Degradation of azinphos-methyl and chlorpyrifos from aqueous solutions by ultrasound treatment

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ABSTRACT

Azinphos-methyl and chlorpyrifos are the organophosphorus pesticides which pose serious threats to the environment including their detrimental effect on humans and, therefore, their removal from the environment is a must. Hence, in the present paper the ultrasound technique was applied to remove the above-mentioned hazardous compounds. For this, the effect of influential parameters such as pH, initial pesticide concentration, frequency, electric power and treatment time on the ultrasound degradation of azinphos-methyl and chlorpyrifos was well investigated and elucidated. The results obtained showed that azinphos-methyl and chlorpyrifos were effectively and rapidly degraded by the ultrasound technique. Thus, the operating optimal conditions (initial pH 9, initial pesticide concentration 1 mg/L, frequency 130 kHz, electric power 500 W and treatment time 20 min) lead to a degradation of 78.50% for azinphos-methyl and of 98.96% for chlorpyrifos with in 20 min of contact time. Two multiple regression-based equations were derived to describe the degradation process of the pesticides by the ultrasound treatment. The result of this study showed that the polynomial equations satisfactorily described the behavior of the present process for various operating conditions.

1. Introduction

The increasing presence of synthetic pesticides in surface water, groundwater and drinking water [1] due to their wide spread use in agriculture and hygiene is a recognized problem worldwide. Among the synthetic pesticides, the organophosphorus pesticides (OPPs) are the most frequently and widely used ones. Recent studies have shown that OPPs have strong inhibitory activity against cholinesterase [2], reproductive toxicity [3], cytotoxicity [4], immunotoxicity [5] endocrine-disrupting effects [6] and genotoxicity [7]. In addition, the joint effect of different pesticides could present higher adverse effects on human health [1] Therefore, the removal of OPPs, especially in drinking water, is an urgent need. Azinphos-methyl and chlorpyrifos (Fig. 1) are widely used pesticides to control most annual grasses and many broad-leaved weeds.

Nowadays, different methods are used to remove OPPs from aqueous solutions such as physical [8,9], photo-catalysis, biological methods [10], irradiation techniques through X-rays [11] gamma-rays [12] and chemical methods [13–15]. Also, the physicochemical methods based on the production and use of hydroxyl radicals, named advanced oxidation processes (AOPs) have shown to be very efficient to remove different organic compounds from aqueous solutions [1–3]. Among the different existing AOPs, during the last years, ultrasound has been effectively applied to degrade a wide variety of pollutants in wastewater [16,17]. The ultrasound process is an attractive technique, since it is chemical free and does not produce secondary pollutants. Furthermore, it is not affected by the toxicity and low biodegradability of the compounds [18]. In the ultrasound process, the main mechanism responsible for pollutant degradation is the acoustic cavitation which causes pyrolysis reactions in water (inside the bubble and/or at the bubble-bulk...
interface) and the generation of free radicals [19] such as OH, H, O and OOH. These free radicals mediate reactions at the bubble-bulk interface and/or in the bulk liquid [20] and are able to oxidize almost all the toxic contaminants present in the environment [21].

Azinphos-methyl and chlorpyrifos are two important and widely used OPPs, so the objective of the present study was to investigate the possible use of ultrasound irradiation as an alternative method for the removal of such compounds from aqueous solutions.

2. Experimental section

2.1. Chemicals

Azinphos-methyl emulsion (20%) and chlorpyrifos emulsion (40.8%) were purchased from Sigma-Aldrich (Germany). Hexane (99%), dichloromethane, acetone and methylacetate were obtained from Merck (Germany). All other reagents were of analytical grade and used as received without further treatment.

2.2. Experimental procedure

The ultrasound process was studied as a function of pH (4, 7 and 9), initial pollutant concentration (1 and 2 mg/L), frequency (35 and 130 KHz), electric power (300 and 500 W) and treatment time (20, 40 and 60 min). The reactions were carried out in an open stainless steel ultrasonic bath (length: 35 cm, wide: 25 cm, height: 54 cm, flow type batch; TI-H-5, ELMA, Germany) (Fig. 2). All tests were performed at 25.0 ± 1.0 °C and under atmospheric pressure. In all experiments, an aqueous solution (250 mL) of the considered pesticide was prepared at the desired concentration, according to the experiment, and then poured into the ultrasonic bath. The pH value of the prepared pesticide solution was adjusted with 1.0 N HCl or 1.0 N NaOH at the beginning of the experiment and remained uncontrolled during the ultrasound irradiation.

