



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

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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 $\text{UV}/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ 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+} .

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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 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 contaminants 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 ($[\text{H}_2\text{O}_2]$), 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, $[\text{H}_2\text{O}_2]$ and $[\text{Fe}^{2+}]$.

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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 ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) 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 $\text{Fe}(\text{OH})_2$ 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, $[\text{H}_2\text{O}_2]$, and $[\text{Fe}^{2+}]$. In this work, a Rayonet™ 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 $[\text{Fe}^{2+}]$ 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 $[\text{H}_2\text{O}_2]$ 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 $[\text{H}_2\text{O}_2]$ was varied while pH was kept at an optimum level. Different levels of $[\text{H}_2\text{O}_2]$ were used until the rate was optimised. Further, at the optimal $[\text{H}_2\text{O}_2]$ and pH, the $[\text{Fe}^{2+}]$ 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 \times 4.6 mm, 5 μm particle size) Alltech column, and a Waters™ 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 pre-determined 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, $[\text{Fe}(\text{OH})]^{2+}$, 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 $\text{Fe}(\text{OH})^{2+}$ could produce HO^\bullet radical and regenerate Fe^{2+} on the absorption of UV light as shown in Eqs. (1) and (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

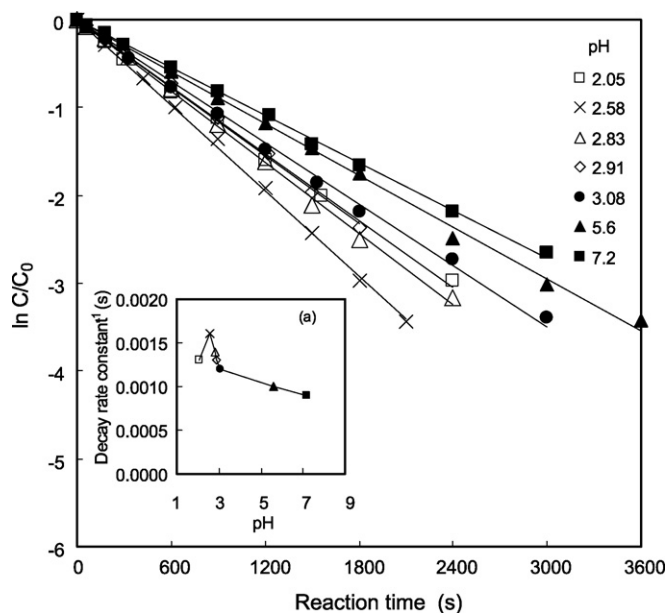
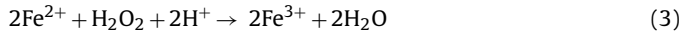


Fig. 1. Pseudo-first-order degradation of alachlor with 0.01 mM of $[\text{Fe}^{2+}]$ and 0.01 mM of $[\text{H}_2\text{O}_2]$ at 253.7 nm at various pH. Inset: Effect of pH on the degradation of alachlor by the UV-FP with 0.01 mM of $[\text{Fe}^{2+}]$ and 0.01 mM $[\text{H}_2\text{O}_2]$ at 253.7 nm.

dropped quickly as the pH further increased. This was an overall result of several reasons. Firstly, the decomposition of H_2O_2 consumed the proton in the presence of ferrous ion as shown in Eq. (3) [9].



A basic environment which provides less H^+ for the reaction, so the formation of $\text{Fe}(\text{OH})^{2+}$ was restricted (Eq. (4)). When pH increased, lesser Fe^{3+} and $\text{Fe}(\text{OH})^{2+}$ was formed, and therefore less HO^\bullet was generated even under the illumination of UV (see Eq. (2)). The overall amount of Fe(II) regenerated was reduced and Fenton's process was retarded.

