	13	50	42
4	0.24	0.11	60	28	200	92
5	0.49	0.15	123	38	408	125
6	0.21	0.09	53	23	175	75
7	0.4	0.12	100	30	333	100
8	0.63	0.2	158	50	525	167
9	0.53	0.19	133	48	442	158
10	0.4	0.17	100	43	333	142
11	0.43	0.16	108	40	358	133
12	0.67	0.22	168	55	558	183
13	0.25	0.12	63	30	208	100
14	0.56	0.18	140	45	467	150
15	0.45	0.16	113	40	375	133

because of decreasing the conductivity during the process, production of colloidal precipitation, or the electrode surface pollution and inactivation during process.

The main reactions occurring in electrocoagulation with aluminum anode and graphite cathode are aluminum oxidation at the anode (Eq. 2) and water reduction at the cathode (Eq. 3). The produced Al^{3+} and OH^- ions react in the bulk to form aluminum hydroxide (Eq. 4). The aluminum hydroxide flocs normally act as adsorbents/traps for pollutants [27].



In the sufficient high potential, compatible reactions may occur including oxidation of diazinon, oxidation of water (Eq. 5), oxidation of chloride (Eq. 6), and reduction of Fe^{3+} to generate ferrous ion as the main Fenton reagent (Eq. 7). The produced chlorine may react with water in pH higher than 3–4 (Eqs. 8, 9) [27].



The regenerate ferrous ion reacts with the low concentrate added hydrogen peroxide to generating the hydroxyl radicals as a highly effective oxidant (Eq. 10).



The oxidative metabolism of diazinon by microsomes has been reported. Desulfuration, hydroxylation of the ring-alkyl side chain, and cleavage of the pyrimidinyl phosphate bond are three main mechanism of this reactions. Diazoxon, hydroxydiazinon, hydroxydiazoxon, pyrimidine, and hydroxypyrimidine are the identified oxidative metabolites of diazinon. Diazoxon and hydroxydiazinon toxicity are similar to diazinon. They are significantly more toxic than the other identified metabolites [28].

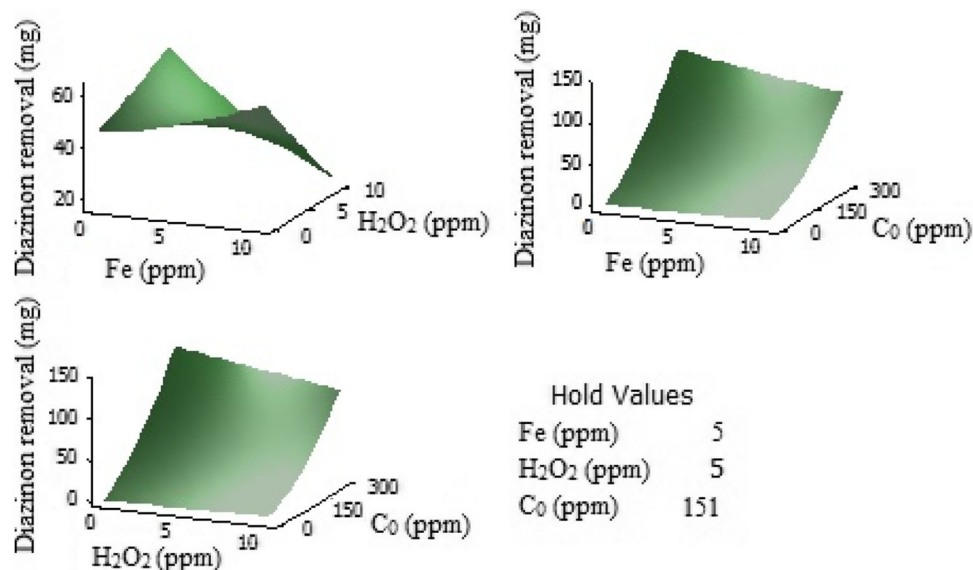
Response surface methodology (RSM) was applied to investigate the parameter influences and interactions. The RSM full quadratic model was developed for diazinon removal. Some parameters were statistically insignificant which were removed. The statistical details of the modified RSM model are presented in Table 3. The goodness parameters of model presented in Table 3 indicate that the RSM model presents a good predictability for diazinon removal.

The best RSM model presented graphically in Fig. 2. Based on the results, concentration of Fenton reagents ($C_{\text{H}_2\text{O}_2}$ and $C_{\text{Fe}^{2+}}$) has positive influences on diazinon removal. The similar result has presented frequently in similar studies. The more concentration of Fenton reagents causes more production of hydroxyl radicals. It causes more diazinon removal. Also, initial concentration of diazinon (C_0) has positive influences on diazinon removal. The more concentration causes faster kinetic of removal reaction. The faster kinetic causes more removal of diazinon in the determined time of reaction (45 min).

