



Application of response surface methodology for the optimization of polycyclic aromatic hydrocarbons degradation from potable water using photo-Fenton oxidation process

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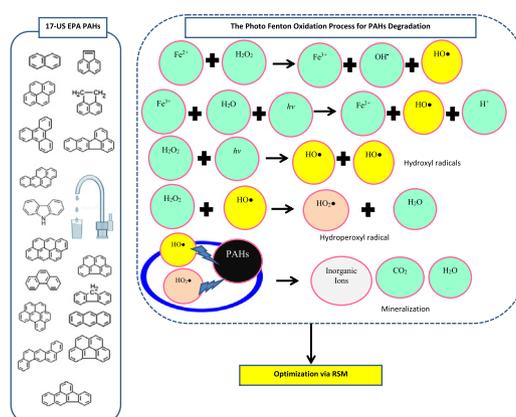
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HIGHLIGHTS

- PAHs are carcinogenic compounds and abundantly found in mixed use area.
- Perak River serves as principal water intakes in Perak Tengah, Perak, Malaysia.
- Conventional water treatment techniques are inefficient for PAHs removal.
- This research studies Photo-Fenton Oxidation Process for PAHs removal in water.
- AOPs may be considered as an alternative to conventional water treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic compounds, composed of benzene rings. The objective of this research was to identify the optimum condition for the degradation of PAHs contaminated water using photo-Fenton oxidation process via response surface methodology (RSM). Aqueous solution was prepared and potable water samples were collected from water treatment plants in Perak Tengah, Perak, Malaysia in September 2016. The reaction time, pH, molarity of H₂O₂ and FeSO₄ were analyzed followed by RSM using aqueous solution. A five level central composite design with quadratic model was used to evaluate the effects and interactions of these parameters. The response variable was the percentage of total organic carbon (TOC) removal. PAHs quantification was done using gas chromatography mass spectrometry analysis. The regression line fitted well with the data with R² value of 0.9757. The lack of fit test gives the highest value of Sum of Squares (15,666.64) with probability F value 0.0001 showing significant quadratic model. The optimum conditions

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Optimization
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were established corresponding to the percentage of TOC removal. The PAHs removal efficiency for potable water samples ranged from 76.4% to 91% following the first order of kinetic rates with R^2 values of >0.95. Conventional water treatment techniques are not effective for PAHs removal. Thus, advanced oxidation processes may be considered as an alternative to conventional water treatment techniques in Malaysia and other developing countries.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that are composed of two or more fused benzene rings (ATSDR, 2017) and abundantly found in mixed use areas (Malakahmad et al., 2018; Masood et al., 2016; Keshavarzifard et al., 2014; Kanzari et al., 2014; Retnam et al., 2013; Mirsadeghi et al., 2011; Patrolecco et al., 2010; Ahrens and Depree, 2010; Saha et al., 2009; Motelay-Massei et al., 2006). Carcinogenic environmental pollutants (US EPA, 1980) enter the aquatic environment from a variety of sources including airborne particulates, industrial effluents, coal-tar, storm-water runoff and point-source petroleum pollution (Malakahmad et al., 2015; Khan et al., 2017; Khan et al., 2016; Grob, 1983).

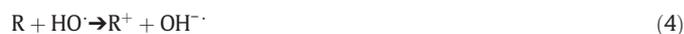
Rivers are vulnerable to pollution (Malakahmad et al., 2015). Factors that may contribute to river pollution like improper environmental management (Santschi et al., 2001), insufficient public awareness (Poon et al., 2016), poor educational background (Wolters et al., 2016), dense population (Mokhtar et al., 2015), poverty (Madulu, 2005), excessive urbanization (Kishida, 2013), and industrialization (Hayzoun et al., 2015), as well as extensive agricultural activities (Jain and Sharma, 2001) are making rivers a potential water-borne transmission media for various diseases. As a result, stakeholders may face highly potential health threats due to the degraded land and water ecosystem (Lourio-Cabana et al., 2011). It has been reported that, 98% of Malaysia's fresh water supply originates from surface water (APEC, 2016). Perak River is located in a mixed use area that serves as the principal water intake for domestic, agricultural and industrial purposes in Perak Tengah, in the Perak, Malaysia and due to that, this river may have been exposed to various anthropogenic pollutants (Malakahmad et al., 2018).

The type of advanced oxidation processes (AOPs) used for the removal of PAHs in this research was photo-Fenton water treatment technique. Photolysis (UV light) plays an important role in the PAHs degradation and other contaminants in water by generation of highly reactive intermediates, mainly hydroxyl radical ($\bullet\text{OH}$), a powerful non-specific oxidant ($E^\circ = 2.8 \text{ V}$) (Pignatello and Huang, 1993).

Several researchers have investigated the photolysis of PAHs under artificial conditions (Rubio-Clemente et al., 2014; Sanches et al., 2011; Jacobs et al., 2008; Shemer and Linden, 2007; Bertilsson and Widenfalk, 2002; Fasnacht and Blough, 2002; Miller and Olejnik, 2001). Under these conditions, the emission of light spectrum may overlap with the absorption spectrum of the substance of interest, causing its degradation (Shemer and Linden, 2007). The wavelengths that can be absorbed by a compound depends on its structure (Sanches et al., 2011). The absorption wavelength of PAHs range from 210 nm to 386 nm (Dabestani and Ivanov, 1999).

Hydrogen peroxide (H_2O_2) is a non-flammable colorless liquid that resembles water, a strong oxidizing agent used in aqueous solution. It contains the peroxide ion (O_2^{2-}), and an extra oxygen atom compared to the more stable water molecule. The bond between the two oxygen atoms, i.e. the peroxide bond, is broken while two $\text{H}-\text{O}$ radicals are formed (Eq. (1)). These radicals quickly react with other substances that form new radicals and a chain reaction takes place. Its application is very selective. By changing the reaction conditions (pH, reaction time and the addition of a catalyzer), H_2O_2 will attack different pollutants (Munter, 2001; Andreozzi et al., 1999; Pignatello and Huang, 1993). It is more powerful than chlorine (Cl_2), chlorine dioxide (ClO_2) and potassium permanganate (KMnO_4). The oxidation potential of H_2O_2 is just below that of ozone (Munter, 2001).

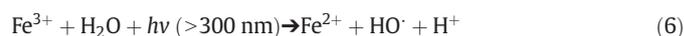
The combination of photolysis and catalytic processes produce profound changes in the chemical structure of pollutants (Pignatello and Huang, 1993). H_2O_2 in the aqueous solution absorbs the incident UV lights and undergoes photo-transformation reactions that generate free hydroxyl radicals (Eq. (1)) (Bokare and Choi, 2014). These free hydroxyl radicals will subsequently decompose the organic pollutants into non-toxic products like CO_2 , H_2O and inorganic salts (Neyens and Baeyens, 2003; Litter and Quici, 2010). The mechanism reaction of the free radicals involves (a) H-addition to $\text{C}=\text{C}$ bonds or to aromatic rings (Eq. (2)); (b) H abstraction from $\text{C}-\text{H}$, $\text{N}-\text{H}$ or $\text{O}-\text{H}$ bonds (Eq. (3)); and (c) electron transfer reactions (Eq. (4)) (Rubio-Clemente et al., 2014; Munter, 2001; Von Sonntag, 2006).



In 1894, Henry John Horstman Fenton published a descriptive study describing how iron (II) ions in the presence of certain oxidizing agents (e.g. H_2O_2) yielded a solution with powerful and extraordinary oxidizing capabilities, and this mixture is typically referred to as the Fenton reagent. Fenton reagent (or Fenton reaction) can be defined as a mixture of hydrogen peroxide (oxidizing agent) and iron (II) ions (catalyst). This method is based on the formation of reactive oxidizing species that effectively degrade the pollutants in solution (Barbusiński, 2009). In the presence of the Fe^{2+} catalyst, H_2O_2 will be decomposed and will generate radical $\text{HO}\cdot$ (Eqs. (5) to (9)) (Bokare and Choi, 2014).

These reactive oxidizing species remove recalcitrant compounds. $\text{Fe}^{3+}/\text{Fe}^{2+}$ can perform catalytic behavior in acidic media (Walling, 1975; Aaron, 2014) (Eqs. (5), (6) and (7)).

The organic compounds present in water are mainly oxidized by $\text{HO}\cdot$ (Eq. (8)), principally by abstracting hydrogen atoms or by adding them to double bonds and aromatic rings (Lundstedt et al., 2006). The ferric ions formed decompose H_2O_2 to regenerate Fe^{2+} and yield $\text{HO}_2\cdot$ (Eq. (9)) (Neyens and Baeyens, 2003; Pignatello et al., 2006).



The general pathway of PAHs degradation with the photo-Fenton reaction consists of the absorption of light by PAHs, causing their excitation (Eq. (9)). The excited PAH can therefore return to the ground state and dissipate its energy (Eq. (10)) (Miller and Olejnik, 2001) or be transformed into a radical cation ($\text{PAH}\cdot^+$) and a solvated electron (e_{aq}^-) (Eq. (11)). Meanwhile, O_2 from the water could react with the e_{aq}^- leading to $\text{O}_2\cdot^-$ or $^1\text{O}_2$ formation (Eqs. (12), (13)) (Fasnacht and Blough, 2002; Miller and Olejnik, 2001). These oxygen species can react with the organic molecule to form intermediates and undergo

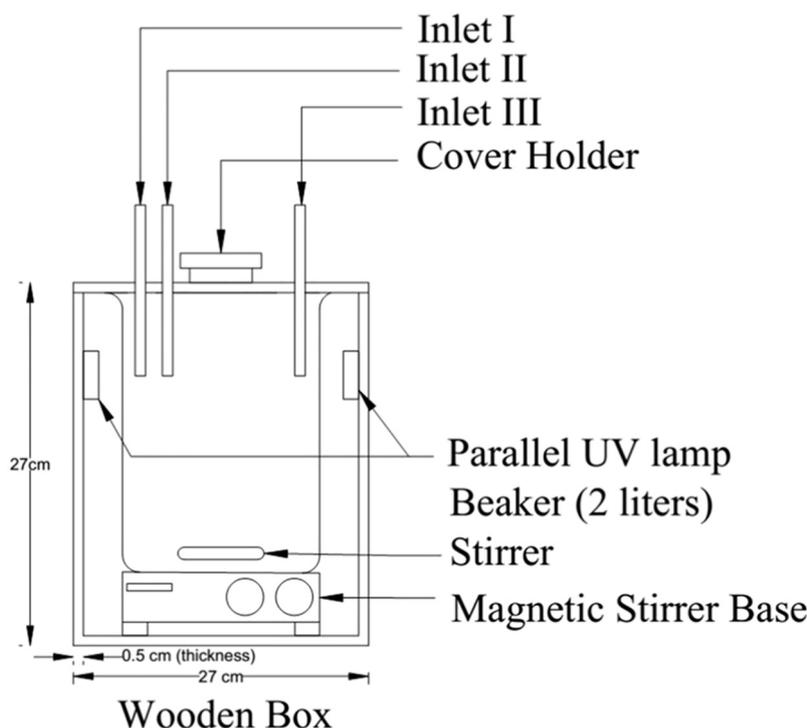
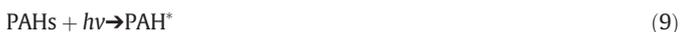


Fig. 1. Schematic diagram of the reactor used.

further oxidation causing the mineralization of the parent compound (Eqs. (14), (15) and (16)).



