Check for updates

Evaluation of wet air oxidation variables for removal of organophosphorus pesticide malathion using Box-Behnken design

Melike Isgoren, Erhan Gengec and Sevil Veli

ABSTRACT

This paper deals with finding optimum reaction conditions for wet air oxidation (WAO) of malathion aqueous solution, by Response Surface Methodology. Reaction conditions, which affect the removal efficiencies most during the non-catalytic WAO system, are: temperature (60–120 °C), applied pressure (20–40 bar), the pH value (3–7), and reaction time (0–120 min). Those were chosen as independent parameters of the model. The interactions between parameters were evaluated by Box-Behnken and the quadratic model fitted very well with the experimental data (29 runs). A higher value of R^2 and adjusted R^2 (>0.91) demonstrated that the model could explain the results successfully. As a result, optimum removal efficiency (97.8%) was obtained at pH 5, 20 bars of pressure, 116 °C, and 96 min. These results showed that Box–Behnken is a suitable design to optimize operating conditions and removal efficiency for non-catalytic WAO process. The EC_{20} value of raw wastewater was measured as 35.40% for malathion (20 mg/L). After the treatment, no toxicity was observed at the optimum reaction conditions. The results show that the WAO is an efficient treatment system for malathion degradation and has the ability of converting malathion to the non-toxic forms.

Key words | advanced oxidation, modeling, response surface methodology, toxicity, wet air oxidation

Melike Isgoren (corresponding author)
Erhan Gengec
Department of Environmental Protection,
Kocaeli University,
41275 Kartepe,
Kocaeli,
Turkey
E-mail: *melike.isgoren@kocaeli.edu.tr*

Sevil Veli
Department of Environmental Engineering,
Kocaeli University,
41100 Izmit
Kocaeli,
Turkey

ABBREVIATIONS

WAO	Wet air oxidation
OPs	Organophosphorus pesticides
EC	Effective concentration
ARH	Activated rice husk
PAC	Powdered activated carbon
NF	Nano filtration
RSM	Response surface methodology
BBD	Box–Behnken design
2FI	Two-factor interaction

INTRODUCTION

The organophosphorus pesticides are a group of very effective and widely used pesticides in the world. In 2001, organophosphorus insecticides represented 70% of the total insecticide usage in the United States and malathion was the most widely used of all (32–44% of total organophosphorus insecticide usage) (Zhang & Pagilla 2010). Malathion (diethyl dimethoxythiophosphorylthio succinate) which was registered in 1956, is a highly toxic organophosphorous insecticide and it is abundantly used in agricultural, industrial and public health areas to kill insects, ants, aphids, bagworm, beetle, cotton leaf worm, mosquito, lice, etc. by inhibiting cholinesterase enzyme (Kumar *et al.* 2014). On the other hand, the experiments of embryo development and *in vitro* fertilization indicated that malathion was an endocrine disruptor and could interfere with reproductive functions. Generally, malathion include a P = S group and naturally occurring oxidants in aquatic media readily oxidize this group to oxons (P = O) which has 61 times more toxicity than malathion (Kralj *et al.* 2007; Kumar *et al.* 2014). Therefore, treatment of malathion and

doi: 10.2166/wst.2016.479

Downloaded from https://iwaponline.com/wst/article-pdf/75/3/619/455391/wst075030619.pdf
by guest

its degradation products (such as malaoxons, isomalathion, etc.) is crucial.

There are a few research reports in the literature that aimed elimination of malathion with advanced treatment systems. Kralj *et al.* (2007) studied mineralization of malathion during UV photolysis and TiO_2 photocatalysis and they achieved to eliminate 75% of theoretically expected P = S groups in 240 min. Likely, Kadam *et al.* (2014), used N-doped TiO_2 nanoparticles in the presence of UV light and they reported 80% malathion mineralization. Yu *et al.* (2010) designed Au-Pd co-modified TiO_2 nanotube film photocatalyst and sustained 98.2% in the photocatalytic reaction in 240 min. Chenna *et al.* (2016) studied effectiveness of hydrogen peroxide photolysis on the degradation of malathion and they reported the complete removal of malathion. Adsorption is another alternative method used by researchers to remove malathion from water. Kumar *et al.* (2014) used activated rice husk (ARH) and powdered activated carbon (PAC) as adsorbent in the adsorption of malathion. But the ARH was not successful as PAC and exhaustive capacity of adsorbents were found as 16.13 and 21.74 mg/g, respectively. Naushad *et al.* (2013) tried De-acidity FF-IP resin and achieved 94% malathion removal with the exhaustive capacity of adsorbent was reported as 3.5 mg/g. (Abdelaty *et al.* 2015) prepared an activated carbon from palm, paper and plastic waste mixture and exhaustive capacity of adsorbent was calculated as 32.1 mg/g. Fly ash of thermal power plant used by Singh *et al.* (2010) for the malathion adsorption and 95% removal was recorded used carbon-cryogel composite as effective removal material. 591 mg/g adsorption capacity was obtained. Ultrasonic treatment, irrigation with UV and Gamma are the other methods applied by Zhang & Pagilla (2010), Shayeghi *et al.* (2012) and Mohamed *et al.* (2009). But these methods applied limited concentrations (0.5–1 mg/L) of malathion which were extracted from the sources of pesticide like apple juice or tealeaves. Another approach followed by the researchers for the elimination of malathion from water is combining two treatment methods. Zhang & Pagilla (2010) combined nano filtration (NF) and photo-Fenton to treat malathion. They used three types of NF membrane. Although membranes could reduce malathion concentration to 0.6 mg/L, low flux rate reported. With photo-Fenton that applied to high concentration effluents of NF, desired levels of malathion mineralization could achieved (0.1 mg/L). Moreira *et al.* (2012) treated the pesticide containing wastewater with combined biological and solar driven TiO_2/UV, TiO_2/H_2O_2/UV and UV, H_2O_2/UV, Fe^{2+}/H_2O_2/UV and Fe^{2+}/H_2O_2 systems. Considering all treatment systems photo-Fenton reaction achieved better results (86% mineralization).

