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Degradation of imidacloprid pesticide in aqueous solution using an eco-friendly electrochemical process

Khadije Yari[a], Alireza Rahmani[a], Ghorban Asgari[a], Qasem Azarian[a],
Amit Bhatnagar[b], Mostafa Leili[a,*]

[a]*Department of Environmental Health Engineering, School of Public Health and Research Center for Health Sciences, Hamadan University of Medical Sciences, Hamadan, Iran, Tel. +98 81 38380398; Fax: +98 81 38380509, emails: m.leili@umsha.ac.ir, mostafa.leili@gmail.com (M. Leili), khadije.yari56@gmail.com (K. Yari), rahmani@umsha.ac.ir (A. Rahmani), asgari@umsha.ac.ir (G. Asgari), gh_azarian@yahoo.com (Q. Azarian)*
[b]*Department of Environmental and Biological Sciences, University of Eastern, Finland, P.O. Box 1627, FI-70211 Kuopio, Finland, emails: amit.bhatnagar@uef.fi, dr.amit10@gmail.com*

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ABSTRACT

The aim of this study was to evaluate the efficiency of electrochemical degradation process in the removal of imidacloprid (IM), a pesticide, from aqueous solutions. Experiments were conducted using a batch glass reactor and two leads as anodes, and stainless steel electrode as a cathode. The influence of various experimental parameters including initial IM concentration (1–150 mg/L), pH (3–11), electrolysis time (20–120 min), current density (12.5–50 mA/cm^2) and NaCl concentration (4.28–26.74 mmol/L) were assessed to determine the optimum conditions. Scanning electron microscopy and X-ray diffraction analyses were used to study the type of materials formed on the electrode surfaces at the electrode preparation stage. The results from this investigation show that at pH = 5, current density = 25 mA/cm^2, electrolysis time = 30 min, initial pesticide concentration = 100 mg/L and NaCl concentration = 10.69 mmol/L are optimum experimental conditions for achieving maximum IM and chemical oxygen demand (COD) removal from water. Accordingly, the maximum IM and COD removal efficiencies of 99.69% and 85.66% were achieved, respectively. At optimum conditions and applied voltage of 23.95 V, the electrical energy consumption was calculated about 5.35 kWh/kg COD. Based on the results, electrochemical degradation method was found to be a highly efficient technology in comparison with existing conventional methods and could be considered as a cost-effective method to remove IM from water and wastewater.

Keywords: Imidacloprid; Electrochemical degradation; Agriculture wastewater; PbO_2 and stainless steel electrodes

1. Introduction

The indiscriminate use of pesticides in agriculture to control pests and other insects and uncontrolled discharge of agricultural wastewater into natural water systems leads to water pollution. Agricultural wastewater contains various agrochemicals that are used for crop protection and yield maximization. There is a growing concern about the effects of these compounds on environment and humans [1,2]. Most of these chemicals are considered to be non-biodegradable and toxic, and the transfer of various pesticide residues via food chains has been extensively investigated in several studies [2–4]. Imidacloprid (IM), $C_9H_{10}ClN_5O_2$, is one of these pesticides with the IUPAC name of 1-6(choloro-3-pyridyl-metyl)-*N*-nitromidazolidin-2-ylideneamine. IM is also sold with other trade names including Confidor, Gaucho, Admire, Advantage, Genesis, Impower, Intercept, Maxforce IC and

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* Corresponding author.

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Merit with a chemical structure that is shown in Fig. 1 [5,6]. IM is used to control different harmful pest species such as sucking pests, resistant strains, whiteflies, thrips, aphids and so forth [6,7].

IM has colorless crystals, weak odor and specific chemical and physical properties. The solubility of IM in water at 20°C and pH 7 is high (610 mg/L) [8]. This pesticide can also cause several diseases and health problems including cancer, defective reproductive outcomes, neurobehavioral and immune function disorders, allergic reactions and skin irritation, disorder of cholinesterase activity and so on [1]. Based on several research studies, the aerosol form of the IM is highly toxic with the LC_{50} value of 0.05 mg/L. The acute oral LD_{50} for moderate toxicity of IM is 500 mg/kg [9,10].

The World Health Organization (WHO) has classified IM in the class II of pollutants, that is, moderately toxic [10,11]. The mechanism of action of this pesticide was inclusive, mainly through disturbing the nervous system, where it acts as an agonist by binding to nicotinic acetylcholine receptors which in turn leads to the accumulation of acetylcholine and finally results in the paralysis and death of insects [12].