Table 3 Statistical details of the RSM model

Parameters	Coef.	St. coef.	<i>t</i> -value	<i>p</i> value	
Constant	-11.2	6.94	-1.61	0.14	
$C_{\text{Fe}^{2+}}$	2.91	1.26	2.31	0.05	
$C_{\text{H}_2\text{O}_2}$	1.26	2.15	0.06		
C_0	0.18	0.05	4.05	0.00	
$(C_0)^2$	7.0×10^{-4}	1.5×10^{-4}	4.79	0.00	
$(C_{\text{Fe}^{2+}} \times C_{\text{H}_2\text{O}_2})$	-0.61	0.24	-2.58	0.03	
Model goodness parameters	R^2	R^2_{adjusted}	<i>p</i> value	<i>F</i> value	RMSE
	0.99	0.98	0.00	136	3.25

Where the unit of $C_{\text{Fe}^{2+}}$, $C_{\text{H}_2\text{O}_2}$, and C_0 in this table is mg/L

Fig. 2 The surface plot of diazinon removal

Since the optimized parameters can be used to identify the parameters influences. The process optimization was probed in this study. Then, RSM algorithm was used to optimize the experimental parameters using the best obtained models. The result of RSM solution is 5, 5, and 151 mg/L for $C_{\text{Fe}^{2+}}$, $C_{\text{H}_2\text{O}_2}$, and C_0 where the maximum diazinon removal was 45 mg. As seen from the results, RSM successfully introduces the good model for the process efficiency.

4 Conclusion

The present study proves the power of electrochemical assisted Fenton as a fast applicable method for diazinon removal. This study also confirms the effective influences of the three investigated parameters including $C_{\text{Fe}^{2+}}$, $C_{\text{H}_2\text{O}_2}$, and C_0 . The RSM design of experiments approach was successfully applied for modeling and optimization of diazinon removal efficiency. The DLLME-GC method was successfully applied for diazinon analysis, too. Since this study is basic study with some limitation, it can be followed by future

more complete studies with more operational parameters studying. The real samples or samples with more complex matrix can be objective of this studies.

References

- Huston, P.L.; Pignatello, J.J.: Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction. *Water Res.* **33**, 1238–1246 (1999)
- Malpass, G.; Miwa, D.; Machado, S.; Olivi, P.; Motheo, A.: Oxidation of the pesticide atrazine at DSA® electrodes. *J. Hazard. Mater.* **137**, 565–572 (2006)
- Moussavi, G.; Hosseini, H.; Alahabadi, A.: The investigation of diazinon pesticide removal from contaminated water by adsorption onto NH_4Cl -induced activated carbon. *Chem. Eng. J.* **214**, 172–179 (2013)
- Ogiso, M.; Tanabe, H.: Removal of residual pesticides from application wastewater with activated carbon [Diazinon, captan, oxinocopper, mancozeb]. *Research bulletin of the Aichi-Ken Agricultural Research Center* (1981)
- Salles, N.A.; Fourcade, F.; Geneste, F.; Floner, D.; Amrane, A.: Relevance of an electrochemical process prior to a biological treatment for the removal of an organophosphorous pesticide, phosmet. *J. Hazard. Mater.* **181**, 617–623 (2010)

