

## Quantification of recalcitrant organic compounds during their removal test by a novel and economical method based on chemical oxygen demand analysis

Abraham Efraim Rodríguez-Mata\*, Leonel Ernesto Amabilis-Sosa\*,†, Adriana Roé-Sosa\*\*,  
José Manuel Barrera-Andrade\*\*\*, Jesús Gabriel Rangel-Peraza\*\*\*\*, and María G. Salinas-Juárez\*\*\*\*\*

\*CONACyT - Instituto Tecnológico de Culiacán, Juan de Dios Bátiz 310, C.P. 80220, Culiacán, Sinaloa, Mexico

\*\*Universidad Tecnológica de Culiacán, Carretera Imala km 2, C.P. 80014, Culiacán, Sinaloa, México

\*\*\*Escuela Superior de Ingeniería Química e Industrias Extractivas, Instituto Politécnico Nacional, Mexico City, Mexico

\*\*\*\*División de Estudios de Posgrado e Investigación, Tecnológico Nacional de México-Instituto Tecnológico de Culiacán, Sinaloa, México

\*\*\*\*\*Departamento de Ingeniería Química, Facultad de Estudios Superiores Zaragoza, UNAM, México

(Received 4 August 2018 • accepted 2 December 2018)

**Abstract**—This article proposes the use of mathematical models obtained by the Pearson correlation between the concentration of various recalcitrant organic compounds (ROCs) measured by chromatographic analysis (ChrA) and experimental chemical oxygen demand (COD). The aim is to reduce the number of samples processed by the ChrA, diminishing the economic costs of analysis. Ten ROCs, including pesticides, colorants, aromatic hydrocarbons and pharmaceuticals compounds, were introduced into four advanced oxidation processes operated at different residence times. Every ROC was tested at each residence time by COD determination and by quantification of concentrations with ChrA. Furthermore, chemical equations for the COD reaction of every ROC were formulated. A linear model was obtained for all the ROCs, after corroborating that the correlation between theoretical and experimental COD was  $>0.99$ , which established the ROC concentration from the experimental COD, omitting the ChrA. Results indicated that it is possible to know concentrations in most of the ROCs by means of the experimental COD with a  $>99\pm0.01\%$  of accuracy, which leads to a cost decrease and even to evaluate methods in developing countries, which often do not have chromatographs and where pollution issues are meaningful.

**Keywords:** Chemical Oxygen Demand, Advanced Oxidation Processes, Linear Correlation, Recalcitrant Organic Compound

### INTRODUCTION

Recalcitrant organic compounds (ROCs) are a large group of substances which, regardless of their organic nature, have low biodegradability and high accumulation levels in certain organisms [1]. These characteristics make them dangerous to ecosystems and public health. For that reason, diverse organizations have recognized these substances as ROCs when they are discharged into the environment such as soil and, or, water.

Among the various ROCs, pesticides are the most used worldwide, being applied in areas around  $6.5$  to  $60\text{ kg ha}^{-1}$ , which adds a total of  $2.5$  million tons per year [2]. Other ROCs which have caused severe environmental damage are the ones produced by the petroleum industry, such as anthracene and derivatives of benzene and both are polycyclic aromatic hydrocarbons (PAHs) [3].

Pesticides and PAHs, which are the two most released ROCs, were the first recognized to cause environmental damage [4]. Pollutants denoted as emerging, such as pharmaceutical and dyes, represent another critical ROCs group. The population growth in-

creased the ROCs production and consumption in the last twenty years, causing a more significant presence in the environmental systems [5].

From the preceding, several research groups have focused on the effect of ROCs on the environment and, on the evaluation of different methods to remove them from wastewater. Also, the industry is the one that defines the ROC or group of ROCs in which research will be done [5,6].

Catalogued as emerging pollutants, there are neither reference data to design their treatment nor kinetic studies defined in official guidelines, causing the majority of research to be carried out in a laboratory using synthetic water samples to control external variables in order to avoid interference and to study degradation pathways [7]. Also, some analytic assays from different experimental designs are required to obtain statistical reproducibility and value and start proposing a significant design and operation data. These assays are the primary step to implement treatment methods in laboratory-scale, pilot-scale and large-scale.

The experimental stage consists of monitoring the pollutant analytically. This monitoring implies having a gas chromatograph or high-performance liquid chromatography depending on the compound. On the one hand, this equipment and its operation tends to be expensive, which is the reason why in a large number of lab-

†To whom correspondence should be addressed.

E-mail: lamabilis@conacyt.mx, leoamabilis@yahoo.com.mx  
Copyright by The Korean Institute of Chemical Engineers.

**Table 1. Recalcitrant organic compounds used in the experimental phase**

Compound	Chemical formula	Initial concentration ( $t_0$ ), mg L <sup>-1</sup>	References
Malathion	C <sub>10</sub> H <sub>19</sub> O <sub>6</sub> PS <sub>2</sub>	120.0	[25,26]
Parathion	C <sub>10</sub> H <sub>14</sub> NO <sub>3</sub> PS	110.0	[27,28]
Endosulfan	C <sub>9</sub> H <sub>6</sub> Cl <sub>6</sub> O <sub>3</sub> S	25.0	[29,30]
Dieldrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub> O	20.0	[31,32]
Ibuprofen	C <sub>15</sub> H <sub>18</sub> O <sub>2</sub>	5.0	[33,34]
Ciprofloxacin	C <sub>17</sub> H <sub>18</sub> FN <sub>3</sub> O <sub>3</sub>	6.0	[35,36]
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	10.0	[37,38]
Anthracene	C <sub>14</sub> H <sub>10</sub>	12.0	[38-40]
Basic Red 12	C <sub>25</sub> H <sub>29</sub> ClN <sub>2</sub>	90.0	[41,42]
Reactive Blue 69	C <sub>23</sub> H <sub>14</sub> BrN <sub>3</sub> Na <sub>2</sub> O <sub>9</sub> S <sub>2</sub>	100.00	[7,33,43]

oratories in developing countries it is not possible to find them, or it is not possible to use them routinely, and it is in these cities where the impact caused by ROCs is higher [8,9].

Besides the chromatographic analysis, the chemical oxygen demand (COD) is also used as referential data, which has features as low cost, representativity, and applicability in international standards. COD is an evaluation index of the wastewater discharge for existing regulations. Several studies performed during the last two decades also denoted the importance of COD, focused on modifying or replacing standard methods [10,11]. Nevertheless, the equivalence between the data found in ChrA and COD is done empirically through several experiments, leading to an increase in costs, time and hazardous wastes. In some cases, this equivalence is not even considered in research.

The principal systems evaluated for ROCs removal are the those based on advanced oxidation such a heterogeneous photocatalysis, photo-Fenton, ozonation and UV/H<sub>2</sub>O<sub>2</sub>, due to their characteristics that make them able to break molecular bonds from organic compounds for their further mineralization. They can also treat high ROCs concentration effluents, something that is important, because levels of these compounds range from 0.1 a 500 µg L<sup>-1</sup> [12], but on industrial effluents, where these type of treatment systems would be used, levels as high as 300 mg L<sup>-1</sup> can be found [13,14].