This pesticide is a systemic chloronicotinyl insecticide with slow degradation properties in soil and having a half-life over 180 d [6,13]. Moreover, the half-lives of IM in vegetation and non-vegetation land are 42–129 and 180 d, respectively [13]. When used, IM can reach the ground and surface waters because of high solubility and mobility, thereby being a serious threat to the environment [14]. The estimated environmental concentrations of IM in different water sources have been detected in wide ranges, from 2.09 to 3,625 ppb [15].

Photolysis and aerobic soil degradation are dominant transformation processes for IM, the latter process being very slow; thus, IM is considered to be persistent in the soil. Because of the characteristics like low propensity to divide the organic carbon from IM as well as high water solubility and low volatility, it is considered to be very mobile in terrestrial environments. IM is readily taken up by the roots of the plants and translocated throughout the plant via the transpiration stream because this pesticide is a xylem-mobile systemic compound [16].

The increasing concentrations of IM in aquatic ecosystem have been detected worldwide [17]. Therefore, due to global shortage of clean water resources and also to protect human health, the choice of appropriate treatment technologies is very important [18]. Advanced oxidation processes (AOPS) have been widely applied to remove chemical contaminants from water and wastewater [19–21], in which anodic oxidation (AO) is considered one of the most common types of AOP methods [19,22]. One of the highly efficient and simple methods for removing recalcitrant pollutants in various industrial wastewaters is electrochemically based method, like AO, which has been successfully used for wastewater treatment. This promising powerful procedure does not produce new toxic materials or by-products, and are easy-controlled and cost-effective method, therefore considered as an environment friendly treatment technology with the acceptable removal efficiency of contaminants [23,24]. The dominant removal mechanism of electrolysis process includes oxidation, reduction and decomposition [23,25]. In this process, toxic organic compounds are converted to end-products such as CO_2 and H_2O through the production of oxidants such as hydroxyl radicals ($^{\bullet}OH$) [26,27]. The $^{\bullet}OH$ radicals with the constant rate of 10^6–10^9 M^{-1} s^{-1} have the highest thermodynamic oxidation potential (2.8 eV), thereby, attacking and destroying many organic molecules. According to Eq. (1), this radical is formed during the water oxidation at the surface of high-oxygen overvoltage anode [28]:

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

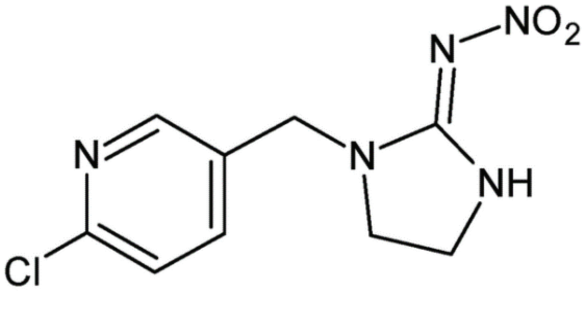

Fig. 1. Chemical structure of imidacloprid.

Electrochemical degradation (ED) of pesticides has recently been widely studied. Sarria Muñoz [28] and Hachami et al. [29] investigated the electrochemical oxidation of methidation and found it very efficient in pesticide oxidation. In the other study, Glavaški et al. [30] assessed the ED of the pesticide dimethenamid-P in different electrolytes and found it as an efficient, non-time consuming, simple and inexpensive method. Garrett et al. [1] examined and compared the ED of malathion, IM and chlorpyrifos in agricultural wastewaters and showed that it was a cost-effective method for treating this types of wastewater.

Therefore, the aim of the current research was to study the IM pesticide removal by ED (AO) from the synthetic wastewater through batch experiments using lead dioxide (PbO_2) and steel electrodes. Furthermore, the effects of different parameters such as pH, current density (CD), electrolysis time, initial pesticide concentration and NaCl concentration on the process efficiency were studied and optimized. The IM mineralization efficiency through COD measurements and energy consumption of the process were also determined. Finally, the surface characteristics of electrodes to understand the mechanisms of the process were further evaluated by X-ray diffraction (XRD) analyses.

