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Decontamination of alachlor herbicide wastewater by a continuous dosing mode ultrasound/Fe^{2+}/H$_2$O$_2$ process

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ABSTRACT

We used a ultrasound/Fe^{2+}/H$_2$O$_2$ process in continuous dosing mode to degrade the alachlor. Experimental results indicated that lower pH levels enhanced the degradation and mineralization of alachlor. The maximum alachlor degradation (initial alachlor concentration of 50 mg/L) was as high as 100% at pH 3 with ultrasound of 100 Watts, 20 mg/L of Fe^{2+}, 2 mg/min of H$_2$O$_2$ and 20°C within 60 min reaction combined with 46.8% total organic carbon removal. Higher reaction temperatures inhibited the degradation of alachlor. Adequate dosages of Fe^{2+} and H$_2$O$_2$ in ultrasound/Fe^{2+}/H$_2$O$_2$ process not only enhance the degradation efficiency of alachlor but also save the operational cost than the sole ultrasound or Fenton process. A continuous dosing mode ultrasound/Fe^{2+}/H$_2$O$_2$ process was proven as an effective method to degrade the alachlor.

Introduction

Alachlor (2-chloro-2′, 6′-diethyl-N-methoxymethylacetanilide), which has been commercially used since 1969, is a member of the chloroacetanilide family of herbicides and is used to inhibit the appearance of annual grasses and many broadleaf weeds in fields growing maize, peanut and soy bean (Tiedje and Hagedorn, 1975). Alachlor can be dissolved in water where its solubility is 240 mg/L at 25°C with moderate toxicity (Torres et al., 2009); this herbicide also has been proven to be a carcinogen by the US EPA (Group B2) and have possible harmful effects to humans (Lauga et al., 2013). Even the alachlor has been proven to be degraded by microbial, adsorption, photolysis, ozonation, or gamma radiolysis (Tiedje and Hagedorn, 1975; Liu et al., 2002; Katsumata et al., 2006; Choi et al., 2010; Qiang et al., 2010), it still can be detected in ground water wells (Chester et al., 1989). Residual pesticides in soil not only appear in the products of vegetables and fruits

but also be transferred to other areas by the underground water system to damage the biological system (Lazhar et al., 2012), so that an effective degradation of alachlor needs to be further concerned.

As the alachlor is toxic to many organisms, conventional biological remediation processes are not suitable to remove the herbicides from contaminated water and therefore alternative treatment methods are required for effective removal of the herbicides (Bagal and Gogate, 2012). Advanced oxidation process (AOP) is a well-known innovative method and has been proven in effectively degrading alachlor or other refractory pesticides, based on the sufficient production of hydroxyl radicals (·OH) in aqueous phase, due to the ·OH is a high-active radical which can easily react with unsaturated chemical structure and degrade the pesticides (Li et al., 2007; Ormad et al., 2010; Ma et al., 2010; Wantala et al., 2011; Xin et al., 2011; Lu et al., 2012). Sonolysis is a kind of AOP and used to degrade alachlor in recent years. Not only the single sonication but also the combination of Fenton's reagent, H$_2$O$_2$, ozone gas with ultrasound have been carried out to degrade the alachlor (Wayment and Casadonte, 2002;

Torres et al., 2009; Bagal and Gogate, 2012).

The combination of ultrasound and Fenton's reagent has been proven to effectively degrade different kinds of refractory compounds (Pradhan and Gogate, 2010; Meshram et al., 2010; Frontistis and Mantzavinos, 2012; Li et al., 2013). Equation (1) shows the reaction of producing ·OH in ultrasound/Fe^{2+}/H_2O_2 process, where the [)))] denotes the ultrasound. In fact, there are two pathways to produce ·OH in ultrasound/Fe^{2+}/H_2O_2 process. The first pathway is shown as Eq. (2), which is a well-known Fenton reaction and the ·OH can be easily produced at acidic condition (Ma, 2012). The second pathway is shown as Eq. (3), where the ultrasonic wave can transfer the energy into the solution phase and excite the water molecule to produce ·OH (Joseph et al., 2009). However, these two pathways are not carried out individually. As the Fe^{2+} reacts with H_2O_2, produced Fe^{3+} in Eq. (2) also reacts with residual H_2O_2 in water sample and produces $Fe-OOH^{2+}$ to quench the production of ·OH (Eq. (4)). The ultrasonic wave not only excite the water molecule to produce ·OH but also decompose the $Fe-OOH^{2+}$ spontaneously to Fe^{2+} (Eq. (5)), and the isolated Fe^{2+} can subsequently react with H_2O_2 to produce more ·OH. Therefore, as the ultrasound is operated with a combination of Fenton's reagent, the ·OH can be continuously and efficiently produced during the reactions to degrade the organic compounds. In addition, organic compounds in the vicinity of a collapsing bubble produced by ultrasonic wave may undergo pyrolysis degradation due to high local temperatures and pressures inside the cavitation bubbles (Eq. (6)) then the degradation and mineralization (Eq. (7)) of organic compounds take place.