During the experimental stage of ROCs removal using advanced oxidation process (AOP), the concentration of the compounds and their COD level present correlation with the different types of time exposure and treatments. Knowing with precision and exactitude the equivalence between the concentration of both compounds with the ChrA and their COD level could reduce the costs, hazardous waste and time. Therefore, these determinations could be possible for institutions which do not have the equipment to research a particular type of ROC in laboratory-scale.

The stoichiometric ratio of the COD is one option to establish a mathematical correlation between the real values of an ROC and its COD values, because part of the principle estimates that all organic compounds are oxidized to CO<sub>2</sub> and H<sub>2</sub>O in acid, chemical and thermal conditions. In this way, the correct use of the equations combined with the results obtained in experimental trials might give representative information with statistical validity in order to know precisely the concentration of a specific ROC, only quantifying the COD.

The present paper aims to validate the theoretical concentrations from different ROCs obtained experimentally by the specific quantifications of COD. This work might represent a useful analytical tool to decrease the cost related to the removal of ROCs, mainly in developing countries which are profoundly affected by this type of pollutant.

## MATERIALS AND METHODS

### 1. Experimental Procedure

A series of solutions were prepared according to the Sigma Aldrich-Merck standards grade Certified Reference Materials under ISO Guide 34: 2009. These solutions were Ibuprofen PHR1004, Ciprofloxacin PHR1167, Ethylbenzene 40036, Anthracene 07671 and a multi-standard SKU-47915-U for pesticides. Likewise, dyes were acquired with analytical certification Basic Red 12 by Aurora Fine Chemicals LLC with number A24.091.418, and CIBA Speciality Chemicals Switzerland supplied Reactive Blue 69.

Based on the type of compound, Sigma standards contain as a solvent the one with the highest chemical affinity; thus they could be diluted with water. For example, the ibuprofen solution contains 10% of methanol (Methanol Chromasolv for HPLC, 99.9%). In that way, the ROCs were different types of pesticides, pharmaceuticals, dyes, and hydrocarbons. The preparation and concentration techniques applied correspond to previous research, in which, characteristics from industrial wastewater with high ROC concentration were emulated leading to a high COD level. Table 1 indicates each of the compounds used during the research.

All the ROCs were tested in four different AOPs. Table 2 lists the AOP which have had high removal efficiency and applicability in a wide range of compounds. In each of the AOP four different characteristic operation times for each process were evaluated

**Table 2. Advanced oxidation processes and its respective operation times used to generate different concentrations**

AOP	Evaluated time, min	References
UV/H <sub>2</sub> O <sub>2</sub>	20, 40, 60, 90	[33,41,42]
Heterogeneous photocatalyst TiO <sub>2</sub>	30, 60, 90, 120	[44-46]
Ozonation	45, 90, 150, 240	[41,47]
Photo-Fenton	20, 40, 60, 90	[48,49]

(Table 2). Concentration of organic compounds was evaluated during the application time of the AOP [5,15]. Different times of treatment were applied to obtain different concentration levels of each of the compounds and treatments indicated in Tables 1 and 2. The theoretical and experimental COD data and chromatographic results of these studies were compared and mathematical models were obtained using this information.

## 2. Analytical Determinations

All analytical determinations were performed according to standard methods. To ensure quality control of the experimental data obtained, intercalibration procedures were carried out with the Certified Materials Reference indicated at the beginning of this section. Specifically, pesticides were quantified by Varian 3700 gas chromatography automatic injector with capillary column DB-35 ms (30 m × 0.25 mm ID, 0.25 μm thickness) with a parallel flow subdivision to an electron micro-capture detector (μECD) and then to a nitrogen-phosphorus detector (NPD) in order to quantify the organochlorine and organophosphate pesticides respectively. Initial chromatographic conditions were injection volume 2 μL, a pulsed splitless injection every 0.8 minutes, purge time of 0.6 minutes, purge flow 35 mL min<sup>-1</sup> and injector temperature of 250 °C. Ultrapure helium at 1.1 mL min<sup>-1</sup> was used as carrier gas [15,16]. The aromatic hydrocarbons were quantified with the same standards as the ones used with pesticides, but with the temperature and volumetric flows indicated in [19,20].

Dyes quantification was performed using a Perkin Elmer HPLC equipment Series 200 with UV-Vis detector. The samples were isocratic eluted using a Waters C18 reversed phase column (25 cm, 4.6 mm, 5 μm). The mobile phase consisted of a solution of ammonia/methanol/water (5 : 15 : 80), and the mobile flow rate was 0.5 mL min<sup>-1</sup> [21].

This equipment was also used for the quantification of the ciprofloxacin and ibuprofen by isocratic reverse phase using Waters C-18 columns (125 mm × 4 mm, 5 μm) coupled with a guard column of silica in mobile phase acetonitrile, flow rate 2.0 mL min<sup>-1</sup> at 25 °C and with UV detector at the wavelength of 278 nm [22].

On the other hand, the COD was determined by the standard method described in [23], and the pH parameter and redox potential (Eh) were measured at the end of each AOP system with a Thermo Scientific Orion Star pH/ORP benchtop meter.

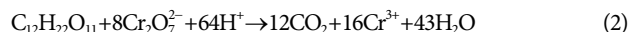
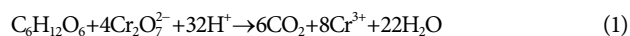
## 2. Analytical Basis of a Mathematical Model that Related the Concentration of Organic Compounds and Chemical Oxygen Demand

### 2-1. Stoichiometric Balances of the Chemical Oxygen Demand Reaction

The fundamental of the COD technique establishes that organic compounds are oxidized to CO<sub>2</sub> and H<sub>2</sub>O because of the action of the dichromate at acidic pH. Eq. (1) indicates the simplest COD reaction, based on the glucose oxidation. According to the calculus, each 180.16 g mol<sup>-1</sup> of glucose, requires 446.97 g mol<sup>-1</sup> of chemical oxygen, which is precisely the COD value. In addition, if both molar masses correspond to milligrams and are dissolved in a liter of water, it is observed a correlation of 1.0 mg L<sup>-1</sup> of glucose per 2.486 mg L<sup>-1</sup> of COD. The correlation implies that the theoretical COD of any glucose concentration can be obtained or even the quantity of glucose needed to reach a COD required. In Eq. (2),

the same calculus can be made using sucrose. In this case, the correlation of 1.0 mg L<sup>-1</sup> of sucrose shows 6.22 mg L<sup>-1</sup> of COD.

Based on the above, the COD equations were posed and balanced, making each of the ten ROCs (Table 1) react with potassium dichromate in acidic pH. This study proposes to find the theoretical COD concentration for each ROC similar to the examples given in Eqs. (1) and (2).