2. Materials and methods

2.1. Electrolytic system

The electrochemical experiments were carried out in an electrolytic cell containing IM pesticide solution (volume: 80 cc; Fig. 2). IM (purity = 95%) was extracted from commercial Confidor 35% SC (Moshkfam Fars Company, MFC©) using Soxhlet extraction with dichloromethane (Merck) and dried in vacuum at 40°C to prepare stock solution [31]. The solutions of desired/working concentrations were prepared by diluting the stock solution with double-distillated water. High-performance liquid chromatography (HPLC) analytical grade of IM (CAS no. 138261-41-3) was purchased from Sigma-Aldrich. The Pb electrode and stainless steel having surface area ≈40 and ≈25 cm^2, respectively, were used as anode and cathode, in all experiments. The distance between two electrodes was 2 cm. The Pb electrode was polished at first and after degreasing, the lead dioxide film was deposited on it. The reactions which resulted in PbO$_2$ production as main degrading agent are shown in Eqs. (2) and (3) [22,32]:

$$\mathrm{Pb} + \mathrm{SO_4^{2-}} \rightarrow \mathrm{PbSO_4} + 2\mathrm{e^-} \tag{2}$$

$$\mathrm{PbSO_4} + 2\mathrm{H_2O} \rightarrow \mathrm{PbO_2} + \mathrm{SO_4^{2-}} + 4\mathrm{H^+} + 2\mathrm{e^-} \tag{3}$$

The energy source was a DC power supply (model GP4303D, LG Precision Co. Ltd., Korea). All experiments were performed in batch mode at ambient temperature (≈25°C) and at atmospheric pressure. A constant stirring of 400 rpm was used in order to provide homogenization in the solution and improve contact of IM with electrodes [33]. The pH was measured by a lab pH meter (model: EC20, HACH Co., USA) and to adjust the pH, 0.01 N hydroxide sodium and sulfuric acid were used. The required CD was adjusted by adding suitable amount of NaCl salt.

2.2. Analytical procedures

To determine the IM concentrations in the influent and effluent samples, HPLC (model LC-2010 AHT, Shimadzu, Japan) equipped with UV detector at a wavelength of 270 nm and Phenomenex C-18 column (250 mm × 4.6 mm) was used. The method was adapted from other studies [1,2,25]. The HPLC method is a rapid, sensitive and reliable procedure that was developed for determination of IM pesticide in aqueous solutions at different pH without the need of derivatization of any compound [34,35]. Furthermore, this method is considered as one of the identity tests by infrared, Hydrogen Nuclear Magnetic Resonance spectra, thermal lens spectrometric and mass spectrometric for determination of IM [12,36]. The solutions of pesticide were prepared in minimal broth containing of 0.7% of IM. Then, the prepared solutions were inoculated with the respective isolates for 72 h. These samples were transferred to microcentrifuge tubes, centrifuged and finally the supernatant was subjected to HPLC [13]. To study the type of material formed in the electrode surfaces after preparation stage XRD (S/max 3080E2 model) was used.

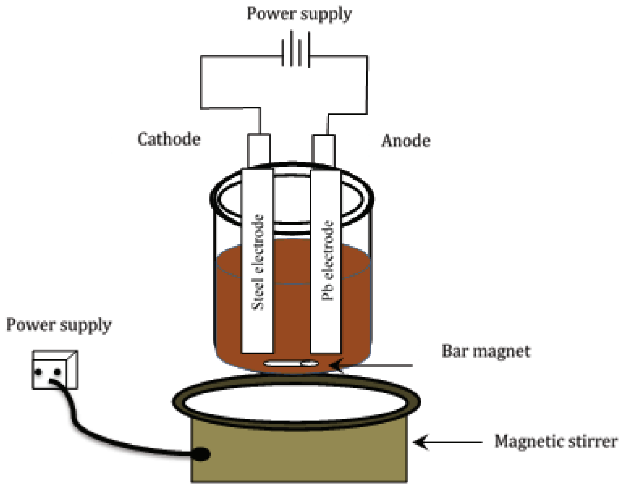

Fig. 2. Experimental setup of electrolytic cell.

