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Research Article

pH CHANGE IN ELECTROCHEMICAL OXIDATION OF IMIDACLOPRID PESTICIDE USING BORON-DOPED DIAMOND ELECTRODES

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ABSTRACT

In this study, pH and ΔpH change in the electrochemical oxidation of imidacloprid (IMD) pesticide using boron-doped diamond (BDD) electrodes was investigated in the presence of Na_2SO_4 electrolyte. The process parameters were operated as imidacloprid concentration (40-200 mg/L), electrolyte concentration (2-10 g/L), current density (4-20 mA/cm^2) and reaction temperature (20-60°C). pH and ΔpH values increased with increasing Na_2SO_4 concentration, current density, and reaction temperature, and decreasing the imidacloprid concentration at 120 min reaction time. The results of this study showed that the pH of the wastewater solution maintained the local pH discharge limits between 6 and 9 after the electrochemical oxidation.

Keywords: *BDD, Boron-doped diamond electrode, Electrolysis, Imidacloprid, Pesticide, Wastewater treatment*

1. INTRODUCTION

The use of pesticides is increasing with growing of world population due to the increase in food demand. Pesticides have become an integral part of the agricultural production all over the world since 20th century in increasing the productivity of plants, the quality of agricultural products, and preventing diseases spread with the insects (Galt, 2008; Bouya *et al*., 2012). However, overconsumption and improper use may cause chemical segregation and ecological damages to the environment (Bouya *et al*., 2012). Uncontrolled consumption of pesticides may cause water, soil and air pollution; and harmful organisms can gain resistance to the pesticides (Bouya *et al*., 2012). Pesticide residues are being contaminating water resources by direct contact with plants or insects in water or on the waterside, by washing soil surfaces or plants by rainwater, and by discharging pharmaceutical industry wastewater to the aquatic environment (Bouya *et al*., 2012).

In order to prevent such risks, many laws were issued in EU countries and in the USA (Gullino *et al*., 1994). In the literature, electrochemical oxidation of 2,4-D, 2,6-D, diazinon, melathion, chloropyrifos, azinphosmethyl, phorate, paraquat, atrazine, thiram, parathion methyl, 2,4-DNP, dichlorvos, myclobutanil, triadimefon and propiconazole pesticides were investigated (Souza *et al*., 2016; Fontmorin *et al*., 2015; Madsen *et al*., 2015; Lazarević-Pašti *et al*., 2012; Cartaxo *et al*., 2015; Steter *et al*., 2016; Malpass *et al*., 2006; Arapoglou *et al*., 2003; Vargas *et al*., 2014; Quiroz *et al*., 2014; Urzúa *et al*., 2013).

It is very important that the wastewater solution should maintain the discharge limits after the treatment. The local pH discharge limit in Turkey is between 6 and 9. Therefore, the pH of the solution should be maintained between 6 and 9 after the treatment. In this study, the effect of process parameters such as imidacloprid concentration, electrolyte concentration, current density and reaction temperature was investigated on pH and ΔpH change in electrochemical oxidation of imidacloprid (IMD) pesticide using boron-doped diamond (BDD) electrodes in the presence of Na_2SO_4 electrolyte. The optimum operating region was determined in order to maintain the local pH discharge limits.

2. MATERIALS AND METHODS

Imidacloprid (IMD) pesticide obtained from Astranova (Turkey) as a concentrated emulsion (350 g/L) and diluted to 40-200 mg/L using double distilled water. Double distilled water was produced using Millipore Simplicity® UV ultrapure water system and GFL-2008 water still. Batch reactor system consists of electrochemical reactor with heating/cooling jacket, Lauda RE 630 S cryostat water bath, Heidolph RZR 2021 mechanical mixer, Goodwill PST-3201 programmable DC power source and Heidolph PD 5206 peristaltic pump. Boron-doped diamond (Nb/BDD) electrodes (CONDIAS, Germany) were used as anode and cathode materials. Total electrode surface area was 260 cm^2. Samples in 10 mL volume were withdrawn from the reaction medium at 5 min time intervals for the analysis. pH was measured using WTW inoLab BNC720 pH meter.