### 2-2. Use of Frost and Pourbaix Diagrams

In Eqs. (1) and (2), the CO<sub>2</sub> and H<sub>2</sub>O were the only products, due to glucose and sucrose only contain C, H and O. However, when the oxidation occurs with organic products which contain, as part of their molecules, other compounds such as nitrogen, phosphorus, chlorine and metals, these have to be presented as products resulting from the equation, only being different because they have been oxidized by the dichromate in acidic pH [24].

In Eq. (3), an example from the reaction between the malathion and the COD is shown, where sulfates and phosphoric acid can be found as products. This equation could not have been balanced if the chemical species from sulfur and phosphorus had not been calculated correctly.

The majority of ROCs contain in their molecular structure other elements in addition to carbon and hydrogen, such as nitrogen (N), phosphorus (P), fluorine (F), bromine (Br), chlorine (Cl) and sodium (Na) (Table 1). Given the above, it was necessary to know the chemical species in which the elements could be found at the end of the reaction, to establish and balance properly every chemical equation. The pH and ORP were quantified at the end of the COD reactions in such a way that the software HSC Chemistry 7 could introduce the values. Frost and Pourbaix diagrams indicate the chemical species and the oxidation state of a specific chemical element. To validate the stoichiometric calculation, chemical species must be experimentally quantified. Chemical species indicated in the Frost and Pourbaix diagrams within the ranges of pH and ORP measured were quantified by ionic chromatography Metrohm Compact IC Flex.

Based on this, chemical equations were formulated and they represented the COD determination from each of the compounds mentioned in Table 1. For each case, the theoretical COD is equal to the oxygen mass required (present in the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) multiplied by the grams-mole from the molecule or organic compound investigated and assuming the use of a liter of water.

### 2-3. General Steps for Model Development

Using the stoichiometric relation (the reaction of each ROC with the dichromate) and the experimental COD determinations and from each ROCs (chromatographic), a model was proposed according to the steps indicated in Fig. 1. Subsequently, a model simulation was made, comparing real data from the ChrA.

With the mathematical model, the mass required of ROCs was obtained for any COD of interest, which is the typical scenario during the ROCs treatment in laboratory scale and even in pilot scale using synthetic water. Theoretical COD is considered the COD of interest in the environmental chemistry field.

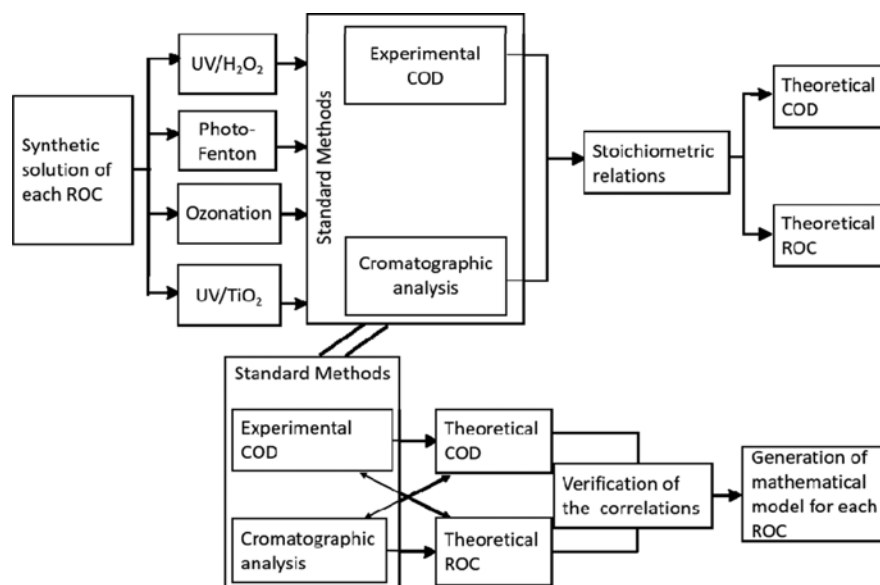


Fig. 1. General sequence for the development of the proposed mathematical model.

### 3. Statistical Analysis and Validation

Each of the experimental COD and ChrA determinations were done five times. Anderson-Darling and Kolmogorov-Smirnov tests were used to corroborate the normality and homogeneity of the results. Then, Pearson correlations were carried out ( $\alpha=0.99$ ) [50].

Even though it was not the research aim, the removal results from the different oxidation processes were compared by an ANOVA analysis with repeated data followed by a Duncan test post hoc

( $\alpha=0.95$ ). All statistical analysis of data was performed using Minitab 15 package.

## RESULTS AND DISCUSSION

### 1. Compounds Removal by Advanced Oxidation Processes

In Figs. 2-5 the removal results from the 10 ROCs evaluated into the four AOP advanced oxidation at different times are shown. It

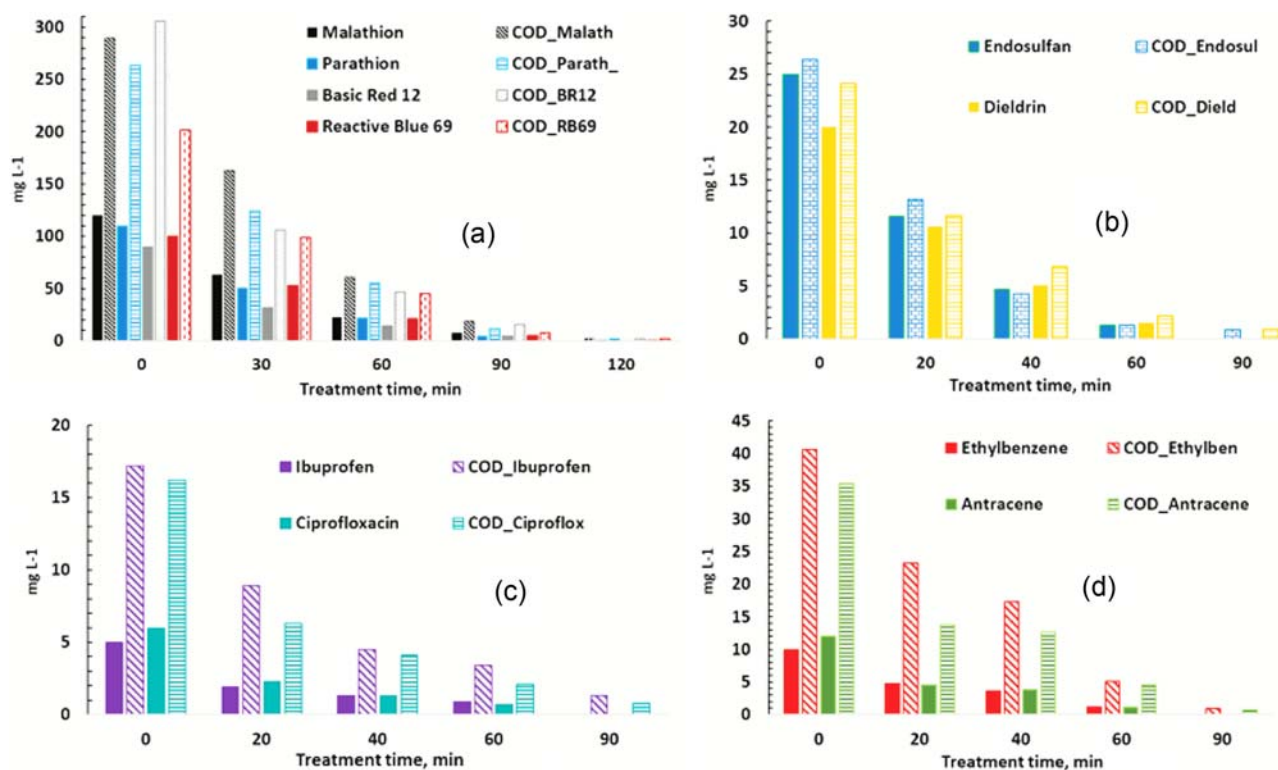


Fig. 2. Removal of recalcitrant organic compounds by the advanced oxidation process UV/H<sub>2</sub>O<sub>2</sub>.