Secondly, the oxidation potential of HO^\bullet decreased with increasing pH [10]. The decay rate constant became slower even if the same amount of HO^\bullet produced at higher pH. Thirdly, the possibility for such retardation could be owing to the formation of iron hydroxide precipitates, $\text{Fe}(\text{OH})_3$. It reduced the concentration of a dissolved fraction of Fe^{2+} in the solution as well as the transmission of the UV light in the solution [11]. Less soluble Fe^{2+} was available in the solution to react with H_2O_2 , leading to a lower amount of HO^\bullet as shown in Eq. (1). Fourthly, the decomposition of H_2O_2 also contributed to the retardation of the reaction rate. The H_2O_2 was unstable and rapidly decayed into water and oxygen at alkaline condition with or without the presence of UV light [12]. These factors could be used to justify the decrease of thealachlor decay rate constant with increasing pH.

3.2. Effect of hydrogen peroxide concentration [H_2O_2]

The degradation ofalachlor with different initial [H_2O_2] was examined and the plot ofalachlor remaining fractions in " $\ln(C/C_0)$ " versus the reaction time was shown in Fig. 2. In the figure, linear relationships ($r^2 > 0.99$) were observed. The kinetic rates were calculated and compared with the concentrations of H_2O_2 in Fig. 3. It was interesting to find that [H_2O_2] would be divided into 3 stages within the tested dosages and could be correlated with a common linear equation as below Eq. (5),

$$k = \alpha \ln[\text{H}_2\text{O}_2] + \beta \quad (5)$$

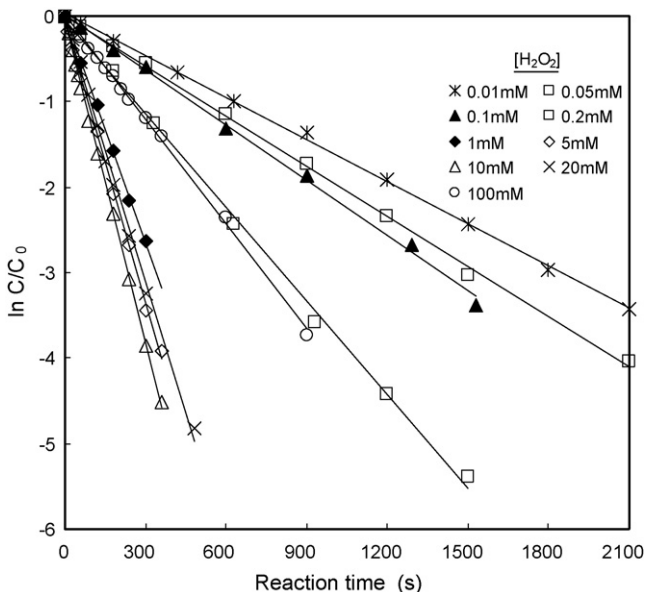


Fig. 2. Pseudo-first order degradation ofalachlor with 0.01 mM of $[\text{Fe}^{2+}]$ at different concentration of $[\text{H}_2\text{O}_2]$ at 253.7 nm.

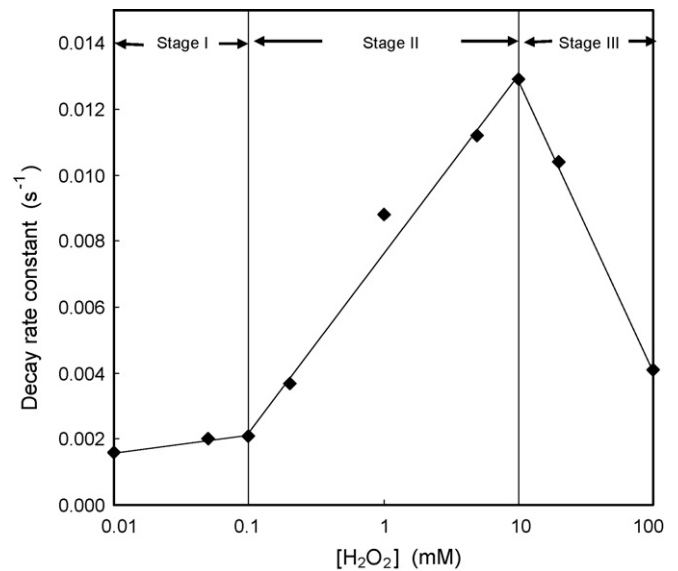


Fig. 3. Effect of H_2O_2 on the degradation ofalachlor by UV-FP with 0.01 mM of $[\text{Fe}^{2+}]$ at pH 2.58 at 253.7 nm.

