Optimisation of Polycyclic Aromatic Hydrocarbon Removal from Contaminated Soil using Modified Fenton Treatment

Venny, S. Gan, and H. K. Ng

Abstract—The performance of modified Fenton (MF) treatment to promote PAH oxidation in artificially contaminated soil was investigated in packed soil column with a hydrogen peroxide (H_2O_2) delivery system simulating in situ injection. Soil samples were spiked with phenanthrene (low molecular weight PAH) and fluoranthene (high molecular weight PAH) to an initial concentration of 500 mg/kg dried soil each. The effectiveness of process parameters H_2O_2/soil, iron/soil, chelating agent/soil weight ratios and reaction time were studied using a 2^4 three level factorial design experiments. Statistically significant quadratic models were developed using Response Surface Methodology (RSM) for degrading PAHs from the soil samples. Optimum operating condition was achieved at mild range of H_2O_2/soil, iron/soil and chelating agent/soil weight ratios, indicating cost efficient method for treating highly contaminated lands.

Keywords—Fenton, polycyclic aromatic hydrocarbon, chelate, response surface methodology

I. INTRODUCTION

POLYCYCLIC aromatic hydrocarbons (PAHs) are chemical compounds that consist of at least two aromatic rings. Their presence in the environment is mainly attributed to anthropogenic activities commonly associated with manufactured gas plants and incomplete combustion of carbon containing fuels. These hydrophobic pollutants are highly toxic and recalcitrant. As such, the contamination of subsurface soils is a serious environmental concern which requires effective remediation tool.

Chemical oxidation technologies based on Fenton's reagent (iron catalysed H_2O_2) combine both economical advantages and effectiveness in destroying organic pollutants such as PAHs at elevated concentration. Fenton oxidation leads to dissociation of the oxidant (H_2O_2) and subsequently the formation of non-specific hydroxyl radicals ($^\bullet OH$) to innocuous compounds such as carbon dioxide, water and inorganic salts [1]. However, low pH values (pH 2-4) often impede the application of conventional Fenton oxidation because iron catalyst is easily precipitated at near neutral pH environment. Chelating agents (CAs) are frequently employed

to overcome the limitation of conventional Fenton oxidation for treating recalcitrant pollutants such as PAHs and chlorophenols [2-5]. This process is also known as the modified Fenton (MF) treatment. Although MF treatments have these advantages, optimisation of reactant dosage and reaction time plays an important role for achieving cost efficient and successful remediation technique which in most cases site- and contaminant-specific. In the present study, the efficacy of MF oxidation using inorganic CA namely sodium pyrophosphate (SP) has been assessed to optimise process parameters: H_2O_2/soil, iron/soil, SP/soil weight ratios and reaction time relating the interactions between each process parameter from statistics point of view.

II. MATERIALS AND METHODS

A. Chemicals

Phenanthrene (PHE, 97%) and fluoranthene (FLUT, Acros, 98%) were purchased from Merck and Fisher Scientific respectively. H_2O_2 (35%), ferric sulphate ($Fe_2(SO_4)_3.xH_2O$, 76%) and SP (99+%) from R&M Chemicals. Dichloromethane (DCM, 99.5%, AR analysis), acetone (99.5%, AR analysis), calcium chloride dehydrate ($CaCl_2$, 99+%, ACS grade), sulphuric acid (H_2SO_4, 98%) and n-hexane ($\geq$ 96%) were purchased from Merck. Acetonitrile (ACN, 99.8%, HPLC grade) was purchased from Rank Synergy, n-pentane (99%, R&M) from Makmal Berjaya and anhydrous sodium sulphate (Na_2SO_4, 99+%) from Fisher Scientific.

B. Soil Characterisation

Surface soil samples (0-10 cm) with no historical contamination were collected from Selangor, Malaysia. The soil samples were air-dried and passed through 2 mm mesh using laboratory sieve shaker (BSE, NL 1015).

The particle size analyses were determined according to the Buoyoucos hydrometer method [6]. The soil bulk density was determined using an oven-dry (130^oC for 20 h) basis per unit volume [6]. The surface area and pore volume of soil sample, on the other hand, were determined by the BJH adsorption-desorption method with a porosimeter (Micromeritics, ASAP 2020) using liquid nitrogen. The soil sample was degassed for 6 h at 120^oC. Meanwhile, the measurements of pH_{H2O}, pH_{CaCl2}, loss on ignition (LOI) and total iron available in the soil sample have been discussed in a previous work [7].