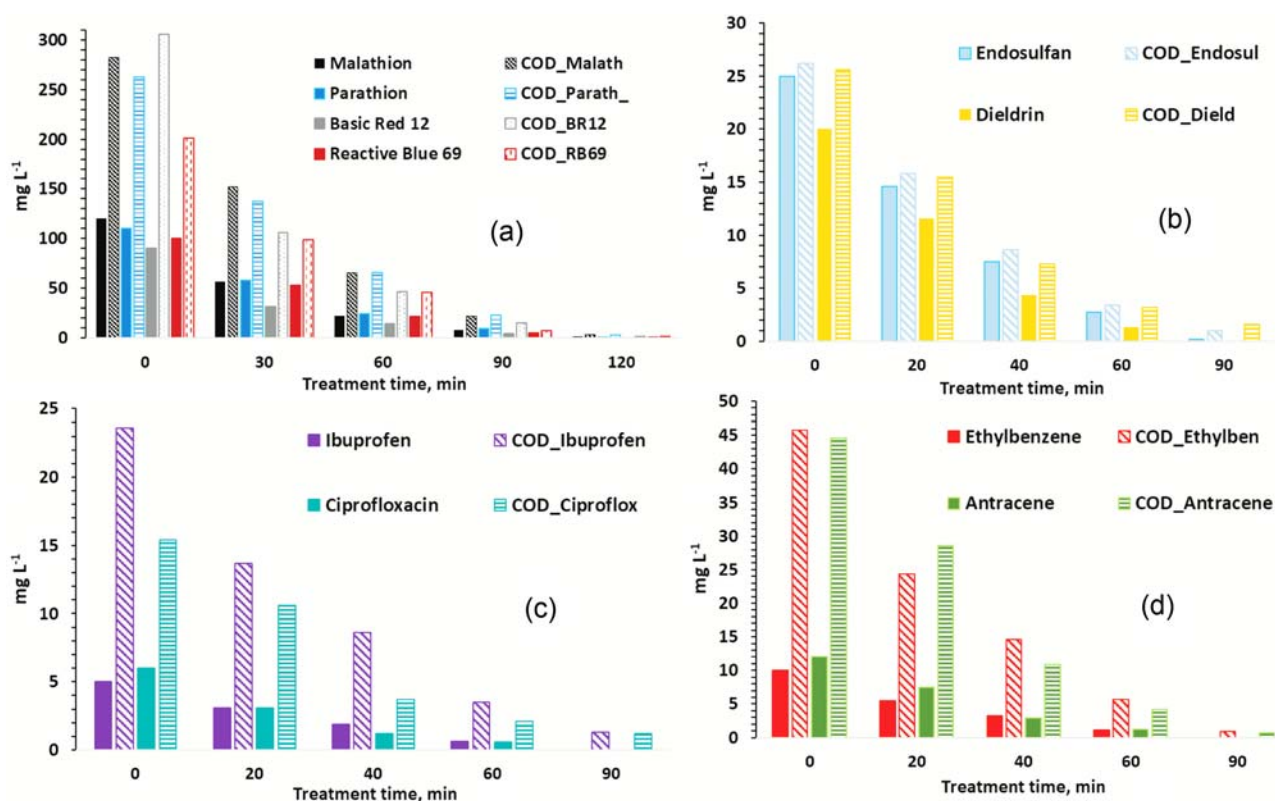


Fig. 3. Removal of recalcitrant organic compounds by photo-Fenton as advanced oxidation process.

can be observed that, to a greater or lesser degree, the pollutant concentration decreases while the exposure time in the AOP increases.

In Fig. 2, the results of ROCs removal using UV/H<sub>2</sub>O<sub>2</sub> are presented. All the compounds were degraded completely after 90 minutes of the treatment, where the ethylbenzene and anthracene degradation was observed in 60 minutes (Fig. 2(d)). In each of the cases a remaining COD concentration was observed even though the ROC molecule was no longer present in the sample; this can be related to the presence of chemical elements different from carbon that also need oxygen from the potassium dichromate (representing a COD concentration) [10], as it can be assumed comparing Eqs. (1) and (2) versus (3) and (6). In the last ones, the phosphorous, sulfur and chlorine need oxygen to change their chemical species in the acidic COD reaction [24].

This remaining concentration corresponds to the values of 0.70 mg L<sup>-1</sup> COD of ibuprofen, ethylbenzene and anthracene during minute 90 of the treatment, which precisely the detection limit in the analytical technique. This fact means that for the four compounds it can be assumed that the COD concentration was reduced to its minimal because their molecular structures only contain chlorine, hydrogen and molecular oxygen (See (7), (9) and (10)); consequently, they do not contain any COD remnant.

The behavior of the ten ROCs during the photo-Fenton treatment is practically the same observed in the UV/H<sub>2</sub>O<sub>2</sub> process (Figs. 2 and 3), because both removal processes lasted 90 minutes. Although in Fig. 3(a) and 3(b) can be observed that the malathion, parathion, and endosulfan were not degraded entirely as it occurred in the UV/H<sub>2</sub>O<sub>2</sub> process (Figs. 2(a) and 2(b)), there were not sig-

nificant differences between both AOPs ( $P > 0.05$ ).

In Fig. 4, the ROCs removal tendency using heterogeneous photocatalysis with UV/TiO<sub>2</sub> is indicated. It can be observed that although 120 minutes of treatment was applied, remnants from malathion, parathion, endosulfan, and dieldrin are still present in the samples. However, they represent only 5% of the initial concentration (Figs. 3(a) and 3(b)). In contrast with the UV/H<sub>2</sub>O<sub>2</sub> and photo-Fenton processes, the AOP UV/TiO<sub>2</sub> presented an ROCs removal of around 75%, which is significantly less than the one presented for the UV/H<sub>2</sub>O<sub>2</sub> and the photo-Fenton (Figs. 2-4). At 120 minutes, the degradation efficiency with UV/H<sub>2</sub>O<sub>2</sub> is practically the same for each of the samples (Fig. 4), due to the production of OH radicals, which is a characteristic radical of this AOP [42,49].