$$Fe^{2+} + H_2O_2 +))) \longrightarrow Fe^{3+} + \cdot OH + OH^- \qquad (1)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \cdot OH + OH^- \qquad (2)$$

$$H_2O_2 +))) \longrightarrow \cdot OH + H\cdot \qquad (3)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe-OOH^{2+} + H^+ \qquad (4)$$

$$Fe-OOH^{2+} +))) \longrightarrow Fe^{2+} + \cdot OOH(fast) \qquad (5)$$
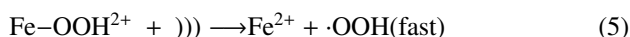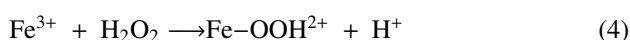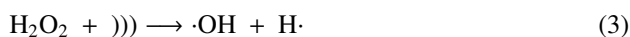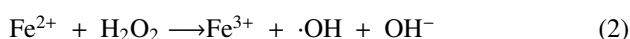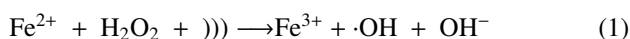
Inside bubble cavity (temperature 5000 K, 600 atm)

$$\text{Organic compounds (g)} \xrightarrow{\text{))))))}} \text{Products} \qquad (6)$$
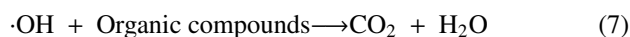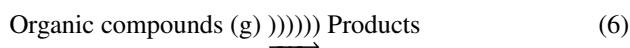
$$\cdot OH + \text{Organic compounds} \longrightarrow CO_2 + H_2O \qquad (7)$$

Even the ultrasound/Fe^{2+}/H_2O_2 process can provide sufficient ·OH production and validly degrade the refractory compounds, this process is generally conducted using a batch dosing mode, i.e., the all chemicals were added into the reactor initially, and is performed in small reactors (0.1–0.3 L). In addition, in batch dosing mode, exceed amounts of H_2O_2 and Fe^{2+} dosing into the solution in the begin of reaction cause the competition reactions among Fe^{2+}, H_2O_2 and ·OH (Li and Song, 2010) and decrease the degradation of pollutants. Therefore, a continuous dosing mode ultrasound/Fe^{2+}/H_2O_2 process was designed

in this study to degrade the alachlor. The objectives of this study were to investigate the effects of different reaction conditions such as pH, Fe^{2+} dosage, H_2O_2 dosage and reaction temperature on the degradation and mineralization of alachlor. The operational costs were also calculated for ultrasound, Fenton and ultrasound/Fe^{2+}/H_2O_2 process to understand the feasibility of this continuous dosing mode ultrasound/Fe^{2+}/H_2O_2 process in pesticide wastewater treatment.

1 Materials and methods

1.1 Standards and reagents

Analytical grade alachlor (99.8%) was purchased from the Sigma-Aldrich Company. Other chemical reagents used in this study including H_2SO_4 (>97%), NaOH (>97%), $FeSO_4\cdot 7H_2O$ (>99.5%) and an aqueous solution of hydrogen peroxide (H_2O_2, 30%, W/W in water) were of the purest grade commercially available and used without further purification. During the analytical process, potassium hydrogen phthalate ($C_8H_5KO_4$) and n-hexane (C_6H_{14}) were used as standard chemicals to determine the total organic carbon (TOC) concentration and isolate alachlor from aqueous solution via a liquid-liquid extraction procedure.