2.3. Mineralization determination and energy consumption

Process performance is evaluated in two ways, one with respect to the extent of reaction completion or IM mineralization (% chemical oxygen demand [COD] removal) of the process and the other with respect to the specific energy consumption (SEC; kWh/kg COD) in the process. COD is also widely used to determine organic pollutants loading in water and wastewater processes; that is, defined as the equivalents number of oxygen consumed in the oxidation of organic materials [37] and was measured as described in the standard methods [38]. The stoichiometry of IM mineralization illustrates that 31 mol of O$_2$ are needed for the complete oxidation of IM (Eq. (4)):

$$2\mathrm{C_9H_{10}ClN_5O_2} + 31\mathrm{O_2} \rightarrow 18\mathrm{CO_2} + 10\mathrm{H_2O} + 10\mathrm{NO_2} + 2\mathrm{Cl} \tag{4}$$

According to Eq. (5), the concentration of IM (mol/m^3) in the electrolyte can be related to the COD (mol O$_2$/m^3) by the following reaction:

$$2[\mathrm{C_9H_{10}ClN_5O_2}] = \frac{\mathrm{COD}}{31} \tag{5}$$

In all experiments, the COD removal efficiency of process was calculated using Eq. (6) [1]:

$$\mathrm{COD_{removal}}\,\% = \left[\mathrm{COD_0} - \frac{\mathrm{COD_{final}}}{\mathrm{COD_0}}\right] \times 100 \tag{6}$$

while current efficiency shows the fraction of the total current passed to degrade the pollutant in the electrolysis process, the term, SEC is the quantity of energy consumed in the process for degradation of 1 kg of COD. For batch reactor, SEC (kWh/kg COD) can be obtained using Eq. (7) [22]:

$$\text{Specific energy consumption} = \frac{V\,\mathrm{It}}{3600 \times 10^3} \times \frac{1}{\Delta C \times V_R \times 10^{-6}} \tag{7}$$

where V is the average cell voltage in volt (V), V_R is the solution volume (L), ΔC is the difference in COD in mg/L, I is the current in ampere (A) and t is the time of electrolysis process (S).

3. Results and discussion

3.1. SEM and XRD characterization

Fig. 3(a) presents the scanning electron microscopy (SEM) of PbO$_2$ electrode with 5,000× magnification. It shows that the PbO$_2$ electrode had small size particles and a very compact crystalline structure which in turn provide more specific surface area and better physical performance for the ED of IM pesticide. Furthermore, the XRD patterns of PbO$_2$ electrode (Fig. 3(b)) demonstrated the characteristic reflections of β-PbO$_2$ with crystal planes at 25°, 32° and 49°.

3.2. Mechanism of electrochemical degradation of IM

The mechanism of electrochemical degradation of pesticides containing wastewaters is complex. However, it is generally stated that two various processes occur at anode electrode: the first direct electrolysis with electrocatalytic activity and the second indirect electrolysis on metal oxide electrode, in which, the rate of direct electrolysis is affected by parameters such as CD, electrode activity, pH and temperature [1]. In addition, the free radicals caused by high catalytic activity are absorbed on the electrode surfaces [26,27]. On the other hand, $^{\bullet}$OH radicals are produced on the anode surface, which in turn, destroy organic contaminants such as IM (Eqs. (8)–(10)) [27,29,39]:

$$\mathrm{PbO_2} + \mathrm{H_2O} \rightarrow \mathrm{PbO_2}\left[{}^{\bullet}\mathrm{OH}\right] + \mathrm{H^+} + \mathrm{e^-} \tag{8}$$

$$\mathrm{PbO_2}\left[{}^{\bullet}\mathrm{OH}\right] + \mathrm{IM_{red}} \rightarrow \mathrm{PbO_2} + \mathrm{IM_{ox}} \tag{9}$$

$$\mathrm{IM_{ox}} \rightarrow \mathrm{mCO_2} + \mathrm{nH_2O} + \mathrm{H^+} + \mathrm{e^-} \tag{10}$$