To date, the application of the photo-Fenton reagent has been reported for the treatment of PAHs from contaminated soil (review paper) (Yap et al., 2012), landfill leachate (Wu et al., 2011), municipal solid waste leachate (Li et al., 2016), sanitary landfill leachate (Tânia et al., 2017), aniline wastewater (Liu et al., 2012), ammunition wastewater (Li et al., 2013) and saline aqueous solutions (Muff and Søgaard, 2011). As for drinking water, the application of Fenton reagent was aided with photo treatment (Ndounla and Pulgarin, 2014; Catalá et al., 2015) or electrolysis (Plakas et al., 2016) not focusing on PAHs removal. Ndounla and Pulgarin (2014) focused on disinfecting the natural drinking water source at two wells in Sahelian region during the rainy season

from bacterial growth. Meanwhile Catalá et al. (2015) worked on drugs removal from natural water by using photo-Fenton treatment. Plakas et al. (2016) has combined Fenton reagent and electrolysis for the removal of organic micropollutants from drinking water which is not specific to PAHs.

Response surface methodology (RSM) by Design Expert Software is one of the statistical modelling methods commonly used in the research field. It provides the best prediction on the parameters optimization and reduces massive laboratorial work based on its statistical modelling prediction (Lenth, 2009). Functions are provided to generate central composite designs. For analysis of the resulting data, the package provides estimation of the response surface, lack of fit, contour plots of the fitted surface, and follow-up analyses such as steepest ascent, canonical analysis, and ridge analysis (Lenth, 2009).

This research aims to identify the optimum condition via response surface methodology (RSM) for the 17-USEPA PAHs degradation in aqueous solution and potable water samples from water treatment plants in Perak Tengah, Perak, Malaysia using the photo-Fenton treatment method. The optimization of the photo-Fenton treatment technique as one of the PAHs removal solutions is presented in this study, suggesting AOPs application may be considered as an alternative water treatment in Malaysia and other developing countries.

2. Methodology

2.1. Batch experiments for the photo-Fenton treatment method

The 17-US EPA PAHs standard was PAHs Mix 64 (2000 mg/L or 2000 µg/mL) in 1 mL (Brand: Dr. Ehrenstorfer, benzene/dichloromethane

Table 1
Experimental range and levels of independent process variables.

Process variables	Code factor	Units	Low actual	High actual	Low coded	High coded
MR	A	MR	0.03	0.2	-1	1
pH	B	N/A	2.5	6.8	-1	1
Time	C	Seconds	100	300	-1	1

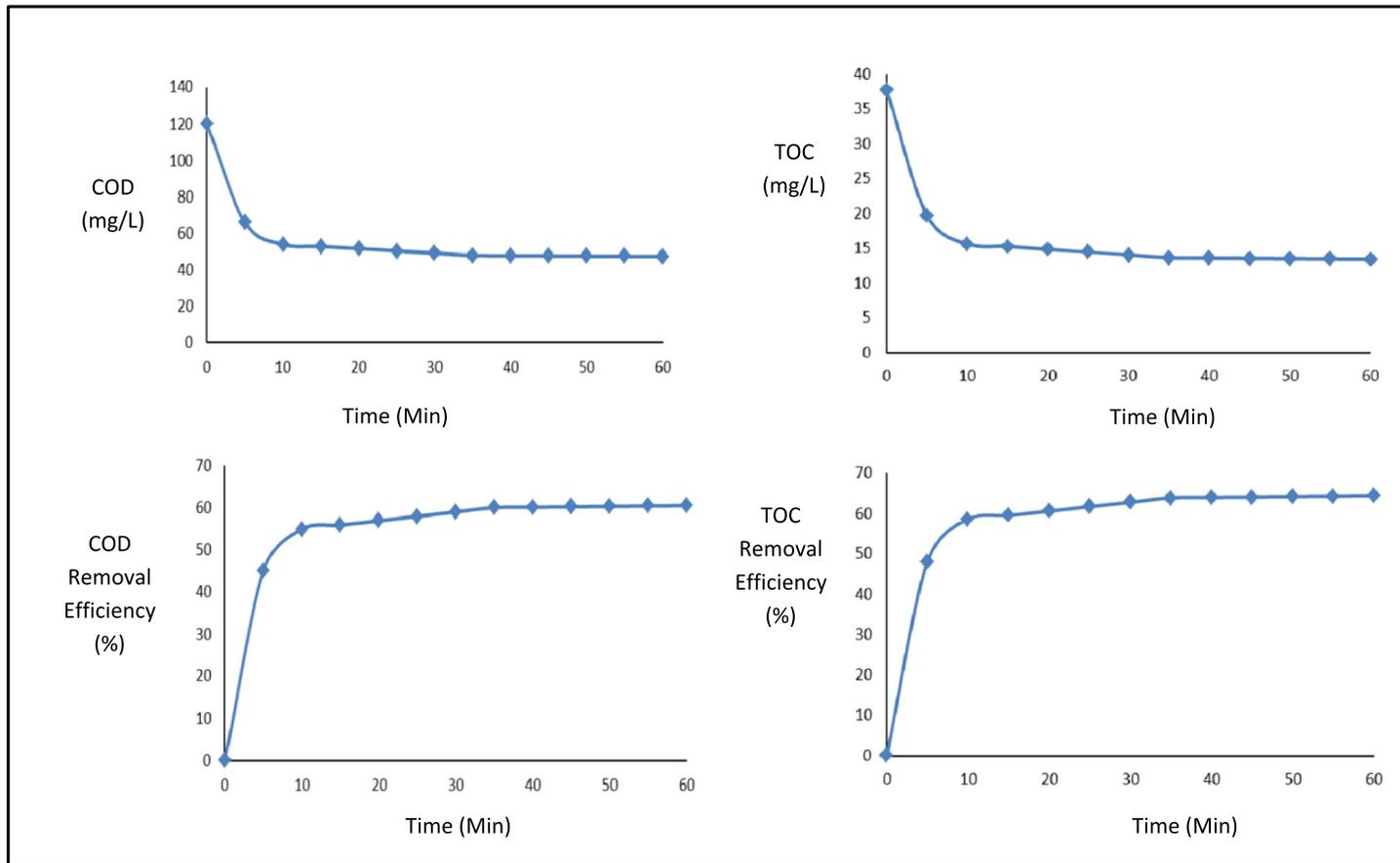


Fig. 2. COD (mg/L) degradation, TOC (mg/L) degradation, COD removal efficiency (%) and TOC removal efficiency (%) over time for the time reaction parameter.

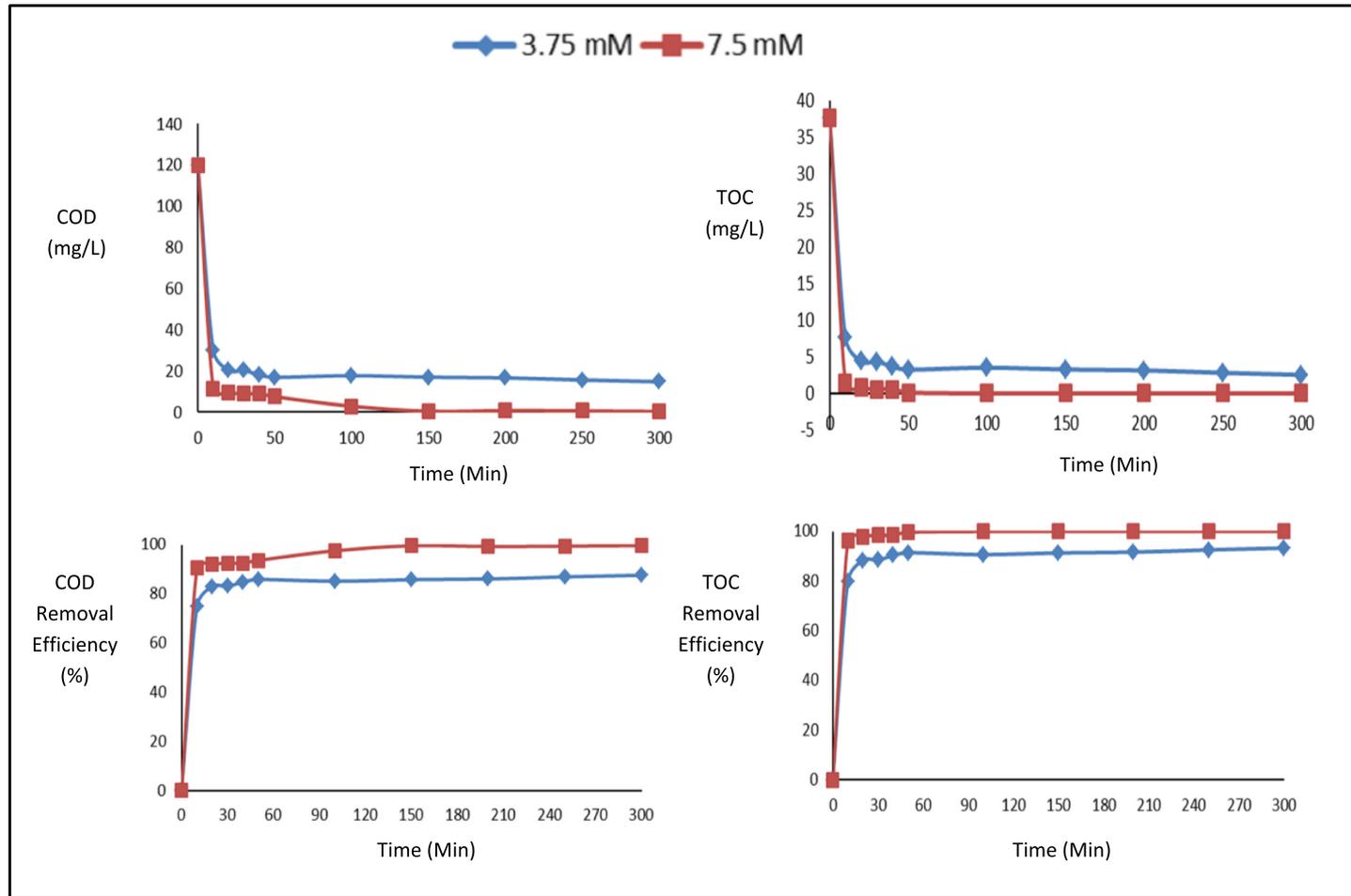


Fig. 3. COD (mg/L) degradation, TOC (mg/L) degradation, COD removal efficiency (%) and TOC removal efficiency (%) over time for the H_2O_2 concentrations tested.