where α and β were the coefficients as stated in Eqs. (6)–(8). Thus, the trend of the decay rate constant by varying the concentration of H_2O_2 was defined as below:

Stage I ($0.01 \leq [\text{H}_2\text{O}_2] \leq 0.1$):

$$k = 0.0002 \ln[\text{H}_2\text{O}_2] + 0.0026 \quad (r^2 = 0.99) \quad (6)$$

Stage II ($0.1 \leq [\text{H}_2\text{O}_2] \leq 10$):

$$k = 0.0023 \ln[\text{H}_2\text{O}_2] + 0.0077 \quad (r^2 = 0.98) \quad (7)$$

Stage III ($10 \leq [\text{H}_2\text{O}_2] \leq 100$):

$$k = -0.0038 \ln[\text{H}_2\text{O}_2] + 0.0218 \quad (r^2 = 0.99) \quad (8)$$

Judging from the slope of Eq. (6), the rate significantly increased with the increment of $[\text{H}_2\text{O}_2]$ as the $[\text{H}_2\text{O}_2] < 0.1$ mM. This indicated that HO^\bullet was deficient in the system when $[\text{H}_2\text{O}_2]$ was very low. From 0.1 to 10 mM, the rate increased sharply with $[\text{H}_2\text{O}_2]$ (Eq. (7)), then the reaction retarded as $[\text{H}_2\text{O}_2]$ was greater than 10 mM (Eq. (8)). The sharp increment of the degradation rate was likely due to the generation of extra HO^\bullet at a higher $[\text{H}_2\text{O}_2]$. Several parallel reactions could produce HO^\bullet in the photo-Fenton process: (i) Fe^{2+} and H_2O_2 could react to form aqueous complex $\text{Fe}(\text{OH})^{2+}$ and OH^\bullet , and the $\text{Fe}(\text{OH})^{2+}$ could further produce OH^\bullet in the presence of UV by photolysis as shown in Eqs. (1) and (2) [7] and (ii) H_2O_2 could generate HO^\bullet by direct photolysis when the wavelength of UV was less than 360 nm [12,13].



Rate retardation was observed when the $[\text{H}_2\text{O}_2]$ increased more than 10 mM. This indicated that excess H_2O_2 was not beneficial to the degradation ofalachlor. In fact, too high of the $[\text{H}_2\text{O}_2]$ had an adverse effect on the reaction owing to the scavenging of HO^\bullet and consequent formation of less reactive hydroperoxyl radicals HOO^\bullet (Eqs. (10)–(12)) [9,14,15]:



The consumption of HO• and the generation of weaker hydroperoxyl radicals HOO• would weaken the overall oxidative power in the solution. In addition, the HOO• could further react with Fe²⁺ and consumed all radicals at the end. The oxidative power of the system was therefore declined significantly. This resulted in the retardation of the reaction and a negative slope was obtained in Fig. 3 (or Eq. (8)).

Because thealachlor decay followed pseudo-first-order kinetic (Eq. (13)), the time to reach desiredalachlor removal (in terms of remaining fraction) could be estimated by substituting Eq. (5) into Eq. (13):

$$\ln \frac{C}{C_0} = -kt \quad (13)$$

$$t = -\frac{\ln(C/C_0)}{\alpha \cdot \ln[H_2O_2] + \beta} \quad (14)$$

where C₀ and C were the concentrations ofalachlor before and after the treatment at time t (s). As stated previously, α and β depended on the concentration of H₂O₂ and they could be determined from Eqs. (6)–(8). The results of arbitrarily selected removal efficiencies were generated in Fig. 4, in which the required reaction time to achieve desired removal efficiencies (by rearranging Eq. (14)) using different doses of H₂O₂ were shown. A typical example in Fig. 4 showed that if a 90% removal ofalachlor is required, then 200 s of retention time could be used with 5 mM of [H₂O₂]. This was a useful tool for the reagent dosage and reactor size determination during a process design.