All the advanced treatment techniques used for malathion treatment have their own advantages and limitations. Complexity of the processes, usage of additional chemicals, causing secondary contaminants, getting the micro pollutants in more intensive form and also taking the contaminants from liquid to solid phase and not being feasible from the economic aspects are the disadvantages of these techniques. Despite the disadvantages, application of advanced treatment technologies are inevitable for hazardous wastes treatment. Wet air oxidation (WAO) has been proven to be one of the most efficient technologies to convert highly concentrated, toxic and hazardous organic compounds to CO_2, H_2O and other innocuous end-products under high temperature and high pressure using oxygen as the oxidant without the emissions of NOx, SO_2, HCl, dioxins, furans, fly ash, etc. (Yang *et al.* 2010). This process is enclosed and has very limited interaction with the environment. WAO is one of the few processes that doesn't return pollution in one form to another (Debellefontaine & Foussard 2000). And there is no chemical added to the system, which have to be separated from water after treatment. In the literature, non-catalytic WAO of phenol, aromatic alcohols, carboxylic acids, formaldehyde and refractory non-biodegradable organic wastewaters were extensively studied before (Stüber *et al.* 2005; Benitez *et al.* 2011; Baroutian *et al.* 2015). However, there is no report about degradation of malathion by WAO.

In the study, Box–Behnken design (BBD) was used for experimental design and data analysis. BBD has the advantage of requiring fewer experiments (29 batches for four variables) than would a full factorial design (256 batches). Another advantage of the BBD is that it does not contain combinations for which all factors are simultaneously at their highest or lowest levels. So these designs are useful in avoiding experiments performed under extreme conditions, for which unsatisfactory results might occur (Kobya *et al.* 2014).

The novelty of this study is the degradation of malathion by the WAO process, optimization of reaction conditions by BBD, and evaluation of the toxicity value before and after treatment for the first time. Moreover, the effects of the variables such as pressure, temperature, pH and reaction time on removal efficiencies were examined by using a batch method. Also, byproduct evaluations were realized by gas chromatography–mass spectrometry (GC-MS).

Downloaded from https://iwaponline.com/wst/article-pdf/75/3/619/455391/wst075030619.pdf
by guest

MATERIAL AND METHODS

Material and samples

Technical grade malathion of 99% purity was obtained from Shenzhen Longshine Chemical Co. Ltd. Ultra-pure water was used for making the synthetic samples. pH adjustments were done with 0.1 M NaOH and 0.1 M H_3PO_4 and measured by pH meter (WTW Inolab pH 720 model). Acetone and acetonitrile (ACN) that were used to prepare malathion sample solution were high-performance liquid chromatography (HPLC) grade. All standards (99% purity) were purchased from Dr. Ehrenstorfer Reference Materials, used to set the method with HPLC-UV for the determination of malathion.

According to the variation of processes in pesticide manufacturing industry, characteristics of wastewater vary extensively. In this study, for the purpose of malathion treatment, synthetic malathion solution was prepared with the 20 mg/L malathion concentration representing the mean concentration value existing in plants that is given in the literature (Zhang & Pagilla 2010).

Wet oxidation procedure

The batch reactions were performed in a hastelloy 0.6 L batch reactor equipped with a magnetically driven stirrer, digitally controlled oil circulated heating jacket, sampling system, and the monometer. Reactor was supplied from Bushi Glassuster, Switzerland. In the standard procedure of non-catalytic wet oxidation 400 mL of sample solution was poured into the reactor. The reactor was closed completely, the circulator was opened and then waited until the internal temperature of the reactor reached to the desired level. After that, the reactor was filled by dried air for obtaining the reaction pressure value that was determined by preliminary experiments. This point was the beginning of the reaction in all experiments. All samples were taken dependently from the system time by means of a special sampling apparatus without changing internal pressure of the reactor. All samples were filtered by 0.45 μm filter paper and analyzed as soon as possible with HPLC-UV.

Analytical procedures

Determination of malathion quantities in the samples were done with Agilent 1260 Infinity HPLC with a UV detector. A 250 mm long C-18 capillary column (Eclipse XDB, Agilent) with an internal diameter of 4.6 mm was used to separate compounds. A 50:50 v/v mixture of ultra-pure water: acetonitrile was used as a mobile phase. Flow rate was set to 1 mL/min (Roe & Lemley 1997). The R^2 values of individual regression lines, which was obtained by measuring diluted series of malathion were 0.9992.

For the byproduct evaluation, samples were injected to the Agilent 5973 GC-MS equipped with DB5, capillary column (30 m, 0.25 mm; film thickness 0.25 mm). Samples were prepared by the extraction with C_{18} SPE cartridges and concentrated in Toluene (%99 Purity, Supra Solve Merck). The injector temperature was held at 280 °C. The oven started at 90 °C, and the temperature was increased with a gradient of 10 °C/min until 290 °C and held constant for 5 min. The injection volume was 1 μL in all cases. Within the aim of byproduct observation, analyses were done at the scan mode to see all the compounds and the results were evaluated with the Agilent Mass Spectral Library. These analyses were done for only qualitative results, not quantitative.

Toxicity tests

Toxicity tests were performed according to the Biotox TM flash method (Aboatox Oy, Turku, Finland), which is based on the bioluminescent response of *Vibrio fischeri* bacteria and incorporates an automatic correction for color and turbidity (Lannalainen *et al.* 1999; Lappalainen*et al.* 2001; Karlsson *et al.* 2010). Luminescence was measured using a high performance Sirius Luminometer and light output was recorded automatically by FB12 Software (Berthold Detection Systems, Pforzheim, Germany). Prior to measurement, freeze-dried *Vibrio fischeri* were rehydrated in reagent diluent (2% NaCl) at 4 °C for at least 30 min and then stabilized at 15 °C for approximately 1 h in a dry cooling block. The samples were prepared by mixing 9 mL sample with 1 mL 20% NaCl and adjusting the pH to 7.0 ± 0.2 if the sample pH was not between 6.0 and 8.5. The samples were subsequently diluted with 2% NaCl solution to obtain a dilution series (1:2, 1:4, 1:8, 1:16, 1:32 and 1:64). Toxicity measurements were performed by initially placing 300 μL diluted samples into luminometer cuvettes (Sarstedt 55.476) and incubating at 15 °C for at least 10 min. Following introduction into the Sirius Luminometer, 300 μL bacterial suspensions were automatically injected into the sample, and bioluminescence was measured, then repeated after 30 min so that the relationship between end point toxicity and peak toxicity could be elucidated. A correction factor was applied based on the response obtained from the non-toxic reference sample (2% NaCl). The inhibition percentage

Downloaded from https://iwaponline.com/wst/article-pdf/75/3/619/455391/wst075030619.pdf
by guest

and the EC_{20} and EC_{50} values were calculated according to the ISO standard method 11348-3 (ISO 2010), where the initial luminescence reading is replaced with the peak value observed immediately after addition of bacteria to the sample.