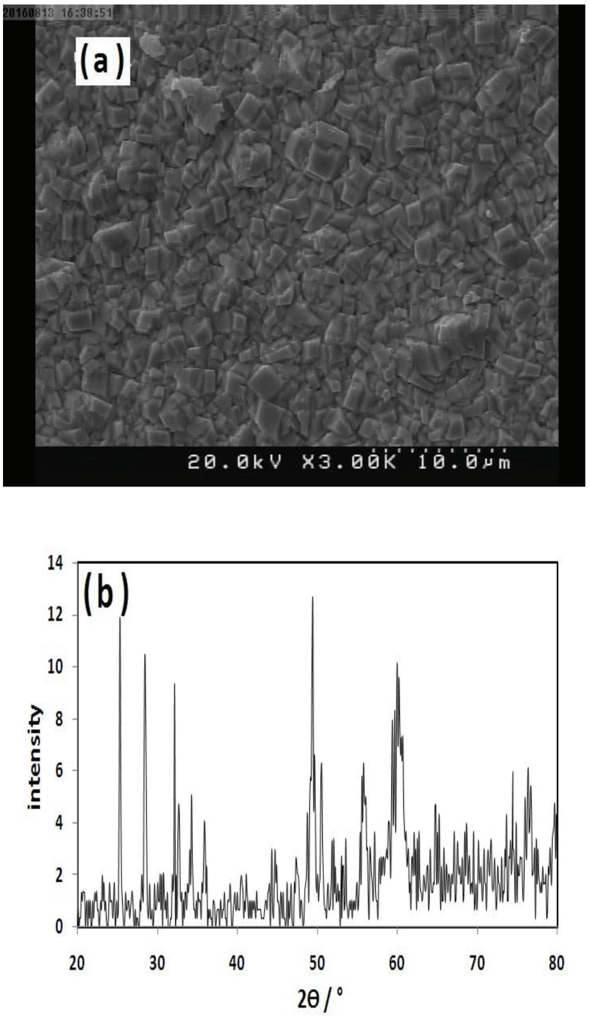

Fig. 3. (a) Scanning electron microscopy (SEM) and (b) XRD patterns of PbO_2 electrode.

where IM_{red} and IM_{ox} are the reduced or initial IM and oxidized IM, respectively.

IM can be said to be degraded in two steps in electrochemical process: capturing electrons in the first step and producing the hydroxyl amine and amine derivatives in the second step [17].

3.3. The effect of solution pH

The solubility of neonicotinoides like IM pesticide in aquatic solutions depends on multiple factors such as pH, temperature and physical state of the pesticide applied [8]. Furthermore, initial pH of aqueous solution was considered as one of the main operating factors that influencing the ED performance [33]. As seen in Figs. 4(a) and (b), removal efficiency of IM and the equivalent COD removal were the highest in the acidic pH of 3 and 5. Furthermore, both IM removal and mineralization efficiency were increased with the increase of electrolysis time up to 30 min (considered as an optimum reaction time) and this trend was remarkable for IM mineralization. It can be said that, the produced $^{\bullet}$OH radicals (Eq. (1)) are more effective in acidic pH than at other pH, therefore acidic conditions are favorable for degradation of organic compounds such as IM through the $^{\bullet}$OH radicals [40]. Moreover, the higher removal efficiency could be due to the production of some ions include Cl^-, Cl_2 and HOCl in the solution which they are more effective in destroying organic compounds at acidic pH of 3 and 5 [32]. Various studies on the AO using PbO_2 electrode containing various pesticides

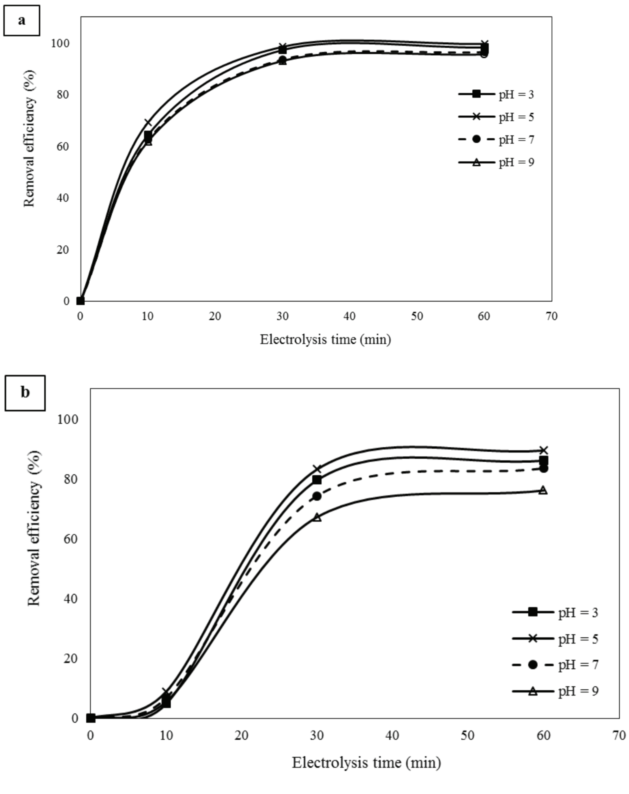

Fig. 4. The effect of solution pH on (a) electrodegradation and (b) mineralization of imidacloprid (C_0 = 100 mg/L, current density = 25 mA/cm^2 and electrolyte concentration = 10.69 mmol/L).

have reported different efficiencies regarding solution pH effects [29,41]. Based on Fig. 4, although the same removal efficiency was obtained at optimum reaction time for pH 3 and 5 (97.18% and 98.42%, respectively), but relatively more mineralization (83.17%) was obtained at pH 5 rather than at pH 3 (79.55%), therefore, taking in to account operational consideration, pH 5 was selected as the optimal pH for the further experiments. Similar results were reported by other studies on the effects of pH in degradation of pesticides like IM [1,26].

