Research Journal of
Environmental
Toxicology

Optimization of Fenton Oxidation Process for Biodegradability Enhancement of a Mature Landfill Leachate Using Response Surface Methodology

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ABSTRACT

Biological methods are not appropriate for mature leachate (5-10 years) due to the presence of bio refractory materials and toxic compounds such as heavy metals. Now-a-days advanced oxidation processes such as Fenton reagent are used for the treatment or biodegradability enhancement of refractory wastewater. In this study, the biodegradability enhancement of mature landfill leachate using Fenton oxidation process in lab scale has been investigated. To optimize Fenton reaction for biodegradability enhancement of leachate, Response surface methodology was used. Design Expert7 was used for statistical analysis of experimental data. The leachate samples have been taken from a 10 years old landfill and oxidation experiments in lab scale were done in different conditions from operational points of view (reaction time, pH, Hydrogen peroxide to Fe (II) ratio). The BOD_5, COD, pH, H_2O_2, Fe^{2+} oxidation time were evaluated in 32 runs, 12 run as pretests and 20 run for optimization. Results from numerical optimization showed that in pH = 3.3, H_2O_2/Fe^{2+} = 15.82 and oxidation time of 130 min, COD removal, BOD_5 and BOD_5/COD ratio variation were 93.1, 0.56 and 0.49%, respectively. In optimal condition that BOD_5/COD ratio will be 0.45, the oxidation time is 130 min, pH = 3-3.5 and H_2O_2/Fe^{2++} ratio = 14-17. This study indicates that Fenton oxidation enhances the biodegradability of the mature leachate. In the optimal condition of Fenton oxidation the BOD_5/COD ratio increased to 80 times greater than initial ratio. Results from experiments will agree to results from model. This agreement confirms accuracy and approach of obtained model.

Key words: Advanced oxidation, biodegradability, landfill leachate, RSM

INTRODUCTION

leachate generated from landfills can be defined as a high strength organic wastewater which is containing the high concentration of recalcitrant organics and toxic mineral matter such as heavy metals (Englehardt *et al.*, 2006). When untreated leachate discharged directly to the environment may cause many environmental and health adverse effects (Zhang *et al.*, 2005). Management of all types of wastewater can play an important role in the protection of public health and the environment (Farrokhi *et al.*, 2008, 2014).

There are many important effective factors on the quality and quantity of leachate, include; seasonal changes, type of landfill method, method of compacting, characteristics of solid waste, structure of landfill and finally the age of landfill (Lopez *et al.*, 2004). The COD of young leachate (leachate from landfill of less than 1-2 years age) is 30-40 times greater than municipal wastewater with the high BOD_5/COD ratio (>0.6) and high concentrations of low molecular weight organics. Therefore biological treatment methods (anaerobic and aerobic) are commonly applied for treatment of young leachate (De Morais and Zamora, 2005). However, biological methods do not have enough efficiencies for treatment of mature leachates (leachate from landfills of more than 5-10 years age), due to their low BOD_5/COD ratios (<0.3) and high fraction of high molecular weight, refractory organics (Lopez *et al.*, 2004). For this reason, there has been increased interest in physicochemical alternative treatment methods for pretreatment and full treatment of mature leachate (Di Iaconi *et al.*, 2006).

The Fenton oxidation process has been extensively studied in recent years and these studies indicate Fenton oxidation process is one of the most cost-effective alternatives for treatment of mature leachate (Deng, 2007; Kajitvichyanukul and Suntronvipart, 2006; Rivas *et al.*, 2003). Typically there are four main stages for Fenton wastewater treatment process includes: oxidation, neutralization, coagulation and solid separation (Gogate and Pandit, 2004).

Fenton reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radical according to the following reaction (Kitts *et al.*, 1999):

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+OH^o+OH$$
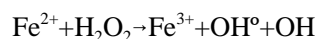
The ferrous iron initiates and catalyzes the decomposition of H_2O_2, resulting in the generation of hydroxyl radical. The generation of hydroxyl radical involves a complex reaction sequence in an aqueous solution (Jiang and Waite, 2003).

