Optimization of Fenton's Oxidation by Box-Behnken Design of Response Surface Methodology for Landfill Leachate

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Abstract

Landfill leachate is one of the major concerns of the present society from environmental point of view. Fenton's reagent serves as an effective treatment method for the removal of pollution load from landfill leachate. In the present study, the efficacy of response surface models was analysed to optimize experimental conditions for maximum removal of chemical oxygen demand, colour, phosphate and sulphate. The optimum conditions obtained by overlaying the responses were found to be initial pH 5, $[H_2O_2]/[Fe^{2+}]$ ratio 4 and $[H_2O_2]$ 80 mM. After Fenton's oxidation, overall reduction in chemical oxygen demand, phosphate, sulphate and colour removal of 84.2%, 93.7%, 97.5% and 82.47% respectively, was achieved. The chemical oxygen demand removal was significantly affected by H_2O_2 concentration and $H_2O_2/FeSO_4$ molar ratio. H_2O_2 concentration and pH had noteworthy influence on phosphate and colour removal. The sulphate removal was significantly affected by $H_2O_2/FeSO_4$ ratio and pH. The estimated overall optimum conditions by overlaying the responses of Box-Behnken design of response surface methodology were found to be initial pH 5, $[H_2O_2]/[Fe^{2+}]$ ratio 4 and $[H_2O_2]$ 80 mM.

Keywords: Landfill leachate, Response surface methodology, Box-Behnken design, Fenton's oxidation

1. Introduction

Land filling i.e. dumping of solid waste is one of the most economical [1] method of waste disposal. However, due to rapid industrialization and population growth land is also becoming devoid for waste dumping [2]. Second issue associated with landfill sites is the production of liquid waste i.e. landfill leachate. Leachate generated as a result of rainwater percolation and moisture content of the solid waste and gases both produced as a combination of biodegradable and non-biodegradable pollutants are basically concerned with emission of noxious gases (e.g. methane) into air and groundwater [3-4]. Landfill leachate (LL) is highly polluted wastewater which may contain large amounts of organic matter, heavy metals, chlorinated organic, inorganic salts, phenols, ammonia nitrogen, phosphate, sulphide and other pollutants [5-7]. Leaching of LL to groundwater leads to its contamination and may also present a danger to the environment and to water species [8]. LL causes xenotoxicity and cytotoxicity on marine biota and human beings due to the presence of different types of wastes including those rich in heavy metals [9]. Thus, leachate needs to be treated before being discharged into the environment in order to avoid negative impacts on environment, land and aquifers [10].

The treatment of LL is based on its quantity and quality. Usually, precipitation followed by biological treatment is used to deal with it. Precipitation process (coagulation, flocculation, and sedimentation) is commonly used to remove soluble metals and anionic species [11]. Biological process (used to reduce biodegradable organic compounds) is highly useful for recently formed leachate with high BOD/COD ratio [12]. Older leachate contains more concentrated and quantitatively high noxious contaminants that are difficult to be removed by biological process. Fenton's process (non-photochemical advanced oxidation processes) serves to remove the high pollution load and can be used as pre-treatment step thus eliminating noxious and refractory contaminants; organic load in terms of chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC) and colour for further biological treatment of LL [13]. Fenton's reagent (aqueous mixtures of Fe (II) and hydrogen peroxide (H_2O_2) is effective, easy to treat, reactive with organic compounds and does not produce toxic compounds during oxidation [14-21]. Fenton's reagent produces highly oxidative hydroxyl radicals (OH˚) which degrades and mineralizes organic pollutants to carbon dioxide and water [22-25]. However, there is no universally adopted optimization for the Fenton's reagent to treat the LL. Extent of removal achieved by Fenton process is further affected by reaction conditions and leachate composition [26]. Most important factors affecting the efficient removal of COD via Fenton process are apt molar ratio of Fenton reagents, H_2O_2 concentration and suitable initial pH [27]. Consequently, a set of conditions for achieving maximum removal efficiency should be critically defined in terms of initial pH and the amount of ferrous ion and hydrogen peroxide [28].

Response surface methodology (RSM) is an assortment of statistical and mathematical tools that has proven to be valuable for multifactor optimization of various processes [29]. Box Behnken Design (BBD) is a far and wide exploited form of RSM, particularly tailored for 3 levels (-1, 0, and +1). BBD is more efficient than other factorial design including Central Composite Design (CCD) and requires fewer experiments [30-31]. The objective of present study is to optimize process conditions for Fenton's oxidation in terms of hydrogen peroxide concentration [H_2O_2], [H_2O_2]/ [$FeSO_4$] molar ratio and initial pH of the reaction by using Box–Behnken design of response surface methodology.

