

Voltammetric behaviour of imidacloprid and its electrochemical mineralization assessment by differential pulse polarography

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Abstract- The development of electrochemical methods for mineralization of agricultural organic pollutant imidacloprid in aquatic environment was investigated. In the present paper, the electrochemically generated strong oxidants destroy the pesticide in the bulk solution by oxidation reaction. The disappearance of pesticide as a function of time was estimated by differential pulse polarograph (DPP). As first, we have studied the electroanalytical behaviour of imidacloprid insecticide by DPP using a dropping mercury electrode (DME) as working electrode and $\text{Hg}/\text{Hg}_2\text{Cl}_2$, $\text{Cl}^-_{(\text{sat})}$ as a reference electrode in Britton-Robinson buffer (pH 3.0–10) as a supporting electrolyte. The results that were obtained showed that, the BRB with pH 8.0 was the best medium for reduction of imidacloprid on the mercury electrode at the peak potential -0.974 V. The range of linearity was found to be from $1.0 \mu\text{g ml}^{-1}$ to $12.0 \mu\text{g ml}^{-1}$ with limit of detection of (LOD) $0.6552 \mu\text{g ml}^{-1}$ and limit of quantification (LOQ) was $2.184 \mu\text{g ml}^{-1}$. The R^2 value was 0.996. DPP method was successfully applied for electrochemical mineralization study of imidacloprid, follows first order kinetic reaction. As observed from different concentrations, the mineralization of insecticide was also increased from 72.38 to 93.36% with the increasing current density. The method used in this work is simple, accurate and economical.

Index Terms- Imidacloprid, Insecticide Differential pulse polarography, Mineralization

I. INTRODUCTION

It is known that ever growing use of pesticides in the agricultural sector has lead to several environmental problems. However enhanced use of pesticides and the problems related to them are yet to attract the attention of scientific community in India. Neonicotinoid insecticide, imidacloprid [1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine] is an important part of agriculture management. Imidacloprid are one of the newer classes of synthetic systemic insecticides with worldwide use in the last three decades.

There are number of physico-chemical methods used by many researchers for the removal of pesticides from aquatic environment, coagulation[1], reverse osmosis[2], microwave plasma detoxification[3], biological method [4-5], advanced oxidation processes[6-7], adsorption[8-12], Fly ash[13], photodegradation[14-20].

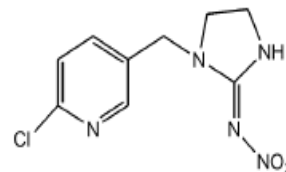


Figure 1: Chemical structure of imidacloprid

Electrochemical mineralization is an advanced technology used for the removal of organic and inorganic impurities from water and wastewater [21-22]. The advantages of electrochemical method are easily controlled and facilitate automation of a process and cost effective. In this method removal efficiency of pesticide in aquatic environment is good [23].

There are various techniques such as the high performance liquid chromatography (HPLC) [24-26], gas chromatography (GC) [27-29], enzyme linked immunosorbant assay (ELISA) [30-34] and radioimmunoassay (RIA) [35] have been developed for the detection and quantification of the imidacloprid, but all these methods have disadvantages such as long analysis time, consume a lot of reagents and expensive. In view of this, it is proposed to develop a cost effective electroanalytical differential pulse polarographic (DPP) method for determination and decontamination of imidacloprid pesticide in aquatic environment.

II. MATERIALS AND METHODS

A. Chemicals

Analytical reagent grade chemicals were used for preparation of solutions in doubly distilled water. The reference standards were imidacloprid, ammonium chloride, ammonium acetate, sodium acetate, ammonium nitrate, acetic acid, phosphoric acid, boric acid and organic solvents such as dichloromethane, hexane, ether etc. were purchased from local mark. Universal BRB buffers were prepared according to the standard procedure with AR chemicals.

B. Standard Solutions

A 1.0 mg ml^{-1} stock solution of the insecticides was prepared by dissolving an appropriate amount of imidacloprid and stored under refrigeration. This solution was stable for at least one month.