However, mineralization of contaminant by AOPs often requires long time of reaction and strong doses of oxidant, often less reactive intermediates are produced that inhibit the degradation of parent compound. Once the recalcitrant compounds have been transformed by means of the chemical treatment, their properties including biodegradability are modified. Often the intermediates have reduced recalcitrance with respect to the parent compound (Marco *et al.*, 1997). Since biological treatment is 10-20 times less expensive than chemical processes, integration of chemical oxidation and biological processes can improve the economy of single process. Response Surface Methodology (RSM) is a statistical modeling technique employed for multiple regression analysis. In this method influences of individual factors as well as their complex interactive influences can be evaluated. One of the most important benefits of RSM is the reduction of the number of tests and experiments (Moradi and Ghanbari, 2014; Ahmad *et al.*, 2007). In recent years optimization of Fenton process for different wastewater and synthetic wastewater using RSM have been studied, but only few researchers report about optimization of Fenton process for leachate treatment using RSM, their report focused on COD, BOD_5 and TOC reduction or level of mineralization of leachate (Amiri and Sabour, 2014). It is rarely seen a report about biodegradability improvement of leachate by Fenton process that optimized using RSM.

In this study, application of Response Surface Methodology (RSM) and Central Composite Design (CCD) for optimization of Fenton oxidation process for biodegradability enhancement of a mature landfill leachate have been investigated. Central composite design is one of the common methods of RSM model that is useful and applicable for design of experiments (Mason *et al.*, 2003). In this method every parameter defined in five levels and in comparison to other experiments design methods have more ability to predict responses.

The main objectives of this study were the determination of Fenton process potential for biodegradability enhancement of mature landfill leachate and to optimize Fenton process for biodegradability improvement of mature leachate using RSM.

MATERIALS AND METHODS

Landfill leachate was collected from the Saravan County Landfill in the city of Rasht in northern Iran which was 10 years landfill. The collected leachate was stored in a plastic bottle at 4°C until use.

For the removal of suspended materials, all samples were filtered through a 40 micron glass filter paper.

All reactions were performed in batch reactor. The reactor was 1 L cylindrical glass, mixing was done by a plastic paddle jointed to an epoxy coated shaft, the shaft was connected to a variable speed electromotor and agitation rates of 180-190 rpm were used in all testes. The pH was controlled by Orion pH meter. Each test began with 500 mL of mature leachate. Each initial pH was adjusted using sulfuric acid.

Required $FeSO_4 \cdot 7H_2O$ was added in to the solution and Fenton reaction was started up after adding H_2O_2. Effluent was collected at a predetermined reaction time. Potential of hydroxyl radical reaction in the collected effluent was quenched by 6N NaOH and 10% Na_2SO_3.

For the study on Fenton oxidation potential for biodegradability enhancement of leachate many parameters such as BOD_5, COD, pH, H_2O_2, Fe^{++}, oxidation time in 32 runs were evaluated, 12 run as pretests and 20 run for optimization. The BOD_5/COD ratio has been used as biodegradability indicator. Definitively BOD_5/COD is indicator of biodegradability (Singh, 2012).

Design Expert7 was used for statistical analysis of experimental data. To optimize three main variables (pH, H_2O_2/Fe^{+2} ratio and reaction time) Response Surface Methodology (RSM) and Central Composite Design (CCD) were used. As shown in Table 1 independent variables including the pH, H_2O_2/Fe^{+2} ratio and reaction time were coded in five level as A, B and C, respectively. Preliminary tests were done for determination of levels before designing the research. The COD (Y1), BOD_5 (Y2) and BOD_5/COD ratio (Y3) were evaluated as important parameters for the evaluation of biodegradability enhancement. The number of tests was calculated from equation as k is the number of factors:

$$CCD = 2^k + 2k + 6$$

Six tests were repeated in central point for evaluation of pure error. Quadratic model as Eq. 1 has been used for analysis of experimental data and prediction of optimum condition:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i . x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{ii \leq j}^{k} \beta_{ij} x_i x_j + \ldots + e \qquad (1)$$