Referring to Fig. 4, a higher percentage removal (R) generally required a longer reaction time, but it could be controlled by regulating the initial concentration of H₂O₂ (i.e., [H₂O₂]₀). In addition, the reaction time was less [H₂O₂]₀-dependence at lower R, while more dependent at higher R. It was found that, for a fixed R, the most effective dosage of H₂O₂ was 10 mM. For [H₂O₂] < 10 mM (defined as stages I and II), the slope of the lines was found to be steeper and more negative. This indicated that the increase of [H₂O₂] in this range would induce a preferred marginal effect to shorten the reaction time, significantly. On the other hand, when [H₂O₂] was further increased (defined as stage III), the slopes of the lines

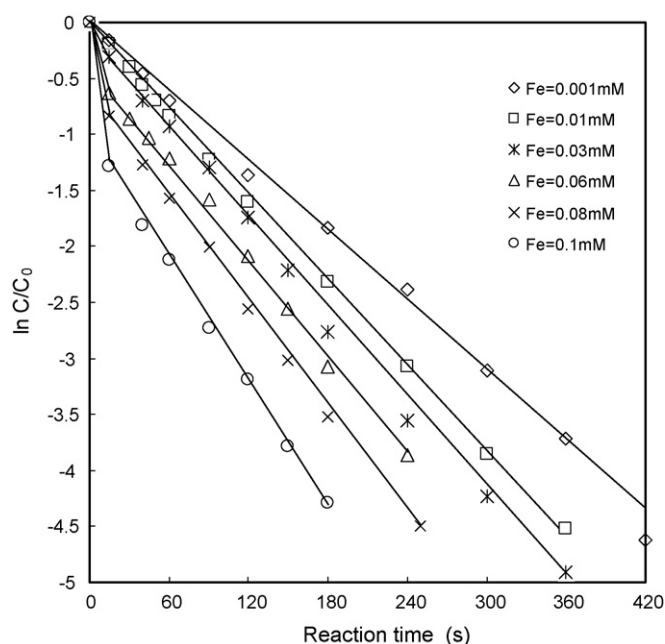


Fig. 5. Pseudo-first-order degradations ofalachlor with 10 mM of [H₂O₂] at different [Fe²⁺] at 253.7 nm at pH 2.58.

were increased and turned into positive. This suggested that the excess [H₂O₂] would result in a longer reaction time to achieve the required performance, or an undesired effect was observed.

In general, the trends of the curves in Fig. 4 might be on account of the relative concentrations between the reagents. An abundant HO• was generated at the beginning of photo-Fenton process while high concentration ofalachlor coexisted in the solution. This could result in a shorter reaction time at lower R. However, when most of thealachlor was decayed in the solution, the [HO•] largely reduced as well, this led to a much lower collision probability betweenalachlor and HO• and a much longer reaction time (in a nonlinear way) would be required to achieve higher percentage removal. In addition, at the later stage of the reaction, the intermediates have accumulated to higher levels; the competition of hydroxyl radicals by the intermediates could further reduce the decay ofalachlor as the removal ofalachlor approached higher percentage. Furthermore, it was interesting to note that, at the same removal percentage, an increase of H₂O₂ from 0.01 to 0.1 mM could only reduce the required treatment time by 30%, but the time was significantly shortened by 82% as the concentration increased from 0.1 to 10 mM. The shortest treatment time was located at 10 mM of H₂O₂ (with much compacted time difference than other dosages). This suggested a proper selection of reagent dosages could significantly minimize the time used for the treatment of intermediates and reduce the reactor size if the optimisation ofalachlor removal was the priority.

3.3. Effect of ferrous ion concentration [Fe²⁺]

By adopting the optimum pH 2.58 and optimum [H₂O₂] at concentration of 10 mM, the degradation ofalachlor was further investigated under different [Fe²⁺] in the UV-FP at 253.7 nm. If the process involved no Fe²⁺, the degradation ofalachlor would mainly depend on UV or UV/H₂O₂, of which the decay rate constant would be much slower [16]. The [Fe²⁺] selected for this study were 0.001, 0.01, 0.03, 0.06, 0.08 and 0.1 mM. The pseudo-first-order decay rate constants ofalachlor were depicted in Fig. 5. Generally, both the rate and the final removal fraction increased with [Fe²⁺], indicating that a higher [Fe²⁺] could efficiently improve the performance

