科技部補助專題研究計畫成果報告
期末報告

流體化床芬頓程序處理新菸鹼類農藥廢水之反應動力與機制

計畫類別：個別型計畫
計畫編號：MOST 106-2221-E-041-001-
執行期間：106年08月01日至107年07月31日
執行單位：嘉藥學校財團法人嘉南藥理大學環境資源管理系(含碩士班)

計畫主持人：盧明俊

計畫參與人員：此計畫無其他參與人員

報告附件：出席國際學術會議心得報告

中華民國 107 年 09 月 07 日

中文摘要：

科學家們已逐漸發現新菸鹼類農藥對環境造成之衝擊。蜜蜂族群崩潰症開始蔓延，這種效應會造成全球糧食減產三分之一以上，人類要面臨的糧食危機即將到來。不僅施用於農田會對蜜蜂產生危害，其農藥生產過程產生農藥空瓶回收清洗產生之廢水排入水體，也會造成生態重大危害，因此本計畫探討含新菸鹼類農藥之廢水處理。目前國內外有關新菸鹼類農藥廢水處理主要是以光觸媒、電化學氧化及臭氧等技術，但仍然處於研究階段，難以放大到實廠應用。本計畫以流體化床芬頓技術各種操作參數，選定最常用之新菸鹼類農藥微處理對象，研究新菸鹼類農藥廢水之處理效率、氧化產物、氧化路徑、礦化率及添加劑之效應。本研究選定的處理對象為新菸鹼類農藥-益達胺，常見的農藥添加劑為丙二醇，結果顯示，含有0.4 mM 益達胺及丙二醇的合成廢水，最佳處理條件為0.8 mM Fe^{2+}及15.5 mM H_2O_2. 增加丙二醇濃度會因為競爭氫氧自由基作用而抑制益達胺分解，本研究最終亦提出益達胺分解途徑。

中文關鍵詞：

流體化床芬頓、廢水處理技術、高級氧化程序、農藥

英文摘要：

Scientists have gradually discovered the impact of neonicotinoid pesticides on the environment. The colonycollapse disorder (CCD) began to spread. This effect may cause the reduction of one-third of global foodproduction. People are going to to face the coming of food crisis soon. Both using pesticide and rinsing therecycle bottles will destroy our environment inducing ecological crisis. Therefore, this project is going to explore the treatment of wastewaters containing neonicotinoids. In the world, there are some literature reporting the treatment of neonicotinoids wastewaters using photocatalytic, electrochemical and ozone technologies. However, they are not easy to be scaled up because of operation cost. This project applied the fluidized-bed Fenton technology(FBF) to investigate the application feasibility by evaluating the treatment efficiencies, oxidation intermediates, mineralization efficiencies with the interference of additive in the commercial pesticides. This project selected Imidacloprid (IMI) as the target pesticide and propylene glycol (PG) was the additive. The FBF process is efficient to treat IMI even in the competing presence of PG. The optimum variables to treat IMI solutions containing 0.4 mM PG were identified as 0.8 mM Fe^{2+} and 15.5 mM H_2O_2, allowing to attain complete IMI removals and considerable COD reductions after 2 h treatment. Increasing concentrations of PG in pesticides formulations, reduces the rate of IMI degradation due to the competitive reaction with the non-selective OH radical and PG. The degradation by-products of IMI were detected by GC-MS analysis and comprehensive oxidation pathway was proposed.

英文關鍵詞： Fluidized-bed Fenton; wastewater treatment technologies; advanced oxidation processes; pesticides

科技部補助專題研究計畫成果報告

（□期中進度報告/■期末報告）

流體化床芬頓程序處理新菸鹼類農藥廢水之反應動力與機制

計畫類別：■ 個別型計畫　　□整合型計畫
計畫編號：MOST　106-2221-E-041-001
執行期間：106 年 8　月 1　日至 107 年 7 月 31　日

執行機構及系所：嘉南藥理大學環境資源管理系

計畫主持人：盧明俊
共同主持人：
計畫參與人員：Carl Francis Z. Lacson, Elaine Joy T. Battung

本計畫除繳交成果報告外，另含下列出國報告，共 _1__ 份：
□執行國際合作與移地研究心得報告
■出席國際學術會議心得報告
□出國參訪及考察心得報告

中　華　民　國 107 年 8 月 31 日

摘要

科學家們已逐漸發現新菸鹼類農藥對環境造成之衝擊。蜜蜂族群崩潰症開始蔓延，這種效應會造成全球糧食減產三分之一以上，人類要面臨的糧食危機即將到來。不僅施用於農田會對蜜蜂產生危害，其農藥生產過程產生農藥空瓶回收清洗產生之廢水排入水體，也會造成生態重大危害，因此本計畫探討含新菸鹼類農藥之廢水處理。目前國內外有關新菸鹼類農藥廢水處理主要是以光觸媒、電化學氧化及臭氧等技術，但仍然處於研究階段，難以放大到實廠應用。本計畫以流體化床芬頓技術各種操作參數，選定最常用之新菸鹼類農藥微處理對象，研究新菸鹼類農藥廢水之處理效率、氧化產物、氧化路徑、礦化率及添加劑之效應。本研究選定的處理對象為新菸鹼類農藥-益達胺，常見的農藥添加劑為丙二醇，結果顯示，含有 0.4 mM 益達胺及丙二醇的合成廢水，最佳處理條件為0.8 mM Fe^{2+} 及15.5 mM H_2O_2.增加丙二醇濃度會因為競爭氫氧自由基作用而抑制益達胺分解，本研究最終亦提出益達胺分解途徑。

關鍵字: 流體化床芬頓、廢水處理技術、高級氧化程序、農藥

Abstract

Scientists have gradually discovered the impact of neonicotinoid pesticides on the environment. The colonycollapse disorder (CCD) began to spread. This effect may cause the reduction of one-third of global foodproduction. People are going to to face the coming of food crisis soon. Both using pesticide and rinsing therecycle bottles will destroy our environment inducing ecological crisis. Therefore, this project is going to explore the treatment of wastewaters containing neonicotinoids. In the world, there are some literature reporting the treatment of neonicotinoids wastewaters using photocatalytic, electrochemical and ozone technologies. However, they are not easy to be scaled up because of operation cost. This project applied the fluidized-bed Fenton technology(FBF) to investigate the application feasibility by evaluating the treatment efficiencies, oxidation intermediates, mineralization efficiencies with the interference of additive in the commercial pesticides. This project selected Imidacloprid (IMI) as the target pesticide and propylene glycol (PG) was the additive. The FBF process is efficient to treat IMI even in the competing presence of PG. The optimum variables to treat IMI solutions containing 0.4 mM PG were identified as 0.8 mM Fe^{2+} and 15.5 mM H_2O_2, allowing to attain complete IMI removals and considerable COD reductions after 2 h treatment. Increasing concentrations of PG in pesticides formulations, reduces the rate of IMI degradation due to the competitive reaction with the non-selective $^{\bullet}OH$ radical and PG. The degradation by-products of IMI were detected by GC-MS analysis and comprehensive oxidation pathway was proposed.

Keywords: Fluidized-bed Fenton; wastewater treatment technologies; advanced oxidation processes; pesticides

1. Introduction

Pesticides play a key role in water–food nexus. Incorrect pest management approaches result on water pollution. Imidacloprid (IMI) is a contaminant of emerging concern used as an alternative to carcinogenic organochloride insecticides such as DDT. The wide range of possible applications of IMI in crops pest control [1], antiparasitic treatments [2], and vector control for dengue mosquitoes [3] resulted in the extensively use of this insecticide which is expected to reach ~24 % share of the agrochemical market [1].