1.2 Experimental apparatus and design

A sonicator (Microson VCX 750, USA, 0–750 W) operated at 20 kHz was used. The output power of the sonicator was maintained at 100 W and the reactor was equipped with oxidation-reduction potential (ORP) and pH meters (Suntex PC-3200, Taiwan). Prior to the experiment, the ORP meter was checked with an ORP standard solution of 220 mV. The reagents of H_2O_2 and Fe^{2+} were pre-adjusted as desire concentrations then added into the reactor drop by drop with a micro-pump, which was defined as a continuous doing mode process; flow rate of H_2O_2 and Fe^{2+} were both 0.5 mL/min and total added volume for 60 min was 60 mL. Oxidation of alachlor by a continuous dosing mode ultrasound/Fe^{2+}/H_2O_2 process was carried out in a cylindrical reactor (working volume of 1 L with a temperature controller) to determine the degradation kinetics at various pH values (3–9), H_2O_2 dosing rates (1–4 mg/min), Fe^{2+} dosages (5–30 mg/L), and temperatures (15–50°C). The initial aqueous alachlor concentration was 50 mg/L, and the reaction pH was pre-adjusted using H_2SO_4 and NaOH solutions. The mixing speed of the solution was controlled at 100 r/min with a magnetic mixer to ensure the adequate mixing of the chemicals. Aeration of the reactor during the reaction was maintained at 0.2 L/min to provide sufficient dissolved oxygen.

1.3 Analytical methods

Alachlor concentration was determined using a gas chromatography/flame ionization detector (GC-FID-Varian GC 3400, Mulgarve, Victoria, Australia) equipped with a DB-1 column (30 m × 0.53 mm i.d., 1.50 μm). Before analysis with GC-FID, each 10 mL alachlor sample was shaken and extracted with 1 mL of *n*-hexane for 30 min at a mixing speed of 150 r/min. After the extraction procedure, 1 μL of the upper solvent layer was collected and injected into the GC-FID in splitless mode. The GC oven temperature was programmed to increase from 50°C (holding time 10 min) to 250°C (holding time 3 min) at a rate of 10°C/min. The injector and detector temperatures were 200 and 290°C, respectively. Nitrogen gas (used as a carrier gas, 15 mL/min), hydrogen gas (33 mL/min) and air (400 mL/min) were used for GC-FID; retention time of alachlor in GC-FID analysis was 19.367 min. Prior to sample analysis, a calibration curve was plotted using known concentrations of alachlor (between 0 and 50 mg/L) and an area response with an R^2 of 0.995; the method detection limit (MDL) of alachlor was 0.03 mg/L. Qualification of alachlor was analyzed by a gas chromatography equipped with a mass spectrometry (GC-MS-QP2010, Shimadzu, Japan) using a DB-5MS column (length 30 m, thickness 0.25 μm, diameter 0.25 mm) in the GC oven. Extraction procedures were same to above steps operated in the GC/FID. The GC oven temperature increased from 50°C (holding time 1 min) to 180°C at a ramp of 30°C/min and then increased to 280°C at a ramp of 10°C/min (holding time 10 min). The injector and detector temperatures were maintained at 250°C and 280°C, respectively. High purity (99.99%) helium was used as a carrier gas (1.5 mL/min) and the sample was analyzed in splitless mode. Mass spectra were obtained by electron-impact at 70 eV using the full-scan mode. The H_2O_2 concentration was measured using the titration with KI. The mineralization of alachlor was investigated by determining the TOC concentration using a total organic carbon analyzer (TOC-500, Shimadzu, Japan); the MDL of TOC was 0.04 mg/L.

2 Results and discussion

2.1 Comparison of ultrasound, Fenton and ultrasound/ Fe²⁺/H₂O₂ process

To investigate the feasibility of a continuous dosing mode ultrasound/Fe^{2+}/H_2O_2 process in the degradation of alachlor, this study was first carried out the alachlor degradation experiments by sole ultrasound (100 W), Fenton (continuous dosing mode, 5 mg/L Fe^{2+} and 2 mg/min H_2O_2) and ultrasound/Fe^{2+}/H_2O_2 process, individually, at pH 3 and 20°C, and compared the results of alachlor degradation, mineralization and operational costs. The