Table 1: Independent variables and their levels in the experimental design as actual and coded

Factor (symbol)	Coded value				
	-1	-0.5	0	0.5	1
	Actual value				
A: pH	2.5	3.0	3.5	4.0	4.5
B: H_2O_2/Fe^{2+} ratio	7	10.5	14.0	17.5	21.0
C: Time (min)	30	60.0	90.0	120.0	150.0

Where:

Y = Response
I = Linear constant
j = Quadratic constant
β = Regression constant
k = Number of studied factors and
e = Random error

Analysis of variances (ANOVA) was used for graphical analyses of the data to obtain the interaction between the process variables and the responses.

The quality of model fitness determined by R^2 (coefficient of determination) and p-value with confidence level of 95% was used for influences of individual variables as well as their interactive influences evaluation. To control the significance and Adequacy of model, calculated F-value (Fisher variation ratio), probability value and Adequate precision were evaluated. Finally to find optimum condition of Fenton process for biodegradability enhancement of leachate, response variables have been compared in an overlaying three dimensional graph.

Analytical methods: All chemicals were purchased from MERK and ALDRICH Company. All chemicals were of analytical grade, 98% and higher (except for H_2O_2 which was 33%). The Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD_5) were measured to investigate the biodegradability enhancement of leachate by Fenton reagent. The pH was measured by Orion pH meter 420 A model and COD and BOD_5 were analyzed according to the standard, 5220-C and 5210-B methods, respectively (APHA *et al.*, 1995).

RESULTS AND DISCUSSION

Landfill leachate characteristics are given in Table 2. It can be seen that the mean BOD_5/COD is less than 0.01.

The low BOD_5/COD ratio and high concentration of NH_3-N and alkalinity as shown in Table 2 indicate that it is a mature, stabilized and non biodegradable leachat (Zhang *et al.*, 2012). Since the Fenton oxidation efficiency is strongly dependent to H_2O_2/COD ratio therefore this parameter was evaluated and the optimal H_2O_2/COD ratio of 2.12 g g^{-1} was obtained which was according to the results of puangrant and Nattapol study on biodegradability of hospital wastewater (Kajitvichyanukul and Suntronvipart, 2006). In all experiments this ratio was constant. In this experimental study 20 run of CCD were performed that results are shown in Table 3.

Table 4 shows regression results of response surface model for COD reduction, BOD_5 and BOD_5/COD variation. Results from Table 4 have been used to determine models coefficients in Eq. 2-4.

Table 2: Landfill leachate characteristics

Parameters	Concentration
pH	6.80
COD (mg L^{-1})	19840.00
BOD_5 (mg L^{-1})	180.00
BOD_5/COD	0.01
EC (msec cm^{-1})	23.40
Alkalinity (mg L^{-1} as $CaCO_3$)	5500.00
NH_3-N (mg L^{-1})	1750.00