IMI is a nicotine-derived insecticide with low mammal toxicity that inhibits the insects' neurotransmitters causing paralysis and fatality with high efficiency [1]. It has been observed a high IMI persistence with half-life for almost one year in aerobic soils. Thus, a great risk for groundwater resources contamination arises due to the high IMI solubility (580 mg L^{-1}) [4]. Recent studies suggest that continuous environmental exposure to IMI might affect non-target organisms such as aquatic organisms [5] and amphibians [6]. Deleterious effects reported can be associated to toxicity and genotoxicity of IMI and its by-products resulting from incomplete degradation [7,8]. IMI has been detected in wastewater treatment plant effluents where slight removals of ~40 % by conventional water treatment technologies have been reported [9,10]. Unfortunately, incomplete degradation can yield even more toxic by-products. In this frame, the development of alternative technologies to efficiently degrade these emergent pollutants until complete mineralization is necessary.

Advanced Oxidation Processes (AOPs) are emerging technologies capable of attaining total organic pollutant mineralization by hydroxyl radical ($^{\bullet}OH$), a high oxidant species ($E^{o}(^{\bullet}OH/H_2O) = 2.80$ V/SHE) generated *in situ* [11-13]. Pesticides removal has been studied by different AOPs including photocatalysis [14,15], ozonation [16,17], photoelectrocatalysis [18,19] and electrochemical oxidation processes [20-22]. Fenton process is considered one of the most satisfactory AOPs due to its easy scalability and low investment cost [23]. Fenton process produces large quantity of $^{\bullet}OH$ from the H_2O_2 decomposition catalyzed by Fe^{2+} following reaction (1) [24-26]. The Fe^{2+} can be regenerated through the Fenton-like reaction (2) that yields hydroperoxyl radical ($HO_2^{\bullet}$) as a weaker oxidant ($E^{o}(HO_2^{\bullet}/H_2O) = 1.65$ V/SHE) [27,28].

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow H_2O + Fe^{3+} + {}^{\bullet}OH \tag{1}$$

$$H_2O_2 + Fe^{3+} + H^+ \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \tag{2}$$

The drawback of the Fenton process is the generation of large quantity of iron sludge that would eventually require supplementary treatment for the separation and for the disposal of solid waste. However when using fluidized-bed reactors in the Fluidized-bed Fenton (FBF) process, both the iron oxides and iron hydroxides form crystals onto the carrier surface (SiO_2 particles) avoiding sludge formation [29,30]. Iron oxides and hydroxides can then further react as heterogeneous catalyst when remaining in fluidized state inside the fluidized-bed column reactor, which improves the kinetics of heterogeneous catalysis [26,31]. The heterogeneous reaction may further enhance the overall organic efficiency removal by FBF in comparison to conventional Fenton oxidation [30-33].

This paper reports the optimization of IMI by FBF treatment. Experiments were conducted in continuous mode using a fluidized-bed reactor where the treated solution was recirculated during the treatment. The effects of independent variables Fe^{2+}, H_2O_2 and propylene glycol (PG) an usual inert ingredient of commercial IMI pesticides preparations on the treatment performance have been evaluated. The degradation of IMI and total organic carbon abatement were determined. The generated intermediates released during the degradation of IMI by $^{\bullet}OH$ were identified by GC-MS and the IMI oxidation pathway by FBF process was proposed.

2. Experimental

2.1. Reagents and chemicals

Imidacloprid ($C_9H_{10}ClN_5O_2$) analytical standard was provided by Huikwang Corporation Taiwan. Hydrogen peroxide (H_2O_2, 35 %) and ferrous sulfate hepta-hydrate ($FeSO_4{\cdot}7\,H_2O$) were acquired from Merck. Analytical grade sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) from Merck were used for pH adjustments. Methanol and acetonitrile of HPLC grade (>99%) used in the chromatographic analysis were purchased from Panreac. PG ($C_3H_8O_2$) and chemicals used as standards were provided by Sigma-Aldrich. High-purity water provided by a Millipore Milli-Q system with resistivity > 18 MΩ cm was used for all the aqueous solution preparation.

2.2. Fluidized-bed Fenton system

Reactions were conducted using a 1.6 L cylindrical glass tube reactor composed of two differentiated zones with different dimensions as fluidized-bed reactor (Fig. 1): (i) the upper zone (height = 25 cm and inner diameter = 5 cm) and (ii) the lower zone (height = 20 cm and inner diameter = 3 cm). Glass beads (50 mm) were set at the bottom of the glass tube reactor to create turbulence and prevent undesirable clogging; to improve flow distribution and to avoid/diminish formation of bubbles from distributor holes. The carriers used were inert SiO_2 particles (0.2-0.5 mm). This reactor design was based after hydrodynamics and fluidization optimization studies in our previous works [30]. A total volume of 1.4 L of synthetic 0.4 mM IMI wastewater was introduced in the reactor. Solution was then recirculated using an Iwaki MD-10-NL12 peristaltic pump during the FBF treatment. The solution was recirculated at a constant flow to ensure fluidization of the SiO_2 carriers. Fluidization state of the carriers was ascertained by keeping expansion, twice of the initial SiO_2 bed height in the reactor column (50 % expansion). Solutions were prepared containing the desired amount of Fe^{2+} as Fenton's catalyst, whereas the required volume of H_2O_2 to reach initial desired concentration was added prior starting experiment (time of treatment 0 min).

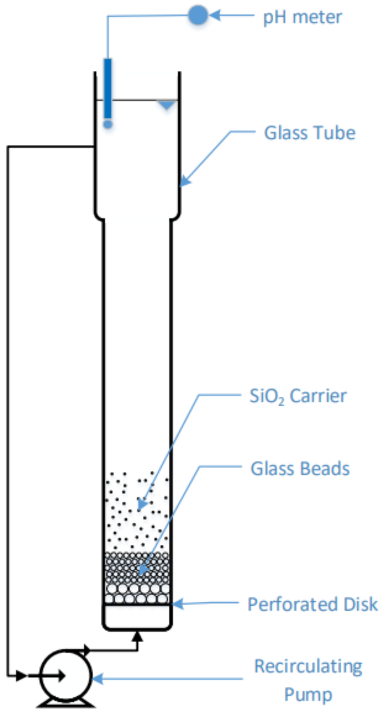


Figure 1 – Fluidized bed Fenton reactor schematics

2.3. Analytical methods and Instruments

Solution pH was continuously monitored using pH/ORP controller (PC-310) manufactured by Shin Shiang Tech Instruments and remained ca. initial value of pH 3.0 during the experiments. The NaOH solution was added to quench the Fenton reaction by precipitation. Samples were diluted and filtered using 0.2 μm syringe filter to remove precipitates prior to analysis. IMI abatement during FBF treatment was quantified by high performance liquid chromatography (HPLC) model P1000 from Thermo Scientific Spectra fitted with an Asahipak ODP-506D C18 column (150 mm × 6.0 mm) at 35 ºC. The photodiode array detector was set at $\lambda = 270$ nm. A 60:40 (v/v) water/acetonitrile mixture was used as mobile phase in isocratic flow mode (1.0 mL min^{-1}). UV-vis spectrophotometer (CT-2400) was used to quantify both the Fe^{2+} and the H_2O_2 residuals using the 1,10-phenanthroline and titanium oxalate standard methods [34], respectively.

Total iron in solution was measured by Atomic Absorption Spectroscopy using a Perkin Elmer Analyst 200 AAS. Mineralization of treated IMI solutions was quantified from the reduction of dissolved organic carbon (DOC), determined on a LiquiTOC Elementar TOC analyzer with reproducible DOC values with ±1% accuracy. Closed titrimetric reflux standard methods using dichromate was used to analyze chemical oxygen demand (COD).

Aromatic intermediates yielded during the FBF process degradation of IMI were identified by GC-MS using Agilent 7890B GC coupled to an Agilent 7693B Injector fitted with an HP-5MS capillary column (30 m x 0.25 mm i.d.) coated with 5% phenyl-methylsiloxane film of 0.25 µm thickness with an Agilent 5977A mass selective detector (MSD). Injection of samples was carried out at 270 °C by splitless mode. The ion source and transfer line temperatures were 230 °C and 300 °C, respectively. The initial temperature of the column was 60 °C within 1 min, raised to 180 °C at the rate of 25 °C min^{-1}, and to 280 °C at the rate of 5 °C/min. When reached, temperature of 280 ºC was held for 5 min. The carrier gas was helium with constant flow rate of 1 mL/min. The electron ionization (70 eV) was utilized to acquire mass spectrometry data gathered with 0.5 s scan interval from 50 to 300 m/z.