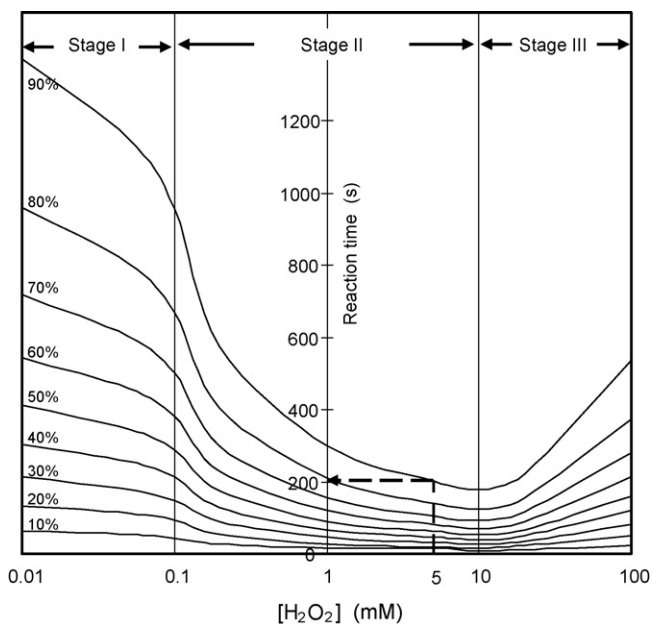


Fig. 4. Time taken for certain percentage removal ofalachlor by different [H₂O₂] with 0.01 mM of [Fe²⁺] at pH 2.58 at 253.7 nm. (The percentages shown in the figure are the removal percentage at different reaction time of the reaction.)

of the alachlor degradation. The reaction time for achieving 90% removal was reduced to 33% when $[\text{Fe}^{2+}]$ increased from 0.001 to 0.1 mM (i.e., the reactor size could be reduced by 3 times). Several reasons were responsible for the higher decay rate constant at higher $[\text{Fe}^{2+}]$. The ferrous ion acted as a catalyst in the photo-Fenton and it could react vigorously with H_2O_2 to produce additional HO^\bullet within a shorter reaction time at a higher $[\text{Fe}^{2+}]$. On the other hand, an increase of $[\text{Fe}^{2+}]$ in the solution would speed up the serial reactions initiated by Fe^{2+} and H_2O_2 so that the generation of $[\text{Fe}(\text{OH})^{2+}]$ and HO^\bullet would be accelerated (as stated in Eq. (1)). Thus, the overall performance on the degradation of alachlor would be improved and the reaction could be completed in a much shorter reaction time.

Referring to Fig. 5, it was interesting to note that the degradation of alachlor followed pseudo-first-order kinetic at Fe^{2+} dosages between 0.001 and 0.01 mM; however, while further increasing the $[\text{Fe}^{2+}]$ (i.e., >0.03 mM), the decay of the alachlor was observed to be divided into a two-stage decay, in which a rapid initial stage was followed by a slower lag stage. Both stages followed pseudo-first-order kinetics, and the higher $[\text{Fe}^{2+}]$ resulted in faster decay rate constants in both the initial and lag reaction stages. The two-stage reaction was observed at higher $[\text{Fe}^{2+}]$, this was likely because at the initial stage of reaction, higher $[\text{Fe}^{2+}]$ could effectively react with abundant H_2O_2 and generate high level of HO^\bullet , which would then immediately react with the alachlor molecule. It was because there were no or very little intermediates existing in the solution at the beginning of the reaction. In consequence, most of the radicals would be used solely for alachlor decay. However, at the lag stage of the reaction, the high concentrations of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions became less important, since the $[\text{H}_2\text{O}_2]$ was greatly reduced and the H_2O_2 turned into the rate-determining factor. The generation rate of $[\text{HO}^\bullet]$ in this stage was lowered, while the intermediates resulting from alachlor have accumulated to a significant amount, the competition for the radicals became more critical. As a result, the decay rate constant of alachlor was observed to be reduced.