3.4. The effect of electrolysis time

The electrolysis time also affects the ED process efficiency. As seen in Fig. 5, IM was effectively removed in 30 min. Although in the first 10 min of reaction time, very good IM removal (73.54%) was obtained, but for better mineralization, 30 min electrolysis time is considered as the optimal time. Although with the increase of electrolysis time from 30 to 120 min, the IM removal efficiency increased to 100%, but in terms of energy consumption and reactor volume requirements, increase in electrolysis time is not required and affordable as it will increase the cost of the process. Nevertheless, a good IM mineralization (85%) was achieved for 30 min.

3.5. The effect of current density

The CD has a significant impact on the removal efficiency of the pollutants like the pesticides and is considered very important factor in controlling electrochemical reaction rates [32]. The influence of the CD on IM removal during the ED is shown in Fig. 6. With the increase of CD from 12.5 to 25 mA/cm^2, removal of IM and equivalent COD was also considerably increased (≈18.41% and 21.88% for IM removal and COD mineralization, respectively). The further increase of CD did not result in increased removal efficiency. For example, only 2% IM removal efficiency was increased with doubling of CD. Moreover, COD removal decreased with the increase of CD above 25 mA/cm^2. These results are in agreement with those obtained by other studies [1,24,25]. At higher current densities (>50 mA/cm^2; results not shown here), removal efficiency of IM almost stayed at constant value. According to Faraday's law, acceleration of materials on electrode's surface and more production of oxidant agents occur because of increase in CD which, in turn, results in higher IM removal efficiency [22]. Hence, in this study, the CD of 25 mA/cm^2 was adopted as the optimum value for the next phases of the experiment. Nevertheless, for current densities higher than the optimum value, the electrode surface is destroyed and oxidation agents are not enough for degradation, therefore contaminants like IM are not significantly removed. This trend was also observed in the study conducted by Turabik et al. [42], where the higher CD than the optimum value caused destruction of $^{\bullet}$OH radicals.

3.6. The effect of initial IM concentration

The initial concentration of pollutants has a significant impact on the removal efficiency. According to Fig. 7, with the increase of initial IM concentration up to 100 mg/L, the removal efficiency of both IM and equivalent COD was also increased. Accordingly, the maximum IM and COD removal efficiencies of 97.2% and 88.57%, respectively, were achieved for initial IM concentration of 100 mg/L. These results indicate that the degradation rate and process efficiency are directly proportional to initial IM concentration. However, the removal efficiencies decreased beyond this concentration and to compensate this, the electrolysis time or CD should also be increased which is not economically affordable. This is in agreement with the data reported by other studies [1,24,33,40].

3.7. The effect of electrolyte concentration

The electrolyte concentration or solution conductivity is a key operational factor that affects on both the system's electrolysis time and removal efficiency. The conductivity of the solution was adjusted by adding a suitable amount of NaCl salt. This salt was used as electrolyte in other studies because

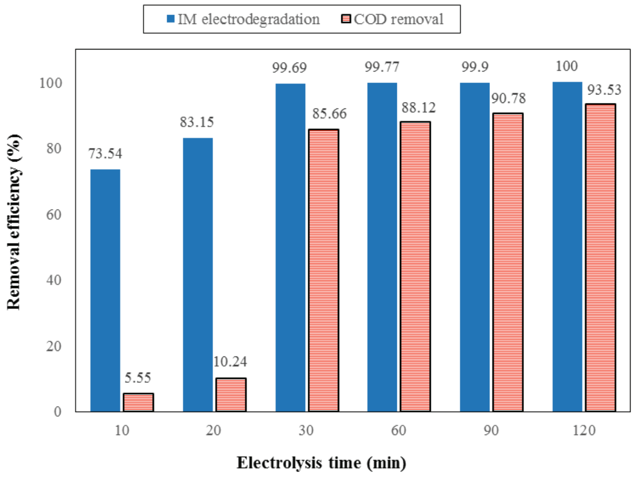

Fig. 5. The effect of contact time on electrodegradation of imidacloprid (C_0 = 100 mg/L, pH = 5, current density = 25 mA/cm^2, electrolyte concentration = 10.69 mmol/L).