profiles of pH values during the reactions of these three experiments were insignificant (pH values were between 3.0 and 3.2, data were not shown) where the effect of pH change during the reaction on the degradation of alachlor could be ignored. As shown by **Fig. 1**, the sole ultrasound was ineffective on the degradation of alachlor; after 60 min reaction, less than 6.5% of alachlor was degraded. In sole ultrasonic process, only three possible reactions such as Eqs. (3), (6) and (7) will take place so that insufficient ·OH can be produced to degrade alachlor. As the Fenton process and ultrasound/Fe^{2+}/H_2O_2 process were carried out, 40% and 44.7% of alachlor were degraded, which was much higher than the sole ultrasonic one. This result is comparable to the observations in previous publications (Sun et al., 2007; Pradhan and Gogate, 2010; Bagal and Gogate, 2012), where the combination of ultrasound and Fenton's reagent can increase the formation of ·OH and increase the degradation of organic compounds. This fact can be further explained by Eqs. (1) to (5) where the combination of ultrasound and Fenton's reagent can continuously and efficiently produce ·OH to degrade the organic compounds.

Table 1 shows the results of alachlor degradation percentage, pseudo first-order der rate constant of alachlor degradation, contribution of mg H_2O_2 usage for degrading alachlor, TOC removal, and operational cost of three oxidation processes. It is found that the results of TOC removal by the sole ultrasound was only 3.6% and increased to 12.3% and 14.9% when the experiments were carried out by Fenton and ultrasound/Fe^{2+}/H_2O_2 processes. The usage of H_2O_2 for degrading the alachlor is substantial information as the AOP is operated. In **Table 1**, each mg H_2O_2 consumption helps the ultrasound/Fe^{2+}/H_2O_2 process to degrade 3.1 mg alachlor, which is greater than the result of Fenton process. As shown in Eqs. (1), (2), (3) and (7), the alachlor can be degraded by two reaction mechanisms such as direct thermal cleavage (inside the ultrasonic cavitation bubbles) and indirect ·OH radical oxidation (in solution phase) so that the addition of H_2O_2 effectively increased the alachlor degradation. This study
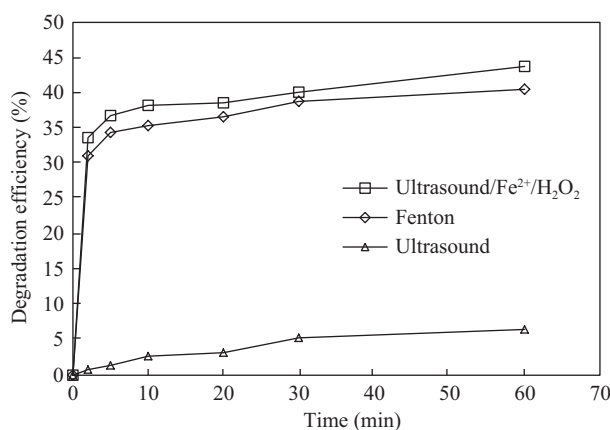

Fig. 1 Degradation of alachlor by different oxidation processes.

Table 1 Alachlor degradation of alachlor, TOC removal, and operational cost of three oxidation processes

	Alachlor degradation	k ($\times 10^{-3}$min^{-1})	Alachlor degradation (mg/mg H$_2$O$_2$)	TOC removal	Operational cost (USD/kg alachlor removal)
Ultrasound	6.5%	1.1	–	3.6%	1795
Fenton	40.0%	2.2	0.4	12.3%	691
Ultrasound/Fe^{2+}/H$_2$O$_2$	44.7%	3.5	3.1	14.9%	1140

also tried to calculate the operational costs of three different oxidation processes. In ultrasound process, the only operational cost is the electric bill and the results (based on the standard electric fee in Taiwan) shown in **Table 1** indicated that removing 1 kg alachlor by the ultrasound needed 1795 USD, which was much higher than Fenton and ultrasound/Fe^{2+}/H$_2$O$_2$ processes. As the Fenton process was carried out, operational cost (including chemical Fe^{2+} and H$_2$O$_2$) for removing 1 kg alachlor decreased to 691 USD. When the ultrasound was combined with Fenton, even the alachlor degradation was increased, the total operational cost for removing 1 kg alachlor increased to 1140 USD. This is a good example that the synergetic effect between Fenton's reagent and ultrasound can enhance the treatment efficiency for degrading refractory compounds but an expensive operational is achieved in.

