Competitive Degradation of Imidacloprid in the Presence of Humic Acids by Fenton Process at Neutral Environment

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Abstract. This study aimed to investigate the imidacloprid degradation in the presence of humic acid by Fenton process. The Fenton degradation experiments were conducted at various H$_2$O$_2$ and Fe$^{2+}$ concentrations to determine the best Fenton reagent dosages. The imidacloprid removal of 87.13% was observed at the Fenton reagent ratio ([H$_2$O$_2$]:[Fe$^{2+}$]) of 6mM:6mM. In the presence of humic acid, the imidacloprid removal was found slightly decreased to 73.39% at the Fenton reagent ratio ([H$_2$O$_2$]:[Fe$^{2+}$]) of 6mM:6mM. The humic acid was found to compete with imidacloprid for hydroxyl radicals. For the molecular weight variation, the addition of ferrous ions in the humic acid solution initiated the reactions between Fe$^{2+}$/Fe$^{3+}$ redox couples and humic acids, breaking the humic acid (molecular weight of 3578) into smaller fractions (molecular weight of 782). These organic fractions were further oxidized into even smaller molecules by hydroxyl radicals (molecular weight of 383) after H$_2$O$_2$ addition.

Keywords: Imidacloprid, Fenton, Humic acid, Hydroxyl radical

1. Introduction

For decades, organic pesticides have been used for pest control due to their significant toxicity and persistence in the environment. Their residuals in the environment may become long term contamination sources and pose a serious threat to the aquatic environment. Therefore, the environmental contamination by the residuals of organic pesticides has drawn a great deal of attention since their extensive uses in agricultural activities [1], [2].

Among the frequently-used pesticides, the imidacloprid, a neonicotinoid insecticide, was firstly developed in 1986. Imidacloprid acts as an agonist on the postsynaptic nicotinic acetylcholine receptors of motor neurones in insects, causing an over-stimulation of the nervous system, and the death of the insect. It has been used for both agricultural and veterinary purposes. Other uses include application to foundations to prevent termite damage, pest control for gardens and turfs, treatment of domestic pets to control fleas, protection of trees from boring insects, and in preservative treatment of some types of lumber products [3], [4]. Its residuals have been reported to have severe deterioration to the aquatic environment as well as ecological community [5]. Meanwhile, the natural organic matter (NOM) is a natural-occurring substance which is ubiquitous in the environment. It may act as a scavenger to compete with other co-dissolved chemicals and impact significantly to the environmental fates of aquatic organic contaminants [6].

To mitigate the organic contamination of the aquatic environment, the Fenton process has been used frequently because of its ready availability of involving reagents and effectiveness in contaminant removal [7]. In this study, the imidacloprid was selected as the target contaminant. The humic acid (HA) was chosen as the representative NOM. The degradation experiment of imidacloprid was conducted at various concentrations of Fenton reagents around pH 7. For competitive study, 10 mg/L of HA was employed, and the molecular weights of HA before and after Fenton degradation were measured.
2. Materials and Method

2.1. Reagents

In this study, the reagent grade imidacloprid with 99.5% purity was purchased from CHEM SERVICE. The humic acid was purchased from ALDRICH. The FeSO$_4$ and H$_2$O$_2$ used were reagent grade chemicals purchased from SANTOKU and SHOWA, respectively. The water used in the experiments was nanopure water. For the pH adjustment, NaOH and H$_2$SO$_4$ used were reagent grade chemicals purchased from Riedel-de Haen and JB Baker, respectively. The quenching agent of KI was purchased from SIGMA.

2.2. Experimental Procedure

All the Fenton degradation experiments were conducted in the 250 ml beakers under the temperature of 22±2°C around pH 7. The initial imidacloprid concentration was 6 ppm. For the degradation experiments, initial concentrations of Fe$^{2+}$ were 3.0, 4.0, 5.0, 6.0 and 7.0 mM, and initial H$_2$O$_2$ concentrations were 3.0, 4.0, 5.0, 6.0 and 7.0 mM. At a given Fe$^{2+}$ concentration, the pesticides were degraded at 5 different H$_2$O$_2$ concentrations. In each experiment, the imidacloprid concentration was moniotored by taking an aliquot of the tested solution at 0, 0.5, 1, 2, 3, 5, 10, 15, 20, 25 and 30 minutes after the reaction took place. The quenching agent of KI was added to stop the reaction immediately after the sample was collected.

2.3. Analytical Method

The imidacloprid samples were analyzed using Waters Alliance HPLC and UV detector. The column used was Waters PAH C18 column. The sample volume injected was 20 μL, and the flow rate was 1 ml/min. The mobile phase was 20% acetonitrile and 80% 0.05% sodium citrate. The UV detector wavelength was 270 nm. The average molecular weight of humic acids was quantified using size exclusion chromatography (SEC) before and after Fenton degradation. The high pressure liquid chromatography was purchased from Thermo Scientific with P1000 pump and UV1000 detector. The detector wavelength was 254 nm and the mobile phase was 0.1 M NaOH aqueous solution at the flowrate of 1 ml/min. The columns (PSS-MCX 1 pre-column with 8x50 mm, and 2 SEC columns (1000 and 10,000,000 A), 8x300 mm each) were purchased from German. The poly (styrene sulfonate) sodium salts of molecular weights of 1100, 3610, 63900 and 2260000 were used for calibration curve construction.