Table 3: Central composite face-centered design and experimental results

		Process variable						Responses		
		A		B		C		COD	BOD_5	BOD_5/COD
Std	Run	Actual	Coded	Actual	Coded	Actual	Coded	removal eff.(%)	variation (%)	ratio variation (%)
18	1	3.5	0.0	14	0.0	90	0.0	86.8	567.0	0.38
5	2	2.5	-1.0	7	-1.0	150	1.0	61.2	567.0	0.13
12	3	3.5	0.0	17.5	0.5	90	0.0	88.9	367.0	0.31
7	4	2.5	-1.0	21	1.0	150	1.0	88.9	433.0	0.36
4	5	4.5	1.0	21	1.0	30	-1.0	37.0	-33.3	0.008
16	6	3.5	0.0	14	0.0	90	0.0	88.9	453.0	0.38
8	7	4.5	1.0	21	1.0	150	1.0	24.4	127.0	0.02
14	8	3.5	0.0	14	0.0	120	0.5	92.4	300.0	0.4
11	9	3.5	0.0	10.5	-0.5	90	0.0	85.7	353.0	0.24
9	10	4.0	-0.5	14	0.0	90	0.0	87.1	453.0	0.3
6	11	4.5	1.0	7	-1.0	150	1.0	49.6	567.0	0.1
1	12	2.5	-1.0	7	-1.0	30	-1.0	24.4	0.0	0.01
20	13	3.5	0.0	14	0.0	90	0.0	87.4	433.0	0.32
19	14	3.5	0.0	14	0.0	90	0.0	90.0	380.0	0.36
2	15	4.5	1.0	7	-1.0	30	-1.0	30.4	-26.6	0.008
3	16	2.5	-1.0	21	1.0	30	-1.0	85.9	367.0	0.25
17	17	3.5	0.0	14	0.0	90	0.0	90.4	367.0	0.37
13	18	3.5	0.0	14	0.0	60	-0.5	89.9	500.0	0.45
10	19	4	0.5	14	0.0	90	0.0	90.6	333.0	0.35
15	20	3.5	0.0	14	0.0	90	0.0	74.8	567.0	0.2

COD: Chemical oxygen demand, BOD_5: Biochemical oxygen demand

Table 4: Regression results of response surface model for COD reduction, BOD_5 and BOD_5/COD variation

	Coefficient estimate				
Factors	Symbol	Value	Standard error	95% CI low	95% CI high
COD					
Intercept	a0	2.20	0.41	1.28	3.11
pH(A)	a1	2.73	0.47	1.69	3.77
H_2O_2/Fe^{+2} ratio (B)	a2	-1.66	0.47	-2.70	0.62
Time(C)	a3	-1.05	0.47	-2.09	-0.0/59
A×B	a4	2.68	0.48	1.61	3.75
A×C	a5	0.83	0.48	-0.24	1.90
B×C	a6	1.62	0.48	0.55	2.69
A^2	a7	2.27	3.15	-4.76	9.29
B^2	a8	2.95	3.15	-4.08	9.97
C^2	a9	2.43	3.15	-4.60	9.45
BOD_5					
Intercept	a0	0.79	0.049	0.68	0.90
pH(A)	a1	-0.14	0.056	-0.26	-0.011
H_2O_2/Fe^{+2} ratio (B)	a2	-0.036	0.056	-0.16	0.089
Time (C)	a3	0.23	0.056	0.10	0.35
A×B	a4	-0.13	0.058	-0.26	0.174
A×C	a5	0.023	0.058	-0.11	0.15
B×C	a6	-0.17	0.058	-0.30	-0.046
A^2	a7	-0.12	0.38	-0.96	0.73
B^2	a8	-0.20	0.38	-1.06	0.65
C^2	a9	0.043	0.38	-0.80	0.89
BOD_5/COD ratio					
Intercept	a0	0.35	0.019	0.31	0.39
pH(A)	a1	-0.070	0.021	-0.12	-0.023
H_2O_2/Fe^{+2} ratio (B)	a2	0.049	0.021	-0.001	0.097
Time (C)	a3	0.035	0.021	-0.013	0.083
A×B	a4	-0.070	0.022	-0.12	-0.021
A×C	a5	-0.017	0.022	-0.066	0.032
B×C	a6	-0.012	0.022	-0.062	0.037
A^2	a7	-0.15	0.14	-0.47	0.18
B^2	a8	-0.35	0.14	-0.67	-0.023
C^2	a9	0.25	0.14	-0.068	0.58

Table 5: ANOVA of quadratic model for COD reduction, BOD_5 and BOD_5/COD variation