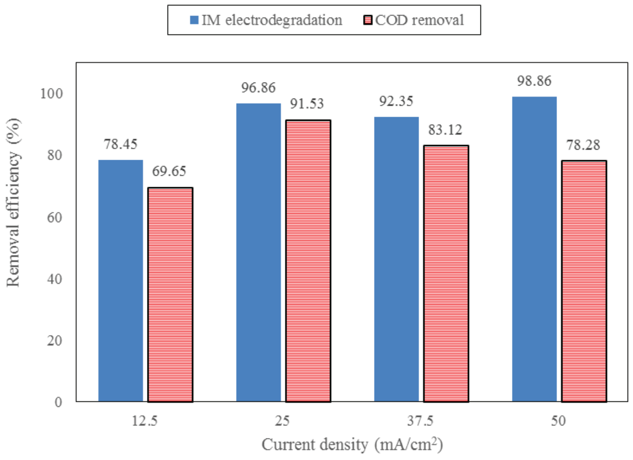

Fig. 6. The effect of current density on electrodegradation of imidacloprid (C_0 = 100 mg/L, pH = 5, electrolysis time = 30 min, electrolyte concentration = 10.69 mmol/L).

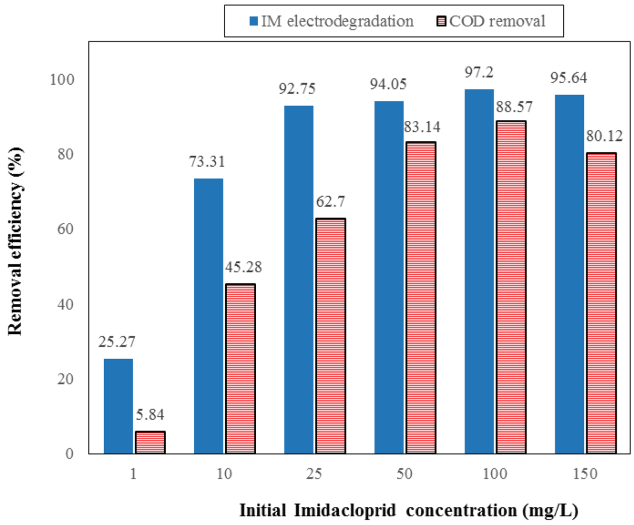

Fig. 7. The effect of initial imidacloprid concentration on electrodegradation efficiency (pH = 5, electrolysis time = 30 min, current density = 25 mA/cm^2, electrolyte concentration = 10.69 mmol/L).

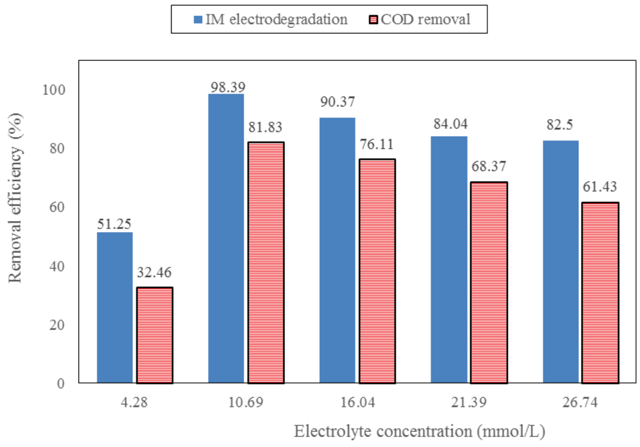

Fig. 8. The effect of electrolyte concentration on electrodegradation of imidacloprid (C_0 = 100 ppm, pH = 5, electrolysis time = 30 min, current density = 25 mA/cm^2).