3. RESULTS AND DISCUSSION

In electrochemical treatment processes, organic pollutants could be removed from wastewater by indirect and direct mechanisms (Brillas and Martínez-Huitle, 2015; Comninellis and Chen, 2010; Körbahti and Artut K, 2010; Körbahti and Taşyürek, 2015; Panizza and Cerisola, 2009). Indirect oxidation occurs in the liquid bulk phase by the mediated oxidants, and direct oxidation at the anode surface (Brillas and Martínez-Huitle, 2015; Comninellis and Chen, 2010; Körbahti and Artut K, 2010; Körbahti and Taşyürek, 2015; Panizza and Cerisola, 2009). Most electrochemical processes are based on indirect oxidation because direct oxidation of organic pollutants are very slow on inert anodes due to the limiting reactions and reaction kinetics (Tarr, 2003; Rajeshwar and Ibanez, 1997).

Boron-doped diamond (BDD) thin-film anodes have better O_2 overpotential than the conventional anodes. Therefore, more hydroxyl radicals adsorb on the electrode surface and organic compounds degrade faster (Comninellis and Chen, 2010; Cañizares *et al*., 2006; Siné *et al*., 2005). Hydroxyl radicals produce by the anodic discharge of water in indirect electrochemical oxidation at BDD anodes. Hydroxyl radicals are not selective for the degradation of organic pollutants (R) that they react with the organic pollutants (R), and mineralize into CO_2 and H_2O (Comninellis and Chen, 2010; Cañizares *et al*., 2006; Siné *et al*., 2005).

$$\boldsymbol{BDD + H_2O \longrightarrow BDD(^{\bullet}OH) + H^+ + e^-} \qquad (1)$$

$$\boldsymbol{BDD(^{\bullet}OH) + R \longrightarrow BDD + CO_2 + H_2O} \qquad (2)$$

In this study, the process parameters were operated as imidacloprid concentration (40-200 mg/L), Na_2SO_4 concentration (2-10 g/L), current density (4-20 mA/cm^2) and reaction temperature (20-60°C) in electrochemical oxidation of imidacloprid (IMD) pesticide using boron-doped diamond (BDD) electrodes. pH and ΔpH change monitored during the electrochemical oxidation and the results are presented in Figures 1 and 2.

Figure 1 (A)-(D) shows the effect of process parameters on pH change. pH values decreased to acidic region in 30 min from the beginning for all runs and then increased to the basic region during the electrochemical oxidation. pH values were increased from their initial value with increasing Na_2SO_4 concentration, current density, and reaction temperature, and decreasing the imidacloprid concentration at 120 min reaction time. pH of the reaction medium decreased from 9.9 to 5.4 with increasing IMD concentration from 40 mg/L to 200 mg/L. Electrolyte type and concentration are important parameters in electrochemical processes that increase or decrease the process efficiency due to the formation of intermediate derivatives (Palma-Goyes *et al*, 2010). Increasing Na_2SO_4 from 2 g/L to 10 g/L, increased pH of the reaction medium from 4.7 to 9.8. In the literature, it was reported that the reaction between hydroxyl radicals and organic contaminants accelerates and removal efficiency increases with increasing the current density and reaction temperature (Brillas *et al*., 2005). pH of the reaction medium increased from 3.9 to 10 with increasing the current density from 4 mA/cm^2 to 20 mA/cm^2. Increasing reaction temperature from 20°C to 60°C slightly increased the pH of the reaction medium from 8.0 to 8.9.