C. Equipments used

Polarographic analyzer model CL-362 supplied by an Elico Ltd, Hyderabad with PC through its RS 232C interface with the help of ELICO's windows based software were used for polarographic measurements. A dropping mercury as a working electrode, saturated calomel as reference and platinum wire as auxiliary electrodes was used. The pH measurements were carried out with the help of Elico pH meter.

D. DPP determination of imidacloprid insecticide

For differential pulse polarographic studies, dilutions of stock solution were prepared in 0.04M BRB buffer solution at pH 8.0 as a supporting electrolyte to obtain concentration ranging from 1.0 $\mu\text{g ml}^{-1}$ to 12.0 $\mu\text{g ml}^{-1}$. A series of electrochemical experiment was performed in an undivided 10 ml cell with three electrodes system. The solutions were degassed prior to analysis by bubbling purified nitrogen gas through the cell for 5 min and differential pulse polarogram of imidacloprid insecticide were recorded at optimum parameters.

E. Electrochemical degradation setup

The electrochemical degradation experiments were conducted by batch process using undivided cell of 100 ml capacity. The anode and cathode were located vertically and parallel to each other with an inter electrode gap of 1.0 cm and area of cross section 1.0 cm^2 (simply conductivity cell). The material used as the anode and cathode was platinum. These electrodes were dipped in the aqueous solution containing definite concentration of imidacloprid and ammonium chloride as supporting electrolytes were added in to the electrolytic cell to increase the conductivity of the solution and to decrease the electrolysis time. The solution was constantly stirred at 200 rpm using a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. A stabilized DC power supply was used as the source of electric current for the experiments. Studies were carried out for the investigation of optimum conditions for the degradation and removal of the imidacloprid solutions by the electrocatalytic oxidation process.

The insecticide imidacloprid in aqueous solution at different time interval were extracted from the electrolysis medium using methylene chloride. The extracts were dried and reconstituted to 0.04 M BRB buffer at pH 8.0. These samples were analyzed Polarographic analyzer using optimum parameters.

III. RESULTS AND DISCUSSION

A. Effect of pH

Before application, a quantitative determination of imidacloprid insecticide, additional characterization of the working electrode was performed. DPP polarogram of imidacloprid were recorded in the pH range 3.0 to 10.0 to study the pH dependence on peak potentials (figure 2.0). It is seen that I_p is maximum in the range of pH 6.0-8.0 for the first peak and pH 3.0-6.0 for the second peak. Consequently, the values of I_p are high for the first peak at pH 8.0, which was chosen as the analytical signal for reduction

of imidacloprid insecticides on the mercury electrode at peak potential(E_p) -0.974V.

Therefore the electrochemical reduction of imidacloprid takes place in two waves by a mechanism commonly proposed for the nitro compounds [36-41].The first one corresponds to a four-electron transfer process to give the hydroxylamine derivative, and the second corresponds to a two-electron transfer get converted in to NH_2 group

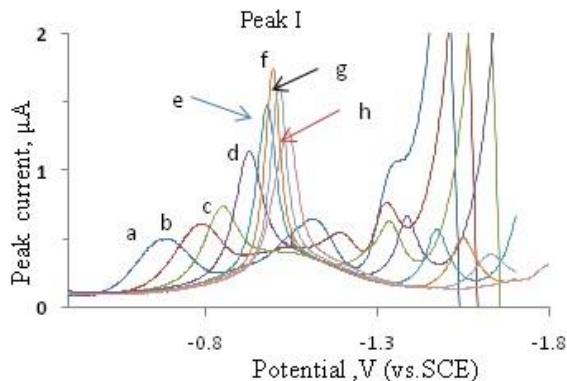


Figure 2: Differential pulse polarographic behavior of 10.0 $\mu\text{g ml}^{-1}$ imidacloprid insecticide at different BRB pH values; (a) 3.0 (b) 4.0 (c) 5.0 (d) 6.0 (e) 7.0 (f) 8.0 (g) 9.0 and (h) 10.0

B. Optimization of instrumental parameters

For optimizing conditions of DPP instrument, the dependence of I_p and E_p of imidacloprid on scan rate, drop time current range and pulse amplitude has been studied. The scan rate was varied from 3 to 12 mV/s and a maximum response for selected pesticide was obtained at 6 mV/s .