C. Modified Fenton Treatment

The soil samples were spiked with 500 mg/kg each of PHE and FLUT using DCM as the carrier solvent. The MF treatment of PAH-contaminated soil was carried out in a glass

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column operated at 28°C without pH adjustment. The experiments were performed using 1.2 kg of spiked soil (resulting soil height in column of approximately 7.5 cm) was packed into a glass column to a density of approximately 1.28 kg/dm³. The glass column was designed with an inner diameter of 12.20 cm and total height of 16 cm. Taking into account the heat and oxygen released during Fenton oxidation, the experiments were conducted with a working volume of 50 %. The Fenton's reagent was delivered to the soil column via perforated glass tube (consists of 4 holes at each side, outer diameter 6 mm, length 400 mm, holes diameter of 2 mm) using a pump (BT100-1F with YZ1515 pump head) operated at a rate of 100 ml/min for the injection of Fe^{3+} solution and 160 ml/min for the injection of both H_2O_2 and SP. Stainless steel mesh (<1 mm, outer diameter 38 mm) was used on the base of the soil column to retain the solid phase. To avoid highly exothermic reactions near the injection point as well as scavenging effect, the H_2O_2 was diluted using distilled water to 15% H_2O_2 solution. The reaction started upon the addition of H_2O_2, followed by the addition of Fe^{3+} and subsequently SP. After certain reaction time (3, 13.5 or 24 h), the solid phase retained in the soil column was divided into two equivalent parts (upper and lower) and consequently analysed for the PAH residual concentration. The pH of column leachate was measured at the end of the reaction using a bench top pH meter BP3001 (Trans Instruments).

D. Automated Soxhlet Extraction (Solid Phase)

PAH extraction analyses were carried out after the MF treatment. For PAH extraction from the solid phase, automated Soxhlet extraction (Gerhardt Soxtherm) was selected because it is not as time consuming as other extraction processes with similar efficiency. The supernatant was separated from the solid phase by vacuum filtering with filter paper (Sartorius Stedim Biotech, each of Grade 292 and 389).

The separated solid phase was placed in a cellulose extraction thimble (Favorit 33x80 mm) and then mixed with anhydrous sodium sulphate (granular Na_2SO_4, initially purified by heating at 400°C for 4 h in a furnace) at a ratio of 2:1 w/w (10 g per 5 g of soil sample) to reduce the moisture level. The Soxhlet extraction was performed according to the US EPA Method 3540C. The soil-Na_2SO_4 mixture was covered with glass wool and extracted with 140 mL of n-pentane for 3 h 18 min, i.e. immersed in boiling solvent at 85°C for 60 min, rinsed for 60 min and evaporated for 78 min. The remaining solvent was subsequently evaporated to dryness using a rotary evaporator (Heidolph).

E. Liquid-liquid Extraction (Aqueous Phase)

The PAHs in the aqueous phase was extracted by means of liquid-liquid extraction using hexane at a ratio of 1:1 v/v. The hexane extracts from triplicate measurements were combined due to very low concentration of PAHs found in the aqueous phase.

TABLE I
CODED AND ACTUAL LEVELS OF INDEPENDENT VARIABLES

Symbol	Factor	Coded level		
		-1	0	+1
X_1	H_2O_2/soil (w/w)	0.050	0.075	0.100
X_2	Fe^{3+}/soil (w/w)	0.000	0.020	0.040
X_3	SP/soil (w/w)	0.000	0.020	0.040
X_4	Reaction time (h)	3.000	13.50	24.00

F. Gas Chromatography (GC) Analysis

The PAHs from both the solid and aqueous extracts were analysed using a GC (Clarus 500 Agilent USA), equipped with a flame ionisation detector (FID) and fused silica capillary column, according to the US EPA Method 8100. Helium was used as the carrier gas. The injector and detector were operated at 290°C and 300°C respectively, whereas the oven was operated at 100°C for 1 min, ramped at a rate of 25°C/min to 310°C and hold for 2 min. Under this condition, individual PAHs were identified by retention times of 8.3 min and 9.6 min for PHE and FLUT respectively.

G. Statistical Analysis

Design Expert 7.1.6 software (Stat-Ease Inc.,) was used for the design, mathematical modelling, regression analysis and optimisation of process parameters involved in the MF treatment. The independent factors considered in the present study were: H_2O_2/soil, Fe^{3+}/soil, SP/soil and reaction time, coded as x_1, x_2, x_3 and x_4 respectively. The low, centre and high levels of each factor are designated according to face centred central composite design (CCD) as -1, 0 and 1 level in conjunction with responses on PAH removal for upper (y_1) and lower part (y_2) of the soil column and leachate pH (y_3). Meanwhile the operating temperature for the MF oxidation was kept constant at ambient temperature of 25°C - 28°C.