2.3. GC analysis

Gas chromatography with flame ionization detector (GC–FID; Varian CP-3800 GC with MS trap detector Varian Saturn 2200, run in El mode) was used to determine the pesticide concentration in the samples. The GC was fitted with a 30 m DB–5 capillary column (internal diameter: 0.25 mm; thickness: 0.25 μm). The method started at 150 °C, which was held for 2 min, then ramped to 270 °C at a rate of 25 °C/min, followed by an increase to 270 °C (held for 2 min). The inlet was
operated in splitless mode. Helium (99.99%) was used as the carrier gas at a flow rate of 1 mL/min. For the extraction of the pesticides the dispersive liquid–liquid micro extraction (DLLME) technique was used. A 5-mL sample was mixed with 500 µL methanol, 70 µL chloroform and 10 µL internal standards (azinphos-methyl or chlorpyrifos). The mixture was then centrifuged for 5 min at 3500 rpm. Then, the supernatant was discarded and the droplets settled at the bottom of the conical test tube were collected by means of a pipette and 1 µL injected into the GC.

2.4. Non-linear regression analysis-based modeling

In this study, two multiple regression-based equations were derived for modeling the degradation of azinphos-methyl and chlorpyrifos in the bulk solution. For the comparative purpose, the experimental data were appraised by a licensed multiple regression software package (Data Fit® V9.0.59, Oakdale Engineering, PA, USA), containing 298 two-dimensional (2D) and 242 three-dimensional (3D) non-linear regression models. The regression analysis was performed based on the Levenberg-Marquardt methodology with double precision as similarly conducted in previous studies [27–50]. The non-linear convergence criteria were selected for the following values of the solution preferences: regression tolerance = 1 × 10–10, maximum number of iterations = 250 and diverging non-linear iteration limit = 10. In the computational analysis, the stepwise selection procedure (SSP) was performed as the combination of the forward selection and backward elimination procedures for variable selection process within the framework of Data Fit® software. The SSP begins with a forward step (with no variables in the model). After the forward step, the p values of the variable coefficients are re-examined and any now insignificant variables are removed in a backward step. This process continues until no variables are either added or removed from the model. The SSP is more generally popular than either the forward or backward procedures.

The experimental data on degradation of azinphos-methyl and chlorpyrifos were imported directly from Microsoft® Excel, used as an open database connectivity data source and then the non-linear regression analysis was performed. As regression models were solved, they were automatically sorted according to the goodness-of-fit criteria into a graphical interface on the DataFit® numeric computing environment. Moreover, regression variables (,..., and ), standard error of the estimate (SEE), coefficient of multiple determination (R²), adjusted coefficient of multiple determination (Ra²) and number of non-linear iterations (NNI) were computed to appraise the performance of the regression models. Furthermore, t-ratios and the corresponding p-values were also calculated for the evaluation of the significance of the regression coefficients. An alpha (α) level of 0.05 (or 95% confidence) was used to emphasize the statistical significance of the model components.

3. Results and discussion

3.1. Effect of contact time and initial concentration on pesticide degradation

As shown in Fig. 3, operating at an initial pH of 7, an ultrasonic frequency of 130 kHz, an electric power of 500 W and an initial pesticide concentration of 1 and 2 mg/L, the removal percentage of both pesticides increased very quickly during the first 20 min and from there onwards it proceeded more slowly until 60 min. Then, it remained constant (data not shown). Also, chlorpyrifos was almost totally removed in 20 min (Fig. 3). However, azinphos-methyl was more resistant to the degradation by the ultrasound treatment (around 60% in 20 min for both concentrations). As for the initial pesticide concentration, the removal efficiency for both pesticides decreased with the increase in the initial pesticide concentration (Fig. 3).

3.2. Effect of pH on pesticide degradation

As can be observed in Fig. 4, the removal of azinphos-methyl was slightly higher at pH 9 and no significant differences were observed for chlorpyrifos removal at the three tested pH values. The other parameters were kept at: initial pesticide concentration 1 mg/L, frequency 130 kHz, electric power 500 W and treatment time 20 min.