In Fig. 5, the removal of organic compounds evaluated by ozonation is indicated. As observed in the other three AOPs, at the end of the process there is almost no ROCs presence and the COD concentration achieved the detection limit for the ethylbenzene, anthracene and ibuprofen. For the rest of the compounds which contain other added molecules to the C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>, COD concentration less than 3.5 mg L<sup>-1</sup> was observed (Figs. 5(a) and 5(b)).

## 2. Recalcitrant Organic Compounds Reactions During the Chemical Oxygen Demand Determination

Eqs. (3) to (12) show the COD reaction balanced for each ROC. The oxidized forms of nitrogen, phosphorus, sulfur, chlorine, fluorine and bromine were identified in the Pourbaix diagrams with a pH of 0.3-0.6 and ORP mean value of +0.85 V. These results were quantified in the AOPs. According to this, in Eqs. (3) and (4) the



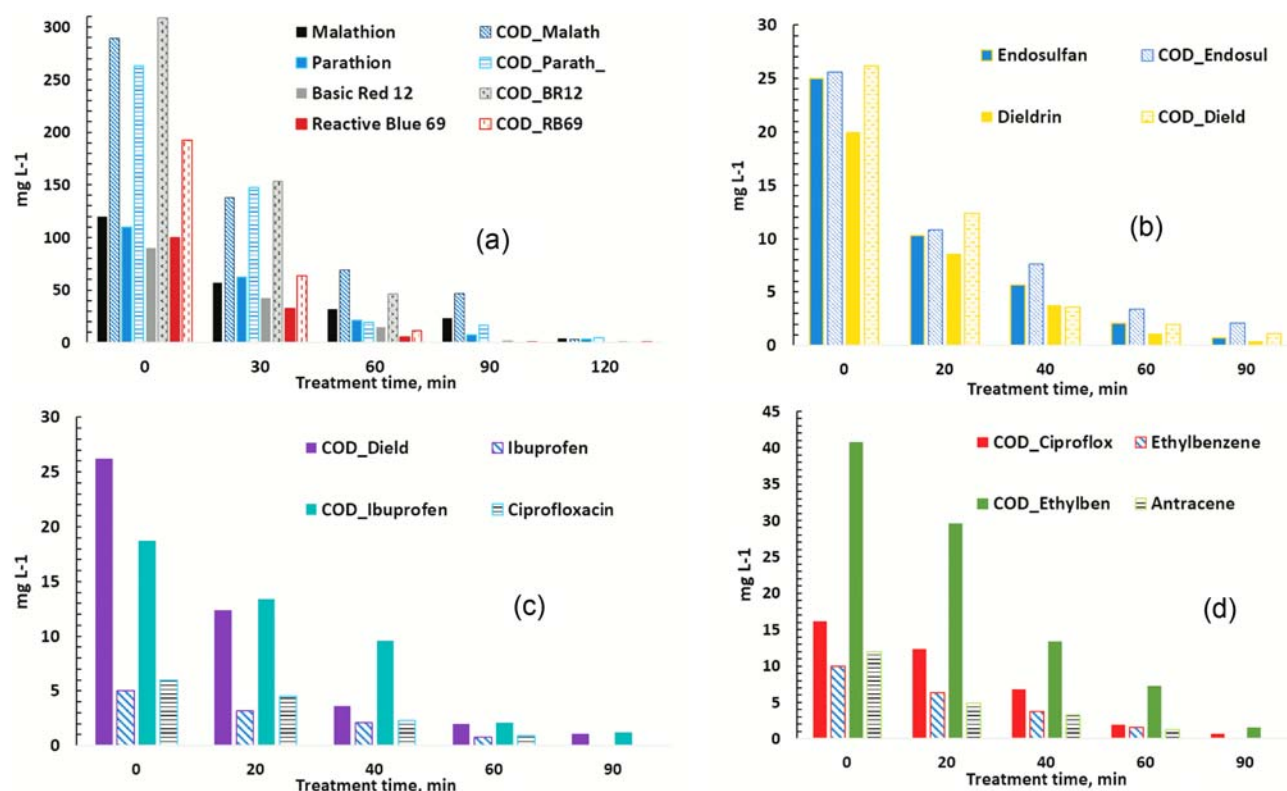


Fig. 4. Removal of recalcitrant organic compounds by the advanced oxidation process UV/TiO<sub>2</sub>.

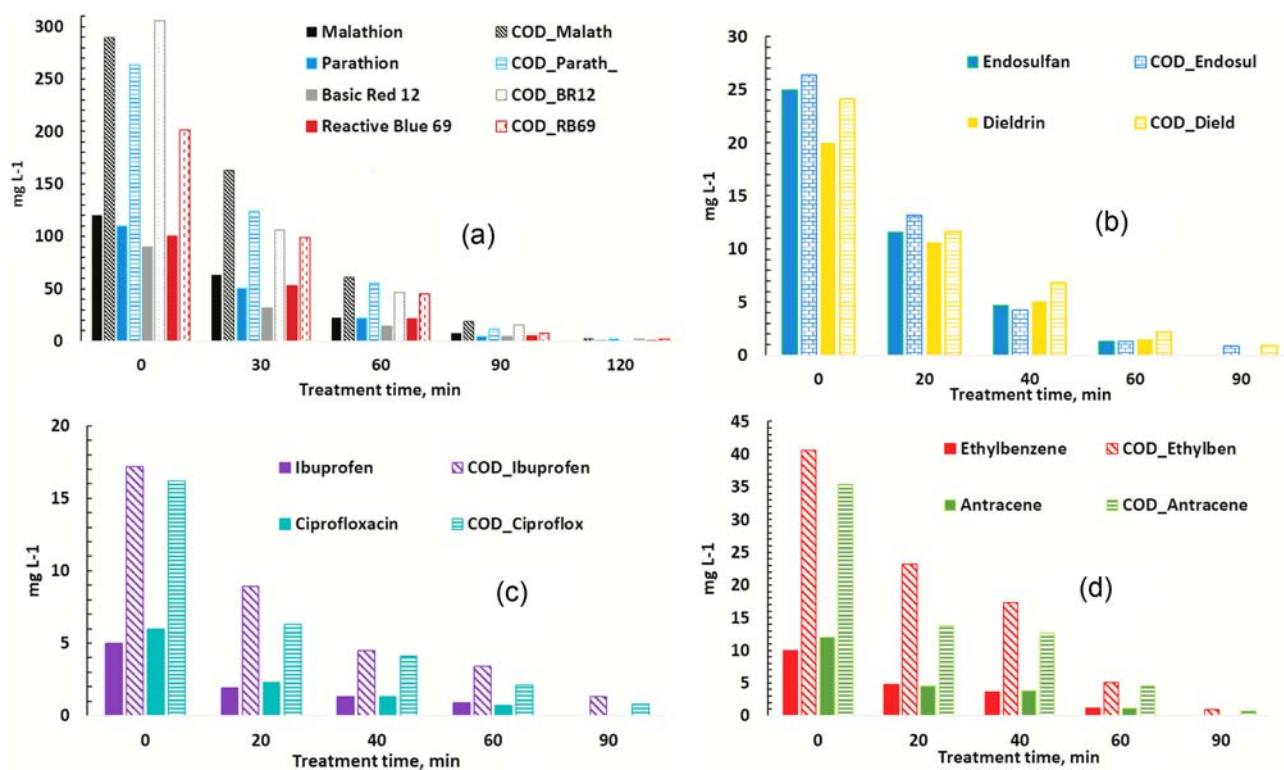


Fig. 5. Removal of recalcitrant organic compounds by ozonation as advanced oxidation process.