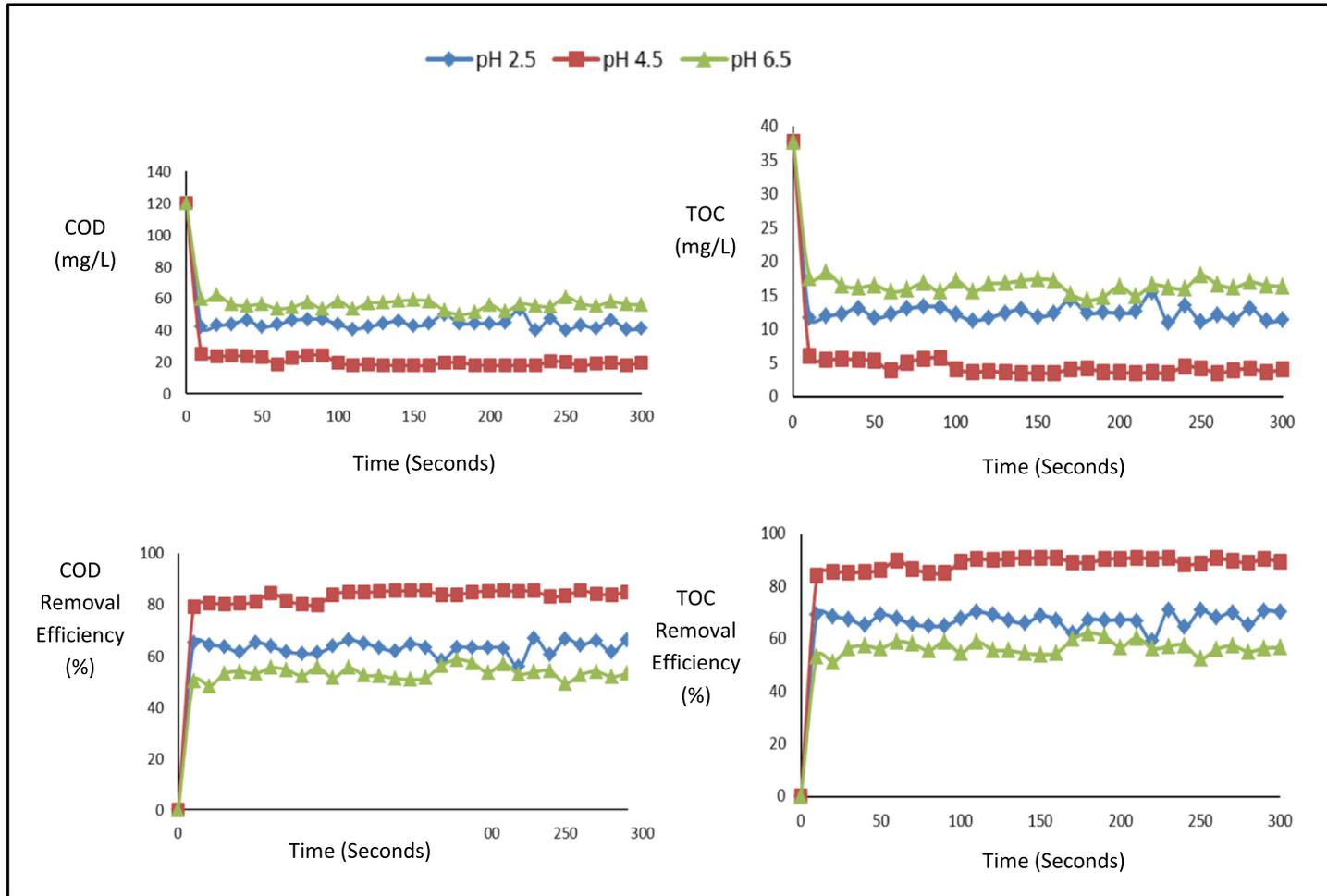


Fig. 4. COD (mg/L) degradation, TOC (mg/L) degradation, COD removal efficiency (%) and TOC removal efficiency (%) over time for the ranges of pH tested.

1:1) which contained 17 types of PAHs. It was purchased from Agilent J & W. The PAHs standard was stored at 5 °C in the dark cold room. The preparation method for the aqueous solution containing PAHs was based on the method used by Sakulthaew et al. (2014) and Sabaté et al. (2001).

The measurement of the chemical oxygen demand (COD) value was performed using the COD analytical equipment (HACH) according to Method 8000. Method 8000 is USEPA approved (5220 D) for wastewater analysis (HACH Company, 1999; APHA, 2005).

The determination of total organic carbon (TOC) was determined using the TOC analyzer (Shimadzu, Japan) (US EPA, 2005). The measurements of TOC were used to monitor the degradation of organic compounds like PAHs during the treatment (Vela et al., 2012). These parameters were also previously reported and used as indications for other types of water pollutants (Vilhunen et al., 2010; Sabhi and Kiwi, 2002; Li et al., 2013).

A reactor was designed with a capacity of 2.0 L using a pyrex beaker; to sustain chemical reactions and due to its stability in a wide range of pHs. Two UV lamps of 4 W with emitting radiation wavelength of 365 nm (Hitachi, F4T5, 4 W, black light, light intensity 400 $\mu\text{Watt}/\text{cm}^2$) were subjected to the sample in room temperature (27 °C) and a rotational frequency of 300 rpm (Fig. 1).

Batch experiments were conducted using the designed reactor with 1 L of aqueous solution. In the beginning of this experiment, the fixed variables were the concentration of PAHs in the prepared aqueous solution (4 $\mu\text{g}/\text{L}$ of PAHs), the actual pH of the aqueous solution (pH 6.96), the theoretically calculated molarity of H_2O_2 (0.0075 M) and FeSO_4 (0.00075 M) (Baker et al., 1999), room temperature (27 °C), rotational

frequency (300 rpm) and UV irradiation (emitting radiation wavelength of 365 nm). The reaction time, pH and MR of $\text{H}_2\text{O}_2:\text{FeSO}_4$ were analyzed. The mixing was carried out by a magnetic stirrer for complete homogeneity during the reaction. Aliquots were withdrawn at the targeted time. The pH of the solution was adjusted to more than pH 10 to decompose the H_2O_2 to oxygen and water to reduce interference in the COD determination. The concentration of iron (Fe) should not exceed 1 mg/L in drinking water standards (MOH, 2016). Nevertheless, the concentration of iron (Fe) after the treatment was 0.38 mg/L.

2.2. Process optimization of PAHs removal by photo-Fenton

A five-level central composite design with quadratic model was used in RSM to evaluate the effects and interactions of these parameters. The response variable was the percentage of TOC removal. Experimental data were analyzed and fitted to a second order polynomial equation using the Design Expert ® software (Version 6). The second order polynomial was employed to attain the interaction between the variables (Eq. (17)).

$$Y = \beta_0 + \sum_{i=1}^k \beta_i \cdot x_i + \sum_{i=1}^k \beta_{ii} \cdot x_i^2 + \sum_{i < j}^k \sum_j^k \beta_{ij} \cdot x_i \cdot x_j + \dots + e \quad (17)$$

The y is the predicted response variable where i and j are the linear and quadratic coefficients, β is the regression coefficient, k is the number of factors studied and optimized in the experiment and e is the

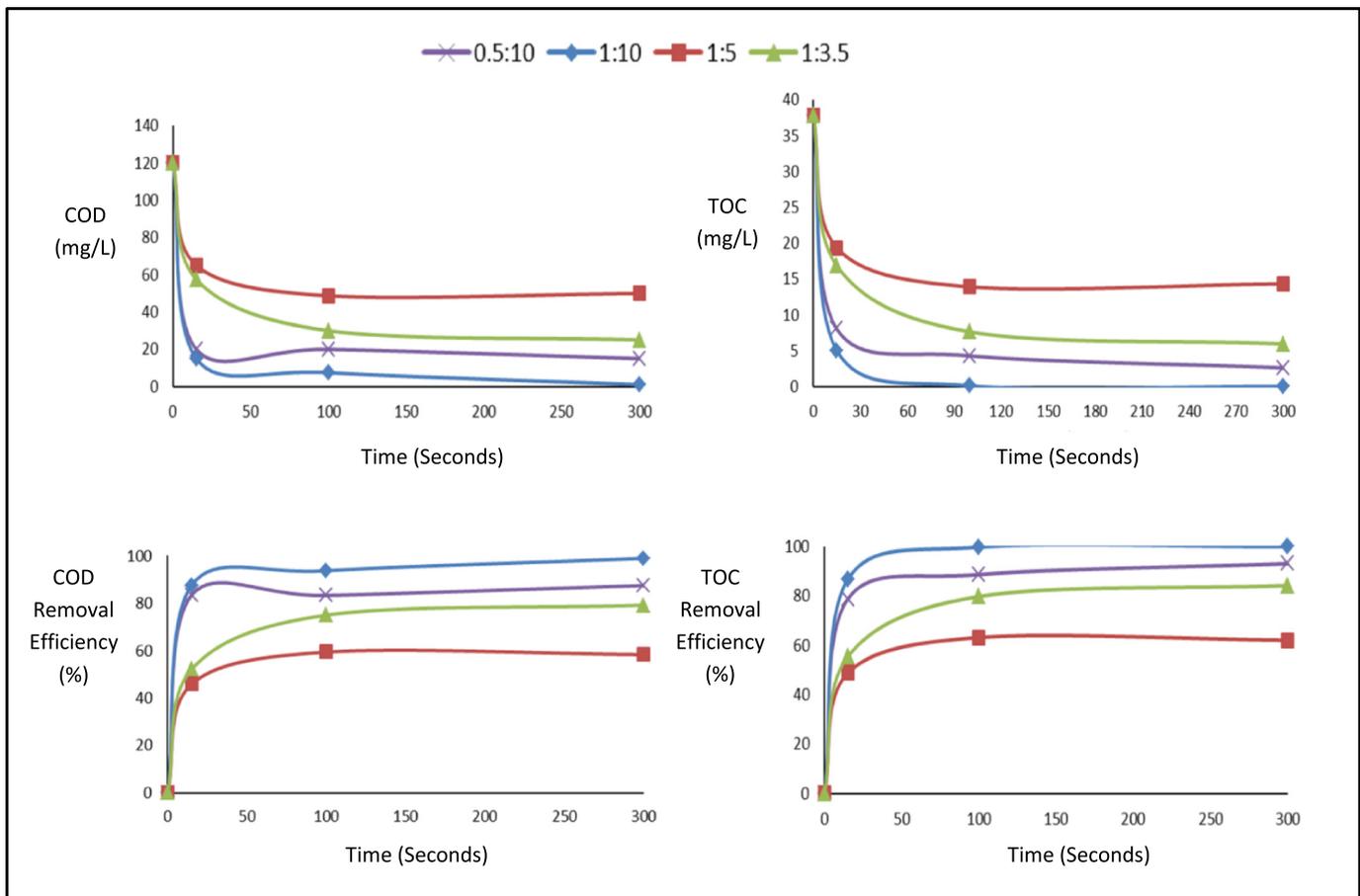


Fig. 5. The effect of molarity ratio of $\text{H}_2\text{O}_2:\text{FeSO}_4$ on COD (mg/L) degradation, TOC (mg/L) degradation, COD removal efficiency (%) and TOC removal efficiency (%) over time for the molarity ratio of $\text{H}_2\text{O}_2:\text{FeSO}_4$ tested.