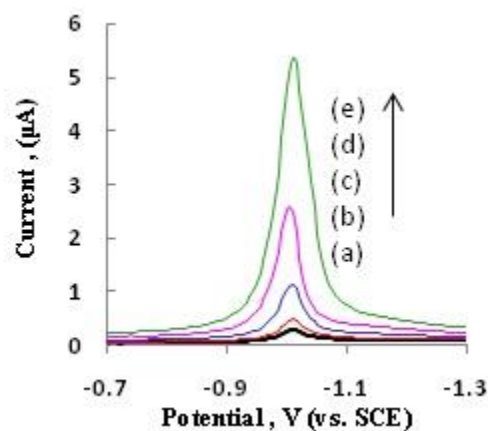


Figure 3: Effect of pulse amplitude on I_p of 10.0 $\mu\text{g ml}^{-1}$ of imidacloprid insecticide at a) 5.0 mV b) 10.0 mV c) 25.0 mV d) 50.0 mV and e) 100.0mV, at pH 8.0, current range 10 μA , scan rate 6 mV/sec , drop time 1sec.

The effect of the pulse amplitude on the I_p of imidacloprid insecticide from the range of 5.0 to 100 mV shows that a maximum value of I_p of selected pesticides were obtained at 100 mV is higher as compared to that obtained by unoptimised parameters, so 100 mV is chosen as optimum pulse amplitude quantification of insecticide with correlation coefficient 0.998as

shown in **Figure 3**. The optimum parameters used for analysis of insecticide are current range 10 μA , data acquisition slow, scan rate 6mV/sec, drop time 1sec, scan type forward, scan range start -0.200V end -1.7 V, pulse amplitude 100 mV and cc compensation is 0%. It was also observed that the I_p is linearly proportional to pulse amplitude according to the following equation [1]

$$I_p (\mu\text{A}) = 0.054x (\text{mV}) - 0.084 \quad [1]$$

C. Calibration and method validation of insecticide

A study was carried out using optimum analytical parameters of DPP at peak potential (E_p) -0.974 V, to observe a relationship between I_p and concentration of insecticide, a calibration curve and polarogram has been prepared by a series of standard solution of imidacloprid as shown in **Figure 4**.

The range of linearity was found to be from 1.0 $\mu\text{g ml}^{-1}$ to 12.0 $\mu\text{g ml}^{-1}$ with limit of detection of (LOD) 0.6552 $\mu\text{g ml}^{-1}$ and limit of quantification (LOQ) was 2.184 $\mu\text{g ml}^{-1}$. The R^2 value was 0.996. For the determination of precision of the developed method, the reproducibility was calculated from 5 independent measurements of 3.0 $\mu\text{g ml}^{-1}$ and 6.0 $\mu\text{g ml}^{-1}$ of imidacloprid solutions on the same day, obtaining relative standard deviations (RSD) of 0.61 % and 0.72% respectively. For the inter-days (within 3 days) accuracy determinations, the RSD for day 1, day 2 and day 3 obtained for measurement of 3.0 $\mu\text{g ml}^{-1}$ are 1.123%, 1.524% and 0.894% respectively and for 6.0 $\mu\text{g ml}^{-1}$ were 1.12 %, 0.51 % and 1.92 %.