phosphorus contained in a pesticide molecule is transformed to H<sub>3</sub>PO<sub>4</sub>. In Eqs. (3), (4), (5) and (12), sulfur is oxidized to SO<sub>4</sub><sup>2-</sup>. In

Eqs. (5), (6) and (11), chlorine is released from organic molecules, appearing as Cl<sup>-</sup>. Nitrogen present in Eqs. (4), (8), (11) and (12) is

**Table 3. The stoichiometric relation between the recalcitrant organic compound mass and the oxygen quantity, present in the dichromate, required to be oxidized (COD reaction)**

Compound	Molar mass, g mole <sup>-1</sup>	Oxygen requirement, mg L <sup>-1</sup>
Malathion	330.35	783.51
Parathion	291.26	671.96
Endosulfan	406.92	447.72
Dieldrin	380.90	447.72
Ibuprofen	230.29	895.44
Ethylbenzene	106.16	447.72
Anthracene	178.22	559.65
Basic Red 12	392.95	1343.16
Reactive Blue 69	668.38	1231.23

The units of both columns are considered in one liter of solution

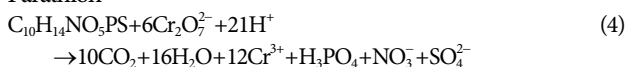
oxidized to NO<sub>3</sub><sup>-</sup>. Sulfur contained in the organic molecule of Eqs. (3), (4), (5) and (12) is oxidized to SO<sub>4</sub><sup>2-</sup>. In Eq. (8), fluorine is converted to HF and, finally, bromine present in the organic molecule of Eq. (12) is released as Br<sup>-</sup>. Subsequently, experimental quantification by ionic chromatographic showed a variation of 1.0% to 5.1%, compared to the obtained by stoichiometry (Eqs. (3) to (12)), which indicates the feasibility of using the Pourbaix diagrams to identify chemical species of interest. The speciation of these chemical elements was found in terms of the combination of pH and ORP [51].

In every case, quantification by ionic chromatography shows a variation of ±4% compared to that obtained by stoichiometry (Eqs. (3) to (12)). On the basis of the above, it was possible to balance each of the chemical Eqs. (3) to (12) and to create Table 3. Based on stoichiometry, the result of relating the ROC concentration with the oxygen concentration present in the dichromate was CO<sub>2</sub> and H<sub>2</sub>O (COD reaction).

#### Malathion



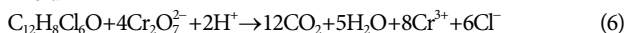
#### Parathion



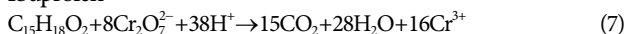
#### Endosulfan



#### Dieldrin



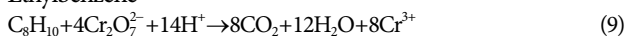
#### Ibuprofen



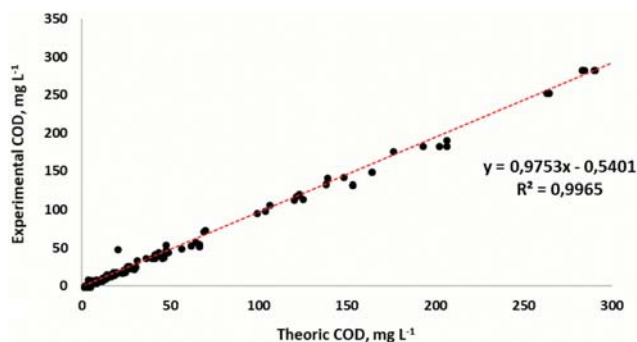
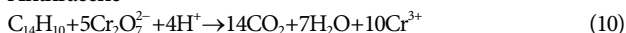
#### Ciprofloxacin



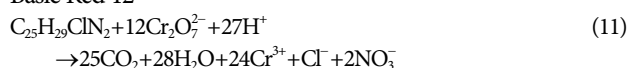
#### Ethylbenzene



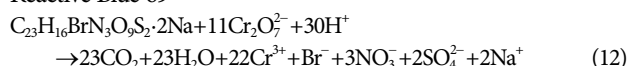
#### Anthracene

**Fig. 6. Correlation between the theoretical and experimental COD. Data obtained by the four AOP with five treatment times in each of them, and the 10 ROCs (n=200 with five replicates).**

#### Basic Red 12



#### Reactive Blue 69



When the degradation results from the 10 ROCs through the four different AOP and the balanced equation from each COD reaction were obtained, the theoretical and experimental COD were correlated, considering all the results altogether (Fig. 6). The correlation coefficient was 0.9965, indicating that the concentration range used during the research and for the ten chemical compounds evaluated, it is possible to prepare synthetic solutions with theoretical COD desired, in order to obtain an experimental value with an acceptable statistical precision (Fig. 6). Also, this permits to establish the concentration range for the COD calibration curves, in which empiricism is always present when the value interval is defined in order to obey the Beer-Lambert law [52]. In the first line of Table 4, a linear model is presented for the relationship observed between both CODs.

In Figs. 7-8, the results of the correlation of the theoretical mal-

**Table 4. Mathematical linear models used to obtain the experimental concentration of recalcitrant organic compounds from the experimental COD**

Mathematical model	R <sup>2</sup> coefficient, %
Malathion=0.417COD-0.7943	99.67
Parathion=0.4238COD+0.00989	99.11
Endosulfan=0.9754COD-0.7763	99.27
Dieldrin=0.8547COD-0.6322	99.02
Ibuprofen=0.2568COD-0.1523	96.12
Ciprofloxacin=0.3944COD-0.1998	97.19
Ethylbenzene=0.2325COD-0.1109	99.07
Anthracene=0.2986COD-0.1304	99.15
Basic Red 12=0.2885COD-0.0239	99.78
Reactive Blue 69=0.4976COD+1.1682	94.7

All chemical compound and COD values are expressed in mg L<sup>-1</sup>  
n=200 with five replicates

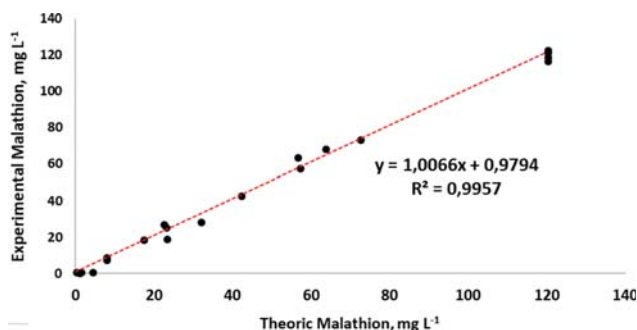


Fig. 7. Correlation between the theoretical malathion concentration (calculation based on the COD reaction) and the real concentration quantified by standard method of gas chromatography ( $n=20$ , five replicates).