Table 2
Central composite design and responses results.

Run	Independent variables (code)			Response
	MR	pH	Reaction time (seconds)	Efficiency of TOC removal (%)
1	0.12 (0)	4.65 (0)	200.00 (0)	94.8
2	0.12 (0)	1.03 (−1)	200.00 (0)	14.5
3	0.20 (1)	2.50 (−1)	100.00 (−1)	47.7
4	0.20 (1)	6.80 (1)	100.00 (−1)	46.4
5	0.03 (−1)	6.80 (1)	300.00 (1)	41.1
6	0.12 (0)	4.65 (0)	200.00 (0)	94.8
7	0.12 (0)	4.65 (0)	200.00 (0)	94.8
8	0.26 (1)	4.65 (0)	200.00 (0)	77.3
9	0.12 (0)	8.27 (1)	200.00 (0)	14.7
10	0.03 (−1)	2.50 (−1)	100.00 (−1)	35.9
11	0.03 (−1)	6.80 (1)	100.00 (−1)	35.9
12	0.03 (−1)	4.65 (0)	200.00 (0)	72.8
13	0.12 (0)	4.65 (0)	200.00 (0)	94.8
14	0.12 (0)	4.65 (0)	200.00 (0)	94.8
15	0.12 (0)	4.65 (0)	200.00 (0)	94.8
16	0.20 (1)	2.50 (−1)	300.00 (1)	50.8
17	0.03 (−1)	2.50 (−1)	300.00 (1)	41.1
18	0.12 (0)	4.65(0)	368.18 (1)	98.2
19	0.20 (1)	6.80 (1)	300.00 (1)	49.9
20	0.12 (0)	4.65 (0)	31.82 (−1)	86.0

random error. Experimental range and levels of independent process variables are shown in Table 1.

2.3. Test on potable water samples from water treatment plants

Potable water samples were collected from three water treatment plants in Perak Tengah, Perak, Malaysia namely WTPP (N 4° 29.84064', E 100° 55.34406'), WTPS (N 4° 22.95438', E 100° 54.13446') and WTPK (N 4° 18.94494', E 100° 52.81428') in September 2016.

As for sample collection and preservation purpose, 1 L amber bottles were pre-cleaned before use. The bottles were washed with phosphate-free detergent and rinsed with tap water. Then, the bottles were washed with 1 mol HNO₃ and rinsed with tap water. The sample containers were rinsed with sample water before they were filled up with sample water. The samples were stored in the cooler room at 4 °C (US EPA, 2014).

The degradation of PAHs using photo-Fenton treatment method in potable water samples from WTPP, WTPS and WTPK was studied based on degradations of total organic carbon (TOC) as well as integrated kinetic rates and quantification of 17-US EPA PAHs concentrations after the treatment via gas chromatography mass spectrometry (GCMS) analysis.

The type of PAHs extraction used was solid phase extraction (APHA, 2005). The solid phase extraction (SPE) method consisted of column HyperSep Retain PEP 60 mg bed weight 3 mL column by Thermo Fisher Scientific Inc. (Product Code: 10505905) was used. The cartridge used was C18 Cartridge: 12102052 Bond Elut C18, 500 mg 6 mL, 30 pk from Agilent J & W. Before loading samples, the cartridge was first

conditioned with 10 mL DCM/n-hexane (1:3, v/v), then with 10 mL methanol to remove air and leach impurity and then with 10 mL ultra-pure water to equilibrate the phase. Next, a 500 mL water sample was loaded at the flow rate of 5.0 mL/min. After loading, the cartridge was kept vacuum for 30 min to remove residual water. The objects retained on the cartridge were eluted by 15 mL/min by 15 mL of DCM/n-hexane (1:3, v/v) at the flow rate of 1 mL/min. The sample re-concentration was done using a type of nitrogen evaporator by Thermo Fisher Scientific namely Reacti-Vap™ Evaporators with 9 ports (Product Code: TS-18825). The samples were collected into a test tube and condensed to dryness under gentle flow of nitrogen at room temperature and re-dissolved with 1 mL of DCM:n-hexane (1:3, v/v). Then, the samples were transferred into the 1.5 mL sept vials, ready for GCMS analysis. Samples need to be analyzed within 40 days after the re-concentration (APHA, 2005; Agilent Technologies, 2011).

Gas chromatography model Clarus 680 and mass spectrometer model Clarus 600 S from Perkin Elmer (USA) using helium as the gas carrier (on a constant pressure of 60 kg²/cm²) with a DB-5MS Ultra Inert 122-5532UI capillary column (30 × 0.25 mm, 0.25 μm film thickness) model from Agilent J & W (USA) was used. The gas carrier was helium and flowed at a constant of 30 cm/s. The Mass Selective Detector (MSD) temperature was varied at 300 °C, Quadrupole at 180 °C and Transfer Line at 290 °C. The scan ranges were 50 to 550 AMU. The injection volume was 1.0 μL and the injector temperature was 320 °C, start temperature at 110 °C for 5 min and end temperature was 320 °C for 8 min. The oven temperature program was started from 110 °C for 5 min with the rate of 5 °C/min and ended at 320 °C for 8 min. The

Table 3
ANOVA for response surface quadratic model.

Source	SS	R ²	DF	MS	F Value	Prob > F	
Quadratic Model	15,666.64	95.13	9	1740.74	44.59	<0.0001	Significant
A	573.29	7.30	1	573.29	14.69	0.0033	Significant
B	0.25	−0.14	1	0.25	6.514E ^{−003}	0.9373	Not significant
C	103.07	2.75	1	103.07	2.64	0.1353	Not significant
A ²	1895.04	−14.41	1	1895.04	48.54	<0.0001	Significant
B ²	13,404.36	−30.37	1	13,404.36	343.36	<0.0001	Significant
C ²	128.04	−2.97	1	128.04	3.28	0.1002	Not significant
AB	0.60	−0.28	1	0.60	0.015	0.9034	Not significant
AC	1.81	−0.48	1	1.81	0.046	0.8341	Not significant
BC	0.020	0.050	1	0.020	5.123E ^{−004}	0.9824	Not significant
Residual	390.39		10	38.04			
Lack of fit	390.39		5	78.08			
Pure error	16,057.03		5	0.000			

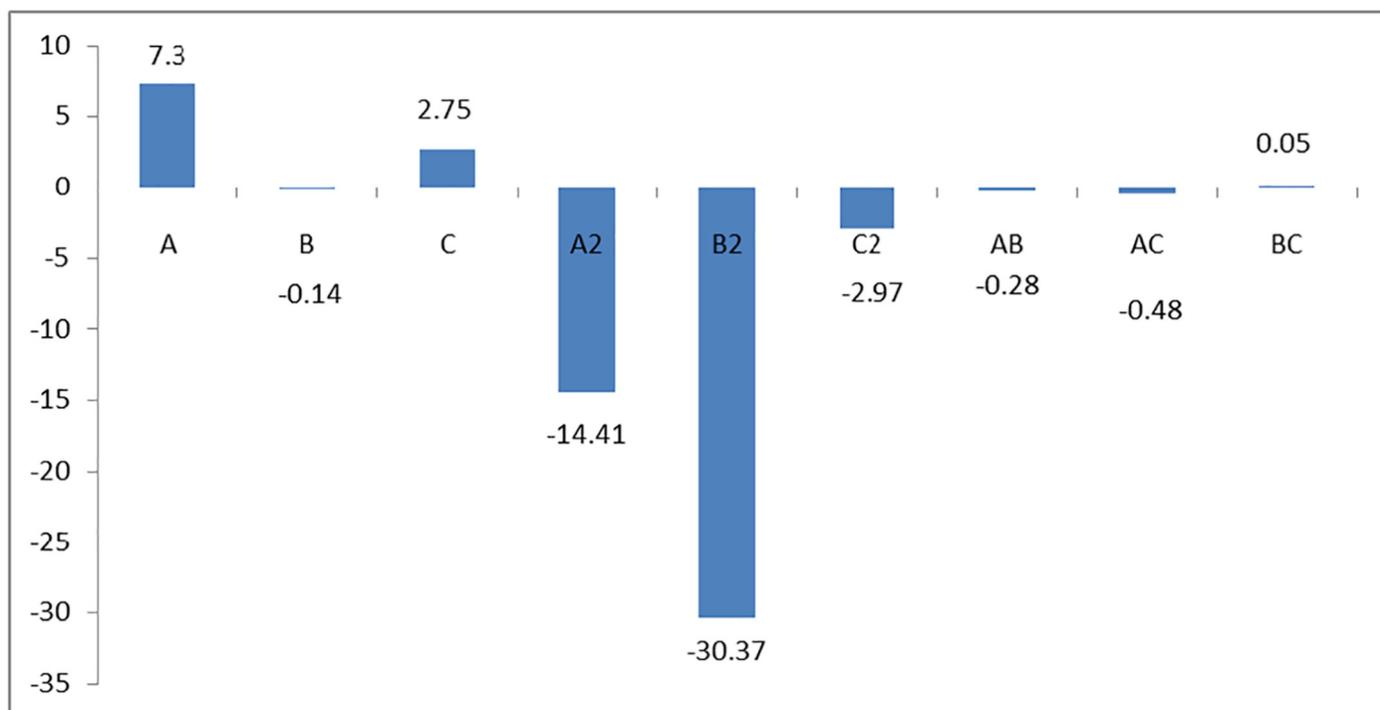


Fig. 6. Coefficient of determination (R^2) for quadratic model and model terms.

injection temperature program was made splitless at 320 °C with total flow/purge flow at 1 mL/min. The total run time was 100 min (Lynam, 2010).

The calibrations curves ($R^2 = 0.99$) and chromatograms for 17 USEPA-PAHs reference standards via GCMS are shown in Appendix A. In GCMS, compounds (e.g. 17 USEPA-PAHs) present in a standard sample of known concentration and volume are analyzed separately from the unknown sample (e.g. extracted water samples) under identical conditions. Standard sample is used to facilitate the qualitative identification and/or quantitative determination of the sample components. The Qvalue is referred to the quality of the peak by mass ratio. If the Qvalue of the search is $\geq 80\%$, that compound will be reported as a tentatively identified compound (TIC) (Hübschmann, 2015). All of the calibration points Qvalue ranged between 86 and 100% and reported as a tentatively identified compound (TIC). The correlation coefficient (R^2) for all calibration curves were ≥ 0.95 . Tentatively Identified Compounds (TICs) are another tool used by EPA to characterize hazardous sites. The identification is not considered “absolute” or “confirmed” until a known standard for the suspect compound can be analyzed on the same instrument which made the tentative identification (Hübschmann, 2015).