3. Results and discussion

3.1. Imidacloprid solutions oxidation by fluidized-bed Fenton

Acidic IMI solutions were treated by means of FBF in continuous-flow mode until reaching complete removal. Initial colorless solutions changed to yellow-brownish color, becoming again colorless after achieving complete removal. The coloration observed at the initial stages of FBF treatment can be attributed to the generation of hydroxylated aromatic by-products that are completely degraded at the end of the treatment by generated $^{\bullet}OH$ from reaction (1). Observed pale-yellowish color can be associated to iron hydroxo-complexes in solution that crystallized on the surface of SiO_2 carriers which by the end of FBF, which contributes reducing the amount of sludge generated from Fenton reaction.

Degradation kinetics of IMI is described by a two-stage process (Fig. 2), similar to the behavior observed during the abatement of pollutants by Fenton process. First stage consists of a rapid IMI degradation by $^{\bullet}OH$ rapidly released from reaction (1) (~55 M^{-1} s^{-1}) consuming the catalytic amounts of Fe^{2+} yielding Fe^{3+}. The great amounts of $^{\bullet}OH$ radical formed in this initial stage quickly react non-selectively with IMI in solution ($E^o(^{\bullet}OH/H_2O)$ = 2.80 V/SHE) [28,35].

The slower second kinetic stage is defined by the regeneration kinetics of the iron catalyst according to Fenton-like reaction (2) (~2 × 10^{-3} M^{-1} s^{-1}), which is several orders of magnitude slower when compared to Fenton's reaction rate [36]. Note that even though $HO_2^{\bullet}$ is produced from (2), this weaker oxidant species ($E^o(HO_2^{\bullet}/H_2O)$ = 1.65 V/SHE) cannot degrade IMI efficiently. Consequently, the Fenton degradation kinetics in the second stage is restricted by the regeneration of the catalyst [28,35]. The relevance of iron catalyst is confirmed from the rapid consumption of Fe^{2+} coincident with the first kinetic stage (Fig. 2), which is followed by the slow Fe^{2+} regeneration that remains with 0.16 mM pseudo-constant concentration during the second stage. It is noteworthy that the iron in solution decreases due to the iron hydroxide crystallization on the SiO_2 carriers, which reduces the sludge formation. Moreover, these iron oxides granules formed on the SiO_2 carriers may act as heterogeneous Fenton catalyst when in fluidized state [30-33].

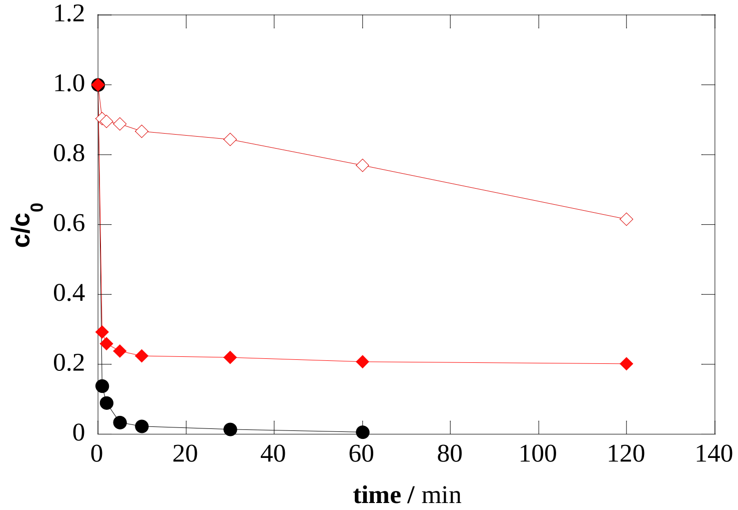


Figure 2- Evolution profile of (●) imidacloprid, (◆) Fenton's catalyst (Fe^{2+}), and total iron in solution (◇) during the treatment of 0.4 mM imidacloprid solutions at pH 3.0 by fluidized-bed Fenton process using SiO_2 carriers, 0.8 mM Fe^{2+} and 15.5 mM H_2O_2. Dashed line distinguishes between first and second kinetic stages.

3.2. Influence of propylene glycol content in the water matrix

Propylene glycol (PG) is a common inert excipient of commercial IMI insecticides. This performs to be both the carrier and the anti-freeze agent in the commercial insecticide. In waters containing IMI, PG is quantified in similar or even superior concentrations due to PG presence as additive in commercial IMI products. Therefore, FBF process must be studied in the presence of PG to evaluate possible deleterious effects on process performance.

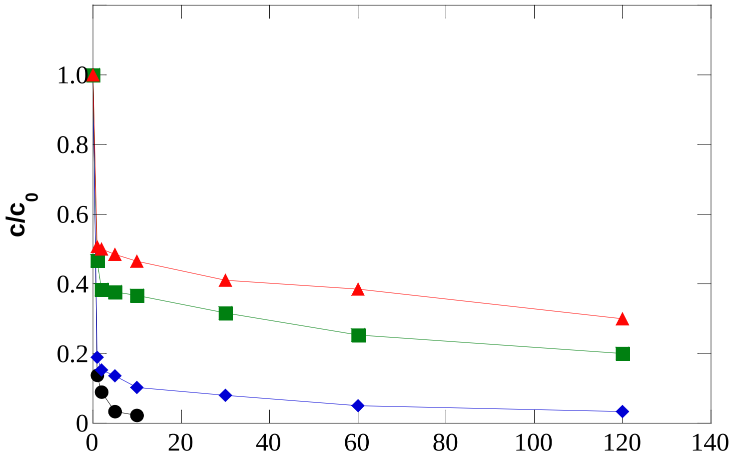


Figure 3- Effect of propylene glycol concentration on fluidized-bed Fenton degradation of imidacloprid using SiO_2 carriers at pH 3.0, 0.8 mM Fe^{2+} and 15.5 mM H_2O_2. Propylene glycol concentration: (●) 0.0 mM, (◆) 0.4 mM, (■) 0.8 mM, (▲) 1.2 mM.

The negative contribution of PG is observed in Fig. 3 where experimental trends suggest that greater times of treatments of IMI are required when PG concentration increases. This trend can be described by the competitive consumption of generated $^{\bullet}OH$ from the Fenton reaction (1) by another target organic in solution. Similar reductions on the degradation kinetics of organics have been observed when natural organic matter or other organic pollutants are in solution [37,38]. Therefore, for increasing concentrations of PG lower mineralization events of IMI should be expected. This results in a considerable decrease on the degradation kinetic absolute rate constant of IMI when $^{\bullet}OH$ is competitively consumed by PG in solution. This trend is also reflected on the percentage of IMI removal under identical experimental conditions. In this frame, AOPs treatment optimization must be conducted in presence of usual concentrations of PG found in commercial products.

3.3. Influence of operational parameters on IMI degradation

The influence of Fe^{2+} initial concentration described by Fig. 4 indicates a dual character where small catalytic concentrations enhance the degradation performance, whereas higher concentrations may result detrimental.

The addition of Fe^{2+} is indispensable to promote the H_2O_2 decomposition yielding $^{\bullet}OH$ according to rection (1), although this beneficial effect occurs at catalytic concentrations of Fe^{2+}. An excess of Fe^{2+} scavenges the $^{\bullet}OH$ according to reaction (4) reducing the FBF overall efficiency [39,40].

