Journal of Hazardous Materials 167 (2009) 199–204

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Reactor model development: The removal performance of ferrous-catalysed photo-oxidation process by examining the reaction parameters

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ARTICLE INFO

Article history:
Received 22 September 2008
Received in revised form 19 December 2008
Accepted 22 December 2008
Available online 30 December 2008

Keywords:
Reactor design chart
Ferrous
Hydrogen peroxide
UV
Alachlor

ABSTRACT

The removal performance of the ferrous catalysed photo-oxidation process was investigated through the examination of major process parameters including pH levels and dosages of ferrous (Fe^{2+}) and hydrogen peroxide (H_2O_2). A common used herbicide, alachlor, was used as a target compound in the degradation process. In the study, alachlor was found to be effectively degraded by hydroxyl radicals ($HO^\bullet$) which were generated by UV/Fe^{2+}/H_2O_2 in the oxidation process. It was interesting to find that the pattern of reaction kinetics of alachlor varied depending on the initial concentrations of Fe^{2+} and H_2O_2. An optimum H_2O_2 dosage was determined. This was practically useful because the overdose of H_2O_2 would cause the process retardation. The conventional pseudo-first-order kinetics and two-stage first-order kinetics were observed at lower and higher Fe^{2+} concentrations, respectively. Models were proposed and used to stimulate the kinetic process. Thus, design charts were established for determining the reaction time (i.e., reactor sizing) required for predetermined removal performance of alachlor under different concentrations of H_2O_2 and Fe^{2+}.

1. Introduction

An increasing demand of chemical herbicides which caused contaminations in a water system has become an important issue over the world. The improper disposal of insecticide and herbicide could lead to contamination of soil, ground water and surface water [1]. Alachlor, 2-chloro-2′, 6′-diethyl-*N*-(methanoxymethyl) acetanilide, was the second most widely used herbicide in the United States on a number of crops to remove annual grasses, broad-leaved weeds in corn and soybean productions. About 26 million pounds were used for agricultural purposes from 1990 to 1993 on the United States [2]. It was a highly toxic compound classified as an endocrine disruptor, where the allowed maximum concentration was $0.002\,\mathrm{mg\,l^{-1}}$. Alachlor has also been classified as the carcinogen of B2 group by the EPA [3]. For the short-term effect, alachlor potentially caused slight skin and eye irritation when people were exposed to it at levels above 2 ppb for relatively short periods of time. A lifetime exposure could damage liver, kidney, spleen, lining of nose and eyelids.

Wastewater containing pesticide was not recommended to be treated biologically, since pesticides were mostly toxic to the microorganisms [4]. Most of the organic pollutants were often treated chemically by single reagent such as chlorine, ozone, UV radiation, hydrogen peroxide (H_2O_2), etc. Sometimes, degradation by conventional treatments might be difficult if the concentration of these pollutants was too low or if they were especially refractory to the reagent added. Therefore, more effective processes for the destruction of such contaminants have been developed, e.g., advanced oxidation process (AOP) which has been successfully used to degrade most of the organic compounds in the polluted water. Most of these AOP generating very reactive free radicals, especially hydroxyl radicals ($HO^\bullet$), have aroused many interests because of their high oxidative power [5].

AOP emerged as attractive options which employ chemical, photochemical, sonochemical or radiolytic techniques to degrade chemical pollutants. The advantages of the various AOP have been well established. One of the AOP, photo-Fenton process (UV–FP), could effectively oxidize a great variety of organic contaminates by the generation of highly oxidative $HO^\bullet$ [1]. The rate of oxidation would depend on radicals, oxygen, and pollutant concentration. Many factors could affect the radical concentration, such as pH, temperature, the presence of ions, the type of pollutant and the presence of scavengers [6]. Regarding the concentration of H_2O_2 ($[H_2O_2]$), the rate constant in generating $HO^\bullet$ increased with the concentration of hydrogen peroxide up to an optimum level. Over this level, the rate decreased gradually due to the overdose of H_2O_2. The aim of this work was to examine the effect of alachlor degradation under various experimental conditions including initial pH, $[H_2O_2]$ and $[Fe^{2+}]$.