3. Results and discussion

3.1. Batch experiments for the photo-Fenton treatment method

Time reaction, molarity of H_2O_2 , pH and molarity ratio of $H_2O_2:FeSO_4$ were the four main parameters tested for the optimization process. For the time reaction parameter, the fixed variables mentioned above maintained the same. The samples were taken for COD and TOC measurements every 15 s for 1 h (Fig. 2). The COD readings showed a trend of positive quadratic line. Three points of time-taken (left point, peak point, right point) were selected.

The initial COD values of 120 mg/L were decreased to 66 mg/L after 5 min and achieved equilibrium after 10 min where the COD values were in the range of 47 mg/L. The COD removal efficiency achieved 60% after 35 min (Fig. 2). In addition, initial TOC (mg/L) was degraded from 37.7 mg/L to 13.4 mg/L after 60 min. The TOC removal efficiency

achieved was 64.4% after 60 min. Thus, the reaction time range of 100 to 300 s was used for the RSM design.

The H_2O_2 concentrations tested were 3.75 mM and 7.5 mM (Fig. 3). Reaction time was fixed at 300 s with unadjusted pH of the sample. The initial COD values of 120 mg/L were decreased to 30 mg/L (3.75 mM) and 11.4 mg/L (7.5 mM) after 10 min. The COD degradation achieved were 87.6% (3.75 mM) and 99.7% (7.5 mM) of COD removal efficiency after 300 s. In addition, initial TOC (mg/L) was degraded from 37.7 mg/L to 2.54 mg/L (3.75 mM) and 0 mg/L (7.5 mM) after 300 s. The TOC removal efficiency achieved were 93% (3.75 mM) and 100% (7.5 mM) after 300 s. Thus, the 7.5 mM was chosen as H_2O_2 concentration for the photo-Fenton treatment.

The ranges of pH tested were pH 2.5, pH 4.5 and pH 6.5 (Fig. 4). Other operational variables such as time (300 s) and H_2O_2 concentration (7.5 mM) were fixed. The initial COD values of 120 mg/L were decreased to 41.9 mg/L (pH 2.5), 25.1 mg/L (pH 4.5) and 59.8 mg/L (pH 6.5) after 10 s. The COD removal efficiency achieved after 300 s were 65.9% (pH 2.5), 83.9% (pH 4.5) and 53.3% (pH 6.5). In addition, initial TOC (mg/L) was degraded from 37.7 mg/L to 11.2 mg/L (pH 2.5), 4.0 mg/L (pH 4.5) and 16.3 mg/L (pH 6.5) after 300 s. The TOC removal efficiency achieved after 300 s were 70% (pH 2.5), 89% (pH 4.5) and 57% (pH 6.5).

The last parameter tested was the molarity ratio of $H_2O_2:FeSO_4$ (Fig. 5). The molarity ratios tested were 0.5:10, 1:10, 1:3.5 and 1:5. The initial COD values of 120 mg/L were decreased to 20 mg/L (0.5:10), 15 mg/L (1:10), 57.5 mg/L (1:3.5) and 65 mg/L (1:5) after 15 s. The COD removal efficiency achieved after 300 s were 87.5% (0.5:10), 98.9% (1:10), 79.2% (1:3.5) and 58.3% (1:5). In addition, initial TOC (mg/L) was degraded from 37.7 mg/L to 2.6 mg/L (0.5:10), 0 mg/L (1:10), 5.9 mg/L (1:3.5) and 14.3 mg/L (1:5) after 300 s. The TOC removal efficiency achieved after 300 s were 93.1% (0.5:10), 100% (1:10), 84.3% (1:3.5) and 62.1% (1:5).

3.2. Process optimization of PAHs removal by UV/ H_2O_2

From the batch experiments, the ranges of time, pH and molar ratios (MR) of $H_2O_2:FeSO_4$ were determined and computed for the response surface methodology (RSM) optimization. The ranges of

Table 4

Fit summary results for response parameters.

Response	Significant model	Std. Dev.	R ²	Adj. R ²	Predicted R ²	F-value
TOC removal	Quadratic model	6.25	0.9757	0.9538	0.7834	44.59

reaction time were from 100 to 300 s. The ranges of molar ratios were from 0.03 to 0.28. Meanwhile, the ranges of pH were from 2.5 to 6.8. The central composite design (CCD) was used to design the experiment to come out with 20 sets of experimental conditions to be tested (Table 2).

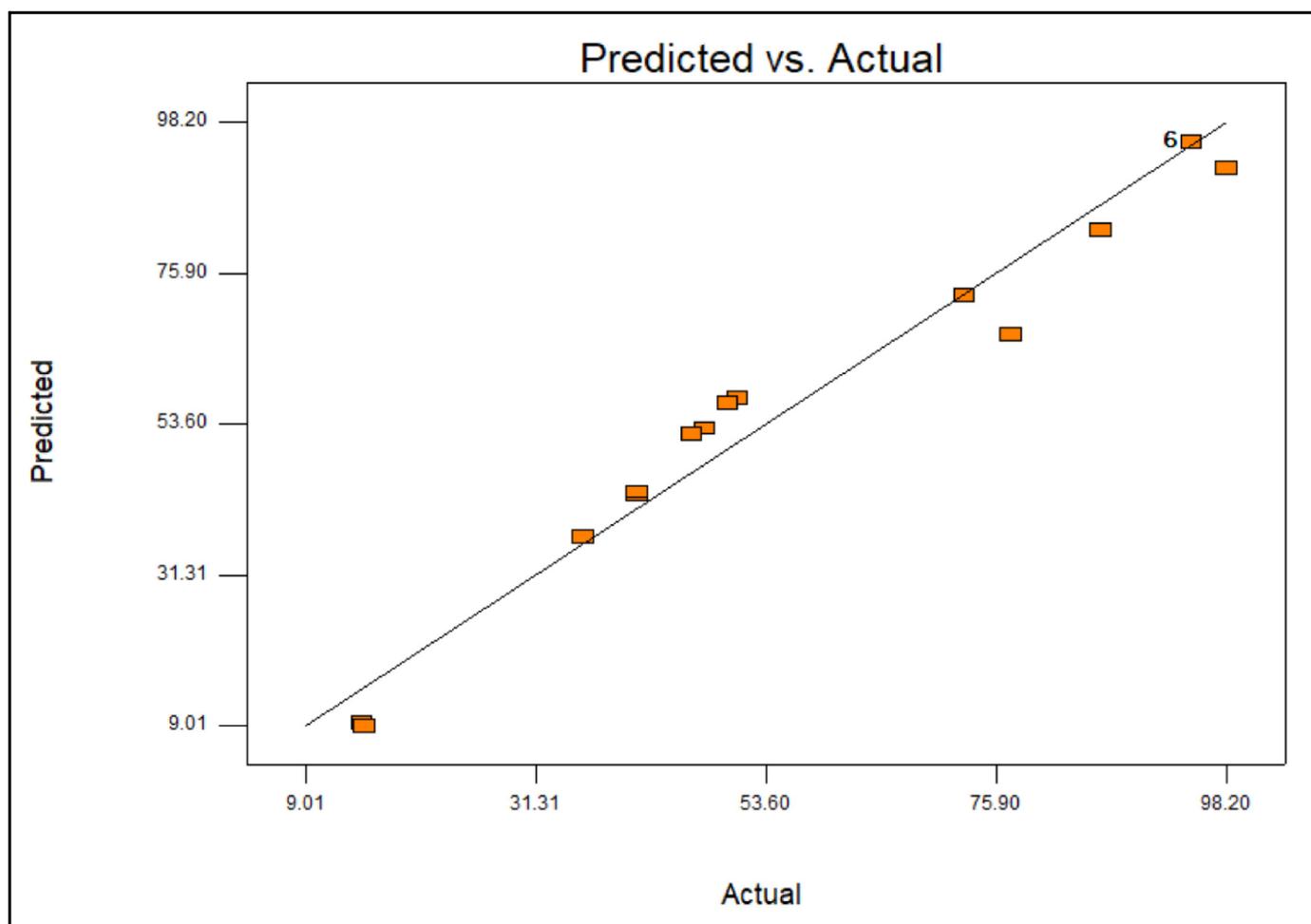
The analysis of variance (ANOVA) results of the established quadratic model for percentage of TOC removal is shown in Table 3. The mean squares (MS) were obtained by dividing the sum of squares (SS) of each of the two sources of variation, the model and the error (residual) variance by the respective degrees of freedom (DF). The *F* value of the model was calculated by dividing the model mean square by residual mean. The model *F* value of 44.59 implies the model is significant. There is only a 0.01% chance that model *F* value this large could occur due to noise. Values of Prob > *F* < 0.0500 shows that the model terms are significant whereas values > 0.1000 indicate that the model terms are not significant. The *R*² coefficient indicates the ratio of sum of squares due to regression (SSR) to total sum of squares (SST). It gives the proportion of the total variation in the response by the model. A high *R*² value, close to 1 is a desirable and reasonable agreement with adjusted *R*² is necessary (Ghafari et al., 2009). *R*² should be at least 0.80 for a good fit of a model (Joglekar and May, 1987).

The coefficient of determination (*R*²) for Quadratic model and model terms are; 95.13 (Quadratic model), 7.30 (A), −0.14 (B), 2.75 (C), −14.41 (A²), −30.37 (B²), −2.97 (C²), −0.28 (AB), −0.48 (AC) and 0.050 (BC). Fig. 6 shows the graph for *R*² of the quadratic model and model terms. Quadratic model and model terms A, A² and B² are significant (Fig. 6). The following regression equation (Eq. (18)) is the empirical model in terms of coded factors for the response after the elimination of the insignificant model.

$$\text{TOC Removal} = 95.13 + 7.30A - 14.41A^2 - 30.37B^2 \quad (18)$$

Overall, the quadratic model is significant for the optimization purpose (Table 4). The *R*² (0.9757) showed that the regression line perfectly fits the data. Adjusted *R*² (Adj. *R*²: 0.9538) is a modification of *R*² that adjusts for the number of explanatory terms in a model. The Adj. *R*² increases only if the new term improves the model more than would be expected by chance. The Adj. *R*² can be negative and will always be less than or equal to *R*². *R*² values smaller than 0.75 usually indicate an insufficient description of the experimental data by the model.

