

## Degradation of Linuron in Water by the Photo-Fenton Reaction

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### Introduction

Recent reports indicate that the illumination of the Fenton system ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ ) can significantly enhance decomposition of many refractory organics. The applications of photo-Fenton cover landfill leachate [1]; the degradation of pesticides and other organics [2]. The enhancement of organic decomposition is believed to be due to photolysis of aqueous complex  $\text{Fe}(\text{OH})^{2+}$  to provide a important source of  $\text{OH}\cdot$  radicals [3]. Further, the photolysis of  $\text{Fe}(\text{OH})^{2+}$  regenerates  $\text{Fe}^{2+}$  ions, that means that photo-Fenton would need less  $\text{Fe}^{2+}$  dosages compared with the conventional Fenton process [4].

In this study, degradation of linuron, which is one of the phenyl urea herbicides, was performed by the photo-Fenton process. The many factors affected on the degradation were evaluated. The progress of mineralization of linuron was monitored by total organic carbon (TOC) content and ionic chromatography. Furthermore, the photoproducts of linuron during this photocatalytic process have been identified by gas chromatography-mass spectrometry (GC/MS). The degradation pathway was proposed on the base of the evidence of the intermediate formation.

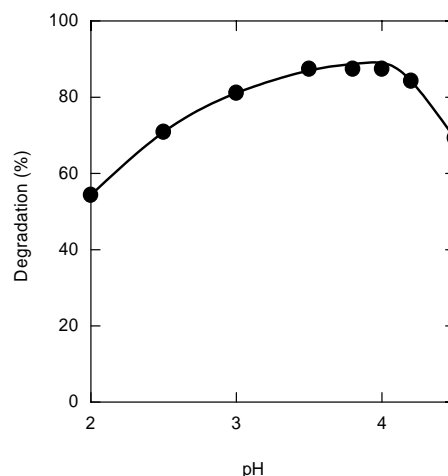
### Experimental

Photodegradation was conducted in a Pyrex glass cell of 30 mL capacity. The reaction mixture inside the cell, consisting of 20 mL of linuron solution ( $10 \text{ mg L}^{-1}$ ) and the precise amount of Fenton reagent, was continuously stirred with a magnetic bar. The pH of the sample solution was adjusted with  $\text{H}_2\text{SO}_4$  and/or  $\text{NaOH}$  solution. In the majority of the experiments, temperature was kept at  $25 \pm 1^\circ\text{C}$  with a water bath. The sample solution was illuminated with a Xe lamp. The intensity of the light ( $2.0 \text{ mW cm}^{-2}$ ) was measured by a UV radio meter.

The progress in the degradation of linuron was followed with a HPLC equipped with a UV detector. The elution was monitored at 250 nm. Concentration of  $\text{Fe}(\text{II})$  consumed was determined by the phenanthroline (phen) method. The progress of mineralization of linuron was monitored by measuring the TOC. TOC of the sample solution was measured with a TOC analyzer. The progress of ammonium, nitrate and chloride ion formations was obtained by ionic chromatography equipped with a conductivity detector. The intermediate products during photodegradation of linuron were extracted by the solid phase extraction. A mixture of dichloromethane and ethyl acetate (1/1, v/v) was used to elute the intermediate products. A GC/MS was used for separation and detection of the intermediate products.

### Results and Discussion

Effect of pH on the degradation of linuron by use of the photo-Fenton process was investigated over the pH range of 2.0 – 5.0. The results are shown in Fig. 1. The degradation percentage of linuron rapidly increased with



**Fig. 1.** Effect of pH on the degradation of linuron by the photo-Fenton reaction.

$[\text{Fe}(\text{II})]_i$ :  $4 \times 10^{-5} \text{ mol L}^{-1}$ ;  $[\text{H}_2\text{O}_2]_i$ :  $4 \times 10^{-4} \text{ mol L}^{-1}$ ; pH: 4.0; reaction time: 5 min; light intensity:  $2.0 \text{ mW cm}^{-2}$ ; reaction temperature:  $25^\circ\text{C}$ .

increasing pH value up to 4.0, decreasing at pH above 4.5. Therefore, the photo-Fenton reaction is strongly affected by the solution of pH. To obtain the optimal initial  $\text{Fe}(\text{II})$  concentration, the investigation was carried out in the range of  $0 - 4 \times 10^{-5} \text{ mol L}^{-1}$  at pH 4. The degradation rate of linuron increased with increasing initial  $\text{Fe}(\text{II})$  concentration. Complete degradation of linuron was reached at  $\text{Fe}(\text{II})$  concentration of above  $2 \times 10^{-5} \text{ mol L}^{-1}$  within 60 min, while low concentration of  $\text{Fe}(\text{II})$  did not allow achieving complete degradation in photo-Fenton process. Especially, when  $\text{Fe}(\text{II})$  concentration was selected as  $4 \times 10^{-5} \text{ mol L}^{-1}$ , linuron was completely degraded after 20 min. Effect of initial  $\text{H}_2\text{O}_2$  concentration on the degradation of linuron was investigated by the use of photo-Fenton process. When concentration of  $\text{H}_2\text{O}_2$  was below  $2 \times 10^{-4} \text{ mol L}^{-1}$ , linuron did not achieve the complete degradation within 60 min.

Concentration of  $\text{Fe}(\text{II})$  decreased with increasing the reaction time up to 1 h and then the concentration reached a plateau value after about 5 h of irradiation. This plateau can be assigned to a photostationary equilibrium between  $\text{Fe}(\text{II})$  and  $\text{Fe}(\text{III})$  that regenerates the absorbing species and gives an interesting catalytic aspect. Accordingly, a continuous formation of  $\text{OH}\cdot$  radicals is observed allowing the complete mineralization of linuron. The progress of the mineralization of the linuron solution was monitored by measuring the TOC. The complete mineralization of linuron was not achieved after 60 min, although linuron was not present in the solution after the irradiation time. This difference indicates that intermediate products were produced during the photocatalytic process. TOC rapidly decreased with increasing the reaction time. TOC remained about 0.4 ppm (ca. 10%) after 25 h irradiation. On the other hand, the formations of ammonium, nitrate and chloride ions during the photocatalytic process were observed. Therefore, linuron could be mineralized by the photo-Fenton process. Furthermore, 8 intermediate products were detected and the degradation pathway of linuron was proposed on the basis of the by-products.

### References

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