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**Table 1**

<table>
<thead>
<tr>
<th>Rank</th>
<th>Regression model</th>
<th>SEE</th>
<th>SR</th>
<th>RSS</th>
<th>R²</th>
<th>Ra²</th>
<th>NNI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Modeling of azinphos-methyl</td>
<td>0.0254</td>
<td>−4.16</td>
<td>0.022</td>
<td>0.998</td>
<td>0.997</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>degradation (Y1)</td>
<td>0.0419</td>
<td>−0.034</td>
<td>0.059</td>
<td>0.995</td>
<td>0.994</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Modeling of chlorpyrifos</td>
<td>0.0504</td>
<td>−0.213</td>
<td>0.089</td>
<td>0.992</td>
<td>0.991</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>degradation (Y2)</td>
<td>0.0345</td>
<td>2.28</td>
<td>0.042</td>
<td>0.996</td>
<td>0.995</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.0384</td>
<td>−0.024</td>
<td>0.0501</td>
<td>0.995</td>
<td>0.995</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.1016</td>
<td>−0.466</td>
<td>0.3610</td>
<td>0.967</td>
<td>0.961</td>
<td>4</td>
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**Table 2**

<table>
<thead>
<tr>
<th>Independent and original variables</th>
<th>SE</th>
<th>t-ratio</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pesticide concentration</td>
<td>8.037 × 10⁻³</td>
<td>132.381</td>
<td>0.00000</td>
</tr>
<tr>
<td>Contact time (×2 = t: min)</td>
<td>2.523 × 10⁻⁴</td>
<td>−12.265</td>
<td>0.00000</td>
</tr>
<tr>
<td>Ultrasound frequency (×3 = f: kHz)</td>
<td>8.460 × 10⁻⁴</td>
<td>−4.321</td>
<td>0.00013</td>
</tr>
<tr>
<td>Electric power (×5 = P: W)</td>
<td>4.019 × 10⁻⁵</td>
<td>−7.970</td>
<td>0.00000</td>
</tr>
<tr>
<td>Reaction pH (×5 = pH)</td>
<td>2.523 × 10⁻³</td>
<td>−5.561</td>
<td>0.00000</td>
</tr>
<tr>
<td>= Constant term</td>
<td>3.079 × 10⁻²</td>
<td>−10.191</td>
<td>0.00000</td>
</tr>
</tbody>
</table>

* Standard error.

b p-values < 0.05 were considered to be significant.

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3.3. Effect of ultrasound frequency on pesticide degradation

The frequency is the most important variable in an ultrasound process and it is reported that irradiation at higher frequencies (e.g. ≥ 100 kHz) increases the reaction rates. However, a definitive explanation for this has not been found [22]. As shown in Fig. 5, pesticide removal increased with the increase of the ultrasound frequency, the optimal frequency being 130 kHz.

Table 3
Model components and regression variable results obtained from the best-fit (first-order polynomial model) model for chlorpyrifos.

<table>
<thead>
<tr>
<th>Independent and original variables</th>
<th>SE$^a$</th>
<th>t-ratio</th>
<th>p-value$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pesticide concentration ($x_1 = C_0$: mg/L)</td>
<td>$1.106 \times 10^{-2}$</td>
<td>92.463</td>
<td>0.00000</td>
</tr>
<tr>
<td>Contact time ($x_2 = t$: min)</td>
<td>$3.470 \times 10^{-4}$</td>
<td>-3.914</td>
<td>0.00041</td>
</tr>
<tr>
<td>Ultrasound frequency ($x_3 = f$: kHz)</td>
<td>$1.164 \times 10^{-4}$</td>
<td>-1.252</td>
<td>0.21917</td>
</tr>
<tr>
<td>Electric power ($x_4 = P$: W)</td>
<td>$5.528 \times 10^{-5}$</td>
<td>-4.408</td>
<td>0.00010</td>
</tr>
<tr>
<td>Reaction pH ($x_5 = pH$)</td>
<td>$3.470 \times 10^{-3}$</td>
<td>-4.454</td>
<td>0.00009</td>
</tr>
<tr>
<td>Constant term</td>
<td>$4.236 \times 10^{-2}$</td>
<td>-16.167</td>
<td>0.00000</td>
</tr>
</tbody>
</table>

$^a$ Standard error.
$^b$ p-values < 0.05 were considered to be significant.