Fit summary determines the nonlinearity based on the outliers observed. Different plots represent different regression

**Fig. 7.** Predicted vs actual values plot for TOC removal efficiency augmentation.

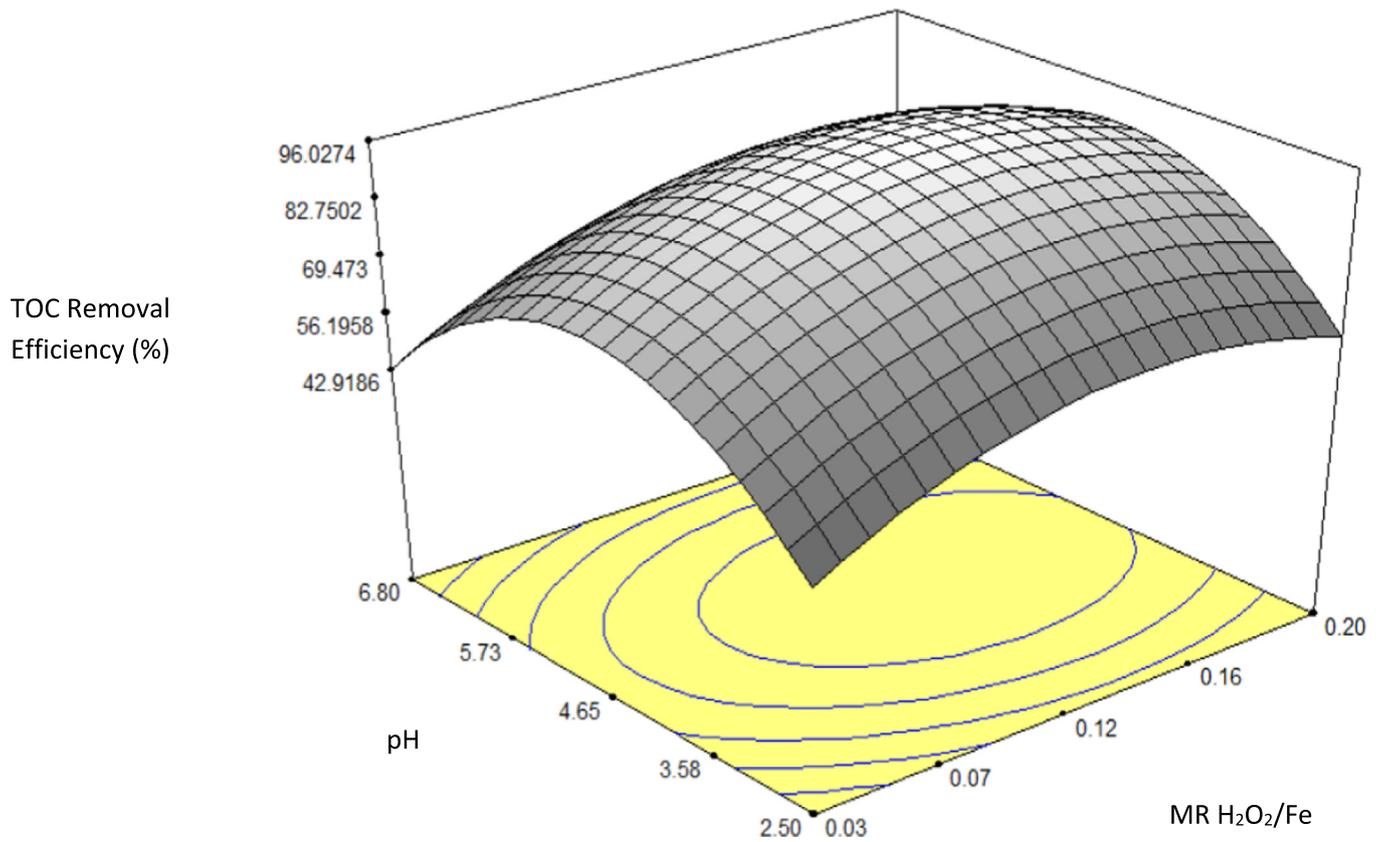


Fig. 8. Three dimensional plots for interactions between TOC removal efficiency, pH and MR.

assumptions such as predicted versus actual (Fig. 7). These are a non-statistical methods based on the inspection of scatterplots. The relationships between the predicted and actual are linear.

This implies that the proposed models are adequate, and that the constant variance assumption was confirmed (Ishak and Malakahmad, 2013).

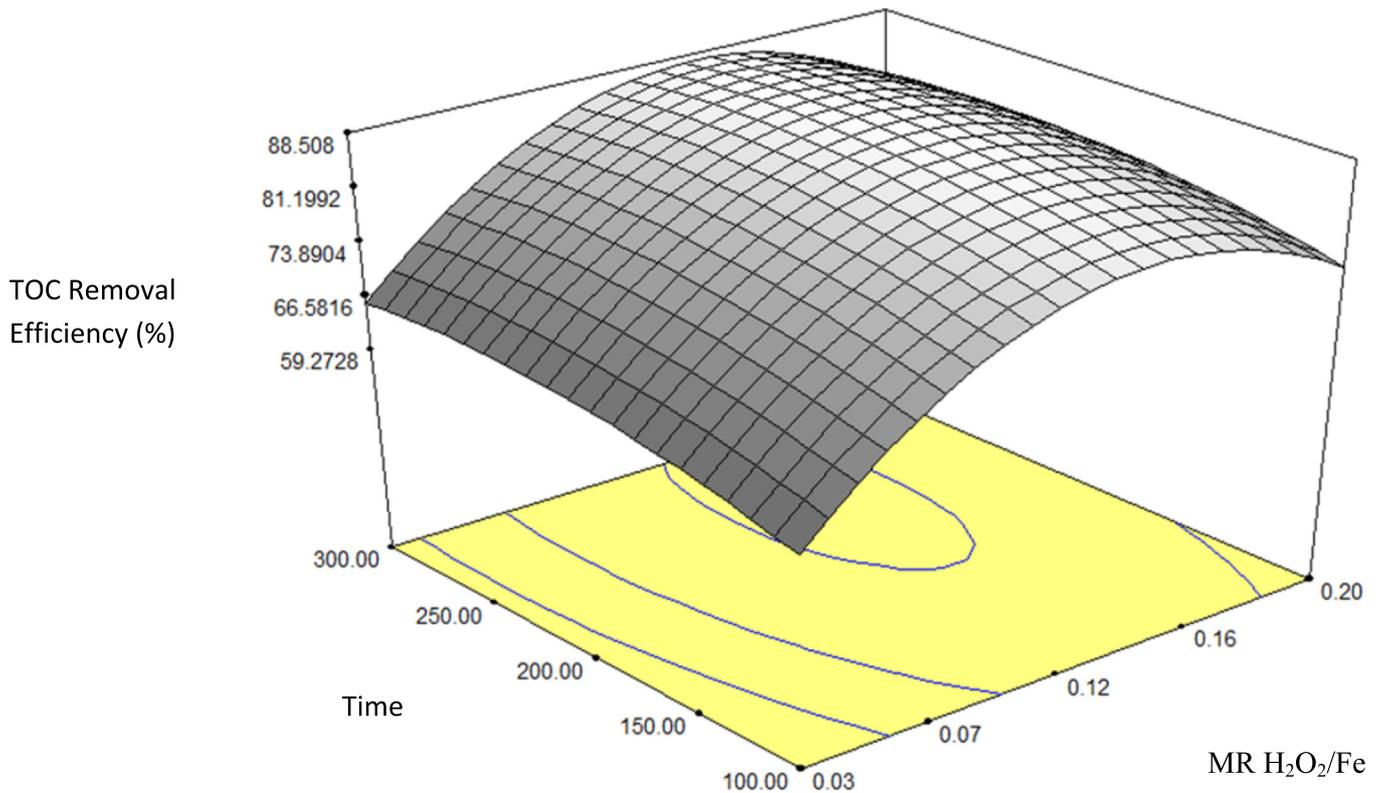


Fig. 9. Three dimensional plots for interactions between TOC removal efficiency, time and MR.

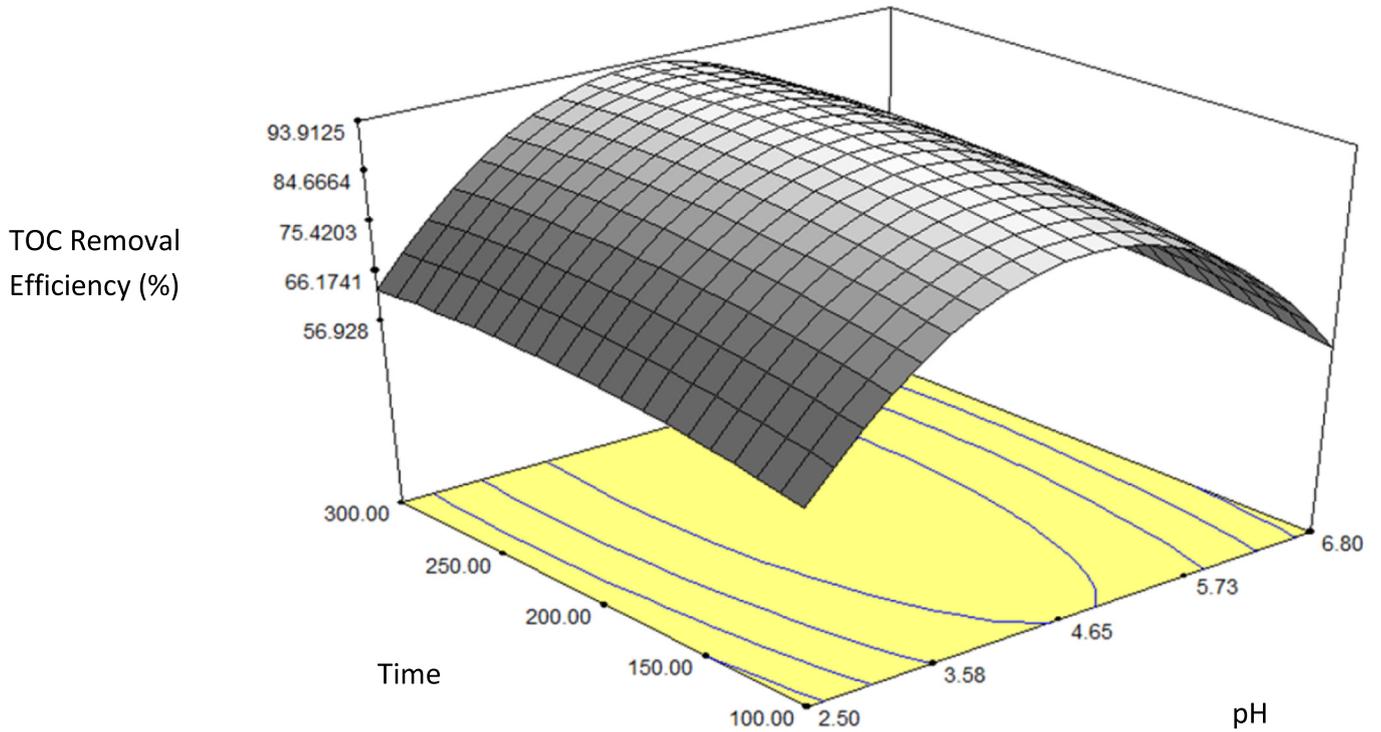


Fig. 10. Three dimensional plots for interactions between TOC removal efficiency, time and pH.