2.2 Effect of pH

It is well-known that the pH level is a key parameter for removing refractory compounds by AOP. Most studies (Bremner et al., 2008; Oturan et al., 2008; Ma et al., 2010) adopted acidic conditions for the ultrasound/Fe^{2+}/H$_2$O$_2$ process for attaining satisfactory degradation efficiency, and the solution pH is an important parameter affecting the kinetics of the ultrasound/Fe^{2+}/H$_2$O$_2$ process. Based on pH changing, the nature of organic compound, the scavenge of ·OH by H$^+$ and the solubility of iron can affect the pollutant treatments (Ma, 2012). Bagal and Gogate (2012) tried to use the ultrasound/Fe^{2+}/H$_2$O$_2$ process to degrade the alachlor and found that pH 3 was the optimal pH level and the degradation efficiency of alachlor reached 86.4%. As pH level was adjusted at 2 or 6, the degradation of alachlor decreased to 85.9% and 71.4%, respectively. Özdemir et al. (2011) used the ultrasound/Fe^{2+}/H$_2$O$_2$ process to decolorize the Dye Orange 127 wastewater found a comparable result, where the decolorization efficiency at pH 3 was greater than that at pH 2.5 and 3.5. This could be explained by two reasons. As the pH value of solution is too low, H$^+$ will catch the ·OH to form H$_2$O and decrease the concentration of ·OH then the degradation efficiency of organic compound decreases. As the pH is greater than pH 4, the produced Fe^{3+} from Fenton reaction easily precipitate so that the formation of ·OH decreases. Nevertheless, the wastewater itself seldom reaches the suitable pH levels. Therefore, determination of optimal reaction pH value is still important for degradation of different target compounds under ultrasound/Fe^{2+}/H$_2$O$_2$ system. In this study, the effect of pH on alachlor degradation by ultrasound/Fe^{2+}/H$_2$O$_2$ process was investigated and the results are shown in **Fig. 2** and **Table 2**.

Table 2 Alachlor degradation and TOC removal in ultrasound/Fe^{2+}/H$_2$O$_2$ process at different pH levels

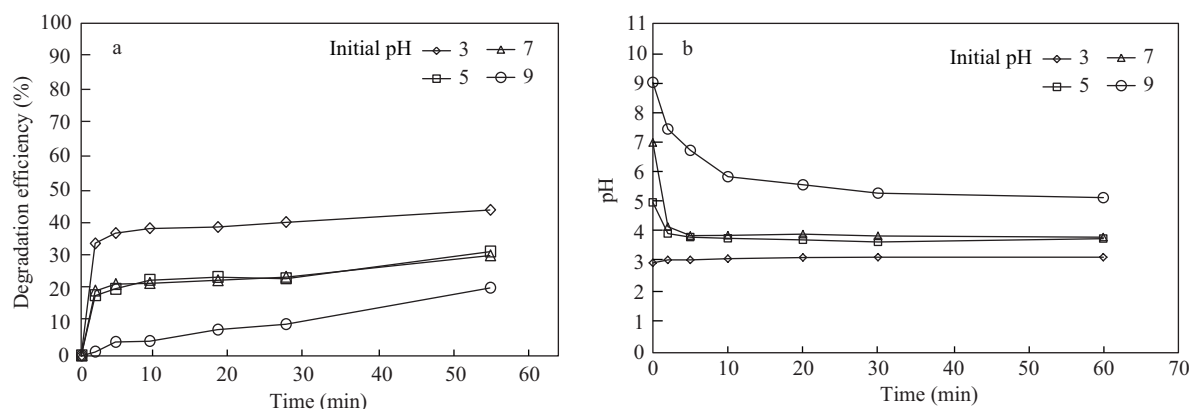| pH	Alachlor degradation	k ($\times 10^{-3}$min^{-1})	Alachlor degradation (mg/mg H$_2$O$_2$)	TOC removal
3	44.7%	3.5	3.1	14.9%
5	31.2%	2.7	2.2	9.5%
7	30.1%	2.3	2.0	8.1%
9	20.3%	2.2	1.4	6.2%

Fig. 2 Degradation of alachlor by the ultrasound/Fe^{2+}/H$_2$O$_2$ process at different pH levels (a) and pH variation with time (b).