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value prob>F
COD					
Model	11312.27	9	1256.92	27.48	<0.0001[s]
A: pH	1617.36	1	1617.36	35.36	0.0001[s]
B: $H_2O_2/Fe+2$ ratio	613.28	1	613.28	13.41	0.0044[s]
C: Time	267.34	1	267.34	5.84	0.0362[s]
A×B	1452.6	1	1452.6	31.75	0.0002[s]
A×C	137.78	1	137.78	3.01	0.1133[ns]
B×C	537.92	1	537.92	11.76	0.0064[s]
A^2	36.38	1	36.38	0.8	0.3934[ns]
B^2	75.87	1	75.87	1.66	0.2268[ns]
C^2	4.09	1	4.09	0.089	0.7710[ns]
Residual	457.34	10	1.86		
Lack of fit	286.55	5	2.37	1.68	0.2922[ns]
Pure error	170.89	5	1.34		
Cor. total	11769.72	19			
$R^2 = 0.96$	Adj $R^2 = 0.93$	Pred $R^2 = 0.87$	AP = 14.3	Press = 1506.3	Mean = 72.73 S.D = 6.76
BOD_5					
Model	580000	9	64980	5.43	0.0071[s]
A: pH	70333	1	70333	5.88	0.0358[s]
B: H_2O_2/Fe^{+2} ratio	5026.5	1	5026.5	0.42	0.5315[ns]
C: Time	195000	1	195000	16.28	0.0024[s]
A×B	57800	1	57800	4.83	0.049[s]
A×C	1800	1	1800	0.15	0.7062[ns]
B×C	108900	1	108900	9.1	0.0130[s]
A^2	1137.89	1	1137.89	0.095	0.7641[ns]
B^2	3216.58	1	3216.58	0.27	0.6154[ns]
C^2	153.88	1	153.88	0.013	0.9120[ns]
Resiual	119650	10	11965		
Lack of fit	81023	5	16204.5	2.1	0.2177[ns]
Pure error	038625	5	7725		
Cor. total	704500	19			
$R^2 = 0.83$	Adj $R^2 = 0.68$	Pred $R^2 = 0.0.32$	AP = 7.32	Press = 484600	Mean = 351.68 S.D = 109.38
BOD_5/COD ratio enhancement					
Model	0.38	9	0.043	11	0.0004[s]
A: pH	0.041	1	0.041	10.5	0.0088[s]
B: $H_2O_2/Fe+2$ ratio	0.021	1	0.021	5.5	0.0413[s]
C: Time	0.011	1	0.011	2.9	0.1196[ns]
A×B	0.038	1	0.038	9.75	0.0108[s]
A×C	0.002	1	0.002	0.51	0.4908[ns]
B×C	0.001	1	0.001	0.26	0.6205[ns]
A^2	0.004	1	0.004	1.02	0.3372[ns]
B^2	0.022	1	0.022	5.72	0.0376[s]
C^2	0.012	1	0.012	3.12	0.1078[ns]
Residual	0.039	10	0.004		
Lack of fit	0.014	5	0.003	0.59	0.71[ns]
Pure error	0.024	5	0.005		
Cor. total	0.42	19			
$R^2 = 0.91$	Adj $R^2 = 0.83$	Pred $R^2 = 0.0.69$	AP = 9.8	Press = 0.13	Mean = 0.062 SD = 0.25

Significant at $p<0.05$,[ns]Not significant at $p<0.05$, AP: Adequate precision, PRESS: Predicted residual error sum of squares

Table 5 shows ANOVA results for predicted parameters regression of response level of quadratic model for COD removal, BOD_5 and BOD_5/COD ratio variations.

As shown in Table 3 the lake of fit test for COD, BOD_5 and BOD_5/COD variations were 1.68, 2.1 and 0.59, respectively, therefore, it is founded that F test insignificant, implying a significant model correlation between variables and COD, BOD5 and BOD/COD percentage variations as process responses.