The interactions between variables; (a) pH and MR (Fig. 8), (b) time and MR (Fig. 9) and (c) time and pH (Fig. 10) are shown in the form of three-dimensional surface plots. In Fig. 8, the percent of TOC removals

varies accordingly. At pH 2.50, the percent of TOC removals were below 51.8% (MR 0.03), 51.8% (MR 0.07), 60.6% (MR in between 0.12 and 0.16) and below 51.8% (MR 0.20). At pH 3.58, the percent of TOC

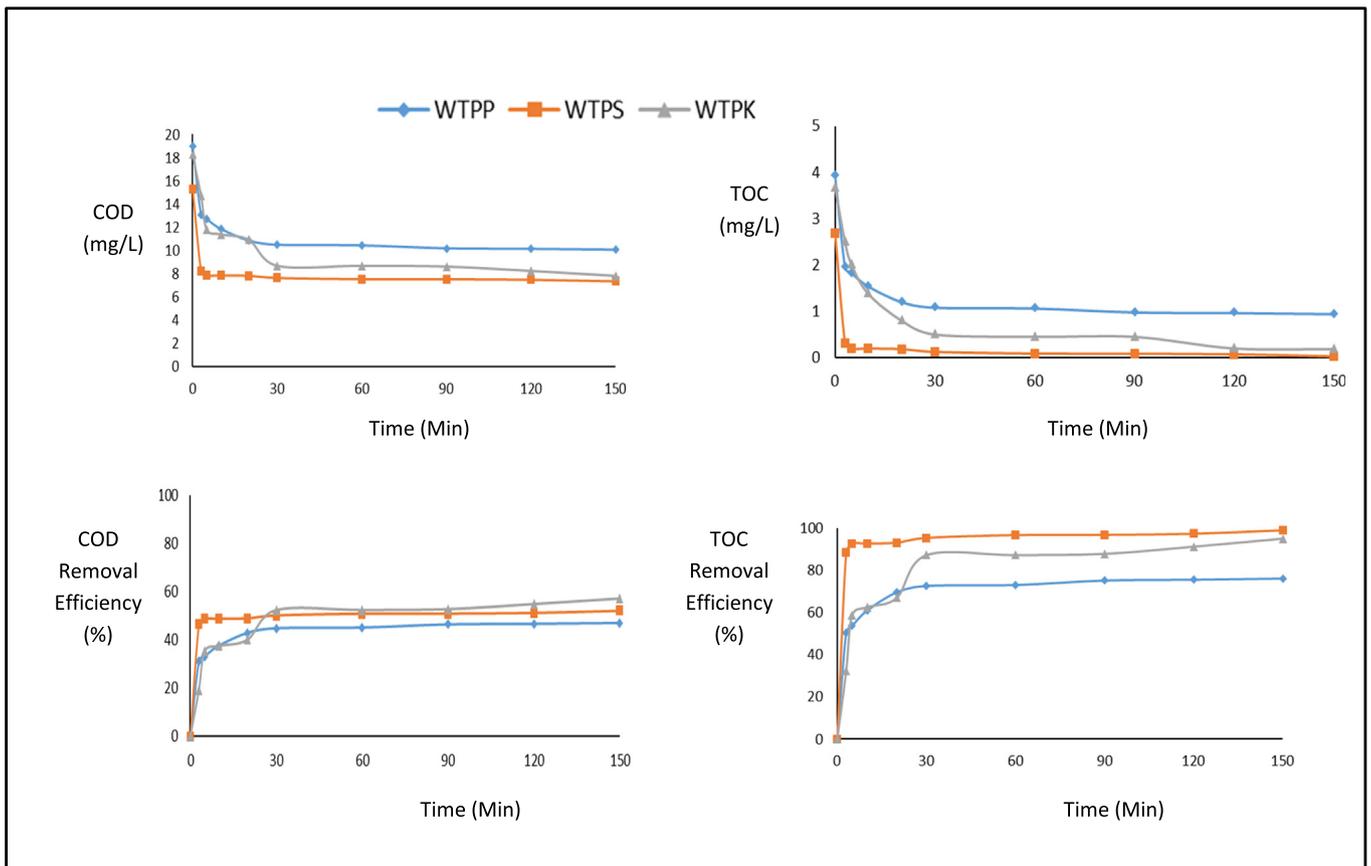


Fig. 11. COD (mg/L) degradation, TOC (mg/L) degradation, COD removal efficiency (%) and TOC removal efficiency (%) under the photo-Fenton treatment.

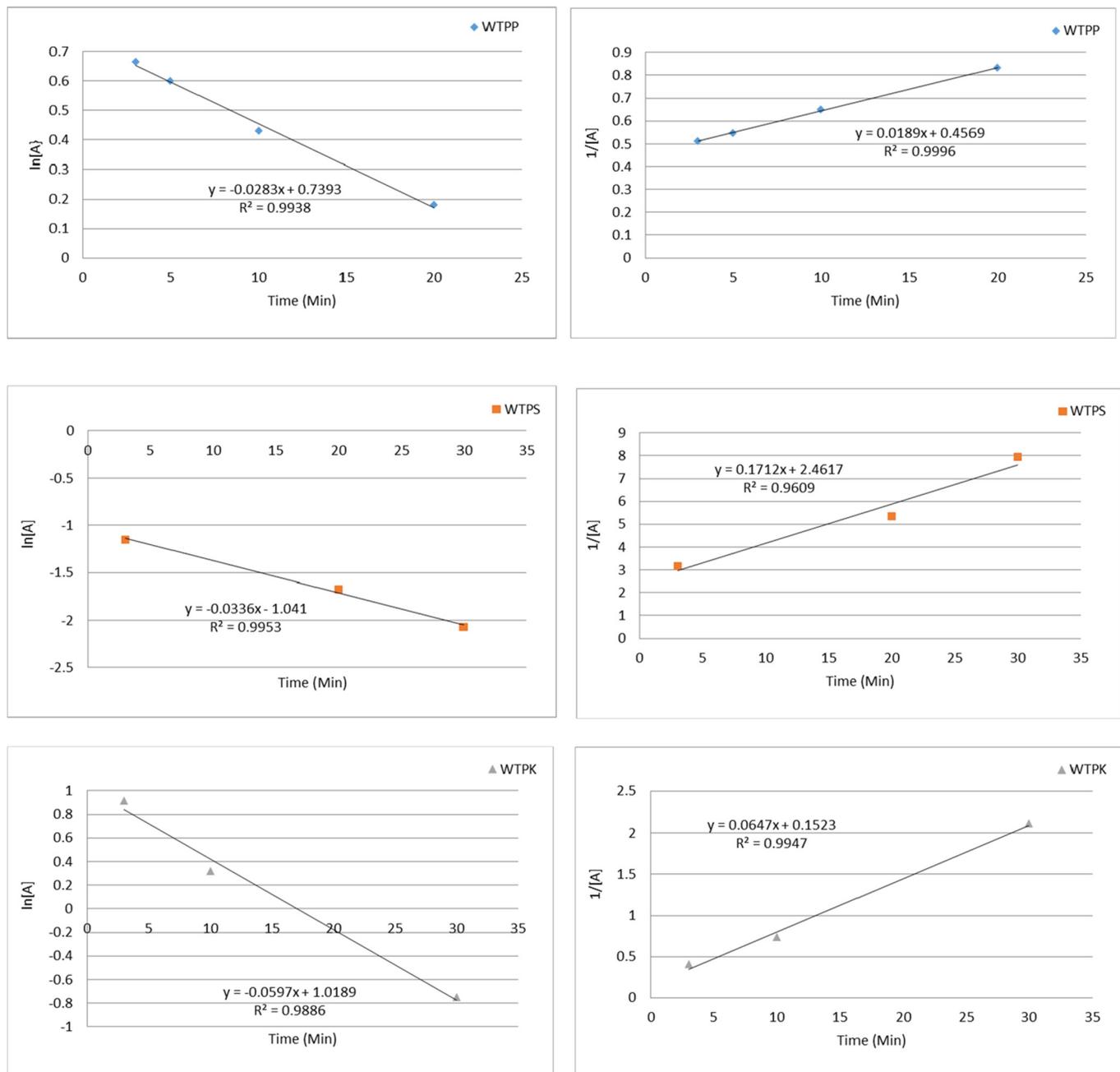


Fig. 12. Integrated rates law plots for photo-Fenton treatment based on TOC degradation.

removals are 51.8% (MR in between 0.03 and 0.07) and 78.3% (MR 0.12). At pH 4.65, the percent of TOC removals are 69.5% (MR in between 0.03 and 0.07), 78.3% (MR 0.07) and 87.2% (MR 0.12). At pH 5.73, the percent of TOC removals are 69.5% (MR in between 0.03 and 0.07) and 78.3% (MR 0.12). At pH 6.8, the percent of TOC removals are 60.6% (MR 0.12).

Fig. 9 shows interactions between time and MR with actual factor pH 5.75. At 100 s, the percent of TOC removal was below 69.5% (MR in between 0.03 and 0.07), 78.3% (MR 0.12 and 0.16). The percent of TOC removals were the same from 150 s to 300 s. The percentage of TOC removals at 200 s was 87.2% at MR 0.12.

Fig. 10 shows interactions between time and pH with actual factor MR 0.10. At 100 s to 300 s, the percentage of TOC removals were below 69.5% (pH 2.5, 3.58, 5.73 and 6.80), 78.3% (pH 3.58) and 87.2% (pH 4.65).

The regression line perfectly fits the data with R^2 value of 0.9757. The lack of fit test gives the highest value of *Sum of Squares* (15,666.64) with

probability F value <0.0001 and pure error equals to 0 indicating a satisfactory quadratic model to the analyzed data. The optimum conditions were established at 0.12 for $H_2O_2:FeSO_4$ MR, 200 s for reaction time and pH at 4.65 corresponding to the percentage of TOC removal of 87.2%.

3.3. Test on potable water samples from WTPP, WTPS and WTPK

In this part, the degradation of PAHs using photo-Fenton treatment method in potable water samples from WTPP, WTPS and WTPK was studied based on degradations of COD and TOC as well as integrated kinetic rates and degradation of 17 PAHs concentrations after the treatment.