Figure 2a shows the profiles of pH values and degradation of alachlor in continuous dosing mode ultrasound/Fe^{2+}/H_2O_2 process at different initial pH levels and 20°C. **Figure 2b** indicates that the pH values decreased at initial pH 5, 7 and 9 based on the addition of $FeSO_4$ (used as Fe^{2+}). As the initial pH levels were 5 and 7, the final pH values were almost 3.8 after 60 min reaction. With the initial pH level was 9, final pH was 5.2. In **Fig. 2a**, the operational condition was designed at 100 W, 5 mg/L Fe^{2+} and 2 mg/min H_2O_2 and the results indicated that the degradation of alachlor at acidic condition was better than at basic condition; alachlor degradation percentages at pH 3, 5, 7 and 9 were 44.7%, 31.2%, 30.1% and 20.3%, respectively, which was an example that lower pH was adequate for the ultrasound/Fe^{2+}/H_2O_2 process. At acidic condition, the organic compounds could easily pass through the cavitation bubbles, decomposed by ·OH in film zone and thermal pyrolysis in gas bubbles. As the compound exists in molecular nature, it is easier to pass through the cavitation bubbles thus giving a better degradation result. In addition, when the solution's pH is greater than 4.0, Fe^{2+}/Fe^{3+} will precipitate in the form of hydroxide, which inhibits the ·OH formation and decreases the degradation of pollutants. At pH 5–8, a higher number of ·OH recombine to form H_2O_2, which leads to a decrease in the number of hydroxyl radicals available for the desired degradation reaction (Bagal and Gogate, 2012). This study also found that the degradation of alachlor at pH 5 and 7 were both approximately 30%, which was similar to the results found in the literature (Katsumata et al., 2006; Bagal and Gogate, 2012).

Table 2 shows the alachlor degradation and TOC removal in ultrasound/Fe^{2+}/H_2O_2 process at different pH levels. Based on the results of alachlor degradation (20.3%–44.7%) and TOC removal (6.2%–14.9%), it is found that less than one third of degraded alachlor were mineralized to CO_2 and most alachlor and its by-products were still present in the wastewater. Even the treatment efficiency of alachlor shown in **Table 2** was unsatisfied, re-

sults of alachlor degradation percentage, pseudo first-order rate constant, mg H_2O_2 usage for degrade mg alachlor, and TOC removal all showed that pH 3 was better than other pH levels, especially when the initial pH levels were greater than 5, TOC removals were all lower than 10%. Hence, more addition of Fe^{2+} and H_2O_2 may be useful to enhance the degradation of alachlor.

2.3 Effect of Fenton's reagent

In Fenton reaction, the reaction between Fe^{2+} and H_2O_2 can produce satisfactory amount of ·OH (Özdemir et al., 2011) so that Sun et al. (2007) and Meshram et al. (2010) both proposed that the addition of Fe^{2+} and H_2O_2 in sonication were profitable to product more ·OH for enhancing the degradation of organic pollutants. However, Li and Song (2010) and Özdemir et al. (2011) found that the exceed addition of Fe^{2+} would react with ·OH to produce Fe^{3+} and quench the reaction between ·OH and organic pollutant then the degradation rate decreased. In addition, exceed addition of Fe^{2+} would produce much amounts of $Fe(OH)_3$ so that the iron-contained sludge after AOP treatment might be increased. Not only Fe^{2+} but also H_2O_2 is an important factor in wastewater treatment by AOP. Sun et al. (2007), Li and Song (2010) and Özdemir et al. (2011) all discussed the effect of H_2O_2 addition on the degradation of organic pollutants and found that the increase of H_2O_2 concentration in the ultrasound/Fe^{2+}/H_2O_2 process were useful to increase the degradation efficiency but additional amounts of H_2O_2 would catch the ·OH and decrease the degradation efficiency of organic pollutants. Based on above description, adequate addition of Fe^{2+} and H_2O_2 is a key parameter in carrying out the ultrasound/Fe^{2+}/H_2O_2 process.