3. Results and Discussion

The degradation experiments of imidacloprid were conducted and the results are presented in Fig. 1. At the Fe$^{2+}$ concentration of 3 mM, the most effective imidacloprid removal (i.e., 16.23%) occurred when H$_2$O$_2$ was at the concentration of 6 mM. At the Fe$^{2+}$ concentration of 4 mM, the most effective imidacloprid removal (i.e., 39.06%) occurred when H$_2$O$_2$ was at the concentration of 5 mM. At the Fe$^{2+}$ concentration of 5 mM, the most effective imidacloprid removal (i.e., 72.78%) occurred when H$_2$O$_2$ was at the concentration of 6 mM. At the Fe$^{2+}$ concentration of 6 mM, the most effective imidacloprid removal (i.e., 87.17%) occurred when H$_2$O$_2$ was at the concentration of 6 mM. At the Fe$^{2+}$ concentration of 7 mM, the most effective imidacloprid removal (i.e., 81.73%) occurred when H$_2$O$_2$ was at the concentration of 7 mM. Apparently, the Fenton reagent ratio (i.e., [H$_2$O$_2$]/[Fe$^{2+}$]) for best imidacloprid removal decreased from 2 to 1 as the Fe$^{2+}$ concentration increased from 3 mM to 7 mM. Overall, the best imidacloprid removal occurred at both the H$_2$O$_2$ and Fe$^{2+}$ concentrations of 6 mM.

As for the competitive degradation experiments, 10 mg/L of humic acid was added into the tested samples, and the degradation results are presented in Fig. 2. One thing worth mentioning is that the dissolved humic acid was used in this study, and the adorption of target contaminant onto the humic acid was considered negligible [8]. At the Fe$^{2+}$ concentration of 3 mM, the most effective imidacloprid removal (i.e., 9.10%) occurred when H$_2$O$_2$ was at the concentration of 5 mM. At the Fe$^{2+}$ concentration of 4 mM, the most effective imidacloprid removal (i.e., 26.10%) occurred when H$_2$O$_2$ was at the concentration of 5 mM. At the Fe$^{2+}$ concentration of 5 mM, the most effective imidacloprid removal (i.e., 60.31%) occurred when H$_2$O$_2$ was at the concentration of 7 mM. Apparently, the Fenton reagent ratio (i.e., [H$_2$O$_2$]/[Fe$^{2+}$]) for best imidacloprid removal decreased from 2 to 1 as the Fe$^{2+}$ concentration increased from 3 mM to 7 mM. Overall, the best imidacloprid removal occurred at both the H$_2$O$_2$ and Fe$^{2+}$ concentrations of 6 mM.

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Similarly, the overall best imidacloprid removal was observed both at H$_2$O$_2$ and Fe$^{2+}$ concentrations of 6 mM. Besides, at the same Fenton reagent dosage, the imidacloprid removal was found relatively higher than that in the presence of humic acid. This is because the humic acid was considered as the alternative target compound to compete with imidacloprid for hydroxyl radicals.

To explore the molecular weight, the molecular weights of the humic acid before, during and after Fenton degradation were measured around 3578, 782, and 383 DA. In the Fenton degradation experiment, the humic acid molecules were broken into smaller fragments after addition of ferrous ions. This is because the reactions between Fe$^{2+}$/Fe$^{3+}$ redox couples and humic acids, causing the molecular fragmentation of the

![Graphs showing degradation of imidacloprid by Fenton process](image)

Fig. 1: Imidacloprid degradation by Fenton process.
investigated humic acids. The resulting fragments were further divided into even smaller pieces after reacting with hydroxyl radicals [9].

4. Conclusion

In this study, the imidacloprid degradation by Fenton process either with or without the presence of humic acid was investigated at neutral environment. The imidacloprid removal was found at 87.13% when the Fenton reagent concentrations ([H\textsubscript{2}O\textsubscript{2}]:[Fe\textsuperscript{2+}]) were at 6mM:6mM. In the presence of humic acid, the imidacloprid removal by Fenton process was found slightly decreased to 73.39% at the Fenton reagent concentrations ([H\textsubscript{2}O\textsubscript{2}]:[Fe\textsuperscript{2+}]) of 6mM:6mM. Apparently, the humic acid was found to compete with imidacloprid for hydroxyl radicals. For the molecular weight variation, the addition of Fe\textsuperscript{2+} in the humic acid solution initiated the reactions between Fe\textsuperscript{2+}/Fe\textsuperscript{3+} redox couples and humic acids, breaking the humic acid (molecular weight of 3578) into smaller fractions (molecular weight of 782). These organic fractions were
further oxidized into even smaller molecules by hydroxyl radicals (molecular weight of 383) after \( \text{H}_2\text{O}_2 \) addition.

5. References