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-} \qquad (4)$$

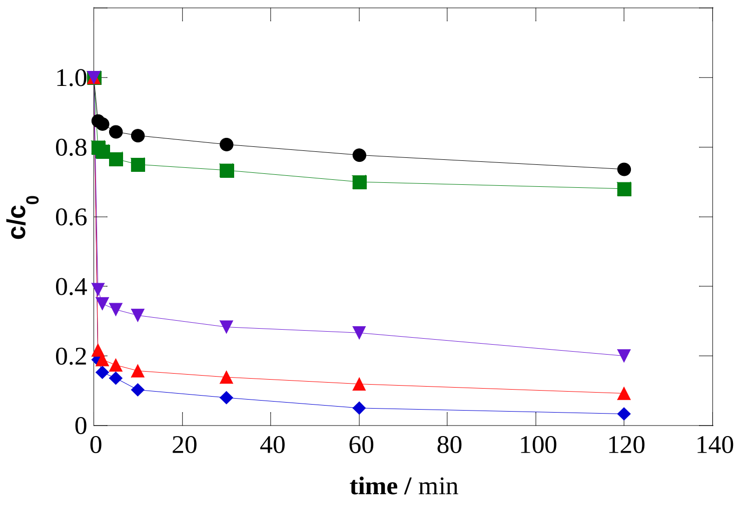


Figure 4- Initial concentration of Fe^{2+} impact on fluidized-bed Fenton process performance using SiO_2 carriers at pH 3.0, 15.5 mM H_2O_2 and 0.4 mM PG. Initial Fe^{2+} concentration: (●) 0.1 mM, (■) 0.2 mM, (◆) 0.8 mM, (▲) 1.4 mM, (▼) 2.0 mM.

Similarly, H_2O_2 concentration is paramount to define optimum conditions of IMI treatment as observed in Fig. 5. The negative effect of an excessive amount of H_2O_2 is associated to parasitic reaction (5) that consumes $^{\bullet}OH$ radical and H_2O_2 yielding the lower oxidant species $HO_2^{\bullet}$ [41,42].

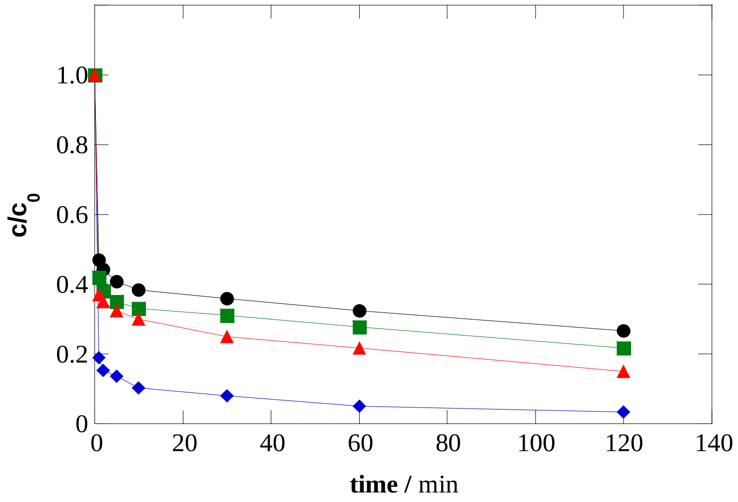


Figure 5- Influence of initial concentration of H_2O_2 on fluidized-bed Fenton process performance using SiO_2 carriers at pH 3.0, 0.8 mM Fe^{2+} and 0.4 mM PG. Initial H_2O_2 concentration: (●) 1.6 mM, (■) 2.0 mM, (▲) 5.0 mM, (◆) 15.5 mM.

Note that the consumption of H_2O_2 not only affects detrimentally the generation of $^{\bullet}OH$ by Fenton's reaction (1), but also reduces the extent of Fe^{2+} regeneration by Fenton-like process (2) [43].

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad (5)$$

The relative concentration of Fe^{2+} and H_2O_2 is one of the most relevant effects on the definition of the optimum treatment conditions. Degradation of IMI attainable by FBF is considerably lower in presence of small concentrations of catalyst Fe^{2+} under high concentrations of H_2O_2 because of the detrimental reaction (5) on the degradation kinetics of IMI and the FBF process performance. Meanwhile, when increasing the Fe^{2+} concentration at a defined H_2O_2 concentration is easily observable an increase on the percentage of IMI attaining a maximum at the optimum Fe^{2+}:H_2O_2 ratio, followed by a decrease caused by the effects of parasitic reaction (4). From Figs. 4 and 5 can be deduced the optimum operational conditions for the FBF treatment of 0.4 mM IMI solutions with 0.4 mM PG defined by the interaction of both variables as 0.8 mM Fe^{2+} and 15.5 mM H_2O_2 concentration during FBF treatment conducted at pH 3.0.

As observed in Fig. 6, complete IMI abatement is attained in 120 min of FBF treatment. The COD quickly decreases an 80 % during the first 15 min of treatment, remaining practically constant afterwards. It can be observed that the FBF treatment is capable to mineralize ~ 40 % of the initial DOC after 120 min of treatment. It is remarkable that conversely to COD, DOC is continuously reduced during the treatment. This trend highlights that the initial attacks of hydroxyl radical yield highly recalcitrant by-products that are not oxidized by dichromate but completely incinerated at the TOC-analyzer furnace.

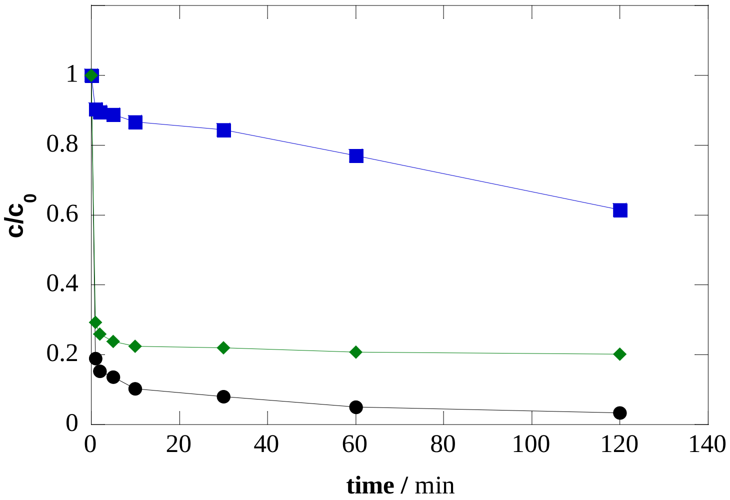
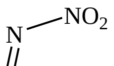


Figure 6- Fluidized-bed Fenton oxidation of 0.4 mM IMI solutions at pH 3.0 under optimum conditions of 0.8 mM Fe^{2+} and 15.5 mM H_2O_2 in presence of 0.4 mM PG. Normalized concentration of: (■) dOC, (◆) COD, and (●) IMI.

3.4. Identification of aromatic intermediates and proposed reaction sequence

Treated solutions under optimized FBF conditions were analyzed by GC-MS and exhibited characteristic peaks related to three different aromatic by-products identified: N-{1-[(6-chloro-3-pyridinyl)methyl]-2-imidazolidinone (t_r= 13.17 min, m/z= 211) , 6-chloronicotinic acid (t_r= 5.94 min, m/z= 156), and 6-chloronicotinaldehyde (t_r= 4.80 min, m/z= 140). Similar by-products have been reported during IMI degradation by means of other AOPs such as photocatalysis [44,45] and electrochemical treatments [46]. A plausible reaction sequence for IMI degradation by the FBF process is proposed in Fig. 7 by considering the oxidation products identified. The degradation pathway described assumes that aromatics are mainly oxidized by $^{\bullet}$OH formed in the bulk according to the Fenton reaction (1), although IMI and by-products slower oxidation with weaker oxidants such $HO_2^{\bullet}$ and H_2O_2 may also take place during FBF treatment.



(A)

(B)

(C) (D) (E)

Figure 7. Reaction sequence proposed for imidacloprid oxidation by fluidized-bed Fenton

The initial $^{\bullet}OH$ attack can results in the breakage of the N-N bond of the nitramino ($RNNO_2$) functional group of IMI (**A**) and dehydrogenation of the imidazole ring to yield N-{1-[(6-chloro-3-pyridinyl)methyl]-2-imidazolidinone (**B**) and nitrate. Consecutive hydroxylation of (**B**) yields 6-chloronicotinic acid (**C**) and/or 6-chloronicotinaldehyde (**D**) from the preferential attack on the methyl carbon of the N-substituent group. Therefore, the additional release of the heterocyclic compound 2-aminoimidazole (**E**) is suggested. The cleavage of the aromatic rings leads to the formation of short-linear carboxylic acids such oxalic and oxamic acid as previous step to complete mineralization to CO_2 [43]. Note that the heterogeneous atoms (N and Cl) may result in the yield of inorganic ionic species such as NO_3^- , NH_4^+, N-volatile species, Cl^- and/or Cl-volatile species [47,48].