As shown in **Table 3**, the degradation of alachlor increased from 16.2% to 100% when the Fe^{2+} dosage increased from 0 to 30 mg/L with 2 mg/min H_2O_2 addition at 20°C, while after 60 min reaction were in a range of 9.8% to 76.6%, which were much lower than the results

Table 3 Alachlor degradation and TOC removal in ultrasound/Fe^{2+}/H_2O_2 process with different Fenton's reagents

		Alachlor degradation	k ($\times 10^{-3}$min^{-1})	Alachlor degradation (mg/mg H_2O_2)	TOC removal	Operational cost (USD/kg alachlor removal)
Fe^{2+} (mg/L)[a]	0	16.2%	2.2	0.4	12.2%	3086
	5	44.7%	3.5	3.1	14.9%	1140
	10	88.0%	21.8	3.6	18.3%	591
	20	99.7%	54.7	4.3	46.8%	541
	30	100%	–	4.5	42.8%	559
H_2O_2 (mg/L)[b]	0	28.9%	2.3	–	21.1%	944
	1	92.8%	16.5	1.2	24.5%	438
	2	99.7%	54.7	4.3	46.8%	541
	3	99.8%	53.7	3.9	28.9%	674
	4	81.7%	23.5	2.8	27.9%	985

[a] H_2O_2: 2 mg/min; [b] Fe^{2+} 20 mg/L.

of ultrasound/Fe^{2+}/H_2O_2 process. This fact indicates that the combination of ultrasound and Fenton's reagent is useful to enhance the degradation efficiency of alachlor. In addition, the alachlor degradation rate constants increased with increasing Fe^{2+} dosages. As 30 mg/L Fe^{2+} was added into the solution, residual alachlor was lower than the MDL with 2 min reaction so that the rate constant could not be calculated. The results of TOC removal and each mg of H_2O_2 usage on the contribution of alachlor degradation both showed that the addition of 20 mg/L Fe^{2+} was the optimal condition as the alachlor was degraded by a continuous dosing mode ultrasound/Fe^{2+}/H_2O_2 process. When the treatment was carried out without Fe^{2+}, i.e. ultrasound/H_2O_2 process, it is found in **Table 3** that the operational cost for removing 1 kg alachlor was 3086 USD. The operational cost decreased with an increase of Fe^{2+} dosage and the result of 20 mg/L Fe^{2+} condition (541 USD) was almost one sixth only than that of the ultrasound/H_2O_2 process. **Table 3** also shows the results in alachlor degradation experiments at different H_2O_2 dosages with 20 mg/L Fe^{2+}. The degradation of alachlor with 1 to 3 mg/min H_2O_2 additions was resembled and all were greater than 90%. In addition, the operational cost for removing 1 kg alachlor with H_2O_2 dosage 1 mg/min was only 438 USD, which was lower than other experimental designs. Even 1 mg H_2O_2/min was the inexpensive one, mineralization of alachlor was only half of the result with 2 mg H_2O_2/min addition. As the H_2O_2 dosages increased to 3 or 4 mg/min, higher operational cost with lower TOC removal were observed so that the condition of 20 mg/L Fe^{2+} and 2 mg H_2O_2/min should be the optimal choice.

2.4 Effect of temperature

Reaction temperature is a key parameter in organic pollutant treatment by the sonochemical process. The energy transferred from a sonicator to reactor leads to the increase of solution temperature and this increase of temperature causes either positive or negative effect to the degradation of organic compounds (Joseph et al., 2009). Frontistis and Mantzavinos (2012) tried to degraded 17α-ethynylestradiol by the ultrasound/Fe^{2+}/H_2O_2 process and proposed that the degradation was favored at the lower temperatures where a complete conversion was achieved after 30 min reaction. The fact that the degradation decreased with increasing liquid bulk temperature was believed to be associated with the effect of temperature on both the bubble formation energy threshold and the intensity of bubble implosion. However, Sun et al. (2007) and Li et al. (2013) found that the increase of reaction temperature was effective on the enhancement of organic compound degradation. Therefore, five different reaction temperatures were carried out to investigate the effect of temperature on the degradation of alachlor in the ultrasound/Fe^{2+}/H_2O_2 process. **Figure 3** shows the results of alachlor degradation by a continuous dosing