In this study 0.04-17% of total variation did not explain by model. High R^2 coefficient ($R^2>0.8$) shows a satisfactory adjustment of quadratic models to experimental results (Montgomery, 2009). Adjusted R^2 values for COD, BOD_5 and BOD_5/COD variations were 0.93, 0.68 and 0.83 it can be seen a strong significance of model.
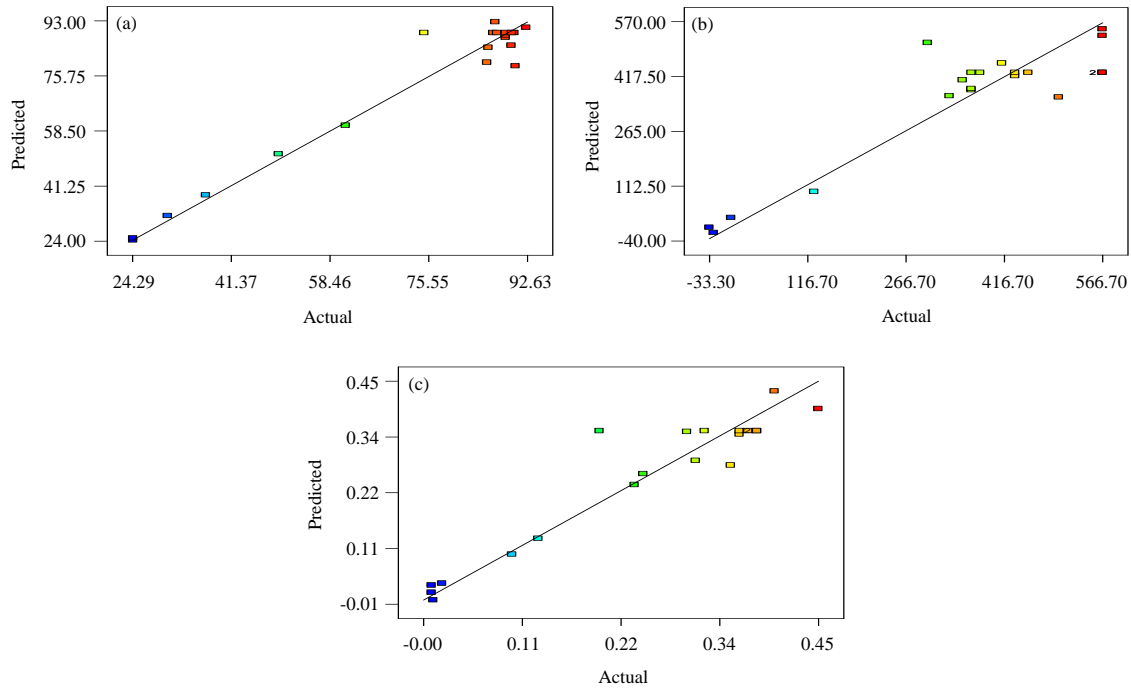
Fig. 1(a-c): Actual and predicted removal (a) COD, (b) BOD_5 and (c) BOD5/COD

Based on the sequential model sum of squares, the models COD removal, BOD_5 and BOD_5/COD ratio variations were selected based on the highest order polynomials where the additional terms were significant and the models were not aliased. The models were coded as Y1, Y2 and Y3 COD, BOD_5 and BOD_5/COD ratio, respectively. The quadratic model for all three terms Y_1, Y_2 and Y_3 were selected as suggested by the software and are shown in Eq. 2-4. The independent variables in the models were pH, H_2O_2/Fe^{+2} ratio and reaction time. All insignificant terms from statistical point of view were removed and the empirical models for each variable resulted as follows:

$$Y_1 = 89.23 - 13.79\ (pH) + 8.49\ (H_2O_2/Fe^{+2}\ ratio) + 5.61\ (Time) - 13.47(pH * H_2O_2/Fe^{+2}\ ratio) - 8.2\ (H_2O_2/Fe^{+2}\ ratio \times Time) \tag{2}$$

$$Y_2 = 428.45 - 90.96\ (pH) + 151.36\ (Time) - 85\ (pH \times H_2O_2/Fe^{+2}\ ratio) - 116.67\ (H_2O_2/Fe^{+2}\ ratio \times Time) \tag{3}$$

$$Y_3 = 0.35 - 0.07\ (pH) + 0.05\ (H_2O_2/Fe^{+2}\ ratio) - 0.069(pH \times H_2O_2/Fe^{+2}\ ratio) - 0.35(H_2O_2/Fe^{+2})^2 \tag{4}$$