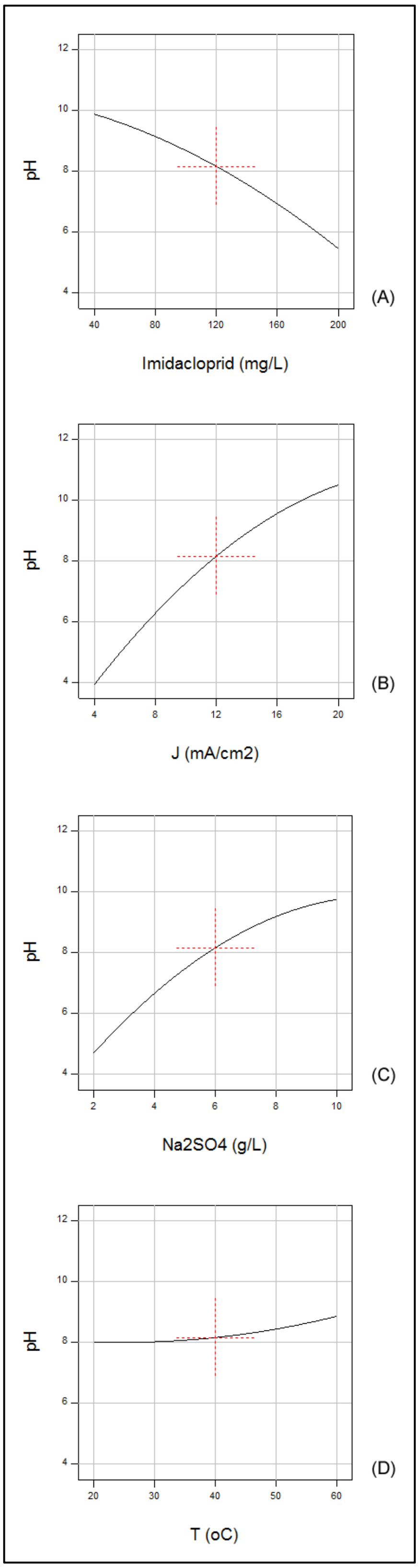

Figure 1. Effect of process parameters on pH change (A) $J=12$ mA/cm^2, Na$_2$SO$_4$=6 g/L, T=40°C, t=120 min; (B) $C_{IMD,o}$=120 mg/L, Na$_2$SO$_4$=6 g/L, T=40°C, t=120 min; (C) $C_{IMD,o}$=120 mg/L, J=12 mA/cm^2, T=40°C, t=120 min; (D) $C_{IMD,o}$=120 mg/L, J=12 mA/cm^2, Na$_2$SO$_4$=6 g/L, t=120 min.

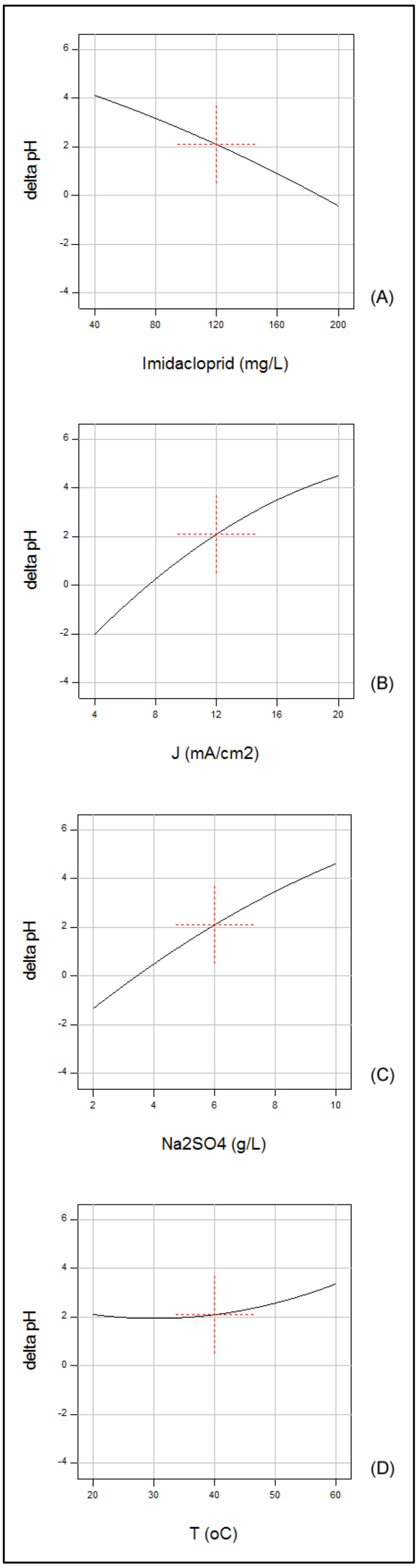

Figure 2. Effect of process parameters on ΔpH change (A) $J=12$ mA/cm^2, Na$_2$SO$_4$=6 g/L, T=40°C, t=120 min; (B) $C_{IMD,o}$=120 mg/L, Na$_2$SO$_4$=6 g/L, T=40°C, t=120 min; (C) $C_{IMD,o}$=120 mg/L, J=12 mA/cm^2, T=40°C, t=120 min; (D) $C_{IMD,o}$=120 mg/L, J=12 mA/cm^2, Na$_2$SO$_4$=6 g/L, t=120 min.

The optimum operating region for pH between 6.0 and 9.0 at 120 min reaction time were determined from Figure 1 (A)-(C) at 85-186 mg/L IMD concentration, 3.3-7.7 g/L Na_2SO_4 concentration, 7.5-14.3 mA/cm^2 current density and 20-60°C reaction temperature.