For statistical calculation, the independent variables X_i have been transformed into x_i in order to allow comparison of factors with different natures and units, as in (1).

$$x_i = \frac{X_i - X_o}{\Delta X} \text{ where } i = 1, 2, \ldots, k. \tag{1}$$

where x_i is the dimensionless coded value of the ith independent variable X_i, X_o is the actual value of X_i at the centre point and ΔX is the step change.

The design of experiment consisted of 2^k (in this case k=4) factorial points, 2k axial points and a centre point with 6 replicates to obtain better prediction of the experimental error. The ranges of independent variables considered are listed in Table I. The ranges of selected parameters were decided based on preliminary experiments in soil slurry [7] and column experiments [8]. An empirical second order polynomial model was employed to describe the interactions between the process dependent variable (response) and independent variables, as in (2).

$$Y = \beta_o + \sum_{i=1}^{k} \beta x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1} \sum_{i \neq j=1}^{k} \beta_{ij} x_i x_{ij} + \varepsilon \tag{2}$$

where Y represents the response (i.e. PAH removal or leachate pH), i , j are linear and quadratic coefficients respectively, while β is regression coefficient. k stands for the number of factors (x) and ε signifies the random error.

Table II shows the experimental matrix of coded and actual values for determination of predicted responses. Analysis of variance (ANOVA) was employed for statistical analyses of the results. The quality of fit of the predicted models was expressed by correlation coefficient (R^2) while its statistical significance was examined by student t-test.

The significance of each model term was evaluated by the P-value (probability) with 95% confidence level. The response surface equations were optimised using numerical evaluation for maximum PAH removal with leachate pH in the range of 4 to 6, considering acidic soil sample used in the present study. Noteworthy, the models were developed with an assumption of equal variance.

TABLE II
EXPERIMENTAL DESIGN MATRIX FOR OVERALL MF TREATMENT

Run no.	Point type	Coded values				Real values				Observed responses		
		x_1	x_2	x_3	x_4	X_1	X_2	X_3	X_4	Y_1	Y_2	Y_3
1	Factorial	-1	-1	-1	-1	0.050	0.000	0.000	3.000	42.73	40.40	3.83
2	Factorial	1	-1	-1	-1	0.100	0.000	0.000	3.000	61.42	51.00	3.87
3	Factorial	-1	1	-1	-1	0.050	0.040	0.000	3.000	62.46	60.71	2.18
4	Factorial	1	1	-1	-1	0.100	0.040	0.000	3.000	72.48	61.98	2.39
5	Factorial	-1	-1	1	-1	0.050	0.000	0.040	3.000	42.73	40.40	6.64
6	Factorial	1	-1	1	-1	0.100	0.000	0.040	3.000	45.35	41.81	5.70
7	Factorial	-1	1	1	-1	0.050	0.040	0.040	3.000	70.77	77.95	2.80
8	Factorial	1	1	1	-1	0.100	0.040	0.040	3.000	80.22	76.82	2.24
9	Factorial	-1	-1	-1	1	0.050	0.000	0.000	24.00	69.98	67.90	3.70
10	Factorial	1	-1	-1	1	0.100	0.000	0.000	24.00	59.81	61.95	3.20
11	Factorial	-1	1	-1	1	0.050	0.040	0.000	24.00	73.70	69.66	2.23
12	Factorial	1	1	-1	1	0.100	0.040	0.000	24.00	78.37	77.05	2.18
13	Factorial	-1	-1	1	1	0.050	0.000	0.040	24.00	19.49	16.11	6.20
14	Factorial	1	-1	1	1	0.100	0.000	0.040	24.00	23.76	11.70	5.83
15	Factorial	-1	1	1	1	0.050	0.040	0.040	24.00	53.52	52.56	2.92
16	Factorial	1	1	1	1	0.100	0.040	0.040	24.00	50.01	47.71	2.80
17	Axial	-1	0	0	0	0.050	0.020	0.020	13.50	82.45	80.27	4.06
18	Axial	1	0	0	0	0.100	0.020	0.020	13.50	72.03	77.35	3.91
19	Axial	0	-1	0	0	0.075	0.000	0.020	13.50	26.54	15.82	5.92
20	Axial	0	1	0	0	0.075	0.040	0.020	13.50	80.19	78.17	2.48
21	Axial	0	0	-1	0	0.075	0.020	0.000	13.50	54.44	48.50	3.58
22	Axial	0	0	1	0	0.075	0.020	0.040	13.50	67.84	73.43	3.26
23	Axial	0	0	0	-1	0.075	0.020	0.020	3.000	73.81	72.86	3.84
24	Axial	0	0	0	1	0.075	0.020	0.020	24.00	72.19	70.77	3.35
25	Center	0	0	0	0	0.075	0.020	0.020	13.50	68.24	63.33	3.36
26	Center	0	0	0	0	0.075	0.020	0.020	13.50	59.44	56.95	2.94
27	Center	0	0	0	0	0.075	0.020	0.020	13.50	62.64	59.36	3.47
28	Center	0	0	0	0	0.075	0.020	0.020	13.50	56.27	59.80	3.29
29	Center	0	0	0	0	0.075	0.020	0.020	13.50	70.60	69.30	2.78
30	Center	0	0	0	0	0.075	0.020	0.020	13.50	71.15	71.45	3.14