2. **Materials and Methods**

2.1 *Sampling and collection of landfill leachate*

Bhalaswa landfill is located in north-west Delhi, India between latitude 28° 42' 30'' and 28° 45' N and longitude 77° 07' 30'' and 77° 11' 54''E (Figure. 1). This site has been operational since 1993. The area of the landfill is about 15 ha [32] and it receives about 2200 tons of waste per day [33]. The sampling of the leachate was done as per the Campbell et al, [34] from the study site and it was stored at $4\ ^{\circ}$C before being used.
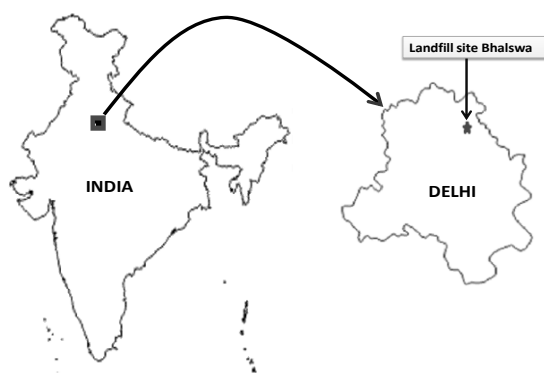

Figure 1: Sampling Site (Bhalaswa landfill)

2.2 *Experimental plan*

Fenton oxidation was conducted in a 500 ml batch reactor filled with 100 ml of leachate sample, after pH adjustment (2.0, 3.5 & 5.0) in separate batches. The solid $FeSO_4·7H_2O$ were added to achieve the targeted Fe^{2+} dosage; then H_2O_2 solution 30% (w/w) was added in a single step in each batch. The mixture was stirred for 30 min at 140 rpm using an orbital shaker cum incubater (Caltar Orbital shaking incubator cum BOD incubator,

NSW India Pvt. Ltd.); then the mixtures were allowed to settle for 1 hr. Aliquot samples in required quantity were drawn from the reactors and heated at 50°C in a water bath for 30 min to remove residual H_2O_2 in solution. COD and rest of the parameters were also measured. Operating conditions for Fenton's reaction are shown in Table 1. All the experiments were carried out at room temperature 25 ± 2^0C under normal lab conditions.

Table 1: Operating conditions for Fenton's reaction

Parameters	Axis Low	Actual Value	Axis High
	-1	0	1
H_2O_2 concentration (m Moles/ l)	40	60	80
H_2O_2/ $FeSO_4$ molar ratio	2	3	4
pH	2	3.5	5

2.3 *Characterization of landfill leachate*
The physico-chemical characteristics of LL were analyzed using "Standard methods of analysis of water and wastewater" [35] and "Manual on water and wastewater analysis" [36]. The COD of the samples were analyzed by closed reflux titrimetric method [35]. pH, total dissolved solid (TDS), salt concentrations and electrical conductivity (EC) were measured digitally by digital multi-response meter (Eutech pH meter Model PC-510 from Eutech Instruments). Phosphate was measured with the ammonium molybdate method using a UV-visible spectrophotometer (T80 UV-Spectrophotometer, PG Instruments Ltd. India) (at wavelength 690 nm). Colour was also measured using UV-Vis spectrophotometer (390 nm).Selected samples were repeatedly analyzed in order to validate/evaluate the produced results. COD, phosphate, sulphate and colour removal were defined as:

$$\eta\ (\%) \quad = (X_i - X_f/ X_i)\ 100 \qquad\qquad (1)$$

Where, X_i and X_f are COD, phosphate, sulphate and colour content before and after Fenton's oxidation respectively.

2.4 *Response surface methodology and Box-Behnken design*
RSM can be successfully employed for the determination of optimum operational conditions and region satisfying the operating specifications [29]. Statistical calculations were carried out according to equation 2 (the variable Xi was coded as Zi) [16, 37]:

$$Z_i = X_i - X_0/\Delta\ X_i \qquad\qquad (2)$$

Where, X_i is the real value of the ith independent variable, X_0 is the real value of an independent variable at the centre point, and ΔX_i is the step change value between low level (-1) and high level ($+1$) [38]. Independent factors used in this study were: initial pH, $[H_2O_2]$ (mol/l), and $[H_2O_2/FeSO_4]$ molar ratio. Responses were recorded in the form of COD, phosphate, colour and sulphate removal efficiency (Y %) and pH, EC, salt concentration and TDS (results not shown). The response variable was fitted by a second-order model in the form of quadratic polynomial equation (3) [39]:

$$Y = \beta o + \Sigma\ \beta iX + \Sigma\ \beta iiXi^2 + \Sigma_i \Sigma_j\ \beta ijXiXj \qquad\qquad (3)$$

Y is the predicted response; β_0 a constant, βi the first-order model coefficient; βii the squared coefficient for the factor i; and βij the linear model coefficient for the interaction between factors i and j. Xi is the coded value of the main effect. Design Expert Software (version 9.1.6, Stat-Ease, Inc., Minneapolis, MN) was employed for the statistical design of experiments and data analysis. The optimum values of selected variables were obtained by solving the regression equation at desired values of the process responses as the optimization criteria. The optimum region was identified by using the main parameters in the overlay plot. The data were subjected to ANOVA and the coefficient of regression (R^2) was estimated to detect the goodness of fit of the model. Regression equations were checked for their adequacy by comparing the experimental values with the predicted data obtained from the equations [39]. Detailed analyses on the model have been presented in the following sections.

3. Results and Discussion

Characteristics of LL vary from site to site and thus for each specific site particular treatment conditions are recommended and different results are obtained [40].The physicochemical characteristics of the raw leachate have been summarized in Table 2. It can be seen from Table 2 that COD of LL was moderate and it was alkaline in nature.