Fig. 6 compared the rate constant in initial stage (k_1) and in lag stage (k_2) in different $[\text{Fe}^{2+}]$. It was found that both constants could be linearised with very good r^2 coefficients (i.e., 0.99 for $\ln k_1$ and 0.91 for k_2). The correlations of the rate constants and $[\text{Fe}^{2+}]$ were listed below,

$$\ln k_1 = 20.943[\text{Fe}^{2+}] - 4.525 \quad (15)$$

$$k_2 = 0.058[\text{Fe}^{2+}] + 0.011 \quad (16)$$

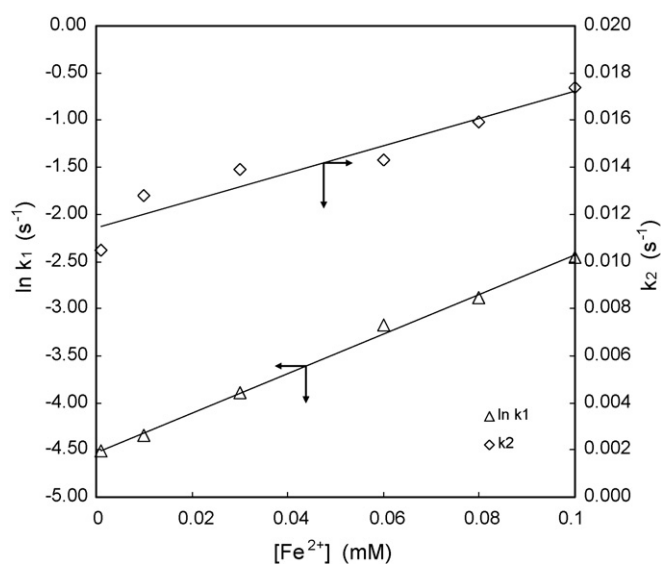


Fig. 6. The variation of the decay rate constants k_1 and k_2 with the $[\text{Fe}^{2+}]$.

Thus, the degradation of alachlor in the initial stage could be finalized as below,

$$\frac{C}{C_{t=0}} = \exp[-\exp(20.943[\text{Fe}^{2+}] - 4.525) \cdot t] \quad (\text{for } t \leq 15 \text{ s}) \quad (17)$$

while the original equation for the lag stage based on pseudo-first-order kinetics would be,

$$\frac{C}{C_{t=15\text{s}}} = \exp[-(0.058[\text{Fe}^{2+}] + 0.011)(t - 15)] \quad (\text{for } t > 15 \text{ s}) \quad (18)$$

Since the term $C_{t=15\text{s}}$ (the end of the initial stage or the beginning of the lag stage) could be determined from Eq. (17) when t equals to 15 (s), the result could be incorporated into Eq. (18). A working model for the lag stage was resulted based on k_1 and k_2 ,

$$\frac{C}{C_{t=0}} = \exp[-\exp(20.943[\text{Fe}^{2+}] - 4.525) \cdot 15] \cdot \exp[-(0.058[\text{Fe}^{2+}] + 0.011)(t - 15)] \quad (19)$$

Accordingly, Fig. 7 was plotted and depicted the time requirement for different R on the degradation of alachlor with respect to $[\text{Fe}^{2+}]$. Referring to the figure, a higher R took a longer reaction time with the same $[\text{Fe}^{2+}]$; in other words, a higher $[\text{Fe}^{2+}]$ could shorten the reaction time under the same R . For $[\text{Fe}^{2+}] < 0.01$ mM, the slope of the lines was found to be steeper. Since the mole ratio of $[\text{H}_2\text{O}_2]$ to $[\text{Fe}^{2+}]$ was very high (i.e., >1000) at this range, this indicated that the slightly increment of $[\text{Fe}^{2+}]$ would induce a significant marginal effect in shortening the reaction time. Such an effect would be gradually reduced when the $[\text{Fe}^{2+}]$ was further increased.