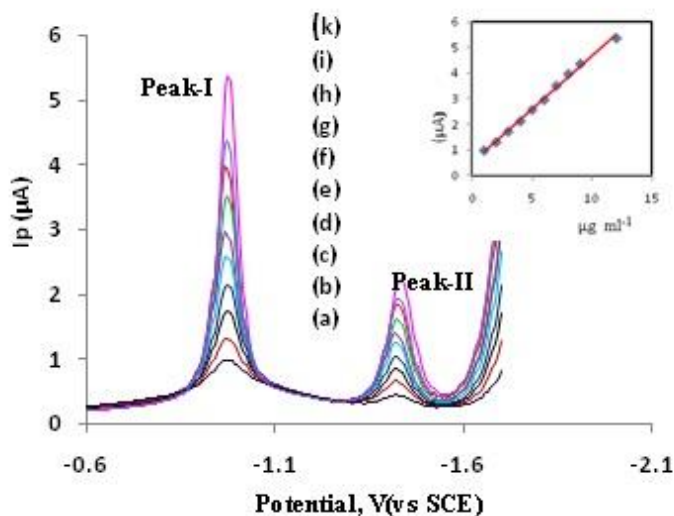


Figure 4: Differential pulse polarogram and calibration curve of imidacloprid insecticide at pH 8.0 in BRB buffer solution as a supporting electrolyte obtained at a) 1.0 $\mu\text{g ml}^{-1}$ b) 2.0 $\mu\text{g ml}^{-1}$ c) 3.0 $\mu\text{g ml}^{-1}$ d) 4.0 $\mu\text{g ml}^{-1}$ e) 5.0 $\mu\text{g ml}^{-1}$ f) 6.0 $\mu\text{g ml}^{-1}$ g) 7.0 $\mu\text{g ml}^{-1}$ h) 8.0 $\mu\text{g ml}^{-1}$ i) 9.0 $\mu\text{g ml}^{-1}$ k) 12.0 $\mu\text{g ml}^{-1}$

In order to determine the accuracy of the proposed method, a recovery study was carried out by the addition of an

amount of three different concentrations of imidacloprid (3.0 $\mu\text{g ml}^{-1}$, 6.0 $\mu\text{g ml}^{-1}$ and 9.0 $\mu\text{g ml}^{-1}$) into the polarographic cell and measuring the peak currents of respective concentrations. The actual amount of imidacloprid found in the cell were calculated using the obtained regression equation ($I_p (\mu\text{A}) = 415.5C + 0.513$). The recoveries obtained were $97.29 \pm 0.79 \%$, $97.26 \pm 0.40 \%$ and $99.47 \pm 0.40 \%$ respectively.

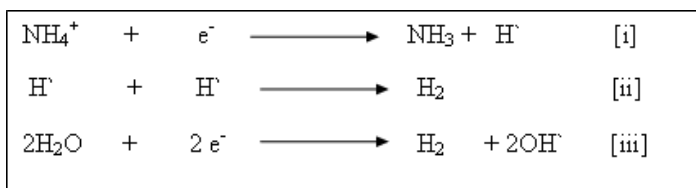
D. Choice of electrode for degradation of insecticide

In order to optimize the process of electrochemical mineralization, the choice of the electrode material plays an important role. The observation on the electrolysis of imidacloprid using different electrodes in an undivided cell was performed. Platinum electrodes showed not only an excellent stability but also offered, higher conductance of current during degradation of insecticides.

E. Effect of supporting electrolytes

The electrochemical degradation of imidacloprid was performed in different electrolytes. It can be seen that in the presence of ammonium chloride, the mineralization efficiency was increased. From this observation it was concluded that the introduction of Cl^- containing electrolytes can enhance the degradation efficiency and shorten the degradation time, which may be attributed to the reaction between the generated chlorine/hypochlorite and the insecticide molecule.

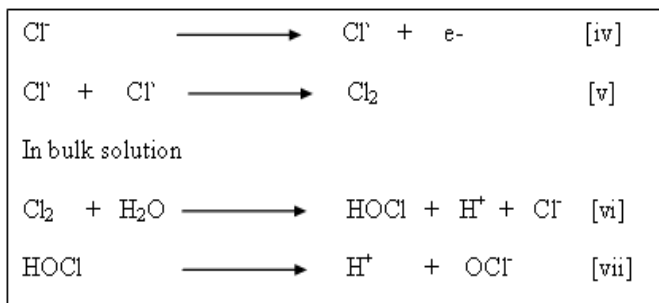
The proposed electrode mechanism is as follows
When ammonium chloride was used as supporting electrolytes for electrochemical degradation of imidacloprid, at cathode ammonium ion get discharged as given below.



Ammonia gas generated was dissolved in water and only hydrogen gas was collected in electrochemical setup. The hydrogen gas formed, during electrolysis is due to combination of hydrogen radicals. The free radicals also get adsorbed on the electrode. This adsorption phenomenon is responsible for the high catalytic activity of electrode.