Table 2: Characterization of landfill leachate

COD	Sulphate (mg L^{-1})	Phosphate (mg L^{-1})	pH	EC	Colour	VSS	VFA	TKN
7360	251	3.85	8.55	27.12	Blackish-brown	550	3912	1932

COD-Chemical oxygen demand; EC-Electrical Conductivity (mS); VSS-Volatile Suspended Solid (mg L^{-1}); VFA-Volatile Fatty Acids (mg L^{-1}); TKN-Total Kjeldahl Nitrogen (mg L^{-1})

The coded variables, their experimental values, and the observed responses are presented in Table 3. The efficiency of Fenton's oxidation under the chosen conditions to remove COD, phosphate, colour and sulphate from the leachate has been summarized in Table 3 and Figure. 2-5.

Table 3: Box–Behnken design matrix for experimental design, observed and predicted response for removal of COD, phosphate, colour and sulphate

Run	Real (coded) values			Response (Y (%))							
				COD		Phosphate		Colour		Sulphate	
	A	B	C	OV	PV	OV	PV	OV	PV	OV	PV
1	80(+1)	3(0)	5(+1)	69.56	69.47	92.8	92.63	97.50	97.21	49.00	47.37
2	60 (0)	3(0)	3.5(0)	64.34	64.39	93.5	91.9	89.30	90.48	81.67	81.38
3	60(0)	4(+1)	2(-1)	71.14	71.62	76.36	76.42	77.30	77.36	71.70	70.03
4	60(0)	2(-1)	2(-1)	75.40	74.93	67.8	67.25	67.10	67.47	68.50	66.54
5	60(0)	3(0)	3.5(0)	64.30	64.39	91.3	91.9	89.70	90.48	82.47	81.38
6	60(0)	2(-1)	5(+1)	61.20	60.72	90.3	90.24	91.30	91.24	55.77	57.44
7	60(0)	3(0)	3.5(0)	64.17	64.39	91.6	91.9	89.70	90.48	82.00	81.38
8	60(0)	3(0)	3.5(0)	65.26	64.39	91.4	91.9	91.70	90.48	81.74	81.38
9	40(-1)	3(0)	2(-1)	71.74	71.83	73.9	74.07	72.00	72.30	53.90	55.53
10	40(-1)	2(-1)	3.5(0)	57.83	58.21	86.5	86.88	83.70	83.04	52.00	52.33
11	60(0)	4(+1)	5(+1)	84.20	84.67	81.6	82.15	83.30	82.93	66.00	67.96
12	80(+1)	2(-1)	3.5(0)	64.00	64.58	82.9	83.13	74.14	74.49	53.90	53.86
13	40(-1)	3(0)	5(+1)	57.50	57.60	88.6	88.28	71.00	71.72	56.00	54.00
14	80(+1)	3(0)	2(-1)	56.50	56.40	77.8	78.12	68.00	67.28	55.00	57.00
15	80(+1)	4(+1)	3.5(0)	67.12	66.74	92	91.62	93.40	94.06	57.09	56.76
16	40(-1)	4(+1)	3.5(0)	77.26	76.69	79.7	79.47	65.40	65.05	63.40	63.44
17	60(0)	3(0)	3.5(0)	63.90	64.39	91.7	91.9	92.00	90.48	79.00	81.38

A- [H_2O_2] m Mol/l; B- [H_2O_2]/$FeSO_4$ molar ratio; C-pH; OV- observed Value; PV-Predicted Value

The Fenton's oxidation removes high percentages for all the responses as initial pH, [H_2O_2] and H_2O_2/$FeSO_4$ molar ratio were identified as per the optimal values (initial pH 2-5, [H_2O_2]/[Fe^{2+}] ratio 2-4 and for H_2O_2 dosage 40-80 mM) reported for Fenton treatment of LL. As defined previously, the responses were considered as percentages of COD, phosphate sulphate, and colour. Regressions significance of all the models was

demonstrated by adequate F-values along with the P-values (less than 0.05 (<0.001) (Table 4-5). It is clear from the lack of fit P-values for the four responses (>0.05) that the models were satisfactory. Determination coefficient R^2 and the multiple correlation coefficient R may be used to check the reliability of the model whereas three parameters of prediction i.e. R^2, adequate precision and F-ratio may be used to evaluate the prediction capability of the models [41].
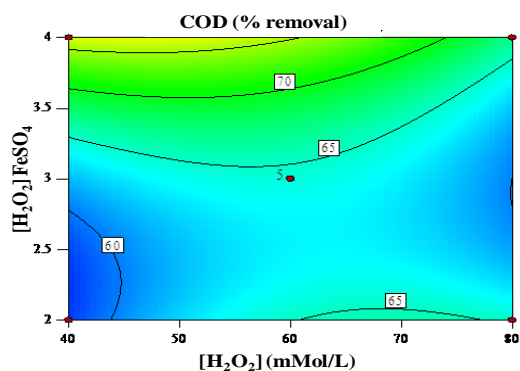