Fig. 7. (a) Agreement between the experimental data and the model outputs for azinphos-methyl ($R^2 = 0.998$), and (b) change of residual error of the first-order polynomial equation ($Y_1$).

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3.4. Effect of electric power on pesticide degradation

To discuss the effect of the electric power on pesticide degradation, the optimal ultrasound frequency (130 kHz) was applied to each run and the other parameters were kept at: initial pesticide concentration 1 mg/L, pH 9 and treatment time 20 min. The optimal electric power for pesticide degradation was 500 W (Fig. 6). The increase in pesticide degradation with the increase in electric power could be due to the increase in temperature and pressure inside the bubbles which further increases the degradation rate of the target compound and/or the generation of free radicals [23].

3.5. Modeling of degradation of azinphos-methyl and chlorpyrifos

In this study, a non-linear regression-based analysis was conducted for modeling the degradation of azinphos-methyl and chlorpyrifos. In this approach, one exponential model and two first-order polynomial models were derived for both azinphos-methyl and chlorpyrifos. Results of the non-linear regression analysis are summarized in Table 1. Regression variable results including the standard error of the estimate (SEE), the t-statistics and the corresponding p-values for the best-fit regression model (herein first-order polynomial models) are presented in Table 1. The polynomial models (Y1 and Y2 for azinphos-methyl and chlorpyrifos, respectively) derived as a function of five input variables [Y = Ce = f, initial pesticide concentration (∝1 = C0: mg/L), contact time (∝2 = t: min), ultrasound frequency (∝3 = f: kHz), electric power (∝5 = P: W), reaction pH (∝5 = pH)] are expressed as follows:

\[ Y_1 = \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_4X_4 + \beta_5X_5 + \beta_0, \]

\[ Ce(\text{azinphos-methyl}) = (1.06)(C0) - \left(3.09 \times 10^{-3}\right) \\
\times (t) - \left(3.66 \times 10^{-4}\right)(f) - \left(3.20 \times 10^{-4}\right) \\
\times (P) - (0.014)(\text{pH}) - 0.314, \]

Fig. 8. (a) Agreement between the experimental data and the model outputs for chlorpyrifos ($R^2 = 0.996$), and (b) change of residual error of the first-order polynomial equation (Y2).
It is reported that the t-ratio represents the ratio of the estimated parameter effect to the estimated parameter standard deviation. Moreover, the p-value is used as a useful statistical tool to check the significance of each of the coefficients. The variable with the larger t-ratio and with the smaller p-value is considered as the more significant parameter in the regression model [24,25]. It is also noted that values that yield Prob(t) factors (or p-values) >0.9 can be omitted until all remaining factors are calculated at once [24–26]. In the study, the significance of each coefficient was determined by Student’s t-test and p-values, which are presented in Tables 2 and 3.

Based on the absolute effects (t-ratio × SE) of the independent variables, the initial pesticide concentration (C1 = 500 mg/L) has more importance than the other variables for the derived first-order polynomial models for both azinphos-methyl and chlorpyrifos in the modeling of pesticide degradation. According to the regression variable results (i.e., t-statistics and the corresponding p-values) presented in Tables 2 and 3, the resulting regression models indicated that the 5 parameters contributed to the final result with different weights and none of them can be neglected without affecting the outcome of the model. Finally, in Figs. 7 and 8 the agreement between the experimental data and the model outputs for azinphos-methyl and chlorpyrifos, respectively, is shown. Looking at the model outputs and deviations (residual errors) of the developed multiple regression-based formulations, it can be concluded that the proposed polynomial equations satisfactorily described the behavior of the present process for various operating conditions.

4. Conclusions

The high ultrasound wave frequency technique was successfully applied to the degradation of the pesticides azinphos-methyl and chlorpyrifos. The results showed that pesticide degradation decreased with the increase in initial pollutant concentration and the decrease in treatment time and frequency. The increase in pH did not affect pesticide degradation. Based on the absolute effects of the independent variables, initial pesticide concentration had more importance with the highest absolute effect compared to the other variables for the derived first-order polynomial models for both pesticides degradation. The result of this study showed that the polynomial equations satisfactorily described the behavior of the present process for various operating conditions. The present study demonstrated that ultrasonic irradiation is a promising process for the removal of azinphos-methyl and chlorpyrifos from aqueous solutions. Further research is needed to determine the degradation products and assess their toxicity.

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