In an indirect oxidation process, the anodic reaction that occurs in electrolysis of ammonium chloride involves the oxidation of chloride ions into chloride radicals. The chlorine radicals can also undergo combination forming strong oxidants molecular chlorine/hypochlorite [42-43]. The insecticide is then destroyed into CO_2 , NO_3^- etc as mineralization products [44] in the bulk solution by oxidation reaction of the generated oxidant. The formation of the reactive chloride species causes an increase in the redox potential of the solution, and can allow the

oxidation of the imidacloprid insecticides in the treated medium [45-47]



F. Electrochemical kinetics study of imidacloprid

The electrochemical degradation of imidacloprid is a simple pseudo-first-order kinetic reaction was attempted. In the indirect electrochemical oxidation process, the insecticide removal rate is proportional to the concentration of the organic compound (pollutant) and to the chlorine/ hypochlorite concentration because the indirect oxidation is mediated by chlorine/hypochlorite. The decreased concentration of insecticide with respect to time is measured by DPP analytical method as shown in **Figure 5**. Therefore, the kinetics for PEST removal is

$$- \frac{d[\text{PEST}]}{dt} = K [\text{PEST}] [\text{Cl}_2] \quad [2]$$

Electrochemical oxidation involves the application of an electrical current to the electrolyte to convert chloride to chlorine / hypochlorite. The chlorine / hypochlorite will oxidize the pesticide and then get reduced to chloride ion. The process is then repeated in a catalytic fashion. Therefore, the concentration of chlorine/hypochlorite during the electrolysis is assumed to be a constant, and so equation [2] can be written as a pseudo-first-order kinetic equation.

$$- \frac{d[\text{PEST}]}{dt} = K [\text{PEST}] \quad [3]$$

The degradation rate constant k can be determined by using following first order rate equation (3)

$$\log C_0/C_t = k t \quad [4]$$

The slope of the plot (not shown) of $\log (C_t/C_0)$ versus time (t) gives the value of rate constant k as shown in figure6.0. Here, C_0 is the initial concentration of neonicotinoids in milligrams per liter, and C_t is unconsumed concentration of neonicotinoids at time (t). **Table 1.0** provides the rate constant and half lives of imidacloprid. High values of correlation coefficients (above 0.98) indicate that the hypothesis of pseudo-first-order reaction of neonicotinoids removal fit well.

The half-life and rate constant are two most important parameters of the persistence of an insecticide. The effect of current density and concentration of insecticide on the two

parameters were studied separately in ammonium chloride medium. From the kinetics study it was observed that as current density at different concentration increases, the half period of decreases and reaction rate coefficient increases as given in Table 1. It was observed that as current density at different concentration increases, the half period of decreases and reaction rate coefficient increases as shown in Table 1.

Table: 1. Electrochemical mineralization of imidacloprid.

Current density (mA)	Regression equation	k (h ⁻¹)	T _{1/2} (hrs)	R ²
[Imidacloprid]= 0.010 mgml ⁻¹ (3.910x10 ⁻⁶ M), E _p = -0.974 V				
50	y=0.075x+0.009	0.1817	3.813	0.993
100	y=0.095x+0.024	0.2427	2.855	0.980
150	y=0.128x+0.004	0.2987	2.320	0.998
200	y=0.15x+0.005	0.3504	1.977	0.996
[Imidacloprid]= 0.015 mgml ⁻¹ (5.866x10 ⁻⁶ M), E _p = -0.974 V				
50	y=0.109x-0.000	0.2510	2.760	0.998
100	y=0.136x+0.006	0.3192	2.171	0.998
150	y=0.145x+0.044	0.3779	1.833	0.990
200	y=0.176x+0.030	0.4353	1.592	0.994