Figure 2: (**a**) Effect of H_2O_2 concentration (mMol/l) and $H_2O_2/FeSO_4$ molar ratio on COD removal at constant pH of 3.5
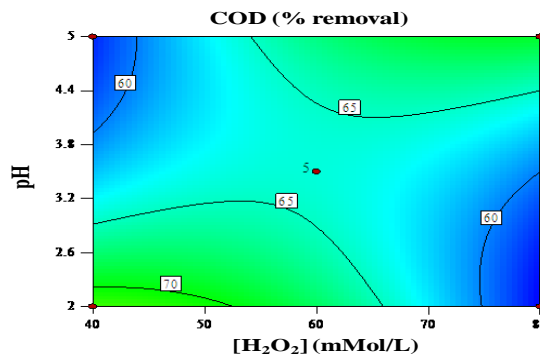
Figure 2: (**b**) Effect of pH and H_2O_2 concentration (mMol/l) at constant $H_2O_2/FeSO4$ molar ratio of 3
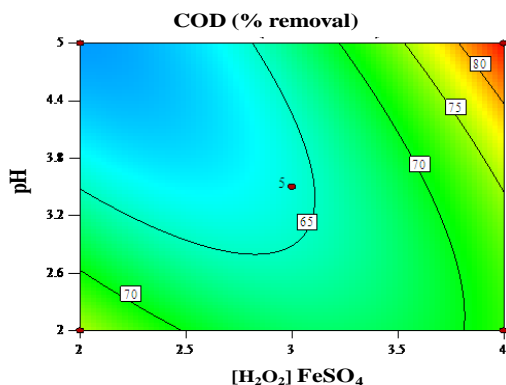
Figure 2: (**c**) Effect of $H_2O_2/FeSO_4$ molar ratio and pH at constant H_2O_2 concentration of 60mMol/l on COD removal efficiency
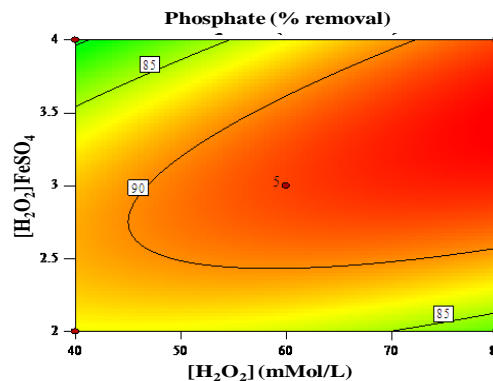

Figure 3: (**a**) Effect of H_2O_2 concentration (mMol/L) and $H_2O_2/FeSO_4$ molar ratio at constant pH of 3.5 on phosphate removal efficiency
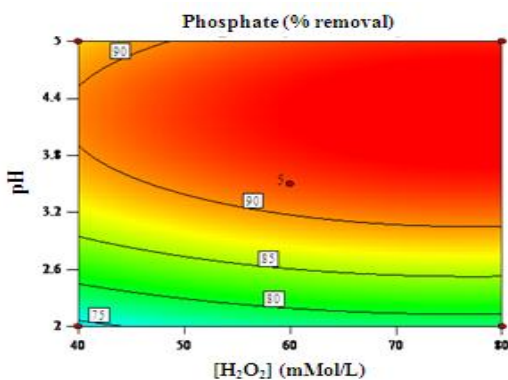

Figure 3: (**b**) Effect of molar H_2O_2 concentration and pH on phosphate removal at a constant $H_2O_2/FeSO_4$ molar ratio of 3.
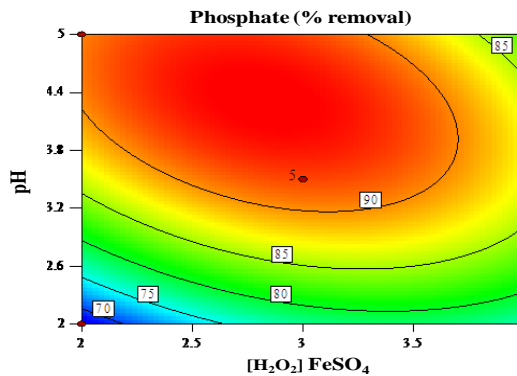

Figure 3: (**c**) Effect of $H_2O_2/FeSO_4$ molar ratio and pH at constant H_2O_2 concentration of 60 mMol/L on removal efficiency of phosphate.
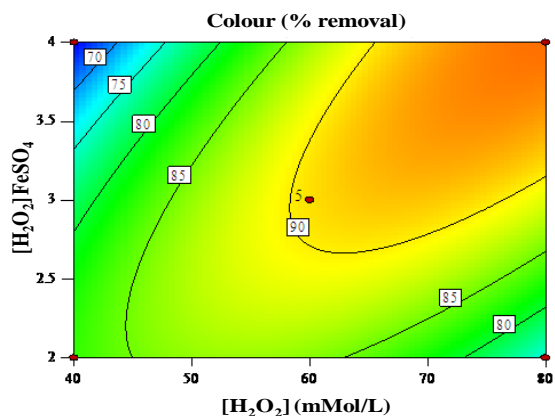
J. Mater. Environ. Sci. 7 (12) (2016) 4456-4466
ISSN: 2028-2508
CODEN: JMESCN

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Figure 4: **(a)** Effect of H_2O_2 concentration (mMol/L) and $H_2O_2/FeSO_4$ molar ratio at constant pH of 3.5
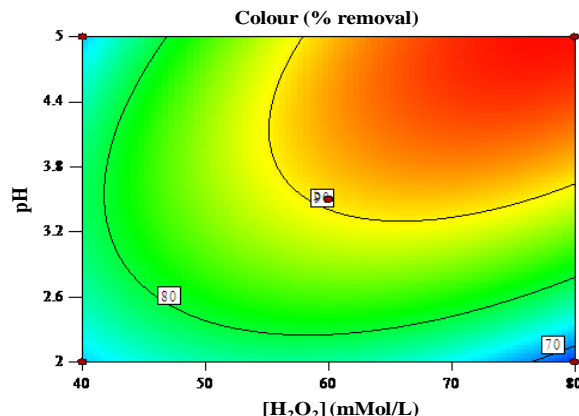