X_1 (H_2O_2/soil, w/w) is calculated as: $X_1 = 0.075 + x_1 (0.025)$
X_2 (Fe^{3+}/soil, w/w) is calculated as: $X_2 = 0.020 + x_2 (0.020)$
X_3 (SP/soil, w/w) is calculated as: $X_3 = 0.020 + x_3 (0.020)$
X_4 (reaction time, h) is calculated as: $X_4 = 13.50 + x_4 (10.50)$

TABLE III
SOIL SAMPLE CHARACTERISATION AND PROPERTIES

Characteristic	Loamy sand
Sand (%)	87.40
Silt (%)	1.38
Clay (%)	11.22
Bulk density (g/mL)[a]	1.30 ± 0.01
Adsorption cumulative surface area (m²/g)	0.28
Desorption cumulative surface area (m²/g)	0.55
Adsorption pore volume (m³/g)	0.005982
Desorption pore volume (m³/g)	0.006342
Moisture content (%)[a]	1.14 ± 0.18
pH$_{H2O}$ at 23.8 ± 0.06 °C [a]	5.41 ± 0.33
pH$_{CaCl2}$ at 23.8 ± 0.06 °C [a]	4.07 ± 0.01
LOI (%)[a]	0.03
Total iron (mg/g)[a]	45.82 ± 1.23

[a]Average of three replicates determinations.

III. RESULTS AND DISCUSSIONS

A. Soil Properties

Fig. 1 depicts the particle size distribution of the soil with the majority of the particles present in the ranges: 0.3-0.6 mm (46.8 wt %). The soil properties are shown in Table III.
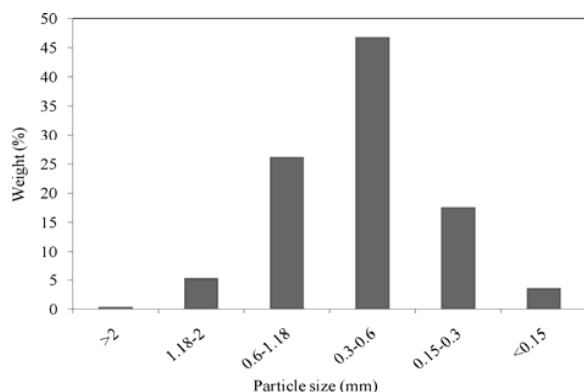

TABLE IV
ANOVA FOR UPPER PAH REMOVAL (Y$_1$)

Source	SS	DF	Mean square	F-value	Prob > F	Remark
Model	6794.49	14	485.32	5.43	0.0012	Significant
X$_1$	36.49	1	36.49	0.41	0.5324	Insignificant
X$_2$	2936.71	1	2936.71	32.87	< 0.0001	Significant
X$_3$	823.02	1	823.02	9.21	0.0084	Significant
X$_4$	145.20	1	145.20	1.63	0.2218	Insignificant
X$_1$X$_2$	1.71	1	1.71	0.02	0.8917	Insignificant
X$_1$X$_3$	6.71	1	6.71	0.08	0.7877	Insignificant
X$_1$X$_4$	129.61	1	129.61	1.45	0.2471	Insignificant
X$_2$X$_3$	307.26	1	307.26	3.44	0.0834	Insignificant
X$_2$X$_4$	7.76	1	7.76	0.09	0.7722	Insignificant
X$_3$X$_4$	1140.34	1	1140.34	12.76	0.0028	Significant
X$_1^2$	192.33	1	192.33	2.15	0.1630	Insignificant
X$_2^2$	603.40	1	603.40	6.75	0.0202	Significant
X$_3^2$	145.25	1	145.25	1.63	0.2217	Insignificant
X$_4^2$	49.61	1	49.61	0.56	0.4677	Insignificant
Residual	1340.25	15	89.35			
LOF	1148.33	10	114.83	2.99	0.1191	Insignificant
PE	191.91	5	38.38			
R^2						0.84
AP						9.46

SS: sum of squares; DF: degree of freedom; LOF: lack of fit; AP: adequate precision; PE: pure error.