mode ultrasound/Fe^{2+}/H_2O_2 process at pH 3, 2 mg/min H_2O_2, 20 mg/L Fe^{2+} and temperatures of 15 to 50°C. It is indicated that the degradation of alachlor at 20°C was significantly higher than other temperatures in the first 2 min reaction. After 60 min reaction, the degradation efficiencies of alachlor were 92.4% to 99.7% when the reaction temperatures were carried out at 20 to 40°C, and only 79% and 85.5% at 15°C and 50°C, respectively. Meshram et al. (2010) and Ma (2012) showed that although the higher reaction temperatures were useful for forming more cavitation bubbles to degrade the organic pollutants, the increase in temperature also led to the collapse of bubbles, so that the increase in temperature would decrease the degradation efficiency for organic pollutants. In addition, Joseph et al. (2009) proposed that the sonication influences favorably both the oxidation and reduction reactions of the targeted pollutant. However, some pollutant may exhibit temperature dependence for an efficient degradation process. Therefore, increase in temperature is useless to increase the degradation of alachlor in this study. **Table 4** shows the results of alachlor degradation and TOC removal in the ultrasound/Fe^{2+}/H_2O_2 process at different temperatures. The highest TOC removal (46.8%) was at 20°C, which indicated that almost half of degraded alachlor was fully mineralized to CO_2. As the temperature increased to 30°C and 50°C, TOC removal decreased to 41.2% and 25.9%; rate constant of alachlor degradation reduced to 47.2×10^{-3} min^{-1} and 14.7×10^{-3} min^{-1}, respectively. This reveals that an adequate reaction temperature not only enhances the degradation efficiency and rate constant of alachlor but also helps to mineralize the alachlor to CO_2 for reducing the toxicity of treated wastewater. Usage of H_2O_2 for degrading alachlor at different reaction temperatures shows a comparable trend to alachlor degradation and TOC removal, where each mg H_2O_2 contributed 4.3 mg alachlor degradation at 20°C and reduced to 1.8 mg at 50°C. Therefore, the reaction temperature of 20°C was found as the optimal temperature.
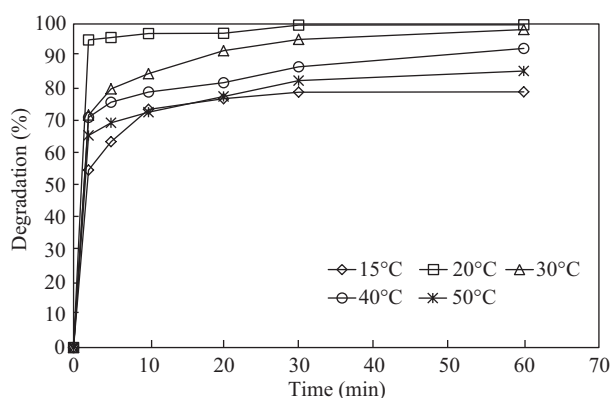

Fig. 3 Degradation of alachlor by the ultrasound/Fe^{2+}/H_2O_2 process at different reaction temperatures.

Table 4 Alachlor degradation and TOC removal in ultrasound/Fe^{2+}/H_2O_2 process at different temperatures

Temperature	Alachlor degradation	k ($\times 10^{-3}$ min^{-1})	Alachlor degradation (mg/mg H_2O_2)	TOC removal
15	79.0%	11.2	4.1	29.5%
20	99.7%	54.7	4.3	46.8%
30	98.3%	47.2	2.3	41.2%
40	92.4%	22.2	2.0	32.4%
50	85.5%	14.7	1.8	25.9%

3 Conclusions

The degradation of alachlor in aqueous solution were investigated by the ultrasound, Fenton and a continuous dosing mode ultrasound/Fe^{2+}/H_2O_2 process under different experimental conditions. More than 99% of alachlor degradation efficiency combined with 46.8% mineralization was achieved in 60 min reaction for the initial alachlor concentration of 50 mg/L and H_2O_2 and Fe^{2+} dosages of 2 mg/min and 20 mg/L, respectively, at pH 3 and 20°C.

Degradation efficiency was enhanced by an increase in H_2O_2 and Fe^{2+} dosages, but an increase in reaction temperature had a negative impact on degradation. The kinetics study indicated that the degradation kinetics of alachlor followed the pseudo first-order kinetics model, with the effects of the experimental parameters on the degradation of alachlor resulting in comparable reaction rate constants. Operational costs of a continuous dosing mode ultrasound/Fe^{2+}/H_2O_2 process based on 1 kg alachlor degradation were obtained, where the adequate addition of H_2O_2 and Fe^{2+} was assistant to increase the degradation of alachlor with economically operational cost.

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