Figure 4: (b) Effect of molar H_2O_2 concentration and pH at constant $H_2O_2/FeSO_4$ molar ratio of 3
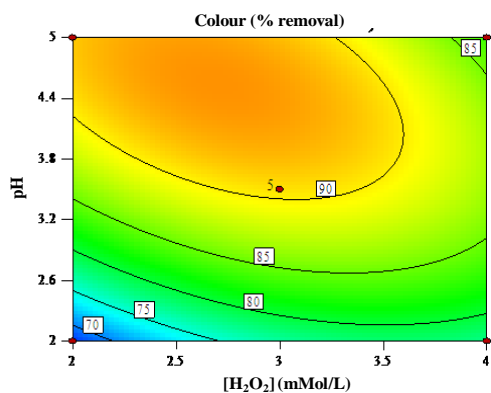

Figure 4: (c) Effect of $H_2O_2/FeSO_4$ molar ratio and pH at constant H_2O_2 concentration of 60 mMol/L on removal efficiency of colour.
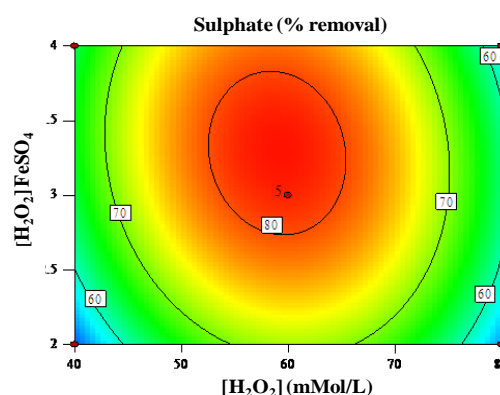

Figure 5: (a) Effect of H_2O_2 concentration (mMol/L) and $H_2O_2/FeSO_4$ molar ratio at constant pH of 3.5
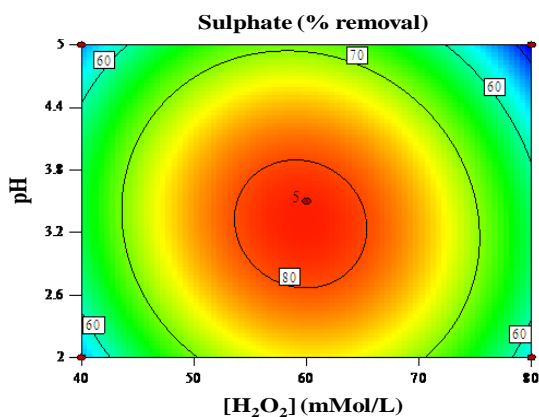

Figure 5: (b) Effect of molar H_2O_2 concentration and pH at constant $H_2O_2/FeSO_4$ molar ratio of 3
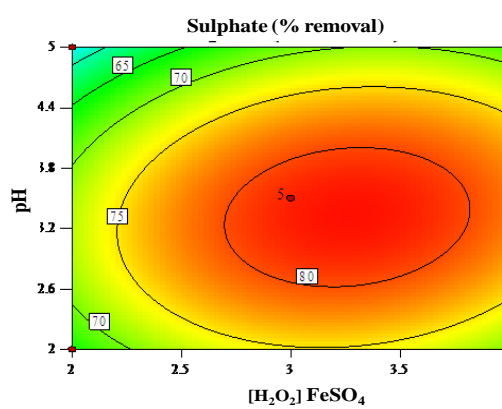

Figure 5: (c) Effect of $H_2O_2/FeSO_4$ molar ratio and pH at a constant H_2O_2 concentration of 60 mMol/L on removal efficiency of sulphate

Table 4: Analysis of variance (ANOVA) variables fitted to quadratic polynomial models

Source	Sum of squares				df	Mean square				F-value				Prob > F			
	COD	P	S	C*		COD	P	S	C*	COD	P	S	C*	COD	P	S	C*
Model	876.38	978.19	2373.9	1816.28	9	97.38	108.69	263.77	201.81	231.17	166.5	53.85	156.58	0	0	0	0
A	6.39	35.28	13.29	209.51	1	6.39	35.28	13.29	209.51	15.17	54.05	2.71	162.56	0.01	0	0.14	0
B	213.11	0.58	98.14	1.25	1	213.11	0.58	98.14	1.25	505.91	0.89	20.04	0.97	0	0.38	0	0.36
C	0.67	412.42	62.33	430.71	1	0.67	412.42	62.33	430.71	1.6	631.8	12.73	334.18	0.25	0	0.01	0
AB	66.5	63.2	16.85	352.69	1	66.5	63.2	16.85	352.69	157.88	96.82	3.44	273.65	0	0	0.11	0
AC	186.32	0.02	16.4	232.56	1	186.32	0.02	16.4	232.56	442.32	0.03	3.35	180.44	0	0.86	0.11	0
BC	185.78	74.48	12.36	82.81	1	185.78	74.48	12.36	82.81	441.03	114.09	2.52	64.25	0	0	0.16	0
A^2	51.6	5.89	1425.21	204.7	1	51.6	5.89	1425.21	204.7	122.5	9.02	290.97	158.82	0	0.02	0	0
B^2	134.85	124.72	171.41	79.58	1	134.85	124.72	171.41	79.58	320.13	191.06	35	61.75	0	0	0	0
C^2	36.19	233.22	380.24	171.52	1	36.19	233.22	380.24	171.52	85.91	357.28	77.63	133.08	0	0	0	0
Residual	2.95	4.57	34.29	9.02	7	0.42	0.65	4.9	1.29								
Lack of Fit	1.89	1.27	26.84	2.61	3	0.63	0.42	8.95	0.87	2.39	0.51	4.8	0.54	0.21	0.69	0.08	0.68
Pure Error	1.06	3.3	7.45	6.41	4	0.26	0.83	1.86	1.6								
Cor. total	879.33	982.76	2408.19	1825.39	16												