TABLE V
ANOVA FOR LOWER PAH REMOVAL (Y$_2$)

Source	SS	DF	Mean square	F-value	Prob > F	Remark
Model	8750.45	14	625.03	5.49	0.0011	Significant
X$_1$	0.11	1	0.11	0.00	0.9759	Insignificant
X$_2$	3627.41	1	3627.41	31.86	< 0.0001	Significant
X$_3$	563.04	1	563.04	4.94	0.0420	Significant
X$_4$	130.85	1	130.85	1.15	0.3007	Insignificant
X$_1$X$_2$	0.07	1	0.07	0.00	0.9809	Insignificant
X$_1$X$_3$	31.12	1	31.12	0.27	0.6088	Insignificant
X$_1$X$_4$	24.93	1	24.93	0.22	0.6466	Insignificant
X$_2$X$_3$	586.53	1	586.53	5.15	0.0384	Significant
X$_2$X$_4$	13.19	1	13.19	0.12	0.7383	Insignificant
X$_3$X$_4$	1835.42	1	1835.42	16.12	0.0011	Significant
X$_1^2$	326.70	1	326.70	2.87	0.1110	Insignificant
X$_2^2$	1097.36	1	1097.36	9.64	0.0073	Significant
X$_3^2$	113.37	1	113.37	1.00	0.3342	Insignificant
X$_4^2$	46.56	1	46.56	0.41	0.5322	Insignificant
Residual	1708.03	15	113.87			
LOF	1537.54	10	153.75	4.51	0.0551	Insignificant
PE	170.50	5	34.10			
R^2						0.84
AP						9.27

SS: sum of squares; DF: degree of freedom; LOF: lack of fit; AP: adequate precision; PE: pure error.

$$y_3 = 3.60 - 1.26\ x_2 + 0.62\ x_3 - 0.50\ x_2 x_3 \qquad (5)$$

The data showed that the proposed approach is a suitable tool for predicting PAH removals and leachate pH. The three models are statistically significant at which there is only 0.01-0.12% chance that the models F-values could occur due to noise. The lack of fit (LOF) F-values for each response (y$_1$–y$_3$) are insignificant relative to the pure error (PE) implying good fitting to the proposed models. The models also accompanied by satisfactory correlation coefficients (R^2) of 0.84, 0.84 and 0.89 for upper, lower PAH removals and leachate pH respectively. Adequate precision (AP) values which measure the signal to noise ratio were found to be higher than four indicate adequate signal for the models to be used to navigate the design space developed by the CCD. From the predicted models, it can be seen that the PAH removal for both upper and lower parts increased with the addition of iron catalyst (x$_2$) but decreased with the addition of SP as the iron chelate (x$_3$) and in some cases with the reaction time (x$_4$). On the contrary, leachate pH decreased with the addition of iron catalyst (x$_2$) but increased with the addition of SP as the iron chelate (x$_3$). The increase in solution pH could be attributed to high pH of the SP reagent used (pH 9-10) which consequently favour iron precipitation and caused lower PAH removal efficiency. Besides, the PAH removal in the lower part of the packed soil column was also found to be slightly lower than the removal in the upper part.

TABLE VI
ANOVA FOR LEACHATE pH (Y_3)

Source	SS	DF	Mean square	F-value	Prob > F	Remark
Model	40.50	10	4.05	15.97	< 0.0001	Significant
X_1	0.33	1	0.33	1.30	0.2676	Insignificant
X_2	28.55	1	28.55	112.60	< 0.0001	Significant
X_3	7.01	1	7.01	27.63	< 0.0001	Significant
X_4	0.06	1	0.06	0.26	0.6190	Insignificant
X_1X_2	0.10	1	0.10	0.39	0.5422	Insignificant
X_1X_3	0.18	1	0.18	0.70	0.4119	Insignificant
X_1X_4	0.00	1	0.00	0.01	0.9181	Insignificant
X_2X_3	3.99	1	3.99	15.74	0.0008	Significant
X_2X_4	0.17	1	0.17	0.65	0.4284	Insignificant
X_3X_4	0.11	1	0.11	0.44	0.5170	Insignificant
Residual	4.82	19	0.25			
LOF	4.47	14	0.32	4.61	0.0505	Insignificant
PE	0.35	5	0.07			
R^2					0.89	
AP					14.04	

SS: sum of squares; DF: degree of freedom; LOF: lack of fit; AP: adequate precision; PE: pure error

The predicted (obtained from the models) versus actual (obtained from laboratory experiments) plots are illustrated in Fig. 2. The data distributed well with the observed values about the straight line (y = x) indicating good agreement between the predicted and the observed data. The normality assumption was also found to be satisfied as the residuals plots corresponded closely to a straight line (Fig. 3).