4. Conclusions

The FBF process is efficient to treat IMI even in the competing presence of PG, its common excipient. Tests were carried out with a 1.6 L fluidized-bed reactor using SiO_2 as carriers for the crystallization of iron hydroxides/oxides to reduce sludge formation after Fenton reaction. The optimum variables to treat IMI solutions containing 0.4 mM PG were identified as 0.8 mM Fe^{2+} and 15.5 mM H_2O_2, allowing to attain complete IMI removals and considerable COD reductions after 2 h treatment. Increasing concentrations of PG in pesticides formulations, reduces the rate of IMI degradation due to the competitive reaction with the non-selective $^{\bullet}$OH radical and PG. The degradation by-products of IMI were detected by GC-MS analysis and comprehensive oxidation pathway was proposed. Fouling/clogging of the fluidized bed reactor due to iron oxides and hydroxides crystallization onto the SiO_2 fluidized particles was not observed. Fouling may became an issue when considering long time operation under continuous flow, hence it must be evaluated in future experiments.

References

[1] Jeschke P, Nauen R, Schindler M, Elbert A. Overview of the status and global strategy for Neonicotinoids. J Agric Food Chem 2010; 59:2897–2908. http://dx.doi.org/10.1021/jf101303q

[2] Dryden MW, Perez HR, Ulitchny D. Control of fleas on pets and in homes by use of imidacloprid or lufenuron and a pyrethrin spray. J Am Vet Med Assoc 1999; 215:36–39.

[3] Riaz MA, Chandor-Proust A, Dauphin-Villemant C, Poupardin R, Jones CM, Strode C, Régent-Kloeckner M, David JP, Reynaud S. Molecular mechanisms associated with increased tolerance to the neonicotinoid insecticide imidacloprid in the dengue vector Aedes aegypti. Aquat Toxicol 2013; 126:326–337. http://dx.doi.org/10.1016/j.aquatox.2012.09.010

[4] Diaz JMC, Martin-Laurent F, Beguet J, Nogales R, Romero E. Fate and effect of imidacloprid on vermicompost-amended soils under dissimilar conditions: Risk for soil functions, structure, and bacterial abundance. Sci Total Environ 2017; 579:1111–1119. https://doi.org/10.1016/j.scitotenv.2016.11.082

[5] Cycoń M, Markowicz A, Borymski S, Wójcik M, Piotrowska-Seget Z. Imidacloprid induces changes in the structure, genetic diversity and catabolic activity of soil microbial communities. J Environ Manage 2013; 131: 55–65. https://doi.org/10.1016/j.jenvman.2013.09.041

[6] Pérez-Iglesias JM, Arcaute CR, Nikoloff N, Dury L, Soloneski S, Natale GS, Larramendy ML. The genotoxic effects of the imidacloprid-based insecticide formulation Glacoxan Imida on Montevideo tree frog Hypsiboas pulchellus tadpoles (Anura, Hylidae). Ecotoxicol Environ Saf 2014; 104:120–126. http://dx.doi.org/10.1016/j.ecoenv.2014.03.002

[7] Duzguner V, Erdogan S. Chronic exposure to imidacloprid induces inflammation and oxidative stress in the liver & central nervous system of rats. Pestic Biochem Physiol 2012; 104:58–64. https://doi.org/10.1016/j.pestbp.2012.06.011

[8] Kapoor U, Srivastava MK, Trivedi P, Garg V, Srivastava LP. Disposition and acute toxicity of imidacloprid in female rats after single exposure. Food Chem Toxicol 2014; 68:190–195. http://dx.doi.org/10.1016/j.fct.2014.03.019

[9] Sadaria AM, Sutton R, Moran K, Teerlink J, Brown JV, Halden RU. Passage of Fiproles and Imidacloprid from urban pest control uses through wastewater treatment plants in Northern California. Environ Toxicol Chem 2017; 36:1473-1482. . http://dx.doi.org/10.1002/etc.3673

[10] Sadaria AM, Supowit SD, Halden RU. Mass balance assessment for six Neonicotinoid Insecticides during conventional wastewater and wetland treatment: Nationwide reconnaissance in United States wastewater. Environ Sci Technol 2016, 50:6199–6206. http://dx.doi.org/10.1021/a6b01032

[11] Garcia-Segura S, Ocon JD, Chong MN. Electrochemical oxidation remediation of realwastewater effluents — A review. Process Safe Environ 2018; 113:48-67. http://dx.doi.org/10.1016/j.psep.2017.09.014

[12] Nidheesh PV, Gandhimathi R, Ramesh ST. Degradation of dyes from aqueous solution by Fenton processes: a review. Environ Sci Pollut Res 2013; 20:2099-2132. https://doi.org/10.1007/s11356-012-1385-z

[13] Laiju AR, Sivasankar T, Nidheesh PV. Iron-loaded mangosteen as a heterogeneous Fenton catalyst for the treatment of landfill leachate. Environ Sci Pollut Res 2014; 21:10900-10907. https://doi.org/10.1007/s11356-014-2883-y

[14] de Luna MDG, Lin JC-T, Gotostos, MJN, Lu M-C. Photocatalytic oxidation of acetaminophen using carbon self-doped titanium dioxide. Sust Environ Res 2016; 26:161-167. http://dx.doi.org/10.1016/j.serj.2016.02.001.

[15] Laciste MT, de Luna MDG, Tolosa NC, Lu M-C, 2017. Degradation of gaseous formaldehyde via visible light photocatalysis using multi-element doped titania nanoparticles. Chemosphere 2017; 182: 174-182. http://dx.doi.org/10.1016/j.chemosphere.2017.05.022

[16] Knopp G, Prasse C, Ternes TA., Cornel P. Elimination of micropollutants and transformation products from a wastewater treatment plant effluent through pilot scale ozonation followed by various activated carbon and biological filters. Water Res 2016; 100:580-592. http://dx.doi.org/10.1016/j.watres.2016.04.069

[17] Mattei C, Wortham H, Quivet E. Heterogeneous atmospheric degradation of pesticides by ozone: Influence of relative humidity and particle type. Sci Total Environ 2018; 625:1544-1553. http://dx.doi.org/10.1016/j.scitotenv.2018.01.049

[18] Dosta S, Robotti M, Garcia-Segura S, Brillas E, Cano IG, Guilemany JM. Influence of atmospheric plasma spraying on the solar photoelectro-catalytic properties of TiO_2 coatings. Appl Catal B: Environ 2016; 189:151-159. https://doi.org/10.1016/j.apcatb.2016.02.048

[19] Garcia-Segura S, Tugaoen HO, Hristovski K, Westerhoff P. Photon flux influence on photoelectrochemical water treatment. Electrochem Commun 2018; 87:63-65.