The effect of process parameters on ΔpH change can be seen in Figure 2 (A)-(D). ΔpH values were calculated using Equation 3. In Equation 3, pH_i is the initial pH value of the reaction medium and pH_f is the final pH value at 120 min.

$$\Delta pH = pH_f - pH_i \tag{3}$$

$\Delta pH < 0$ indicates $pH_f < pH_i$, $\Delta pH = 0$ indicates $pH_f = pH_i$, and $\Delta pH > 0$ indicates $pH_f > pH_i$. ΔpH values were increased with increasing Na_2SO_4 concentration, current density, and reaction temperature, and decreasing the imidacloprid concentration at 120 min reaction time. ΔpH of the reaction medium decreased from +4.1 to -0.4 with increasing IMD concentration from 40 mg/L to 200 mg/L. Increasing Na_2SO_4 from 2 g/L to 10 g/L, increased ΔpH from -1.4 to +4.6. ΔpH increased from -2.0 to +4.5 with increasing the current density from 4 mA/cm^2 to 20 mA/cm^2. Increasing reaction temperature from 20°C to 60°C slightly increased the ΔpH of the reaction medium from +2.0 to +3.4.

The point for ΔpH = 0 at 120 min reaction time were determined at 188 mg/L IMD concentration, 3.5 g/L Na_2SO_4 concentration and 7.6 mA/cm^2 current density from Figure 2 (A)-(C).

The electrolysis of an aqueous solution of sodium sulphate using inert electrodes produces hydrogen at the cathode and oxygen at the anode. Hydrogen ions are being removed from solution and leaving an excess of hydroxyl ions which makes the solution alkaline at the cathode, and hydroxyl ions are being removed and leaving an excess of hydrogen ions which makes the solution acidic at the anode (Comninellis and Chen, 2010).

4. CONCLUSION

In this study, pH and ΔpH change in the electrochemical oxidation of imidacloprid (IMD) pesticide using boron-doped diamond (BDD) electrodes was investigated in the presence of Na_2SO_4 electrolyte. pH and ΔpH values increased with increasing Na_2SO_4 concentration, current density, and reaction temperature, and decreasing the imidacloprid concentration at 120 min reaction time. pH values decreased to acidic region in 30 min from the beginning for all runs and then increased to the basic region during the electrochemical oxidation. It can be concluded that pH decreased due to the production of hydroxyl radicals at the BDD anode and oxygen evolution reaction. pH of the reaction medium increased to the alkaline region while these reactions are getting slower during electrochemical oxidation. The optimum operating region for pH between 6.0 and 9.0 at 120 min reaction time were determined at 85-186 mg/L IMD concentration, 3.3-7.7 g/L Na_2SO_4 concentration, 7.5-14.3 mA/cm^2 current density and 20-60°C reaction temperature. The results of this study showed that the pH of the wastewater solution maintained the local pH discharge limits between 6 and 9 after the electrochemical oxidation, being an advantage for the neutralization of treated wastewater without using any chemicals.

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REFERENCES

Arapoglou, D., Vlyssides, A., Israilides, C., Zorpas, A. and Karlis, P. (2003). “Detoxification of methyl-parathion pesticide in aqueous solutions by electrochemical oxidation”. *Journal of Hazardous Materials*, Vol. 98, No. 1-3, pp. 191-199.

Brillas, E. and Martínez-Huitle, C.A. (2015). “Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review”. *Applied Catalysis B: Environmental*, Vol. 166-167, pp. 603-643.

Brillas, E., Sirés, I., Arias, C., Cabot, P.L., Centellas, F., Rodríguez, R.M. and Garrido, J.A. (2005). “Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode”. *Chemosphere*, Vol. 58, No. 4, pp. 399-406.

Cañizares, P., Sáez, C., Lobato, J. and Rodrigo, M.A. (2006). “Detoxification of synthetic industrial wastewaters using electrochemical oxidation with boron-doped diamond anodes”. *Journal of Chemical Technology & Biotechnology*, Vol. 81, No. 3, pp. 352-358.

Cartaxo, M.A.M., Borges, C.M., Pereira, M.I.S. and Mendonça, M.H. (2015). “Electrochemical oxidation of paraquat in neutral medium”. *Electrochimica Acta*, Vol. 176, pp. 1010-1018.

Comninellis, Ch. and Chen, G. (2010). *Electrochemistry for the Environment*, Springer, USA.

Fontmorin, J.M., Fourcade, F., Geneste, F., Soutrel, I., Floner, D. and Amrane, A. (2015). “Direct electrochemical oxidation of a pesticide, 2,4-dichlorophenoxyacetic acid, at the surface of a graphite felt electrode: Biodegradability improvement”. *Comptes Rendus Chimie*, Vol. 18, No. 1, pp. 32-38.