It has been observed that the PAH removal for the MF treatment was indirectly proportional to the addition of SP, implying high dependency towards solution pH (Fig. 4 and 5). It also seems that excessive H_2O_2 had a negative influence on PAH degradation. It is likely due to scavenging effect from the production of hydroperoxyl radical ($HO_2^\bullet$), which is a species with weaker oxidising power than $^\bullet OH$ radicals, as shown in (6).

$$H_2O_2 + {}^\bullet OH \rightarrow HO_2^\bullet + H_2O \qquad (6)$$

C. Optimisation and Validation

In order to determine an optimum operating condition, numerical optimisation method (Design Expert) was applied for maximum PAH removals and leachate pH in the range of 4 to 6, taken into account the acidity of the soil sample used and often soil fertility takes place near neutral pH. Under these constraints, the optimised condition was obtained for highest desirability of 0.76 at H_2O_2/soil of 0.05, Fe^{3+}/soil of 0.025, SP/soil of 0.04 and reaction time of 3 h resulted in 85.95% and 74.47% of upper and lower PAH removal efficiencies

TABLE VII
MODEL OPTIMISATION AND VALIDATION

Response	X_1	X_2	X_3	X_4	Observed	Predicted
Y_1 (%)	0.05	0.025	0.04	3	79.42	85.95
Y_2 (%)	0.05	0.025	0.04	3	68.06	74.47
Y_3	0.05	0.025	0.04	3	4.42	4.00

with a resulting leachate pH of 4. Model reliability and validation were confirmed by conducting another set of laboratory experiment at the optimum condition. Table VII

presents a comparison between the simulated and the laboratory experiment results. The observed experimental data were found to agree well with the predicted values, i.e. the upper and lower PAH removal of 79.42% and 68.08% with a resulting leachate pH of 4.42.
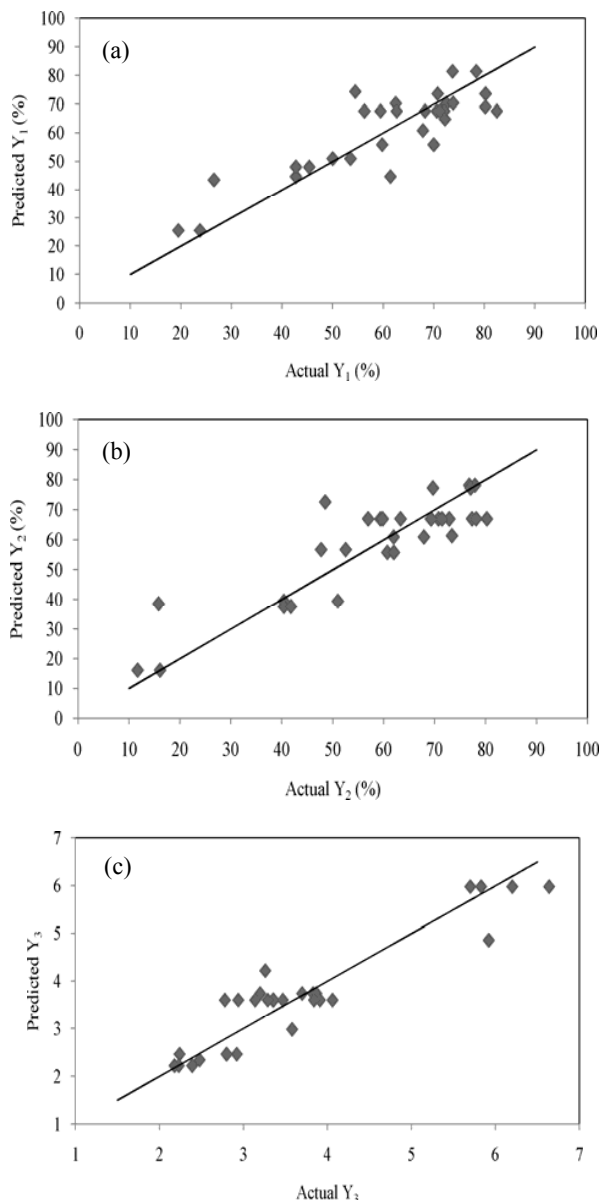