The experimental design and data analysis

Response surface methodology (RSM) is used for improving and optimizing the processes, which is a collection of mathematical and statistical techniques. The main advantage of this technique is to provide opportunity for evaluating the relative significance of several affecting factors in the presence of complex interactions (Kobya *et al.* 2009; Khuri & Mukhopadhyay 2010). The BBD is experimental design, which is used generally with RSM to fit a model by least squares technique. BBD was used as experimental design to describe the effects of three process independent variables (pressure, initial pH, time and temperature). The number of runs (N) required for the development of BBD is defined as $N = 2k(k - 1 + C_0)$, (where k is number of factors and C_0 is the number of central points) (Ferreira *et al.* 2007). BBD has the advantage of requiring fewer experiments (29 batches for four variables) instead of a full factorial design (81 batches). Process factors and their levels are presented in Table 1. The independent variables' ranges and levels were determined from preliminary experiments, which give minimum and maximum removal efficiency of malathion, for a well-defined model.

RESULTS AND DISCUSSION

Results of statistical analysis

Linear, two-factor interaction (2FI), quadratic and cubic models were used in this study in order to obtain the appropriate regression equations. Results indicated that the quadratic model is in good agreement with results. A higher value of R^2 (0.91) demonstrated that the model could explain the response successfully. The quadratic equation model for predicting the optimal conditions can be shown according to Equation (1):

$$y = \beta_0 + \sum_{i-1}^{k} \beta_i x_i + \sum_{i-1}^{k} \beta_{ii} x_i^2 + \sum_{i-1}^{k-1} \sum_{i-1}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

where the predicted response (y), is therefore correlated to the set of regression coefficients (β): the intercept (β_0), linear (β_1, β_2, β_3), interaction (β_{12}, β_{12}, β_{23}), and quadratic coefficients (β_{11}, β_{22}, β_{33}), k, is the number of factors analyzed and optimized in the experiment and ϵ, is the random error.

The estimated coefficients of functions are given in Equation (2). The following regression models were applied to examine both individual and synergistic effects of pressure (x_1), temperature (x_2), time (x_3) and pH (x_4) in terms of coded factors. Positive and negative signs in front of the terms mean a synergistic effect and antagonistic effect, respectively. The pressure, temperature, and time had a positive influence on the removal on the contrary of the pH.

$$\begin{aligned}\text{Malathion removal (\%)} = {} & +35.56 + 2.65 \times x_1 + 32.11 \times x_2 \\ & + 21.24 \times x_3 - 0.74 \times x_4 - 1.64 \times x_1 \times x_2 - 0.18 \times x_1 \times x_3 \\ & - 1.45 \times x_1 \times x_4 + 14.99 \times x_2 \times x_3 - 3.01 \times x_2 \times x_4 \\ & - 3.81 \times x_3 \times x_4 + 0.58 \times x_1^2 + 21.51 \times x_2^2 + -6.45 \times x_3^2 \\ & - 4.14 \times x_4^2 \end{aligned} \quad (2)$$

Analysis of variance (ANOVA) for quadratic model was presented in Table 2. The statistical significance of quadratic models was checked by the Fisher variation test (F test) and model terms were evaluated by the probability (P value) with 95% confidence level. F value of the model (9.61) implies the significance of model. There is only a 0.01% chance that a 'model F value' could occur due to noise. Values of 'Prob > F' less than 0.0500 indicate that model terms are significant, and values greater than 0.1000 indicate that the model terms are not significant.

Actual values, which were measured response data for each run, and the predicted values that calculated from the model and generated by using the approximating functions (Equation (2)) lay close to the diagonal line in Figure 1. This situation shows that developed model was adequate for the prediction of each response.

Table 1 | Process variables and their levels

Factor	Name	Units	−1 Actual	Mean	+1 Actual
x_1	Pressure	bar	20	30	40
x_2	Temperature	°C	60	90	120
x_3	Time	min	0	60	120
x_4	pH	–	3	5	7

Effect of reaction conditions

Effect of reaction conditions, pressure, temperature, pH and reaction time on WAO was studied (Suranjana *et al.* 2008). The actual designs of this work were presented in Table 3 and 3D surface plots in Figure 2 visualize the effects of

Downloaded from https://iwaponline.com/wst/article-pdf/75/3/619/455391/wst075030619.pdf
by guest

Table 2 | ANOVA results for BBD model

Source	Sum of squares	df	Mean square	F value	Prob > F	Remarks
Model	22,939.46	14	1,638.53	9.61	<0.0001	significant
x_1	84.27	1	84.27	0.49	0.4936	
x_2	12,376.48	1	12,376.48	72.56	<0.0001	
x_3	5,412.80	1	5,412.80	31.74	<0.0001	
x_4	6.60	1	6.60	0.04	0.8469	
$x_{1\times}x_2$	10.82	1	10.82	0.06	0.8048	
$x_{1\times}x_3$	0.12	1	0.13	<0.001	0.9787	
$x_{1\times}x_4$	8.38	1	8.38	0.05	0.8278	
$x_{2\times}x_3$	899.10	1	899.10	5.27	0.0376	
$x_{2\times}x_4$	36.30	1	36.30	0.21	0.6516	
$x_{3\times}x_4$	58.06	1	58.06	0.34	0.5689	
x_1^2	2.16	1	2.16	0.01	0.9121	
x_2^2	3001.63	1	3001.63	17.60	0.0009	
x_3^2	269.51	1	269.51	1.58	0.2293	
x_4^2	111.22	1	111.22	0.65	0.4329	
Residual	2,387.82	14	170.56			
Lack of Fit	2,386.83	10	238.68	962.43	<0.0001	significant
Pure Error	0.99	4	0.25			
Cor. Total	25,327.28	28				