6. Samet, Y.; Agengui, L.; Abdelhédi, R.: Electrochemical degradation of chlorpyrifos pesticide in aqueous solutions by anodic oxidation at boron-doped diamond electrodes. *Chem. Eng. J.* **161**, 167–172 (2010)
7. Badawy, M.I.; Ghaly, M.Y.; Gad-Allah, T.A.: Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater. *Desalination* **194**, 166–175 (2006)
8. Guivarch, E.; Oturan, N.; Oturan, M.A.: Removal of organophosphorus pesticides from water by electrogenerated Fenton's reagent. *Environ. Chem. Lett.* **1**, 165–168 (2003)
9. Pirsaeheb, M.; Dargahi, A.; Hazrati, S.; Fazlzadehdavil, M.: Removal of diazinon and 2, 4-dichlorophenoxyacetic acid (2, 4-D) from aqueous solutions by granular-activated carbon. *Desalin. Water Treat.* **52**(22–24), 4350–4355 (2014)
10. Real, F.J.; Benitez, F.J.; Acero, J.L.; Gonzalez, M.: Removal of diazinon by various advanced oxidation processes. *J. Chem. Technol. Biotechnol.* **82**, 566–574 (2007)
11. Wu, J.; Luan, T.; Lan, C.; Lo, W.; Chan, G.: Efficacy evaluation of low-concentration of ozonated water in removal of residual diazinon, parathion, methyl-parathion and cypermethrin on vegetable. *J. Food Eng.* **79**, 803–809 (2007)
12. Ballesteros Martín, M.; Sánchez Pérez, J.; Casas López, J.; Oller, I.; Malato, S. Rodríguez: Degradation of a four-pesticide mixture by combined photo-Fenton and biological oxidation. *Water Res.* **43**, 653–660 (2009)
13. Malato, S.; Blanco, J.; Cáceres, J.; Fernández-Alba, A.; Agüera, A.; Rodríguez, A.: Photocatalytic treatment of water-soluble pesticides by photo-Fenton and TiO₂ using solar energy. *Catal. Today* **76**, 209–220 (2002)
14. Mason, T.J.; Collings, A.; Sumel, A.: Sonic and ultrasonic removal of chemical contaminants from soil in the laboratory and on a large scale. *Ultrason. Sonochemistry* **11**, 205–210 (2004)
15. Belgiorno, V.; Rizzo, L.; Fatta, D.; Della Rocca, C.; Lofrano, G.; Nikolaou, A.; Naddeo, V.; Meric, S.: Review on endocrine disrupting-emerging compounds in urban wastewater: occurrence and removal by photocatalysis and ultrasonic irradiation for wastewater reuse. *Desalination* **215**, 166–176 (2007)
16. Jolival, C.; Brenon, S.; Caminade, E.; Mougin, C.; Pontié, M.: Immobilization of laccase from *Trametes versicolor* on a modified PVDF microfiltration membrane: characterization of the grafted support and application in removing a phenylurea pesticide in wastewater. *J. Membr. Sci.* **180**, 103–113 (2000)
17. Amooey, A.A.; Ghasemi, S.; Mirsoleimani-azizi, S.M.; Gholaminezhad, Z.; Chaichi, M.J.: Removal of Diazinon from aqueous solution by electrocoagulation process using aluminum electrodes. *Korean J. Chem. Eng.* **31**, 1016–1020 (2014)
18. Bazrafshan, E.; Mahvi, A.; Nasser, S.; Shaieghi, M.: Performance evaluation of electrocoagulation process for diazinon removal from aqueous environments by using iron electrodes. *Iran. J. Environ. Health Sci. Eng.* **4**, 127–132 (2007)
19. Diagne, M.; Oturan, N.; Oturan, M.A.: Removal of methyl parathion from water by electrochemically generated Fenton's reagent. *Chemosphere* **66**, 841–848 (2007)
20. Feleke, Z.; Sakakibara, Y.: A bio-electrochemical reactor coupled with adsorber for the removal of nitrate and inhibitory pesticide. *Water Res.* **36**, 3092–3102 (2002)
21. Martínez-Huitle, C.A.; De Battisti, A.; Ferro, S.; Reyna, S.; Cerro-López, M.N.; Quiro, M.A.: Removal of the pesticide methamidophos from aqueous solutions by electrooxidation using Pb/PbO₂, Ti/SnO₂, and Si/BDD electrodes. *Environ. Sci. Technol.* **42**, 6929–6935 (2008)
22. Sires, I.; Garrido, J.A.; Rodríguez, R.M.; Brillas, E.; Oturan, N.; Oturan, M.A.: Catalytic behavior of the Fe ³⁺ /Fe ²⁺ system in the electro-Fenton degradation of the antimicrobial chlorophene. *Appl. Catal. B Environ.* **72**, 382–394 (2007)
23. Da Pozzo, A.; Merli, C.; Sirés, I.; Garrido, J.A.; Rodríguez, R.M.; Brillas, E.: Removal of the herbicide amitrole from water by anodic oxidation and electro-Fenton. *Environ. Chem. Lett.* **3**, 7–11 (2005)
24. Yatmaz, H.C.; Uzman, Y.: Degradation of pesticide monochrotophos from aqueous solutions by electrochemical methods. *Int. J. Electrochem. Science* **4**, 614–626 (2009)
25. Daraei, H.; Maleki, A.; Mahvi, A.H.; Zandsalimi, Y.; Alaei, L.; Gharibi, F.: Synthesis of ZnO nano-sono-catalyst for degradation of reactive dye focusing on energy consumption: operational parameters influence, modeling, and optimization. *Desalin. Water Treat.* **52**(34–36), 6745–6755 (2014)
26. Daraei, H.; Kamali, H.: Response surface modelling for optimization of 2-chlorophenol removal from water by nanoscale iron and iron powder. *Am. J. Environ. Prot.* **3**, 144–151 (2014)
27. Ghoneim, M.M.; El-Desoky, H.S.; Zidan, N.M.: Electro-Fenton oxidation of Sunset Yellow FCF azo-dye in aqueous solutions. *Desalination* **274**, 22–30 (2011)
28. Wang, Q.; Lemley, A.T.: Oxidation of diazinon by anodic Fenton treatment. *Water Res.* **36**, 3237–3244 (2002)