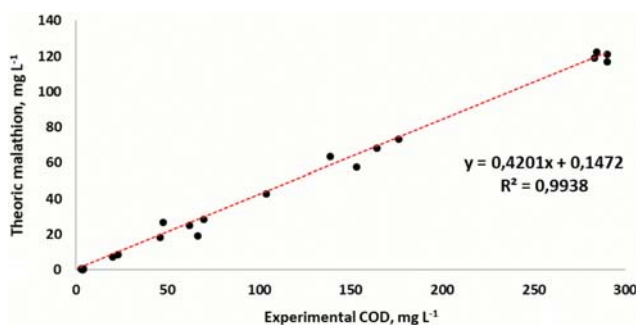


Fig. 8. Correlation between the experimental COD and the theoretical malathion concentration quantified by stoichiometry ( $n=20$  with five replicates).

athion concentration are presented, for example, with its experimental concentration ( $R^2=0.9957$ ) and the correlation of the experimental COD and the theoretical malathion concentration ( $R^2=0.9938$ ). These results are relevant because they are the intermediate steps in the sequence to make the correlation between the experimental COD and each ROC concentration. This means that it was first necessary to obtain the results in Figs. 7 and 8 to then make the correlation in Fig. 9, in which was finally established the mathematical model that correlates the experimental COD concentration (which would be measured in the laboratory) with the

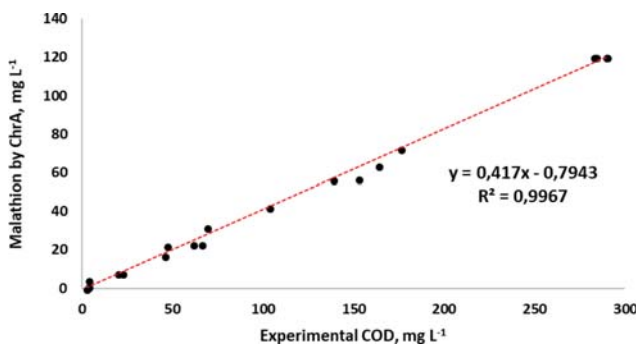


Fig. 9. Correlation between the experimental COD and the malathion concentration quantified by gas chromatography, both under standard methods ( $n=20$  five replicates).

needed ROC by using chromatography.

To set an example, the mathematical model shown in Fig. 9 indicated that a 99.67% of certainty is achieved when calculating the real malathion concentration by using a certified reference material. These results were obtained only quantifying the COD in the laboratory. This calculation applies to malathion concentrations ranging from 0 to 120  $\text{mg L}^{-1}$ .

Following the same procedure for malathion, the other nine mathematical models corresponding each ROC were made, making it possible to obtain the ROC concentration from its respective experimental COD determination. These results are shown in Table 4.

The correlation coefficients from ibuprofen, ciprofloxacin and reactive blue 69 were found under 0.99, which means that the mathematical model is not viable to use in laboratories where the protocols ask for a more accurate analysis (Table 4). Nevertheless, the correlation coefficients were found around 0.95; thus these models could be used in laboratory trials where the determination of concentrations range from a specific ROC is the main objective.

Both ibuprofen and ciprofloxacin molecular structures were not mineralized even though being exposed to AOP. In fact [35,53] report the complete degradation of the antibiotics molecules was reported using the  $\text{UV}/\text{H}_2\text{O}_2$  and  $\text{UV}/\text{S}_2\text{O}_8^{2-}$  processes, but with the presence of secondary metabolites with cyclic structure and double bonds was noticed. Furthermore, the ciprofloxacin contains in its structure two anthraquinones, and one of them joined to a cyclic compound with a fluorine radical, causing a higher resistance to mineralization [24,45]. This chemical ciprofloxacin structure is very similar to the one of Blue Reactive 69, but this, besides containing anthraquinones, also has four double bonds and in one of them has a bromide joined, which leads to the display of at least four secondary metabolites even though losing the coloration quickly due to the molecular breakage of the chromophore group [7]. In fact, in Table 4 it can be observed that the lowest correlation coefficient (0.947) corresponds to Blue Reactive 69.

## CONCLUSIONS

The suggested methodology allows establishing the linear mathematical models for environmentally representative organic compounds such as antibiotics, hydrocarbons, pesticides and dyes. The methodology is extremely convenient for environmental engineering and a useful tool to optimize time and resources in water management for developed and developing countries.

Based on the data obtained in laboratory experiments, it is recommended to conduct pilot-scale research with specific industrial effluents such as those from the pharmaceutical, textile, agricultural, or petroleum industries. The results will enable the presence of other industrial wastewater compounds to be considered in the mathematical model.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge the collaboration of chemical engineering and postgraduate students for their hard work in the laboratory. Also, thanks to the technicians of the laboratories involved, for their advice on the use of chromatography.



## FUNDING

This work was financially supported by the National Council of Science and Technology of Mexico, through the financing of post-graduate studies in master and doctoral degrees in engineering. Likewise, for the support given through the project Cátedras CONACyT 2572.

## DECLARATION OF INTEREST STATEMENT

The authors state that there are no conflicts of interest.