[20] Nidheesh PV, Gandhimathi R. Trends in electro-Fenton process for water and wastewater treatment: An overview. Desalination 2012; 299:1-132. https://doi.org/10.1016/j.desal.2012.05.011

[21] Pérez T, Garcia-Segura S, El-Ghenymy A, Nava JL, Brillas E. Solar photoelectro-Fenton degradation of the antibiotic metronidazole using a flow plant with a Pt/air-diffusion cell and a CPC photoreactor. Electrochim Acta 2015; 165:173-181. http://dx.doi.org/10.1016/j.electacta.2015.02.243

[22] Rubí-Juárez H, Cotillas S, Sáez C, Cañizares P, Barrera-Díaz C, Rodrigo MA. Removal of herbicide glyphosate by conductive-diamond electrochemical oxidation. Appl Catal B: Environ 2016; 188:305-312. http://dx.doi.org/10.1016/j.apcatb.2016.02.006

[23] Prousek J, Palacková E, Marková L. Fenton and Fenton-like AOPs for wastewater treatment: From laboratory to plant scale application. Sep Sci Technol 2017; 42:1505-1520. https://doi.org/10.1080/01496390701290151

[24] Nidheesh PV, Rajan R. Removal of rhodamine B from a water medium using hydroxyl and sulphate radicals generated by iron loaded activated carbon. RSC Adv 2016; 6:5330-5340. https://doi.org/10.1039/C5RA19987E

[25] Silva TFCV, Fonseca A, Saraiva I, Boaventura RAR, Vilar VJP. Scale-up and cost analysis of a photo-Fenton system for sanitary landfill leachate treatment. Chem Eng J 2016; 283: 76-88. https://doi.org/10.1016/j.cej.2015.07.063

[26] Nidheesh PV. Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: a review. RSC Adv 2015; 5:40552-40577. https://doi.org/10.1039/C5RA02023A

[27] Garcia-Segura S., Brillas E. Applied photoelectrocatalysis on the degradation of organicpollutants in wastewaters. J Photoch Photobio C: Photochem Rev 2017; 31:1-35. https://doi.org/10.1016/j.jphotochemrev.2017.01.005

[28] Babuponnusami A, Muthukumar K. A review on Fenton and improvements to the Fenton process for wastewater treatment. J Environ Chem Eng 2014; 2: 557-572. https://doi.org/10.1016/j.jece.2013.10.011

[29] Boonrattanakij N, Lu M-C, Anotai J. Iron crystallization in a fluidized-bed Fenton process. Water Res 2011; 45:3255-3262. http://dx.doi.org/10.1016/j.watres.2011.03.045

[30] Garcia-Segura S, Bellotindos LM, Huang Y-H, Brillas E, Lu M-C. Fluidized-bed Fenton process as alternative wastewater treatment technology – A review. J Taiwan Inst Chem Eng 2016; 67:211-225. https://doi.org/10.1016/j.jtice.2016.07.021

[31] Xavier S, Gandhimathi R, Nidheesh PV, Ramesh ST. Comparison of homogeneous and heterogeneous Fenton processes for the removal of reactive dye Magenta MB from aqueous solution. Deaslin Water Treat 2015; 53:109-118. https://doi.org/10.1080/19443994.2013.844083

[32] Matira EM, Chen T-C, Lu M-C, Dalida MLP. Degradation of dimethyl sulfoxide through fluidized-bed Fenton process. J Hazard Mater 2015; 300:218-226. http://dx.doi.org/10.1016/j.jhazmat.2015.06.069

[33] Tisa F, Raman AAA, Daud WMAW. Applicability of fluidized bed reactor in recalcitrant compound degradation through advanced oxidation processes: A review. J Environ Manage 2014; 146:260-275. https://doi.org/10.1016/j.jenvman.2014.07.032

[34] APHA. Standard methods for the Examination of Water and Wastewater . 21st ed. Washington DC, United States: American Public Health Association

[35] Boonrattanakij N, Sakul W, Garcia-Segura S, Lu M-C. Implementation of fluidized-bed Fenton as pre-treatment to reduce chemical oxygen demand of wastewater from screw manufacture: Influence of reagents feeding mode. Sep Purif Technol 2017; 202:275-280. https://doi.org/10.1016/j.seppur.2018.03.075

[36] Wang N, Zheng T, Zhang G, Wang P. A review on Fenton-like processes for organic wastewater treatment. J Environ Chem Eng 2016; 4:762–787. https://doi.org/10.1016/j.jece.2015.12.016

[37] Wang F, Wu Y, Gao Y, Li H, Chen Z. Effect of humic acid. Oxalate and phosphate on Fenton-like oxidation of microcystin-LR by nanoscale zero-valent iron. Sep Purif Technol 2016; 170:337-343. https://doi.org/10.1016/j.seppur.2016.06.046

[38] Wilde ML, Schneider M, Kümmerer K. Fenton process on single and mixture components of phenothiazine pharmaceuticals: Assessment of intermediaries, fate, and preliminary ecotoxicity. Sci Total Environ 2017; 583:36-52. https://doi.org/10.1016/j.scitotenv.2016.12.184

[39] Foteinis S, Monteagudo JM, Durán A, Chatzisymeon E. Environmental sustainability of the solar photo-Fenton process for wastewater treatment and pharmaceuticals mineralization at semi-industrial scale. Sci Total Environ 2018; 612: 605-612. https://doi.org/10.1016/j.scitotenv.2017.08.277

[40] Garcia-Segura S, Salazar R, Brillas E. Mineralization of phthalic acid by solar photoelectro-Fenton with a stirred boron-doped diamond/air-diffusion tank reactor: Influence of Fe^{3+} and Cu^{2+} catalysts and identification of oxidation products. Electrochim Acta 2013; 113:609-619. https://doi.org/10.1016/j.electacta.2013.09.097

[41] Papoutsakis S, Pulgarin C, Oller I, Sánchez-Moreno R, Malato S. Enhancement of the Fenton and photo-Fenton processes by components found in wastewater from the industrial processing of natural products: The possibilities of cork boiling wastewater reuse. Chem Eng J 2016; 304:890-896. https://doi.org/10.1016/j.cej.2016.07.021

[42] Anotai J, Tanvanit P, Garcia-Segura S, Lu M.-C. Electro-assisted Fenton treatment of ammunition wastewater containing nitramine explosives. Process Saf Environ 2017; 109:429-436. https://doi.org/10.1016/j.psep.2017.04.018

[43] Garcia-Segura S, Brillas E, Cornejo-Ponce L, Salazar, R. Effect of the Fe^{3+}/Cu^{2+} ratio on the removal of the recalcitrant. Solar Energy 2016; 124:242–253. http://dx.doi.org/10.1016/j.solener.2015.11.033

[44] Agüera A, Almansa E, Malato S, Maldonado MI, Fernández-Alba AR. Evaluation of photocatalytic degradation of imidacloprid in industrial water by GC-MS and LC-MS. Analusis 1998; 26:245–250. https://doi.org/10.1051/analusis:1998168

[45] Kitsiou V, Filippidis N, Mantzavinos D, Poulios I. Heterogeneous and homogeneous photocatalytic degradation of the insecticide imidacloprid in aqueous solutions. Appl Catal B : Environ 2009; 86:27–35. https://doi.org/10.1016/j.apcatb.2008.07.018

[46] Iglesias O, Gómez J, Pazos M, Sanromán MA. Electro-Fenton oxidation of imidacloprid by Fe alginate gel beads. Appl Catal B: Environ 2014; 144, 416–424. https://doi.org/10.1016/j.apcatb.2013.07.046

[47] Garcia-Segura S, Mostafa E, Baltruschat H. Could NOx be released during mineralization of pollutants containing nitrogen by hydroxyl radical? Ascertaining the release of N-volatile species. Appl Catal B: Environ 2017; 207: 376-384. http://dx.doi.org/10.1016/j.apcatb.2017.02.046

[48] Mostafa E, Reinsberg P, Garcia-Segura S, Baltruschat H. Chlorine species evolution during electrochlorination on boron-doped diamond anodes: *In-situ* electrogeneration of Cl_2, Cl_2O

and ClO_2. Electrochim Acta 2018, 281:831-840. https://doi.org/10.1016/j.electacta.2018.05.099

MOST MECO-TECO Sandwich Scholarship Program Internship Report

1. Basic Information

Name of Student	Reyson M. Feliciano
Internship Duration	From 2017/08/01 to 2018/01/28
Name of Taiwan Supervisor	Dr. Ming-Chun Lu
Name of Taiwan Supervisor's Institution	Chia Nan University of Pharmacy and Science

2. Internship Report **(this part is to be completed by student)**

(a) Briefly outline the research/activities conducted in Taiwan institution

The following are the major research/activities conducted in Taiwan:

- (i) Conduct experimental runs for the investigation of the operating parameters that affect desorption of Dibenzothiophene Sulfone (DBTO) adsorbed in the surface of Neutral Activated Alumina (NAA) namely eluent dosage, eluent type, solvent ratio, adsorbate amount, agitation, temperature, and contact time. On the other hand, both Acidic Activated Alumina (AAA) and Basic Activated Alumina (BAA) are also investigated for comparative study with operating parameters agitation, temperature, adsorbate amount, and eluent type.
- (ii) Optimized and modeled the experimental data for the desorption investigation on NAA, AAA, and BAA.
- (iii) Conduct experimental runs for kinetic study of all adsorbents.
- (iv) Analyzed all the samples for total Sulfur analysis using X-ray Fluorescence Sulfur in oil Analyzer; and for adsorbent characterization during after each process i.e adsorption, desorption, and regeneration, using FTIR, BET, XRD, SEM, and EDS for a deep understanding of the experimental results.
- (v) Utilized the experimental data for the determination of Isothermal model and Thermodynamics on the study.