A-H$_2$O$_2$ concentration;   B-H$_2$O$_2$/FeSO$_4$ molar ratio; C- pH; P-phosphate; S-sulphate; C*-Colour

Table 5: Analysis of variance for the four responses				
	COD	**Phosphate**	**Colour**	**Sulphate**
Std. Dev.	0.65	0.81	1.14	2.21
Mean	66.79	85.28	82.15	65.24
C.V. %	0.97	0.95	1.38	3.39
R-Squared	0.9966	0.9954	0.9951	0.9858
Adj. R-Squared	0.9923	0.9894	0.9887	0.9657
Pred. R-Squared	0.9637	0.9741	0.9716	0.8169
Adeq. Precision	56.802	40.958	36.932	20.034

The closer the value of R to 1, the better is the correlation between the predicted and experimental values. Values of R^2, varied from 0.99 to 0.97 demonstrating reasonable correlation amid predicted and experiential outcome (Table 5). Also, the adjusted R^2 values of 0.9657–0.9923 showed the lack of R^2 inflation effect due to introduction of insignificant variables [40]. Predicted R^2 values of 0.82- 0.97 were in good agreement with the ''adjusted R^2'' of 0.97 – 0.99 indicating that the response surface designs can be used for navigating the design space. Adequate precision which measures the signal to noise ratio (range of predicted response in relation to its average prediction error needs to be greater than 4) ranging from 20.034 to 56.802 represents an adequate signal. Low values of coefficient of variation (0.95–3.37%) indicate good precision and reliability of the experiments. Correlation plots of predicted versus actual values showed that all four responses display satisfactory conformity between observed data and integrated models (Figure. 6a-d).
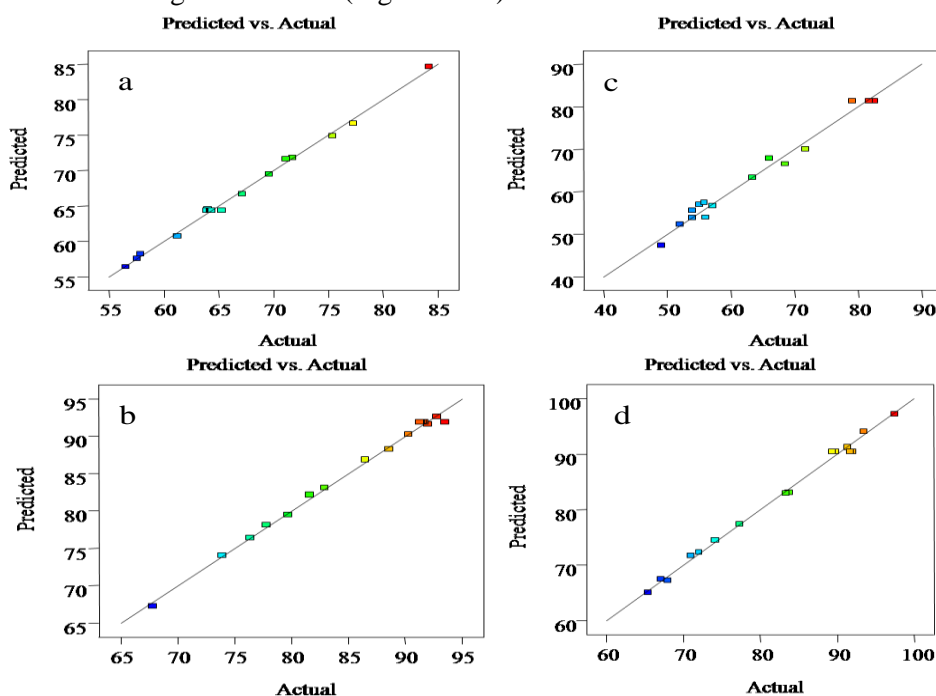

Figure 6: Correlation of actual and predicted removal efficiency for (a) COD (b) Phosphate (c) colour and (d) sulphate