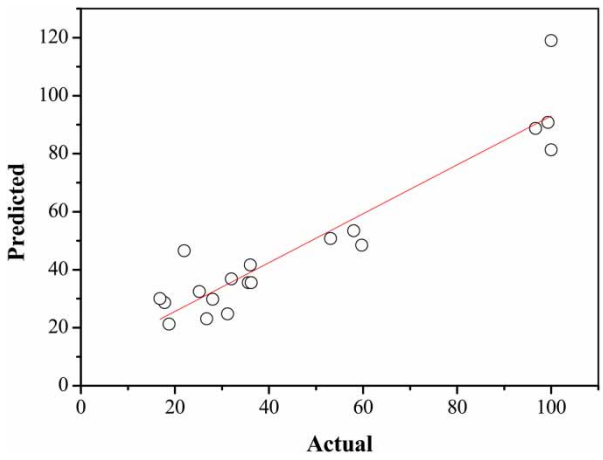


Figure 1 | Comparisons of predicted and experimental values.

experimental factors on removal efficiencies of malathion. In addition, to examine the effects of all factors on response, the perturbation plot shows how the response changes as each factor moves from the chosen reference point, with all other factors held constant at the reference value. In Figure 3, a reference point is chosen at the middle of the design space.

As seen in Figure 3, the positive influence of the variables on removal efficiencies were changed as temperature > time > pressure. On the other, the pH had a negative influence on the removal efficiency.

The system pressure is one of the most important parameters in WAO. It is clear that the increasing of pressure (from 20 bar to 40 bar) causes increasing of removal efficiencies as seen in Equation (2) and Table 3 (16.81% (Run 22) to 25.21% (Run 1)) when all factors held constant except pressure (Garg *et al.* 2010). In addition, run 8 (40 bar) and run 20 (20 bar) showed similar trend at 60 °C, 60 min, pH 5. However, very low increasing of removal efficiencies was observed at runs 15 and 16 (120 °C, 60 min, pH 5) with the same pressure changes. The reason of this result is that almost complete degradation of malathion (99%) occurred at 20 bar and there is no need for excess of the oxygen. These results show that higher total pressure causes higher malathion removal efficiency. When the total pressure of the system increases, the mass transfer of O_2 into liquid phase increases, causing the higher dissolved O_2 level. In this way, formation of strong oxidation species (O_2, HO_2, etc.) which are responsible for the oxidation of persistent organics in the liquid phase, become easy (Yang *et al.* 2010; Benitez *et al.* 2011). Pressure is also essential for WAO systems, to force organics to remain in the liquid phase and prevent organics from vaporizing at high temperatures.

Downloaded from https://iwaponline.com/wst/article-pdf/75/3/619/455391/wst075030619.pdf
by guest

Table 3 | Experimental design of experiments by BBD

Run	Pressure (bar)	Temperature (°C)	Time (min)	pH (−)	Removal efficiencies (%)
1	40	90	60	7	25.21
2	30	60	60	7	26.77
3	30	120	60	3	97.1
4	30	120	60	7	100
5	30	90	120	7	36
6	30	120	120	5	100
7	30	90	60	5	35.6
8	40	60	60	5	28.01
9	40	90	120	5	58
10	30	90	60	5	35.6
11	30	90	0	3	12.41
12	20	90	120	5	59.72
13	30	60	120	5	31.2
14	30	90	60	5	35.6
15	20	120	60	5	96.66
16	40	120	60	5	99.34
17	30	60	60	3	11.82
18	30	90	60	5	34.8
19	30	90	0	7	10.56
20	20	60	60	5	18.75
21	20	90	0	5	13.01
22	20	90	60	7	16.81
23	30	90	60	5	36.2
24	40	90	60	3	32.01
25	40	90	0	5	12
26	30	60	0	5	13.17
27	30	120	0	5	22
28	20	90	60	3	17.82
29	30	90	120	3	53.09

Another extremely important factor in WAO process is temperature. According to Arrhenius' law, the reaction gets faster when the reaction temperature gets higher (Peng *et al.* 2008). The effect of temperature was examined in the runs 2 and 4, 6 and 13, 3 and 17, 15 and 20, 16 and 8, when all factors held constant except the reaction temperature. As seen in runs 2 and 4 (30 bar, 60 min, pH 7), when the temperature increased from 60 °C to 120 °C, malathion degradation efficiency increased from 26% to 100%. All results of these group experiments showed that when the reaction temperature is 60 °C, only a part of malathion degradation occurred. However, if the reaction temperature is 120 °C, almost all of malathion was degraded