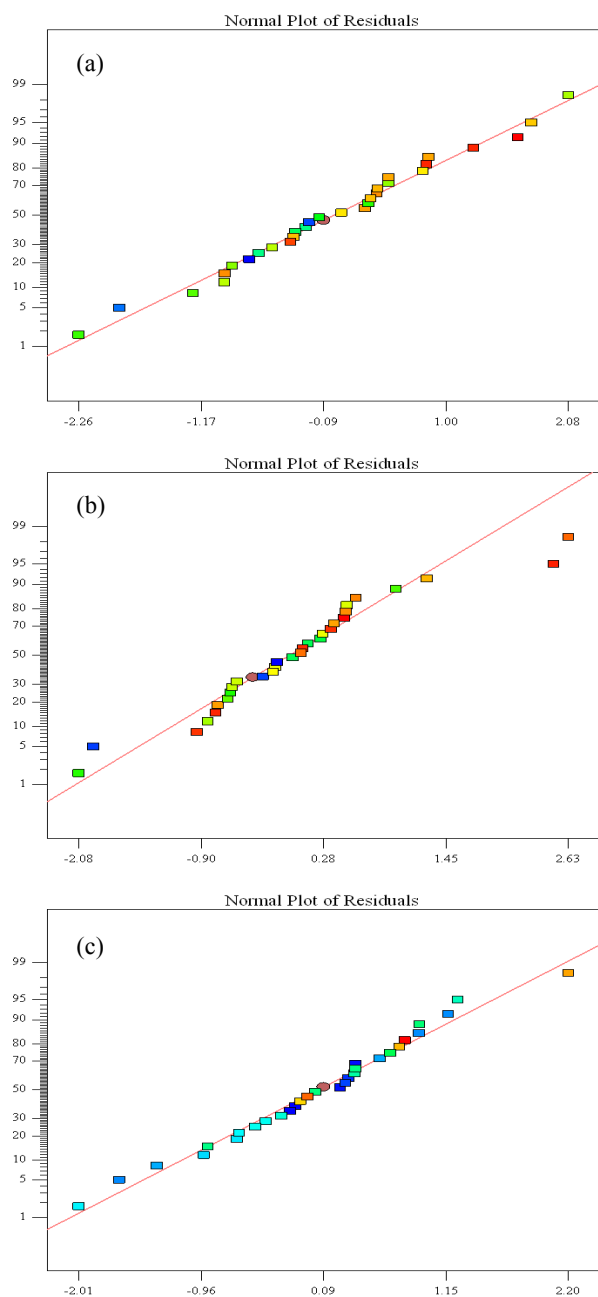Fig. 2 Predicted versus actual plot for (a) upper PAH removal, (b) lower PAH removal and (c) leachate pH