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doi:10.1016/j.jhazmat.2008.12.099

2. Methodology

2.1. Chemicals

Alachlor (2-chloro-2′,6′-diethyl-*N*-methoxymethylacetanilide) at 99.5% was obtained from Chem Service, Inc. Iron (II) sulfate-7-hydrate ($FeSO_4{\cdot}7H_2O$) and hydrogen peroxide (30% w/w) was purchased from Riedel-de Haen Co. and Junsei Chemical Ltd. (Japan). The Fe^{2+} and H_2O_2 solutions were freshly prepared for each experiment to minimize errors resulting from precipitations and self-decomposition, where the Fe^{2+} was prepared in the acidic solution (pH 2) to prevent the formation of $Fe(OH)_2$ precipitation. Acetonitrile and methanol were HPLC grade and obtained from Tedia Company. Methanol was prepared as a quenching solution and acetonitrile was used to prepare the mobile phase in HPLC analysis. Sulfuric acid and sodium hydroxide were used to adjust the initial pH of the solutions. High-purity (distilled-deionised) water was produced from a Bamstead NANO water treatment system using distilled water feed and used to prepare all the solutions. All chemicals were used as received without further purification. All solutions were degassed before being used in HPLC system.

2.2. Procedure

The stock solution of alachlor was prepared at 0.573 mM. A homogenous solution of alachlor was added with predetermined doses of Fe^{2+}. The reaction was initiated by adding H_2O_2 and switching on the pre-heated UV system simultaneously to investigate the effects of pH, $[H_2O_2]$, and $[Fe^{2+}]$. In this work, a Rayonet^{TM} photochemical reactor was employed as the UV system for the experiments. Only one parameter was varied in each batch of tests while other experimental parameters were kept to be unchanged. For the study on pH effect, 10 ml of 0.573 mM alachlor was mixed with 180 ml deionised water and 5 ml of 0.01 mM of $[Fe^{2+}]$ in a 300 ml quartz beaker. The pH level of the mixture was adjusted to the required value. The vessel was placed at the centre of the UV system equipped with two 253.7 nm monochromatic lamps, a magnetic stirrer and a cooling fan. The reaction was initiated by adding 5 ml of 0.01 mM of $[H_2O_2]$ and switching on UV lamps simultaneously. The total final volume of reaction solution was 200 ml and the initial concentration of alachlor was 28.67 μM. The pH value was varied in each batch of tests until a highest rate was obtained. After obtaining the optimum pH, the $[H_2O_2]$ was varied while pH was kept at an optimum level. Different levels of $[H_2O_2]$ were used until the rate was optimised. Further, at the optimal $[H_2O_2]$ and pH, the $[Fe^{2+}]$ was then varied to investigate its effect on the degradation rate. For each batch of the experiments described above, 1 ml of sample was taken at selected time intervals and mixed with the same amount of methanol to quench the reaction. The quenched samples were quantified by liquid chromatography (LC). All the experiments were conducted in duplicate.

2.3. Instrumental analysis

Each illuminated sample was quantified by LC, which consisted of a pump (Waters 515), a C18 (250 mm × 4.6 mm, 5 μm particle size) Alltech column, and a Waters^{TM} 486 Tunable Absorbance Detector, which is capable of measuring the light absorbance, ranging from 190 to 280 nm. The mobile phase was made up of 50% (v/v) acetonitrile and 50% distilled-deionized water (pre-mixed with 0.15% acetic acid). It was delivered at a flow rate of 1.5 ml min^{-1} and resulted in an alachlor peak at a retention time of about 10 min. The detection wavelength for alachlor was 200 nm, which was predetermined as the maximum absorption wavelength (λ_{max}) by a Biochrom Libra S12 UV–visible Spectrophotometer.