(b) Describe the achievement/findings from this research

- (i) The operating parameters have significant effect to the desorption of DBTO from all adsorbents with the following trend from highest effect to lowest:
  - a. For NAA: time>solvent type>agitation>adsorbate amount>eluent dosage>temperature>eluent ratio
  - b. For AAA and BAA: solvent type>agitation>adsorbate amount>temperature
- (ii) The highest percent DBTO desorption in every adsorbent follows the following trend: NAA>AAA>BAA

- (iii) The highest regeneration efficiency on each adsorbent at 2nd cycle follows the trend: NAA>AAA>BAA
- (iv) For kinetic study, the DBTO desorption of NAA fits most in the 2nd order kinetic model in all parameters which suggests that chemisorption is the rate limiting step in the process.
- (v) For the optimization on the desorption study, the following parametric values are best conditions for the optimal desorption of DBTO from each adsorbent:
  - a. For NAA: 120 rpm, 25 ˚C, 25 mL Acetone only, and 1 hr desorption time in a highest adsorbate amount.
  - b. For BAA and AAA: 120 rpm, 45 ˚C, 25 mL Acetone only and 1 hr desorption time in a highest adsorbate amount.
- (vi) For desorption isotherm study, all adsorbent types follow Langmuir isotherm which implies formation of monolayer coverage of adsorbate on the surface of the adsorbents. The result is also consistent to the

adsorption isotherm of Activated Alumina in the previous study.

(vii) An increased temperature increases the percent DBTO desorption in all adsorbent types which implies that the DBTO desorption of Activated Alumina proceeds endothermic process.

(viii) The FTIR results shown activity of the functional groups present in the Activated Alumina after adsorption compared to fresh and desorbed Activated Alumina.

(ix) Other adsorbent characterization tests are ongoing.

(c) Comment on the assistance/supervision/research infrastructure/facility offered by your Taiwan supervisor and comment whether the internship is beneficial to your personal and professional career developments.

My host Professor conducts weekly group meetings for the reporting of his students' progress both in manuscript and experiment status. During the meetings, he even cultivates communication, critical and analytical thinking skills in us making us prepared and well-developed for outside future work or for a higher academic study. The infrastructure and facility are very satisfactory that it typically suits for my research work needs. Though other test equipment is not available in the host institution, my host Professor finds alternatives and connects to other institutions to provide test analysis for my research study needs.

(d) Provide any suggestions/comments to improve the Sandwich Scholarship Program

In my case, the host institution does not provide all test analysis for my research study. In compensation or assistance to obtain other test analysis, with due respect, may the commendable Sandwhich Scholarship Program also provide conditional financial budget for test analysis of samples of which the host institution/department have not acquired test equipment for such analysis.

3. Remarks by the Supervisor (**this part is to be written by Taiwan Supervisor**)

Please provide overall comments on the student's performance/achievement during the internship period, and advise if you would accept more Philippines students under the Sandwich Scholarship Program.

Reyson worked very well during his staying in my laboratory. Every week he submitted his working results and discussed with me at the weekly meeting. Afterwards, he revised his experimental conditions if necessary and completed all the expected works in the next week before the next weekly meeting.

Reyson's research topic is how to regenerate the adsorbent for the recovery of transportation fuels desulfurization sorbents. Firstly, he started to review the recent researches on different regeneration methods in recovery of spent adsorbents used in desulfurization of transportation fuel. He also discussed about the affectivity and efficiency of the adsorbent regeneration methods, its corresponding parameters, the underlying desorption mechanism, and its different advantages and disadvantages in application, in a comparative frame. Secondly, he will discuss all the data to reach the objectives. Finally, an optimum operation condition and desorption model will be proposed.

Due to the Sandwich Scholarship Program, Reyson has the opportunity to complete his experimental work for his master thesis in Taiwan. He also got a lot of friends in Taiwan, especially students in my school. They can learn each other and improve mutual understanding; this is an invaluable achievement of this program. Therefore, I hope I can continuously accept more Philippines students under the Sandwich Scholarship Program.

科技部補助專題研究計畫出席國際學術會議心得報告

日期： 107 年 8 月 30 日

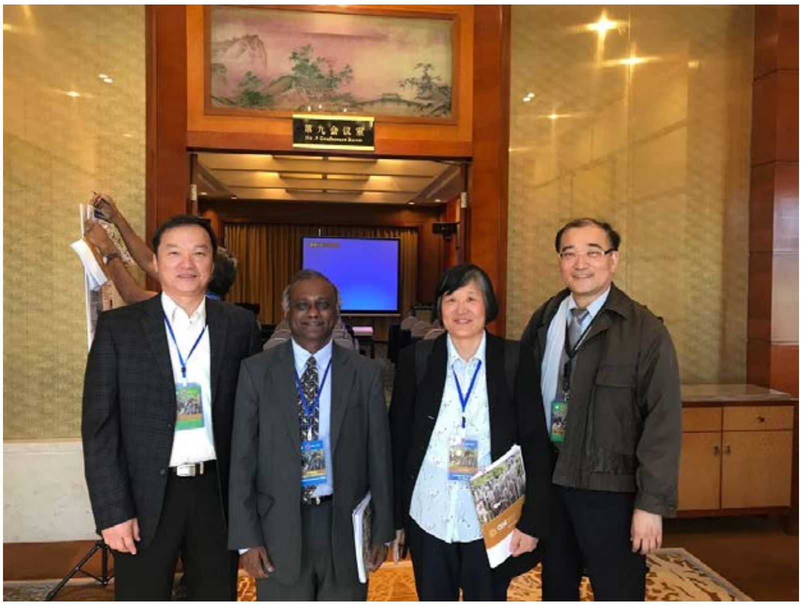
計畫編號	MOST 106-2221-E-041-001		
計畫名稱	流體化床芬頓程序處理新菸鹼類農藥廢水之反應動力與機制		
出國人員姓名	盧明俊	服務機構及職稱	嘉南藥理大學環境資源管理系
會議時間	106年11月11日至106年11月15日	會議地點	中國 昆明
會議名稱	(中文)第10屆挑戰環境科學與工程國際研討會 (英文) The 10th International Conference on Challenges in Environmental Science & Engineering		
發表題目	(中文)以流體化床芬頓技術分解益達胺 (英文) Degradation of imidacloprid by fluidized-bed Fenton process		

一、 參加會議經過

本次大會是在中國昆明舉行，大會前一天(11/10)即抵達昆明，隔天早上前往會場-20世紀金源大飯店會議廳報到，參與會議開幕，此次是第10屆，如同大會主題所有研究都是著眼於各種環境科學與工程之研究，本會共有來自全球16個國家之學者專家參與發表口頭論文與張貼海報，本會所有與會者，依大會所規劃的議題，安排在不同會場發表，休息期間則是參觀所張貼出來海報與作者討論，會議共進行三天。