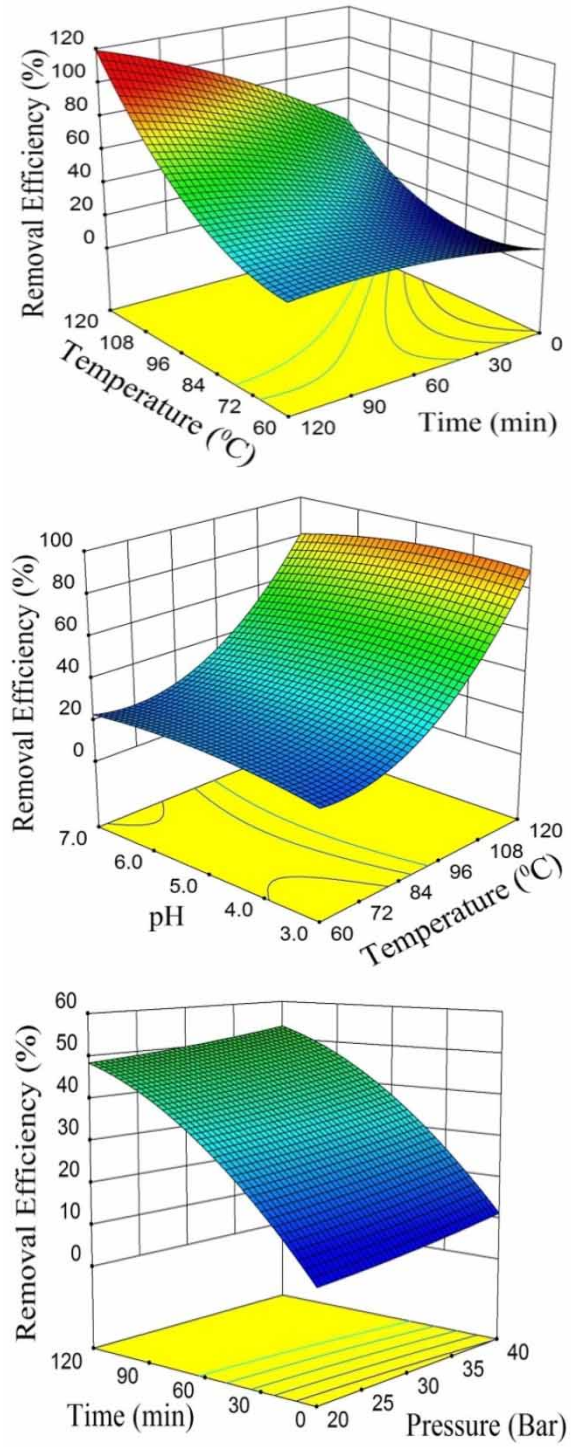


Figure 2 | Effects of the variables on malathion removal efficiencies (with 20 ppm malathion concentration, at different reaction conditions).

in a short time with the changing proportions according to the other reaction conditions. Effect of temperature on the malathion degradation can be seen clearly from the Figures 2 and 3.

Downloaded from https://iwaponline.com/wst/article-pdf/75/3/619/455391/wst075030619.pdf
by guest

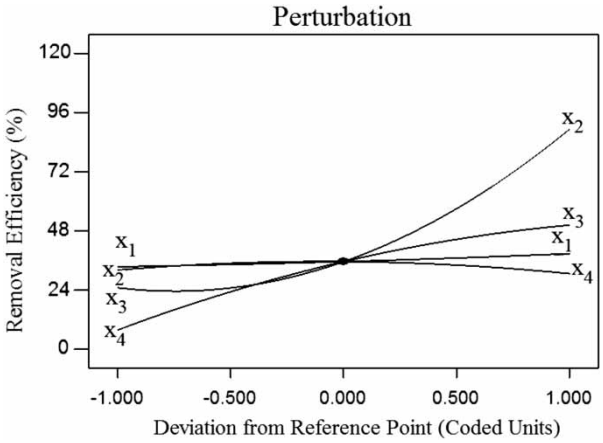


Figure 3 | Perturbation graph for removal efficiencies (x_1: pressure, x_2: temperature, x_3: time, and x_4: pH).

The researchers reported that a rapid degradation of organics occurs at higher temperatures, but when the reaction temperatures are low, degradation rate becomes slower and much longer reaction times would be required (Gomes *et al.* 2008; Baroutian *et al.* 2015). When the literature reviewed for the non-catalytic wet air oxidation process of malathion, 99% removal efficiency is reported (Copa & Momont 1995). But the temperature that was used in past applications was between 200 and 280 °C. It is much greater than our applied temperature that also causes more energy consumption and is not sufficient for economic aspects.

In our study, during the time to reach higher temperatures (90 °C or 120 °C), 10–15% malathion degradation was observed. These results showed that the partial degradation of malathion happened in the system without addition of external oxygen. This phenomenon probably occurs due to the combination of hydrolysis and oxidation processes caused by the oxygen, which is available in the reactor headspace. Moreover, these results show good agreement with literature (Dudala *et al.* 2014).

The effect of pH is another investigated parameter, which has the undeniable effects on the oxidation reactions. The results showed that decreasing of pH cause increasing of removal efficiencies. When the pressure, temperature and reaction time were held constant for each couple of runs (1 and 24; 2 and 17; 3 and 4; 5 and 29; 22 and 28), malathion was more degraded in the lower pH value. For example, the malathion removal efficiencies decreased from 26.77% to 11.82% for the pH value of 7 and 3 (runs 2 and 17).

However, as seen from Figures 2 and 3 when compared to other parameters, pH has the lowest influence on the removal of malathion, especially on the experiments with low efficiencies (runs 1 and 24, 22 and 28, etc.). Besides that, pH adjustment has some disadvantages such as causing high chemical costs, operational difficulties and disposal limits at low and high pH.

Optimization results

The optimization processes include maximizing and/or minimizing of dependent and/or independent variables and responses. Primarily, for analyzing the effect of each variable on response, the appropriate model was established (Equation (2)). Then the goals were selected as maximizing removal efficiency and minimizing the other experimental conditions except pH, which were selected in range. Considering these goals, optimum removal efficiency (97.8%) was obtained at pH 5, 20 bars of pressure, 116 °C, and 96 min (Table 4).