Fig. 7 revealed a possible approach for process optimisation if the $[\text{Fe}^{2+}]$ was used as the final controlling factor for the design (associated with the result of H_2O_2 optimisation using Fig. 4). A proper dosage of Fe^{2+} could be determined from the figure, which was critical for the cost estimation on the process design. In this study, within the test range of $[\text{Fe}^{2+}]$, the higher $[\text{Fe}^{2+}]$ would achieve higher R if the selected reaction time was the same; however, it led higher cost on the materials. Thus, the benefit of higher marginal effect at a higher mole ratio of $[\text{H}_2\text{O}_2]$ to $[\text{Fe}^{2+}]$ (i.e., lower $[\text{Fe}^{2+}]$) should be considered as a design alternative as well. Fig. 7 could provide reference information on the cost analysis in the process

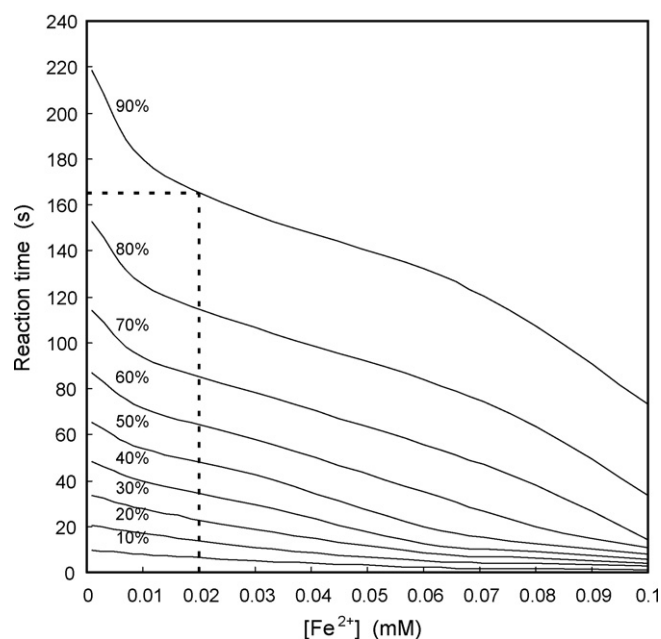


Fig. 7. Time taken for certain percentage removal of alachlor by different $[\text{Fe}^{2+}]$ with 10 mM of $[\text{H}_2\text{O}_2]$ at pH 2.58 at 253.7 nm. (The percentages shown in the figure are the removal percentage at different reaction time of the reaction.)

design. Example shown on the figure suggesting the retention time required for 90% removal of alachlor by using 0.02 mM of $[\text{Fe}^{2+}]$ would be 165 s.

4. Conclusion

The decay of alachlor by a photo-Fenton process was studied by varying process parameters including pH and concentrations of H_2O_2 and Fe^{2+} . The optimum condition of the process was observed at a pH of 2.58, 10 mM of $[\text{H}_2\text{O}_2]$, and various $[\text{Fe}^{2+}]$ depending on the cost analysis. Regarding the pH effect, the Fe(III)-hydroxyl complexes which have the highest light absorption coefficient and quantum yield for HO^\bullet radical production in the reaction was concluded to be predominant at the observed optimum pH. The removal of alachlor was generally more efficient with increasing H_2O_2 dosage. However, the reaction was retarded when the $[\text{H}_2\text{O}_2]$ was overdosed due to the scavengers of HO^\bullet by extra H_2O_2 and resulted in the formation of less reactive HOO^\bullet . When the $[\text{H}_2\text{O}_2]$ was greater than 10 mM, longer reaction time would be required to achieve the same R . In addition, the decay rate constant and the R of alachlor were found to be increased with the $[\text{Fe}^{2+}]$. Owing to the generation rate of $\text{Fe}(\text{OH})^{2+}$ speeding up by higher $[\text{Fe}^{2+}]$, more HO^\bullet would be generated in a shorter time upon the UV illumination. When the initial concentration of $[\text{Fe}^{2+}]$ was low (i.e., 0.001–0.03 mM), the decay followed a pseudo-first-order kinetic. As the concentration was higher than 0.03 mM, the two-stage first-order kinetics was observed. The rate of the initial stage was faster than the lag stage. A mathematical model with respect to different experimental parameters was successfully developed to predict the reaction in this work. The reaction time for the same R of alachlor was predictable and the corresponding design charts were depicted accordingly.

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