Galt, R.E. (2008). “Beyond the circle of poison: Significant shifts in the global pesticide complex, 1976-2008”. *Global Environmental Change*, Vol. 18, No. 4, pp. 786-799.

Gullino, M.L. and Kuijpers, L.A.M. (1994). “Social and Political Implications of Managing Plant Diseases with Restricted Fungicides in Europe”. *Annual Review of Phytopathology*, Vol. 32, No. 1, pp. 559-581.

Körbahti, B.K. and Artut, K. (2010). “Electrochemical oil/water demulsification and purification of bilge water using Pt/Ir electrodes”. *Desalination*, Vol. 258, No. 1-3, pp. 219-228.

Körbahti, B.K. and Taşyürek, S. (2015). “Electrochemical oxidation of ampicillin antibiotic at boron-doped diamond electrodes and process optimization using response surface methodology”. *Environmental Science and Pollution Research,* Vol. 22, No. 5, pp. 3265-3278.

Lazarević-Pašti, T.D., Bondžić, A.M., Pašti, I.A. and Vasić, V.M. (2012). “Indirect electrochemical oxidation of organophosphorous pesticides for efficient detection via acetylcholinesterase test”. *Pesticide Biochemistry and Physiology,* Vol. 104, No. 3, pp. 236-242.

Madsen, H.T., Søgaard, E.G. and Muff, J. (2015). “Study of degradation intermediates formed during electrochemical oxidation of pesticide residue 2,6-dichlorobenzamide (BAM) in chloride medium at boron doped diamond (BDD) and platinum anodes”. *Chemosphere*, Vol. 120, pp. 756-763.

Malpass, G.R.P., Miwa, D.W., Machado, S.A.S., Olivi, P. and Motheo, A.J. (2006). “Oxidation of the pesticide atrazine at DSA® electrodes”. *Journal of Hazardous Materials*, Vol. 137, No. 1, pp. 565-572.

Palma-Goyes, R.E., Guzmán-Duque, F.L., Peñuela, G., González, I., Nava, J.L. and Torres-Palma, R.A. (2010). “Electrochemical degradation of crystal violet with BDD electrodes: Effect of electrochemical parameters and identification of organic by-products”. *Chemosphere*, Vol. 81, No. 1, pp. 26-32.

Panizza, M. and Cerisola, G. (2009). “Direct and Mediated Anodic Oxidation of Organic Pollutants”. *Chemical Reviews,* Vol. 109, No. 12, pp. 6541-6569.

Quiroz, M.A., Sánchez-Salas, J.L., Reyna, S., Bandala, E.R., Peralta-Hernández, J.M. and Martínez-Huitle, C.A. (2014). “Degradation of 1-hydroxy-2,4-dinitrobenzene from aqueous solutions by electrochemical oxidation: Role of anodic material”. *Journal of Hazardous Materials*, Vol. 268, pp. 6-13.

Rajeshwar, K. and Ibanez, J.G. (1997). *Environmental Electrochemistry,* Academic Press, USA.

Siné, G. and Comninellis, Ch. (2005). “Nafion®-assisted deposition of microemulsion-synthesized platinum nanoparticles on BDD”. *Electrochimica Acta,* Vol. 50, No. 11, pp. 2249-2254.

Souza, F.L., Saéz, C., Lanza, M.R.V., Cañizares, P. and Rodrigo, M.A. (2016). “Removal of pesticide 2,4-D by conductive-diamond photoelectrochemical oxidation”. *Applied Catalysis B: Environmental*, Vol. 180, pp. 733-739.

Steter, J.R., Kossuga, M.H. and Motheo, A.J. (2016). “Mechanistic proposal for the electrochemical and sonoelectrochemical oxidation of thiram on a boron-doped diamond anode”. *Ultrasonics Sonochemistry,* Vol. 28, pp. 21-30.

Tarr, M.A. (2003). *Chemical Degradation Methods for Wastes and Pollutants*, CRC Press, USA.

Urzúa, J., González-Vargas, C., Sepúlveda, F., Ureta-Zañartu, M.S. and Salazar, R. (2013). “Degradation of conazole fungicides in water by electrochemical oxidation”. *Chemosphere*, Vol. 93, No. 11, pp. 2774-2781.

Vargas, R., Díaz, S., Viele, L., Núñez, O., Borrás, C., Mostany, J. and Scharifker, B.R. (2014). “Electrochemical oxidation of dichlorvos on SnO_2-Sb_2O_5 electrodes”. *Applied Catalysis B: Environmental*, Vol. 144, pp. 107-111.