Toxicity results

The toxicity levels of wastewater were measured by kinetic luminescent bacteria test. The light emission was measured and recorded from the moment of dispensing of the bacterial suspension to the sample until the maximum value has been reached and after a contact time of 30 min. The ratios of inhibitory effect (Figure 4) and EC_{20} (effective concentration which resulted in 20% light reduction compared to the control sample) values (Figure 5) were measured by means of dilution series. As mentioned in the experimental section, the monitoring of toxicity levels were realized by dilution of

Table 4 | Variables' level and optimization results according to goals

		Limit		Weight			
Name	**Goal**	**Lower**	**Upper**	**Lower**	**Upper**	**Importance**	**Optimization results**
Pressure (Bar)	Minimize	20	40	1	1	3	20
Temperature (°C)	Minimize	60	120	1	1	3	116
Time (min)	Minimize	0	120	1	1	3	96
pH (–)	In range	5	7	1	1	3	5
Removal efficiency (%)	Maximize	10.56	100	5	1	5	97.8

Downloaded from https://iwaponline.com/wst/article-pdf/75/3/619/455391/wst075030619.pdf
by guest

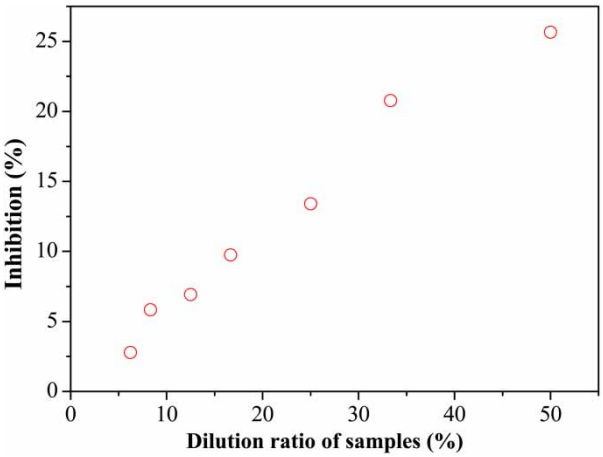


Figure 4 | Inhibition rate of 20 mg/L malathion based on dilution ratio of samples (dilution of malathion samples were realized with 2% NaCl solution to obtain a dilution series).

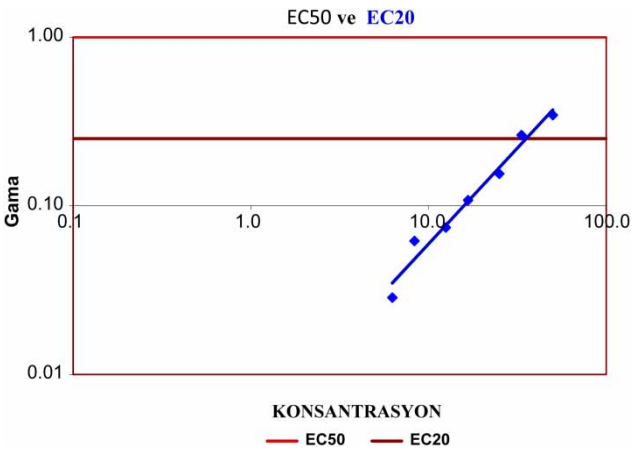


Figure 5 | EC_{50} and EC_{20} plot of 20 mg/L malathion sample.

malathion sample (20 mg/L) with 2% NaCl solution to obtain a dilution series (1:2, 1:4, 1:8, 1:16, 1:32 and 1:64).

For evaluation of the relationship between concentration and inhibitory effect by using a linear regression technique, the gamma values (ratio of light lost), Γ, were calculated for each dilution level of the test sample after 30 min using Equation (3):

$$\Gamma_{30} = \frac{\overline{H_t}}{100 - H_t} \tag{3}$$

where H_t is the inhibitory effect of a sample after the contact time (30 min). EC_{20} for the 20 mg/L malathion solution was calculated as 35.40% by means of the gamma values (Figure 4).

After treatment at optimum reaction conditions (pH 5, 20 bars of pressure, 116 °C and 96 min), EC_{20} value of sample was measured as near 0%. Figure 6 gives the inhibition rate (%) vs. dilution factor of treated sample. These data showed

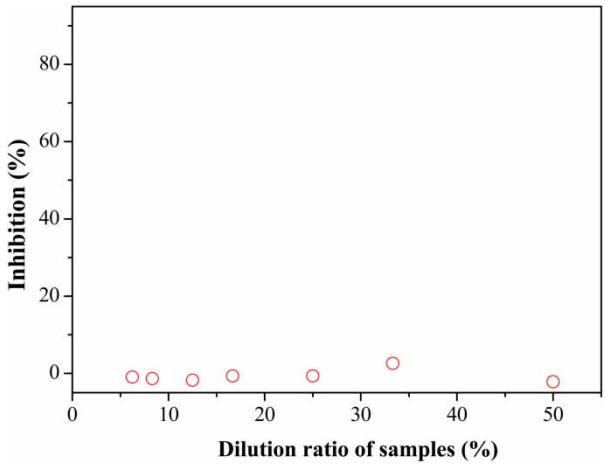


Figure 6 | Inhibition rate of sample (after WAO treatment in optimum conditions) based on dilution ratio of samples.

that at the end of the runs, malathion is completely removed and byproducts which have toxicity higher than malathion (malaoxon, izomalathion, etc.) is not formed or formed in very low quantities. The toxicity results prove that the WAO is an important alternative for treatment of malathion and it is also crucial in converting malathion to the non-toxic forms different from the water treatment techniques given in the literature (Kralj *et al.* 2007).

Non-catalytic wet oxidation kinetics

A first-order reaction depends on the concentration of only one reactant and the first order rate with respect to a reactant A is:

$$-\frac{d[A]}{d_t} = k[A] = r \tag{4}$$

where the A, is reactant concentration and k is rate constant which has units of 1/s, and arranging it with the integration we obtained the equation below:

$$\ln[A] = -kt + \ln[A]_0 \tag{5}$$

By plotting ln[*A*] vs. time gives the straight line with a slope of −k. As seen in Figure 7, which are the results of experiments made in different temperatures, malathion reduction rates in non-catalytic WAO were found to be first-order with high values of R^2 (>0.99). The k_1, k_2, k_3, for 60 °C, 90 °C, 120 °C were calculated as 0.002 1/min, 0.006 1/min, 0.049 1/min, respectively.