Contour plots were developed as a function of two factors at a time, holding other factors at a fixed level (centre level). $H_2O_2/FeSO_4$ molar ratio exerted a more important role in the COD removal as compared to both H_2O_2 molar concentration and initial pH (Figure. 2a-c). Amiri and Sabour, [40] also reported that $[H_2O_2]/[Fe^{2+}]$ ratio and Fe^{2+} dosage had significant influence on COD removal. With increase in $H_2O_2/FeSO_4$ molar ratio from 2 to 4, the percent COD removal efficiency first increased gradually and then after reaching value of 3 it increased sharply from 58.36% to more than 76.34%. It has been specified that 60–90% of COD can be removed from the effluent with the help of Fenton oxidation [42]. At higher COD strengths, more COD was removed with the same amount of dosage e.g. initial COD being 1000, 2000, and 3000 mg l^{-1}; COD removal efficiency (H_2O_2/Fe^{2+}) = 0.075 M/0.05 M) was 61.3%, 49.4%, and 37.5% respectively [43]. On the other hand, with increase of molar

concentration of H_2O_2 from 40 to 80mMol/l, the process efficiency increased gradually from 58.3% to slightly more than 65.5%. Kang and Hwang, [44] also reported that COD removal effectiveness was highest around a pH of 3.5 and increased by increasing the H_2O_2 dose. Saddle points in Figure 2(a-b) suggest maximum COD removal will be at the extremes. Figure 2 (b) plots the effect of pH and H_2O_2 concentration on COD removal at a constant $[H_2O_2]/ [Fe^{2+}]$ molar ratio of 3. Deng, [45] and [46] also established a most favourable H_2O_2/Fe^{2+} molar ratio of 3 while using Fenton's oxidation process for LL. Cortez et al, [46] reported that maximum COD removal efficiency increased almost linearly with the increase of H_2O_2/Fe^{2+} until a molar ratio of 3 and any further increase in this ratio did not show noteworthy elimination. This might be due to the scavenging effect of peroxide on the hydroxyl radicals, which presumably became stronger as the ratio H_2O_2/Fe^{2+} rapidly increased. Deng, [46] and Lopez et al, [47] also described an optimum initial pH of 3. At lower pH (<3) value the COD removal efficiency decreased sharply. One of the reasons may be increased scavenging of $^.OH$ by H^+ [48]. On the other hand, COD removal efficiency dropped significantly when pH was higher than 3, which can be attributed to increasing rate of self-decomposition of H_2O_2, deactivation of iron ions into iron oxyhydroxides, the increased scavenging effect of carbonate and bicarbonate on $^.OH$, and the decreased oxidation potential of $^.OH$. Therefore, COD removal efficiency depends strongly on the initial pH of the solution. Cortez et al, [46] reported a COD removal efficiency of 60.9% at a molar ratio H_2O_2/Fe^{2+} of 3, a Fe^{2+} dosage of 4 mmol·L^{-1}, pH 3, and a reaction time of 40 min.

Figure 3 (a-c) shows the 2-D contour plots for phosphate removal resulting from interaction of two factors at a time while keeping third factor constant. Significance of the variable on the response factor is indicated by the slope of the plot [38]. It is clear from the figures, Phosphate removal was not much affected by variation in H_2O_2 concentration within the chosen range and showed more or less similar removal. However, it was highest at $[H_2O_2]/ [FeSO_4]$ molar ratio of 3 and decreased with both increase and decrease in the molar ratio. Decreasing pH had a negative effect on phosphate removal whereas increase in pH above 3.5 had an initial positive effect which then declined gradually. It can be seen from the figures (Figure 3 a-c) that H_2O_2 concentration and pH had positive effect on phosphate removal increasing from 74 (at pH 2 and molar ratio around 40) to 90% (at pH 4.7 and H_2O_2 concentration of 40mMol/l). With increase in molar concentration of H_2O_2, phosphate removal increased gradually from 74% to 78%. On the other hand phosphate removal was highest at the central $[H_2O_2]/ [FeSO_4]$ ratio of 3 and declined with both increase as well as decrease in molar ratio.

Figure 4 (a-c) shows the 2-D contour plots of the interaction of various factors for colour removal. Colour removal decreased from 83% (at 40mMol/l $[H_2O_2]$ and $[H_2O_2]/ [FeSO_4]$ molar ratio of 2) to 66% (at 40mMol/l $[H_2O_2]$ and $[H_2O_2]/ [FeSO_4]$ molar ratio of 4). Colour removal increased with increase in molar $[H_2O_2]$ attaining a maximum value of 86% at 60mMol/l (and $[H_2O_2]/ [FeSO_4]$ molar ratio of 2, and then decreased up to 76.8% (at 80mMol/l $[H_2O_2]$ and $[H_2O_2]/ [FeSO_4]$ molar ratio of 2. Yilmaz et al, [20] reported 89.4% colour removal under the optimal operation conditions (initial pH 3, 2000 mg/L Fe^{2+}, 5,000 mg/L H_2O_2). Figure 4(b) shows the contour plot of colour removal as a function of pH and $[H_2O_2]$ at a fix $[H_2O_2]/ [FeSO_4]$ molar ratio of 3. It was observed that colour removal first increased with increasing pH reaching a maximum value of 78% at pH 4 and then decreased with further increase 72% at pH 5. With increasing $[H_2O_2]$, colour removal increased from 72.7% to 76.8% (at 65mMol/l) and then declined with further increase finally reaching a value of 67% at 80mMol/l H_2O_2. Keeping $[H_2O_2]$ constant at 60 mMol/l, colour removal increased with increase in pH from 67% at pH 2 to 91% at $[H_2O_2]/ [FeSO_4]$ molar ratio of 2 and pH 5. Colour removal also increased with increasing molar ratio up to 77.6%. The results are in accordance with the previous studies as [49] also reported colour removal effectiveness as high as 92% using Fenton treatment for mature LL. Erkan and Apaydin, [50] reported colour removal efficiencies of 74–97%; 4–97%; and 14–98% for young, middle-aged and stabilized leachate respectively. As seen from the slope, pH had a much pronounced effect on colour removal as compared to $[H_2O_2]$ and $[H_2O_2]/ [FeSO_4]$ molar ratio. Interaction of the three factors showed maximum removal of 92.5% at $[H_2O_2]$ molar concentration of 80mMol/l, $[H_2O_2]/ [FeSO_4]$ molar ratio of 3, and pH 5.