本人論文題目為「以流體化床芬頓技術分解益達胺」。探討含新菸鹼類農藥-益達胺之廢水處理。本論文以流體化床芬頓技術各種操作參數，研究含益達胺廢水之處理效率、氧化產物、氧化路徑、礦化率及添加劑之效應及益達胺分解途徑。會議期間與來自各國的學者交流，討論環境科技之發展與趨勢，在此期間也與台灣與會的學者專家共同分享研究心得。會議共舉辦三天圓滿結束。除學術經驗分享外，也與主辦單位交流舉辦國際研討會之經驗，照片一即為與大會主辦人合照，照片二為口頭論文發表

現場，照片三為海報論文發表現場。



照片一、與大會主辦人合照

照片二、口頭論文發表現場

照片三、海報論文發表現場

二、與會心得

這次出國參加的會議是 CESE 2017，發表「以流體化床芬頓技術分解益達胺」。在會議的過程中不只聽到了一些與自己研究有相關的演講外，還可以接收其它相關的研究，以增加自己的知識。藉由參加這次研討會，不但增加了許多新知也得到許多的資訊，而這些資訊讓我可以了解各國實驗室的研究實力，可以藉此調整自己研究方向。

會議中大家所討論的是，目前的各種有關新菸鹼類農藥廢水處理氧化處理研究，主要是光觸媒、芬頓法、電化學氧化及臭氧等技術。光觸媒技術雖然已發展多年，但還是因為光源及催化劑表面毒化現象，還是難以應用至廢水處理。電化學直接氧化程序因為電極價格問題，而且處理能量有限之缺點，所以仍然處於研究階段，難以放大到實廠應用。而臭氧程序因臭氧溶解度的問題，在淨水方面比較能夠發揮其特性，對於高濃度之工業水處理仍有困難。至於結合各種程序之處理效率可以滿意，但是程序複雜，而且加入超過理論值 100 倍的氧化劑量，操作成本過高。因此，新菸鹼類農藥廢水處理仍有相當大之研究空間。而本研究之成果，可提供新菸鹼類農藥廢水處理另一種新選擇。

最後要感謝科技部補助出國的經費，本次出席該會議與大會其他與會人員交換意見，獲益良多。

三、發表論文摘要

Theme Number: I Sub-topic: Advances in Water and Wastewater Treatment

Degradation of imidacloprid by fluidized-bed Fenton process

Elaine Joy T. Battung a, Mark Daniel G. De Luna b, Ming-Chun Lu c*

a Environmental Engineering Program, National Graduate School of Engineering, University of the Philippines, 1101 Diliman, Quezon City, Philippines (E-mail: etbattung@up.edu.ph)
b Department of Chemical Engineering, University of the Philippines, 1101 Diliman, Quezon City, Philippines (E-mail:mgdeluna@gmail.com)
c Department of Environmental Resources and Management, Chia Nan University of Pharmacy and Science, Tainan, Taiwan (E-mail:mmclu@mail.cnu.edu.tw)

Corresponding author
Ming-Chun Lu, Department of Environmental Resources and Management, Chia Nan University of Pharmacy and Science, Tainan, Taiwan (E-mail:mmclu@mail.cnu.edu.tw)

Abstract

Imidacloprid ($C_9H_{10}ClN_5O_2$) (IMD), one of the most widely-used neonicotinoid pesticides, has been proven resistant to conventional treatment processes. The increase in its usage has led to a rise in its detection in surface waters, and along therewith is its adverse effects on non-target organisms. This research focuses on the use of Fenton's reagent in a fluidized bed reactor in degrading IMD. The effects of pH and Fenton’s reagent concentration on the extent and kinetics of IMD degradation were determined. These parameters were optimized using response surface methodology (RSM). It was observed that increasing the H2O2 and Fe2+ concentrations up to certain values improved the removal efficiency of the system. The optimum pH was established to be around 2.8 to 3.0. The model equation for the extent of removal derived from RSM accurately predicted both the IMD removal and iron removal at the optimized conditions (H2O2: IMD = 5.2:1; H2O2: Fe = 3.3:1). 98.8 % IMD removal was achieved after two hours. It was also found that IMD degradation followed first-order kinetics with respect to initial pollutant concentration. Furthermore, the removal efficiencies of the fluidized-bed Fenton system and conventional Fenton system were compared. Without the carriers, a decrease in the rate of reaction in the Fe3+/H2O2 stage was observed, which led to lower removal efficiency. This study shows that fluidized-bed Fenton process could be used to effectively treat IMD-contaminated waters.

Keywords: Fluidized bed reactor, Advanced Oxidation Processes, Neonicotinoid, Imidacloprid

List of Figures

List of Tables

四、建議

五、攜回資料名稱及內容

研討會程序手冊及論文集電子檔

六、其他

106年度專題研究計畫成果彙整表

計畫主持人：盧明俊　**計畫編號：**106-2221-E-041-001-

計畫名稱：流體化床芬頓程序處理新菸鹼類農藥廢水之反應動力與機制

成果項目					量化	單位	質化 （說明：各成果項目請附佐證資料或細項說明，如期刊名稱、年份、卷期、起訖頁數、證號...等）
國內	學術性論文	期刊論文			1	篇	投稿於Sustainable Environmental Research ，已接受發表，預計２０１９年刊出
		研討會論文			0		
		專書			0	本	
		專書論文			0	章	
		技術報告			0	篇	
		其他			0	篇	
	智慧財產權及成果	專利權	發明專利	申請中	0	件	
				已獲得	0		
			新型/設計專利		0		
		商標權			0		
		營業秘密			0		
		積體電路電路布局權			0		
		著作權			0		
		品種權			0		
		其他			0		
	技術移轉	件數			0	件	
		收入			0	千元	
國外	學術性論文	期刊論文			0	篇	
		研討會論文			0		
		專書			0	本	
		專書論文			0	章	
		技術報告			0	篇	
		其他			0	篇	
	智慧財產權及成果	專利權	發明專利	申請中	0	件	
				已獲得	0		
			新型/設計專利		0		
		商標權			0		
		營業秘密			0		
		積體電路電路布局權			0		
		著作權			0		

		品種權	0		
		其他	0		
	技術移轉	件數	0	件	
		收入	0	千元	
參與計畫人力	本國籍	大專生	0	人次	
		碩士生	0		
		博士生	0		
		博士後研究員	0		
		專任助理	0		
	非本國籍	大專生	0		
		碩士生	2		本研究共有兩位菲律賓籍之訪問學生參與研究
		博士生	0		
		博士後研究員	0		
		專任助理	0		
其他成果 （無法以量化表達之成果如辦理學術活動、獲得獎項、重要國際合作、研究成果國際影響力及其他協助產業技術發展之具體效益事項等，請以文字敘述填列。）					

科技部補助專題研究計畫成果自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現（簡要敘述成果是否具有政策應用參考價值及具影響公共利益之重大發現）或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估
■達成目標
□未達成目標（請說明，以100字為限）
　　□實驗失敗
　　□因故實驗中斷
　　□其他原因
說明：

2. 研究成果在學術期刊發表或申請專利等情形（請於其他欄註明專利及技轉之證號、合約、申請及洽談等詳細資訊）
論文：□已發表　■未發表之文稿　□撰寫中　□無
專利：□已獲得　□申請中　■無
技轉：□已技轉　□洽談中　■無
其他：（以200字為限）

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性，以500字為限）
由於新菸鹼類農藥對環境造成之衝擊。蜜蜂族群崩潰症開始蔓延，這種效應會造成全球糧食減產三分之一以上，人類要面臨的糧食危機即將到來，所以本研究之結果可以做為政府制訂政策減緩農藥對環境衝擊時之參考。另外，由目前的國內外研究顯示，新菸鹼類農藥廢水的處理技術尚未成熟，本案之進行，可以為此等農藥之去除提供另一個選擇，尤其在國際學術上，除了對生態衝擊研究上，也能夠在新菸鹼類農藥處理領域中占有重要貢獻。

4. 主要發現
本研究具有政策應用參考價值：□否　■是，建議提供機關行政院環境保護署，
（勾選「是」者，請列舉建議可提供施政參考之業務主管機關）
本研究具影響公共利益之重大發現：■否　□是
說明：（以150字為限）