Fig. 3 Normal % probability versus studentised residuals for (a) upper PAH removal, (b) lower PAH removal and (c) leachate pH
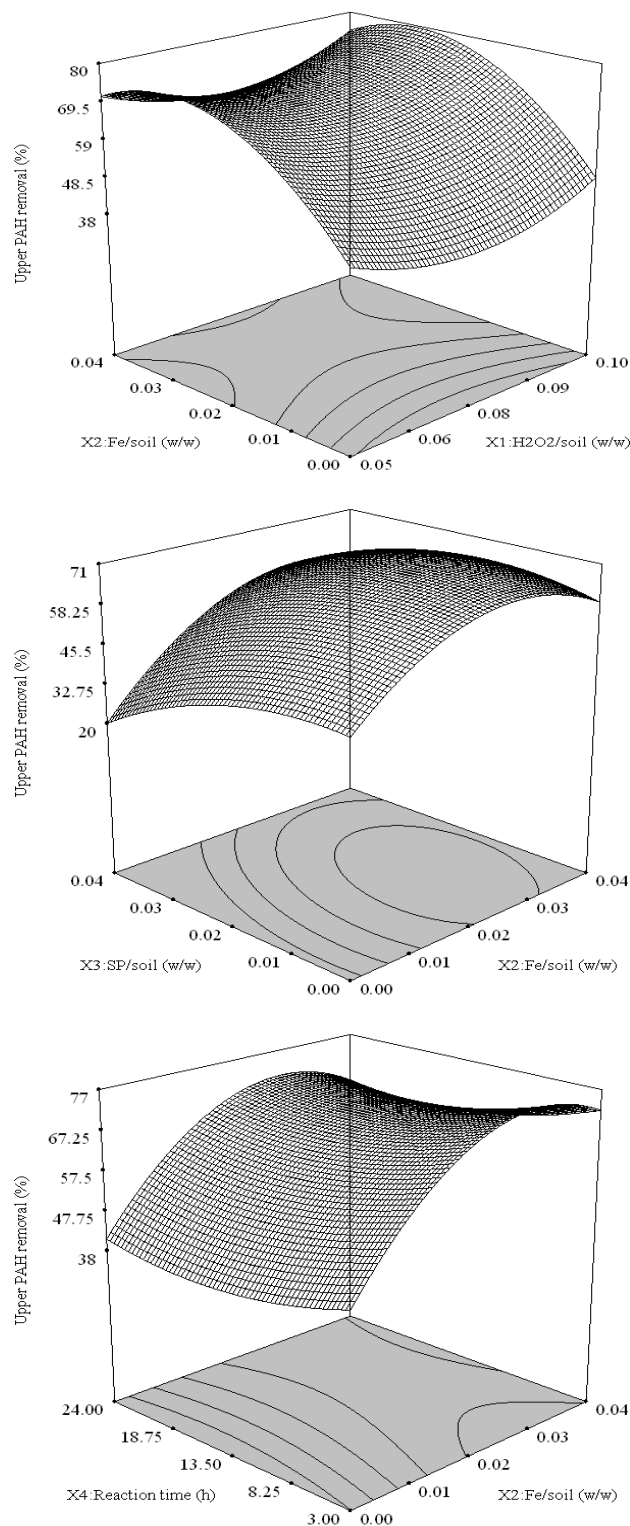
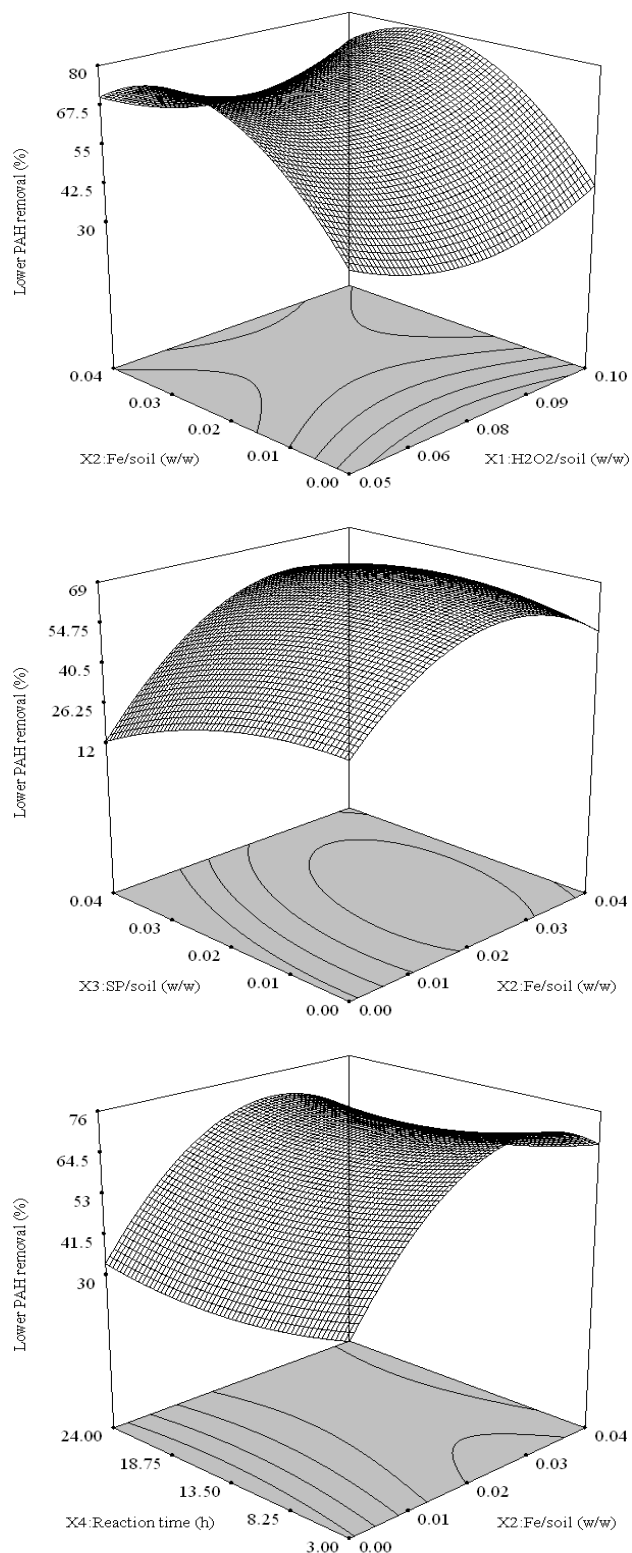Fig. 4 Three-dimensional surface plots for upper PAH removal

Fig. 5 Three-dimensional surface plots for lower PAH
removal

IV. CONCLUDING REMARKS

The MF treatment is a promising approach to remediate PAH-contaminated soils at natural soil pH. An optimum operating condition for this MF treatment was observed at H_2O_2/soil of 0.05, Fe^{3+}/soil of 0.025, SP/soil of 0.04 and reaction time of 3 h resulted in 79.42% and 68.08% of upper and lower PAH removal efficiencies and leachate pH of 4.42. Overall, RSM analysis was able to quantify the effect of parameter interactions being investigated using minimum experimental runs with statistically reliable results for PAH removal and leachate pH.

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