The concentration of chemical oxygen demand (COD) and its gradual degradation upon photo-Fenton treatment was recorded (Fig. 11). The initial COD were 19.0 mg/L (WTPP), 15.3 mg/L (WTPS) and 18.2 mg/L (WTPK) accordingly. After 3 min of treatment, the COD

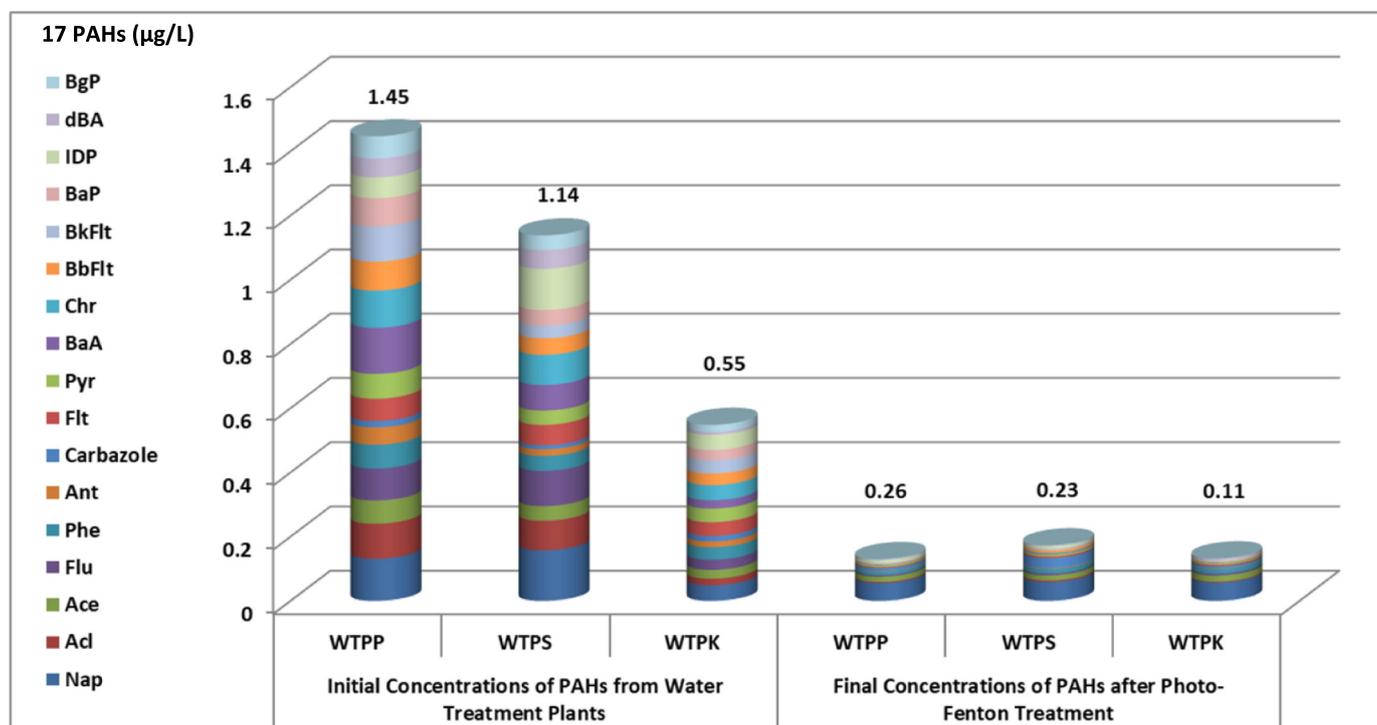


Fig. 13. The degradation of 17 PAHs ($\mu\text{g/L}$) after the photo-Fenton treatment.

readings were decreased to 13.1 mg/L (WTPP), 8.2 mg/L (WTPS) and 14.7 mg/L (WTPK). Although the treatment was prolonged up to 150 min, the reductions in the COD values were within the ranges of 7 mg/L to 10 mg/L. The final COD values were 10.1 mg/L (WTPP), 7.3 mg/L (WTPS) and 7.8 mg/L (WTPK). The COD degradation achieved were 47.0% (WTPP), 52.1% (WTPS) and 57.1% (WTPK).

According to National Water Quality Standards for Malaysia, the COD values before treatment (15.3 mg/L to 19.0 mg/L) are categorized as Class IIA equivalent to >10 mg/L and <25 mg/L. The COD values after treatment for WTPS and WTPK were categorized as Class I equivalent to <10 mg/L and Class II for WTPP equivalent to >10 mg/L and <25 mg/L.

Next, the concentration of total organic carbon (TOC) and its gradual degradation upon respective treatment was taken into account to represent PAHs concentration (Fig. 11). The initial TOCs were 3.929 mg/L (WTPP), 2.692 mg/L (WTPS) and 3.675 mg/L (WTPK). The treatment time and H_2O_2 concentration for UV/ H_2O_2 treatment were determined based on optimization results. For this treatment, the TOC readings dropped after 3 min to 1.947 mg/L (WTPP), 0.315 mg/L (WTPS) and 2.494 mg/L (WTPK). The TOC readings for WTPP, WTPS and WTPK were maintained below the 2 mg/L of TOC and the final readings taken after 150 min were 0.9406 mg/L (WTPP), 0.0278 mg/L (WTPS) and 0.185 mg/L (WTPK). The TOC removal efficiency achieved after 150 min were 76.1% (WTPP), 99% (WTPS) and 95% (WTPK). TOC monitoring results for potable water prior to primary disinfection using chlorine should generally not exceed 2.0 mg/L (US EPA, 2005). The TOC values before the UV/ H_2O_2 treatment exceeded 2.0 mg/L: The final TOC values after the treatment finally achieved the ranges of below 2.0 mg/L. TOC regulation however, is not stated in the National Water Quality Standards for Malaysia.

A kinetic rates study is the study of rates of chemical reactions or the speed of chemical reactions. The first order kinetic rates ($\ln[A]$ vs time) indicates a reaction that depends on the concentration of only one reactant. Meanwhile, a second-order reaction ($1/[A]$ vs time) will depend on the concentration(s) of one second-order reactant or two first-order reactants. The variable A is a concentration or the values of some function of concentration (Cornish-Bowden, 2012). The kinetic rates based on first ($\ln[A]$ vs time) and second order ($1/[A]$ vs time) were plotted and

shown in Fig. 12. The rate constants (k) from the first order were WTPP (0.0283/min), WTPS (0.0336/min) and WTPK (0.0597/min). The rate constants (k) from the second order were WTPP (0.0189/mg/L/min), WTPS (0.1712/mg/L/min) and WTPK (0.0647/mg/L/min). The kinetic rates from photo-Fenton treatments for WTPP, WTPS and WTPK followed first order with R^2 higher than the second order, equivalent to >0.95.

The initial PAHs concentrations were 1.4466 $\mu\text{g/L}$ (WTPP), 1.1382 $\mu\text{g/L}$ (WTPS) and 0.5485 $\mu\text{g/L}$ (WTPK). The PAHs final concentrations after treatment were 0.1301 $\mu\text{g/L}$ (WTPP), 0.1731 $\mu\text{g/L}$ (WTPS) and 0.1326 $\mu\text{g/L}$ (WTPK) (Fig. 13). The percentages of PAHs removal for photo-Fenton treatment were 91% (WTPP), 87.7% (WTPS) and 76.4% (WTPK).

4. Conclusion

The study on PAHs degradation on PAHs contaminated water via UV/ H_2O_2 treatment method and identification of the optimum conditions for both simulated solution and actual water samples were achieved. PAHs removal efficiency from the photo-Fenton ranged from 76.4% to 91%. The reaction time of UV/ H_2O_2 treatment was 90 s based on its kinetic rate at 0.0283/min to 0.0597/min. The presence of 17-US EPA PAHs contamination in potable water for public water supply in Perak Tengah showed that conventional water treatment does not remove PAHs compounds. This research studied the photo-Fenton water treatment technique as one of the solutions for PAHs removal. Therefore, water treatment that applies AOPs could be considered as an alternative for conventional water treatment in Malaysia and other developing countries in the near future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

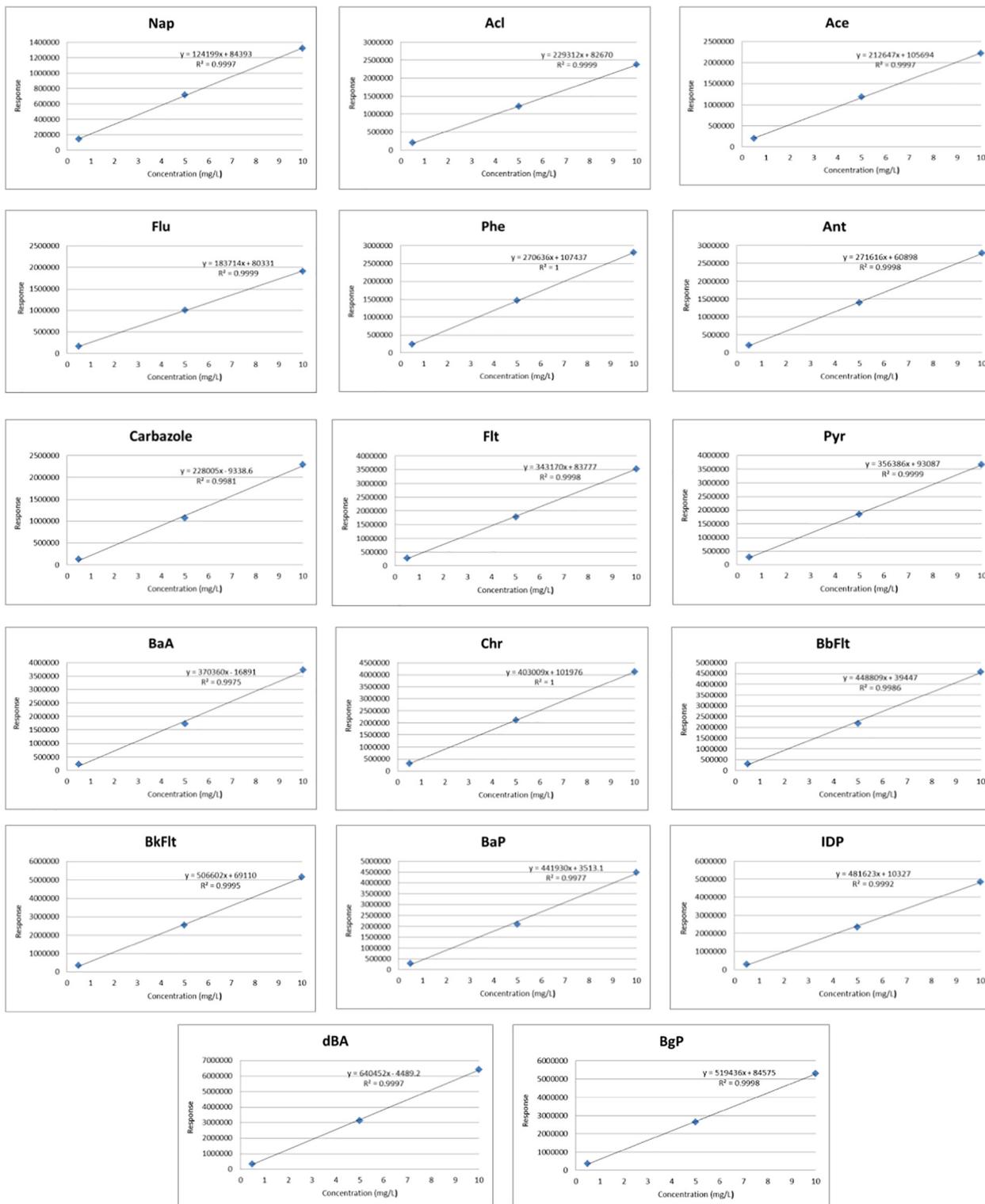
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Appendix A

A.1 Calibration curves for 17 USEPA PAHs reference standard via GCMS



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