3. Results and discussion

3.1. Effect of pH on the photo-Fenton process

The effect of different initial pH levels on the degradation rates of alachlor using UV–FP was firstly investigated in this work. Pseudo-first-order kinetic was observed with a high r^2 coefficient over 0.99. Fig. 1 showed the linearised pseudo-first-order decay curves of alachlor by photo-Fenton process. The pH levels varied from 2.05 to 7.2 which covers a range from acidic to neutral condition. The overall removal was over 90% at 3000s. The highest and the lowest rates were located at pH 2.58 and pH 7.2 respectively. The decay rate constant increased firstly and then decreased as the pH level increased from acidic to neutral conditions within the tested range. A plot of decay rate constant at tested pH range was summarized in Fig. 1 (inset). In the figure, the photo-Fenton reaction was strictly affected by the pH. In general, an acidic environment was more favourable for the alachlor degradation, where the reaction rate was found to be optimum at 2.58. A further increment of pH level from 2.58 to 3.08, the decay rate constant decreased rapidly and an extended decline between pH 3.08 and 7.2 was observed. Thus, the optimum pH was observed at 2.58.

For the Fenton process, Fe^{3+} was generated by oxidizing Fe^{2+} and formed Fe(III)-hydroxyl complexes, $[Fe(OH)]^{2+}$, which was reported to be highly soluble and predominates at acidic pH range [7]. Referring to Fig. 1, when the pH level increased from 2.05 to 2.58, the degradation rate of alachlor increased as well. Since the $Fe(OH)^{2+}$ could produce $HO^{\bullet}$ radical and regenerate Fe^{2+} on the absorption of UV light as shown in Eqs. (1) and (2).

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + HO^{\bullet} \quad (1)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} \quad (2)$$

As $HO^{\bullet}$ became the main species to degrade alachlor in the UV–FP, the degradation rate increased with the amount of $HO^{\bullet}$ existed in the system. However, negative effect was observed at extremely low pH. H_2O_2 solvated protons to form oxonium ions (H_3O^+), which strengthens the stability of H_2O_2 [8]. The reactivity of the H_2O_2 with Fe^{2+} ion was therefore reduced. On the other hand, after reaching the optimum pH of 2.58, the decay rate constant

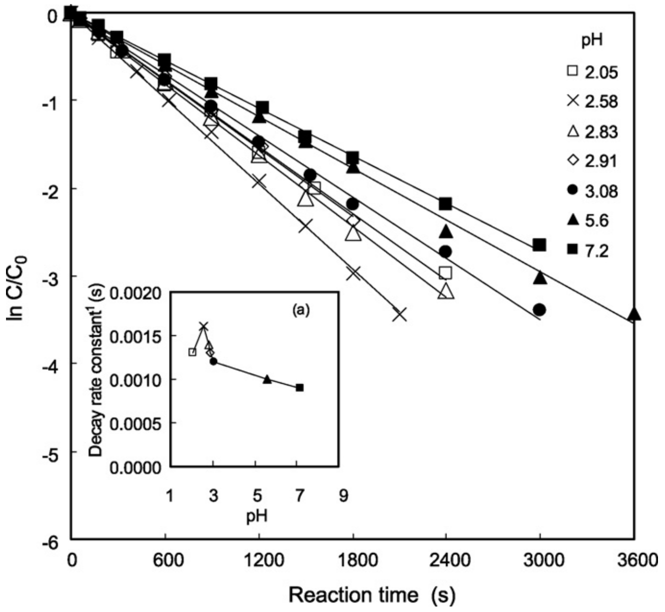

Fig. 1. Pseudo-first-order degradation of alachlor with 0.01 mM of $[Fe^{2+}]$ and 0.01 mM of $[H_2O_2]$ at 253.7 nm at various pH. Inset: Effect of pH on the degradation of alachlor by the UV–FP with 0.01 mM of $[Fe^{2+}]$ and 0.01 mM $[H_2O_2]$ at 253.7 nm.