Figure 5(a-c) shows contour plots for interaction of the variables on sulphate removal efficiency. Sulphate removal was maximum at pH 3.5, $H_2O_2/FeSO_4 = 3$ and H_2O_2 concentration of 60 mMol/l. A sharp variation was observed with increase as well as decrease in pH. Sulphate removal exhibited gradual change with increasing and decreasing $[H_2O_2]/ [FeSO_4]$ molar ratio and molar H_2O_2 concentration.

Optimization node of RSM merges the individual interests into an identified value and then explores to maximize this function thus facilitating the determination of optimum value of the responses [50]. In accordance with the optimization step, the preferred target meant for each factor (initial pH, $[H_2O_2]$ and H_2O_2/Fe^{2+} molar ratio) was

selected "within the range" whereas the responses (COD, TOC, and colour removal efficiency) were defined as "maximum" to accomplish peak performance [50]. An overlay plot illustrating the optimum region in which all the responses simultaneously meet their desirable conditions and contain all the response contours in a single plot [40]. Contour plot and overlay plot have been shown in Figure 7 (a and b).
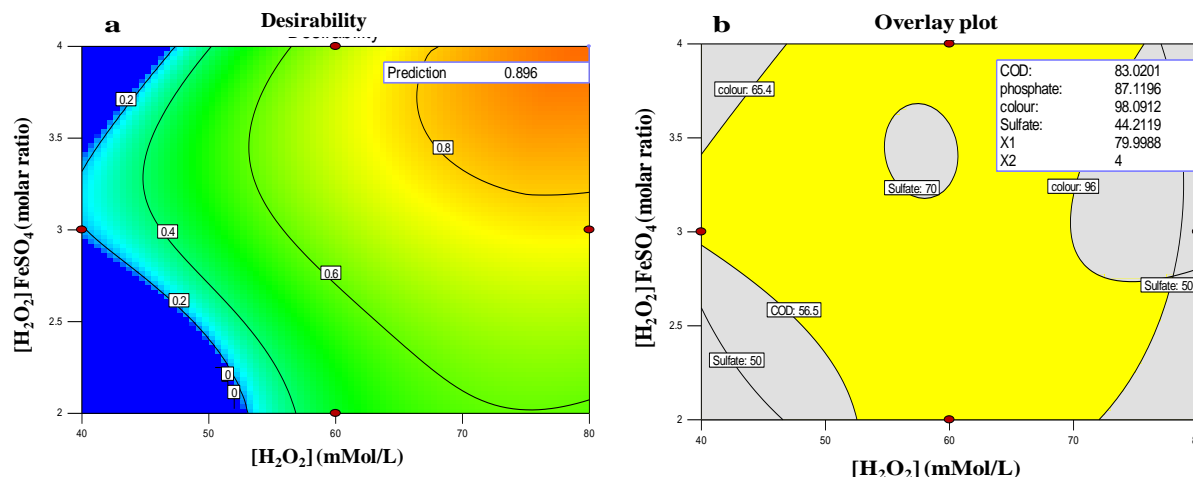

Figure 7: (a) Contour plot showing desirability of predicted conditions representing the optimized region **(b)** Overlay plot

The most favourable operational conditions exhibiting maximum 83% removal of COD, 87% removal of phosphate, 98% removal of colour and 44% removal of sulphate were achieved at optimum conditions of pH 5, 80mMol/l [H_2O_2] and H_2O_2/$FeSO_4$ molar ratio of 4 (Figure. 7b). Lak et al, [17] reported 50.76% COD removal at optimum conditions of initial pH of 5.8 and [H_2O_2]/ [Fe^{2+}] molar ratio of 8. According to Amiri and Sabour, [40], optimum operational conditions obtained by overlay plot, were found to be initial pH of 5.7 and [H_2O_2]/ [Fe^{2+}] ratio of 17.72. However, COD removal of 83% seems absolutely reasonable in comparison with the values previously accounted in the literature [17].

Conclusions

In the present study, modeling and optimization of experimental parameters in Fentone oxidation process was done by Box Behnken Design (BBD) of response surface methodology (RSM). The analysis of variance (ANOVA) results indicated (1) the interaction of H_2O_2 conc. and H_2O_2/$FeSO_4$ were significant on percent COD removal (2) H_2O_2 conc. and pH was significant on percent phosphate and colour removal (3) H_2O_2/$FeSO_4$ and pH were significant on percent sulphate removal. By Fenton's oxidation, the maximum removal of COD (84.2%), phosphate (93.7%), sulphate (97.5%) and colour (82.5%) were achieved. In the design range, the statistical analysis of the proposed quadratic models seemed completely adequate with adjusted R^2 values (0.9657 to 0.9923).Validation of predicted models was confirmed by precision and F-ratio also. Overall optimum conditions obtained by overlaying the responses were found to be initial pH 5, [H_2O_2]/ [Fe^{2+}] ratio 4 and [H_2O_2] 80 mM.

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(2016) ; http://www.jmaterenvironsci.com/