of higher efficiency compared with other salts [38]. When chlorides are present in the solution, the Cl_2 and OCl^- are the products that result from the AO. The presence of chlorides in optimum concentrations (Fig. 8) resulted in an increase in the removal efficiency through the increase of CD and shortened electrolysis time. This increase could be due to the increase of the redox potential of the solution as well as the contribution of strong oxidizing agents (Eqs. (11)–(13)) [1,22,25]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{11}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{12}$$

$$\text{Pesticide} + OCl^- \rightarrow CO_2 + H_2O + Cl^- \tag{13}$$

To assess electrolyte concentration effects on the IM removal efficiency, the NaCl concentrations of 0.02, 0.05, 0.075, 0.1 and 1.25 g/80 mL (corresponds to 4.28, 10.69, 16.04, 21.39 and 26.74 mmol/L, respectively) were used as a supporting electrolyte. Our findings also confirm that by the increase of NaCl concentration from 4.28 to 10.69 mmol/L (optimum value), IM removal also increase but further increase of NaCl concentration (beyond the optimum value), does not improve IM removal. On the contrary, IM and COD removal percentage decreased mainly due to decrease of solution conductivity. Two major causes can be considered as reason for decrease in efficiency on the increase of salt concentration: (i) it could be due to oxidation of spraying salt instead of IM at higher dose of electrolyte concentration, because IM resistance to oxidation is higher than that of NaCl and thus the latter was more easily oxidized and consumed the produced degrading radicals; (ii) generation of Cl^- ions during the electrolysis process which, in turn, enter the electrode pores and cause deterioration and destroy the formed lead dioxide passive layer from the electrode surface, induces of the pseudo-COD and leads to reduced efficiency [43]. Thus, the electrolyte concentration of 10.69 mmol/L was adopted as the optimum electrolyte concentration, which was well under the inhibitory effect limit of NaCl on the COD measurement [44].

3.8. Energy consumption and Pb corrosion issues

In the current study, energy consumption was calculated using Eq. (7) and the results have been given in Fig. 9. In electrochemical cells, energy consumption is influenced by four important parameters: CD, average input voltage to the cell, retention time and organic loading rate. As can be clearly seen from Fig. 9, at optimum conditions, that is, CD = 25 mA/cm^2), reaction time = 30 min and average applied voltage of 23.95 V, the amount of electrical energy consumption obtained was ca. 5.35 kWh/kg COD. One of the main arguments on electrochemical reactor process is the electrical energy consumption of the system. According to Zhou et al. [45], if the energy consumption of an electrochemical process is less than 40–50 kwh/kg COD, it can compete with other AOPs. Since the obtained electrolysis time was very low, it can be claimed that this method is preferable compared with other processes in terms of energy consumption and is suitable for industries with very low volume of wastewater.

Regarding some issues about Pb corrosion and its transport to wastewater or to the environment, it should be noted that pure Pb was covered by the formation of PbO_2 layer, which in turn, increased the resistance against corrosion. Furthermore, corrosion is usually more at high current densities and at high pH, but the lower ranges used in this study could logically result in little corrosion [46,47].

4. Conclusions

In this study, ED of IM was assessed. PbO_2 and steel electrodes were used and the various operational parameters were optimized and applied to remove IM from aqueous solutions. At solution pH of 5, electrolysis time of 30 min, CD of 25 mA/cm^2, initial IM concentration of 100 mg/L and electrolyte concentration of 10.69 mmol/L optimum IM removal was achieved. The corresponding removal efficiency was 97.30%

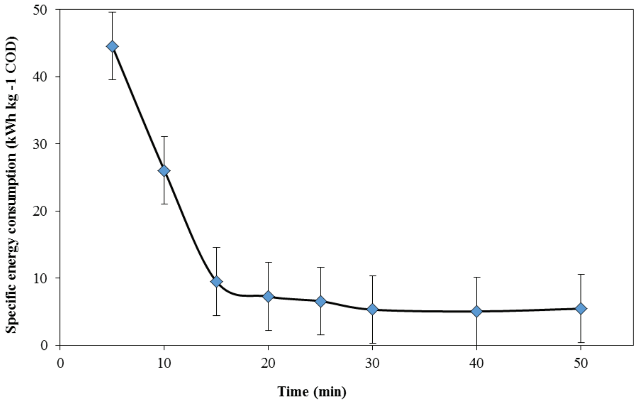

Fig. 9. The specific energy consumption for anodic oxidation of imidacloprid in the optimum conditions (pH = 5, current density = 25 mA/cm^2, electrolysis time = 30 min, C_0 = 100 mg/L and NaCl (electrolyte) concentration = 10.69 mmol/L).

for IM and 88.65% for COD. Furthermore, IM degradation does not require high electrical energy; hence, the ED of IM on Pb/stainless steel electrode can be easily achieved. This study suggests that ED of IM by Pb and stainless steel electrodes can be considered as a promising and economically viable technology for the treatment of IM containing wastewater.

Acknowledgments

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