## REFERENCES

- G. Zhang and M. Mastalerz, *Chem. Soc. Rev.*, **43**(6), 1934 (2014).
- F. P. Carvalho, *Food Energy Secur.*, **6**(2), 48 (2017).
- H. Jin, S. Liu, W. Wei, D. Zhang, Z. Cheng and L. Guo, *Energy Fuels*, **29**(10), 6342 (2015).
- Environmental Protection Agency of United States, <https://www.epa.gov/international-cooperation/persistent-organic-pollutants-global-issue-global-response>.
- L. C. Sander, M. M. Schantz and S. A. Wise, in *Liquid Chromatography Applications*, Ed. by S. Fanali, C. F. Poole, P. R. Haddad and M. L. Riekkola, Elsevier Inc., New York (2017).
- L. A. Schaidler, K. M. Rodgers and R. A. Rudel, *Environ. Sci. Technol.*, **51**(13), 7304 (2017).
- J. M. Barrera-Andrade, J. A. García-M, A. E. Jiménez-G, R. Zanella-S, L. S. Gelover-S and M. C. Duran-Dominguez-de-Bazua, *J. Adv. Oxid. Technol.*, **17**(1), 152 (2014).
- J. E. Hardoy, D. Mitlin and D. Satterthwaite, *Environmental problems in an urbanizing world: finding solutions in cities in Africa, Asia and Latin America*, 2<sup>nd</sup> Ed., Routledge, Abingdon-on-Thames, 464 (2013).
- J. M. Dean, *International Trade and the Environment*, 1<sup>st</sup> Ed., Taylor and Francis, London, 60 (2017).
- J. Li, G. Luo, L. J. He, J. Xu and J. Lyu, *Crit. Rev. Anal. Chem.*, **48**(1), 47 (2018).
- R. B. Geerdink, R. S. van den Hurk and O. J. Epema, *Anal. Chim. Acta.*, **961**, 1 (2017).
- A. A. Bletsou, J. Jeon, J. Hollender, E. Archontaki and N. S. Thomaidis, *TrAC, Trends Anal. Chem.*, **66**, 32 (2015).
- J. L. Liu and M. H. Won, *Environ. Int.*, **59**, 208 (2013).
- W. L. Liew, M. A. Kassim, K. Muda, S. K. Loh and A. C. Affam, *J. Environ.*, **149**, 222 (2015).
- R. Meffe and I. de Bustamante, *Sci. Total Environ.*, **481**, 280 (2014).
- A. Klančar, J. Trontelj, A. Kristl, A. Meglič, T. Rozina, M. Z. Justin and R. Roškar, *Ecol. Eng.*, **97**, 186 (2016).
- F. Ahmadi, Y. Assadi, S. M. Hosseini and M. Rezaee, *J. Chromatogr. A.*, **1101**, 1 (2006).
- H. P. Li, G. C. Li and J. F. Jen, *J. Chromatogr. A.*, **1012**, 2 (2003).
- J. N. Bianchin, G. Nardini, J. Merib, A. N. Dias, E. Martendal and E. Carasek, *J. Chromatogr. A.*, **1233**, 22 (2012).
- P. Poinot, F. Qin, M. Lemoine, V. Yvon, J. Ledauphin and J. L. Gailard, *J. Food Compos. Anal.*, **35**(2), 83 (2014).
- M. Kucharska and J. Grabka, *Talanta*, **80**(3), 1045 (2010).
- J. L. Santos, I. Aparicio, E. Alonso and M. Callejón, *Anal. Chim. Acta*, **550**(1-2), 116 (2005).
- E. W. Rice, R. B. Baird, A. D. Eaton and L. S. Clesceri, *Standard Methods for the Examination of Water and Wastewater*, 22<sup>th</sup> Ed., American Public Health Association, Water Environment Federation, Denver, 1496 (2012).
- S. Manahan, *Environmental Chemistry*, 10<sup>th</sup> Ed., CRC press, Boca Raton, FL, 752 (2017).
- M. Behloul, H. Grib, N. Drouiche, N. Abdi, H. Lounici and N. Mameri, *Sep. Sci. Technol.*, **48**(4), 664 (2013).
- D. M. Fouad and M. B. Mohamed, *J. Nanomater.*, **2012**(2), 1 (2012).
- P. V. Laxma Reddy and K. H. Kim, *J. Hazard. Mater.*, **285**, 325 (2015).
- O. Autin, J. Hart, P. Jarvis, J. MacAdam, S. A. Parsons and B. Jefferson, *Water Resour.*, **47**(6), 2041 (2013).
- N. S. Shah, X. He, H. M. Khan, J. A. Khan, K. E. O'Shea, D. L. Boccelli and D. D. Dionysiou, *J. Hazard. Mater.*, **263**, 584 (2013).
- M. A. Oturan and J. J. Aaron, *Crit. Rev. Environ. Sci. Technol.*, **44**(23), 2577 (2014).
- X. T. Bui, T. P. T. Vo, H. H. Ngo, W. S. Guo and T. T. Nguyen, *Sci. Total Environ.*, **563**, 1050 (2014).
- D. Yang, S. Qi, J. Zhang, C. Wu and X. Xing, *Ecotoxicol. Environ. Saf.*, **89**, 59 (2013).
- W. A. Al-Amrani, P. E. Lim, C. E. Seng and W. W. Wan Ngah, *J. Taiwan Inst. Chem. Eng.*, **45**, 609 (2014).
- L. Feng, van E. D. Hullebusch, M. A. Rodrigo, G. Esposito and M. A. Oturan, *Chem. Eng. J.*, **228**, 944 (2013).
- D. P. Mohapatra, S. K. Brar, R. D. Tyagi, P. Picard and R. Y. Surampalli, *Sci. Total Environ.*, **470**, 58 (2014).
- X. Liu, P. Lv, G. Yao, C. Ma, Y. Tang, Y. Wu and Y. Yan, *Colloids Surf.*, **441**, 420 (2014).
- L. P. Ramteke and P. R. Gogate, *Process Saf. Environ. Prot.*, **95**, 146 (2015).
- Z. W. Cheng, L. Feng, J. M. Chen, J. M. Yu and Y. F. Jiang, *J. Hazard. Mater.*, **254**, 354 (2013).
- Y. Zhang, C. S. Guo, J. Xu, Y. Z. Tian, G. L. Shi and Y. C. Feng, *Water Res.*, **46**(9), 3065 (2012).
- P. Singh, K. Mondal and A. Sharma, *J. Colloid Interface Sci.*, **394**, 208 (2013).
- A. Buthiyappan, A. R. A. Aziz and W. M. A. W. Daud, *Rev. Chem. Eng.*, **32**(1), 1 (2014).
- F. H. Borba, A. N. Modenes, F. R. Espinoza-Quinones, D. R. Manenti, R. Bergamasco and N. D. Mora, *Environ. Technol.*, **34**, 653 (2013).
- F. I. Hai, K. Yamamoto and K. Fukushi, *Crit. Rev. Environ. Sci. Technol.*, **374**(4), 315 (2007).
- F. M. Amaral, M. T. Kato, L. Florêncio and S. Gavazza, *Bioresour. Technol.*, **163**, 364 (2014).
- M. Bahrani and A. Nezamzadeh-Ejhi, *Mater. Sci. Semicond. Process.*, **30**, 275 (2015).
- A. Nezamzadeh-Ejhi and F. Khodabakhshi-Chermahini, *J. Ind. Eng. Chem.*, **20**, 695 (2014).
- U. Hübner, B. Seiwert, T. Reemtsma and M. Jekel, *Water Res.*, **49**, 34 (2014).
- N. H. M. Azmi Ayodele, O. B. Vadivelu, V. M. Asif and B. H. Hameed, *J. Taiwan Inst. Chem. Eng.*, **45**, 1459 (2014).

49. J. Blanco, F. Torrades, M. Morrón, M. Brouta-Agnésa and J. García-Montaño, *Chem. Eng. J.*, **240**, 469 (2014).
50. D. Montgomery and C. Jennings, *Introduction to Statistical Quality Control*, 7<sup>th</sup> Ed., John Wiley & Sons Inc., London, 754 (2012).
51. B. W. Berry, M. C. Martínez-Rivera and C. Tommos, *Proc. Natl Acad. Sci.*, **109**(25), 9739 (2012).
52. T. Yang, L. Zhang, A. Wang and H. Gao, *Inf. Sci.*, **235**, 55 (2013).
53. M. Kwon, S. Kim, Y. Yoon, Y. Jung, T. M. Hwang, J. Lee and J. W. Kang, *Chem. Eng. J.*, **269**, 379 (2015).