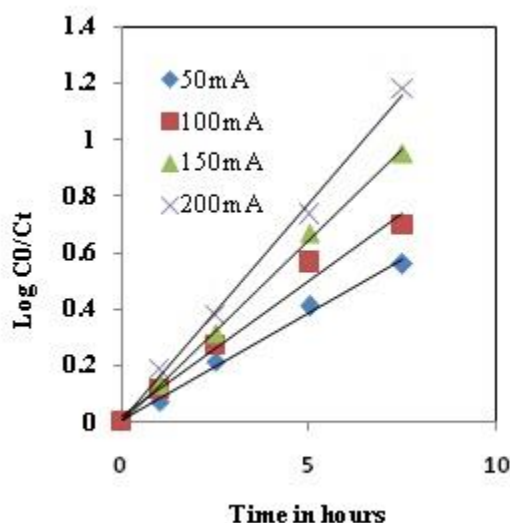


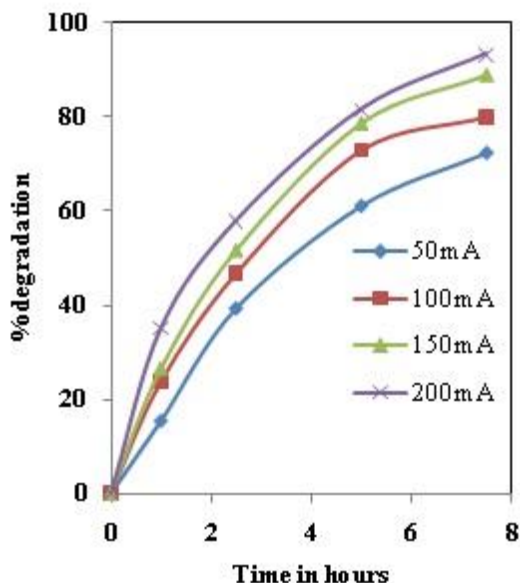
Figure 6: Electrochemical degradation kinetics of imidacloprid insecticide at various current densities at 0.010 mg ml⁻¹

G. Electrochemical mineralization of imidacloprid

The electrochemical degradation and mineralization of neonicotinoid insecticide imidacloprid in an aqueous has been investigated. DPP study was employed for the mineralization study of imidacloprid solutions to measure the peak current at optimum parameters after extraction in dichloromethane before and after electrolysis. The mineralization efficiency was calculated using the relation [5]

$$\%E = \frac{C_0 - C_t}{C_0} \times 100 \quad [5]$$

Where, C_0 is the initial concentration and C_t is the final concentration value at a time (t) of insecticide solution, respectively.



Figures 7.0: Electrochemical degradation of imidacloprid insecticide at different current density and concentration 0.010 mg ml^{-1}

Initially, the decontamination of insecticide from aquatic environment in different initial concentrations (0.01 , 0.015 and 0.020 mgml^{-1}) was investigated by indirect electro-oxidation process using platinum electrodes as both anode and cathode at a current density of 50 mA in NH_4Cl electrolyte solution for 7.5 hrs. As the initial concentration of insecticide was increased 0.01 mgml^{-1} to 0.020 mg ml^{-1} , insecticide degradation efficiencies were increased to 72.38% , 84.95% and 88.24% respectively as shown in figure 7.0. The energy consumptions at 0.010 mg ml^{-1} and different current density from $50, 100, 150$ and 200 mA of insecticide were 0.07812×10^{-3} , 0.333×10^{-3} , 0.3125×10^{-3} , and $0.2916 \times 10^{-3} \text{ kWhm}^{-3}$ for 7.5 hrs. The sanitization of imidacloprid insecticide from aqueous solutions in different initial concentrations was also investigated by electrochemical

method with different current density of from $50, 100, 150, 200 \text{ mA}$ in NH_4Cl electrolyte solution at the same time. As the current density at 0.01 mgml^{-1} insecticide concentration was increased to 200 mA , imidacloprid degradation efficiencies of 50 mA were increased from 72.38 to 93.36% As observed from different concentrations, the degradation of insecticide were also increased with the increasing current density, but not at expected level..

H. Conclusion

In this work, electroanalytical DPP technique was successfully applied for the electrochemical degradation and kinetic study of imidacloprid follow first order kinetic reaction. The results show that current density influences the % degradation, rate of reaction and half life of the imidacloprid insecticides. Finally, it can be concluded that the proposed DPP method which are sensitive, accurate, precise, fast and low cost methods were successfully developed for the determination of insecticide in water environment. This method has a great potential as an alternative method for this application in the future.

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