On the other hand, based on the data obtained for the removal kinetics at different oxidation temperatures,

Downloaded from https://iwaponline.com/wst/article-pdf/75/3/619/455391/wst075030619.pdf
by guest

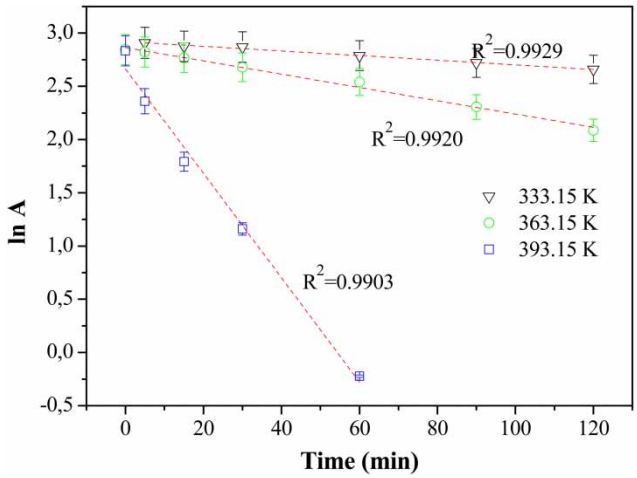


Figure 7 | First order kinetics of malathion degradation in different reaction temperatures in WAO (reaction conditions; 20 mg/L malathion conc., 20 bar pressure, stirring at 400 rpm).

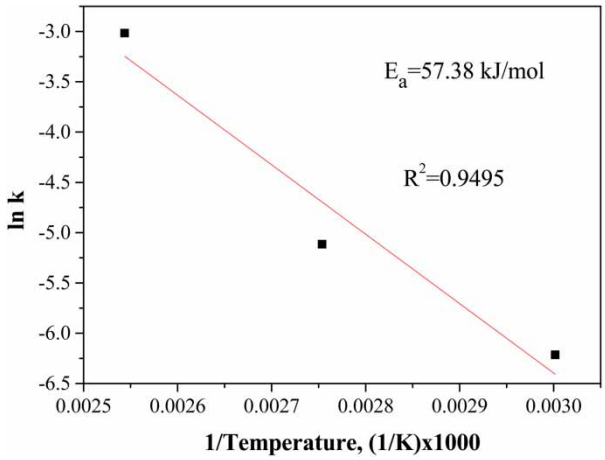


Figure 8 | Temperature dependence of malathion WAO: Arrhenius parameters for WAO of malathion.

thermodynamic parameters can be found by using the Equation (6):

$$k = A \times \exp\left(\frac{-Ea}{RT}\right) \quad (6)$$

where k is the first order reaction rate constant (in 1/min), Ea, is the activation energy (in kJ/mol), and A is the pre-exponential factor (in 1/min).

Determining the activation energy from values of k, observed in different temperatures, is possible by plotting the ln k vs. 1/T, where the T is temperature in Kelvin. This plot gives a straight line having the $-E_a/R$ value as a slope. For the wet oxidation of malathion reaction, the value of *Ea* was found as 57.38 kJ/mol (Figure 8).

Byproduct evaluation

Byproducts of the samples, treated at optimum reaction conditions, analyzed with GC-MS at scan mode for qualitative determination. Byproducts, given by the Agilent Spectral Library with high spectrographic fit (>90%), were malathion-*O*-analog, 2-methoxycarbonyl-1-methylvinyl dimethyl phosphate ($C_7H_{13}O_6P$), which are not observed in the sample before the oxidation process.

CONCLUSION

In this study, WAO process was applied to removal of malathion. The selected process variables (pressure, temperature, time, and pH) were designed and analyzed by BBD. Results indicated that the quadratic model is consistent. A higher value of R^2 (0.91) demonstrated that the model could explain the responses successfully. Model has given the optimum removal efficiency (97.8%) obtained at pH 5, 20 bars, 116 °C, and 96 min. These results showed that BBD is a suitable method to optimize operating conditions in WAO. In addition, toxicity tests show that WAO system converts the malathion to non-toxic forms which led to possible discharge of wastewater to natural sources. These results showed that WAO process is an efficient system in removal of malathion.

ACKNOWLEDGEMENTS

The authors thank Kocaeli University, Scientific Research Project Funding (KOUBAP) for their financial support (Project number: 2013/073). The authors have declared no conflict of interest.

REFERENCES

Abdelaty, M., Abdullah, Z., Al-tamrah, S. A., Abdel, A. & Soylak, M. 2015 Activated carbon from waste as an efficient adsorbent for malathion for detection and removal purposes. *Journal of Industrial and Engineering Chemistry* **32**, 336–344.

Baroutian, S., Smit, A.-M., Andrews, J., Young, B. & Gapes, D. 2015 Hydrothermal degradation of organic matter in municipal sludge using non-catalytic wet oxidation. *Chemical Engineering Journal* **260**, 846–854.

Benitez, F. J., García, J., Acero, J. L., Real, F. J. & Roldan, G. 2011 Non-catalytic and catalytic wet air oxidation of pharmaceuticals in ultra-pure and natural waters. *Process Safety and Environmental Protection* **89** (5), 334–341.

Chenna, M., Messaoudi, K., Drouiche, N. & Lounici, H. 2016 Study and modeling of the organophosphorus compound

Downloaded from https://iwaponline.com/wst/article-pdf/75/3/619/455391/wst075030619.pdf
by guest

degradation by photolysis of hydrogen peroxide in aqueous media by using experimental response surface design. *Journal of Industrial and Engineering Chemistry* **33**, 307–315.

Copa, W. M. & Momont, J. A. 1995 Wet air oxidation of energetics and chemical agent surrogates. *Journal of Energetic Materials* **13** (3-4), 235–258.

Debellefontaine, H. & Foussard, J. N. 2000 Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe. *Waste Management* **20** (1), 15–25.

Dudala, P. S., Dhakhwa, S. & Garg, A. 2014 Biodegradability enhancement of synthetic pulping liquor (generated from sugarcane Baggase digestion) by non-catalytic wet oxidation process. *Journal of Environmental Chemical Engineering* **2** (2), 1182–1185.

Ferreira, S. L. C., Bruns, R. E., Ferreira, H. S., Matos, G. D., David, J. M., Brandão, G. C., da Silva, E. G. P., Portugal, L. A., dos Reis, P. S., Souza, A. S. & dos Santos, W. N. L. 2007 Box-Behnken design: an alternative for the optimization of analytical methods. *Analytica Chimica Acta* **597** (2), 179–186.

Garg, A., Mishra, I. M. & Chand, S. 2010 Oxidative phenol degradation using non-noble metal based catalysts. *CLEAN – Soil, Air, Water* **38** (1), NA–NA.

Gomes, H. T., Machado, B. F., Ribeiro, A., Moreira, I., Rosário, M., Silva, A. M. T., Figueiredo, J. L. & Faria, J. L. 2008 Catalytic properties of carbon materials for wet oxidation of aniline. *Journal of Hazardous Materials* **159** (2–3), 420–426.

ISO 2010 Water quality – Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (luminescent bacteria test) – Part 3: Method using freeze-dried bacteria.

Kadam, A. N., Dhabbe, R. S., Kokate, M. R., Gaikwad, Y. B. & Garadkar, K. M. 2014 Preparation of N doped TiO_2 via microwave-assisted method and its photocatalytic activity for degradation of malathion. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **133**, 669–676.

Karlsson, K., Viklander, M., Scholes, L. & Revitt, M. 2010 Heavy metal concentrations and toxicity in water and sediment from stormwater ponds and sedimentation tanks. *Journal of Hazardous Materials* **178** (1–3), 612–618.

Khuri, A. I. & Mukhopadhyay, S. 2010 Response surface methodology. *WIRES Computational Statistics* **2**, 128–149.

Kobya, M., Demirbas, E. & Akyol, A. 2009 Electrochemical treatment and operating cost analysis of textile wastewater using sacrificial iron electrodes. *Water Science and Technology* **60** (9), 2261–2270.

Kobya, M., Gengec, E., Sensoy, M. T. & Demirbas, E. 2014 Treatment of textile dyeing wastewater by electrocoagulation using Fe and Al electrodes: optimisation of operating parameters using central composite design. *Coloration Technology* **130** (3), 226–235.

Kralj, M. B., Černigoj, U., Franko, M. & Trebše, P. 2007 Comparison of photocatalysis and photolysis of malathion, isomalathion, malaoxon, and commercial malathion-products and toxicity studies. *Water Research* **41** (19), 4504–4514.

Kumar, P., Singh, H., Kapur, M. & Mondal, M. K. 2014 Comparative study of malathion removal from aqueous solution by agricultural and commercial adsorbents. *Journal of Water Process Engineering* **3**, 67–73.

Lannalainen, J., Juvonen, R., Vaajasaari, K. & Karp, M. 1999 A new flash method for measuring the toxicity of solid and colored samples. *Chemosphere* **38** (5), 1069–1083.

Lappalainen, J., Juvonen, R., Nurmi, J. & Karp, M. 2001 Automated color correction method for *Vibrio fischeri* toxicity test. Comparison of standard and kinetic assays. *Chemosphere* **45** (4-5), 635–641.

Mohamed, K. A., Basfar, A. A., Al-Kahtani, H. A. & Al-Hamad, K. S. 2009 Radiolytic degradation of malathion and lindane in aqueous solutions. *Radiation Physics and Chemistry* **78** (11), 994–1000.

Moreira, F. C., Vilar, V. J. P., Ferreira, A. C. C., Felipe, R. A., Dezotti, M., Sousa, M. A., Gonçalves, C., Boaventura, R. A. R. & Alpendurada, M. F. 2012 Treatment of a pesticide-containing wastewater using combined biological and solar-driven AOPs at pilot scale. *Chemical Engineering Journal* **209**, 429–441.

Naushad, M., Alothman, Z. A. & Khan, M. R. 2013 Removal of malathion from aqueous solution using De-Acidite FF-IP resin and determination by UPLC-MS/MS: equilibrium, kinetics and thermodynamics studies. *Talanta* **115**, 15–23.

Peng, Y., Fu, D., Liu, R., Zhang, F. & Liang, X. 2008 $NaNO_2/FeCl_3$ catalyzed wet oxidation of the azo dye acid Orange 7. *Chemosphere* **71** (5), 990–997.

Roe, B. & Lemley, T. 1997 Treatment of two insecticides in an electrochemical Fenton system. *Journal of Environmental Science and Health. Part. B, Pesticides, Food Contaminants, and Agricultural Wastes* **32** (2), 261–281.

Shayeghi, M., Dehghani, M. H., Alimohammadi, M. & Goodini, K. 2012 Using ultraviolet irradiation for removal of malathion pesticide in water. *Journal of Arthropod-Borne Diseases* **6** (1), 45–53.

Singh, V. K., Singh, R. S., Tiwari, P. N., Singh, J. K., Gode, F. & Sharma, Y. C. 2010 Removal of malathion from aqueous solutions and waste water using Fly ash. *Journal of Water Resource and Protection* **2** (4), 322–320.

Stüber, F., Font, J., Eftaxias, A., Paradowska, M., Suarez, M. E., Fortuny, A., Bengoa, C. & Fabregat, A. 2005 Chemical Wet oxidation for the abatement of refractory non-biodegradable organic wastewater pollutants. *Process Safety and Environmental Protection* **83** (4), 371–380.

Suranjana, C., Krishna Gopal, B. & Parimal, P. 2008 Catalytic destruction of 4-Chlorophenol in water. *CLEAN – Soil, Air, Water* **36** (5–6), 488–497.

Yang, S., Liu, Z., Huang, X. & Zhang, B. 2010 Wet air oxidation of epoxy acrylate monomer industrial wastewater. *Journal of Hazardous Materials* **178** (1–3), 786–791.

Yu, H., Wang, X., Sun, H. & Huo, M. 2010 Photocatalytic degradation of malathion in aqueous solution using an Au-Pd-TiO2 nanotube film. *Journal of Hazardous Materials* **184** (1–3), 753–758.

Zhang, Y. & Pagilla, K. 2010 Treatment of malathion pesticide wastewater with nanofiltration and photo-Fenton oxidation. *Desalination* **263** (1-3), 36–44.

First received 27 March 2016; accepted in revised form 29 September 2016. Available online 22 November 2016

Downloaded from https://iwaponline.com/wst/article-pdf/75/3/619/455391/wst075030619.pdf
by guest