As shown in Table 5 all obtained quadratic models were significant (F<0.007, prob>F). Adequate Precision (AP) of model for COD removal, BOD_5 and BOD_5/COD ratio variations were 14.3, 7.32 and 9.8, respectively. They were greater than 4 that indicated adequate signal and it is concluded that predicted data could be used to navigate the design space defined by the CCD (Mason *et al.*, 2003). As shown in Table 5 the lake of fit test for COD, BOD_5 and BOD_5/COD variations were 1.68, 2.1 and 0.59, respectively, therefore it is founded that F-test insignificant, implying a significant model correlation between variables and COD, BOD_5 and BOD_5/COD variations as process responses Adequacy of model could be assessed by diagnostic plot such as normal probability plots of Studentised of residual and predicted versus actual values. Figure 1 shows actual and predicted
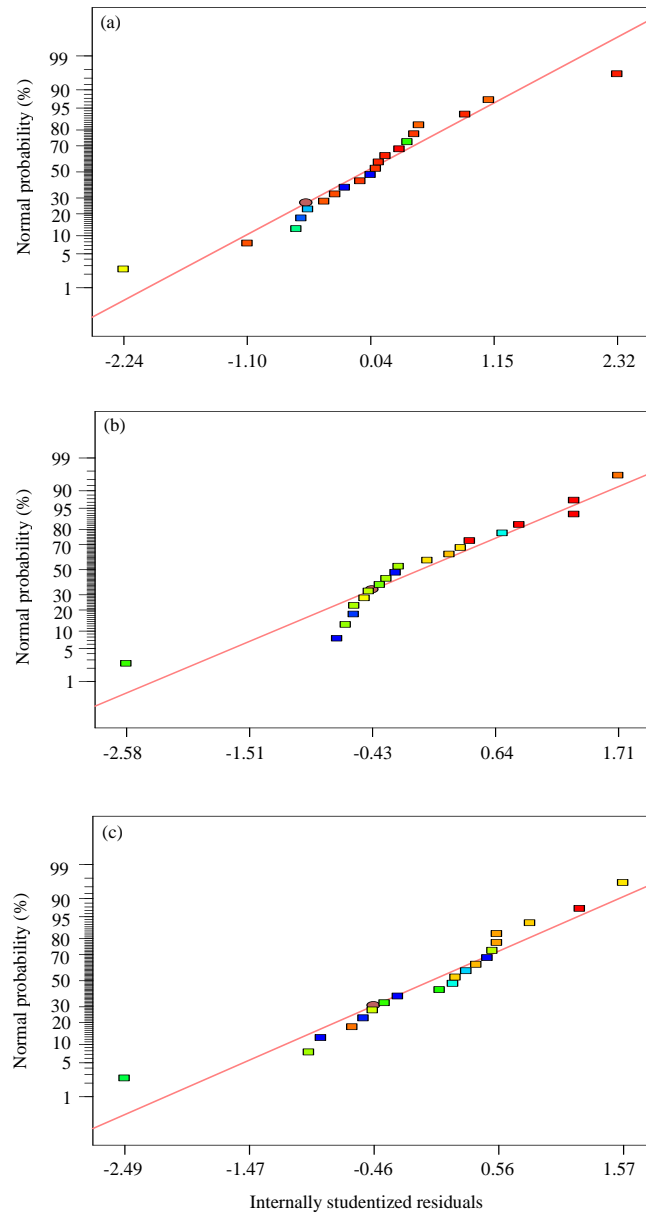
Fig. 2(a-c): Normal probability versus studentized residuals (a) COD, (b) BOD_5 and (c) BOD_5/COD

values for COD removal, BOD_5 and BOD_5/COD variations. Figure 2 shows normal probability versus studentized residues. As shown in Fig. 1 and 2, there are a strong correlation between real data and the ones obtained from quadratic model about COD removal, BOD_5 and BOD_5/COD variations and so adequacy of the model was confirmed for prediction of COD removal and BOD_5, BOD_5/COD variations. Furthermore outlier t-value was about 3.5± that was indicated approximation of model to response surface is acceptable.
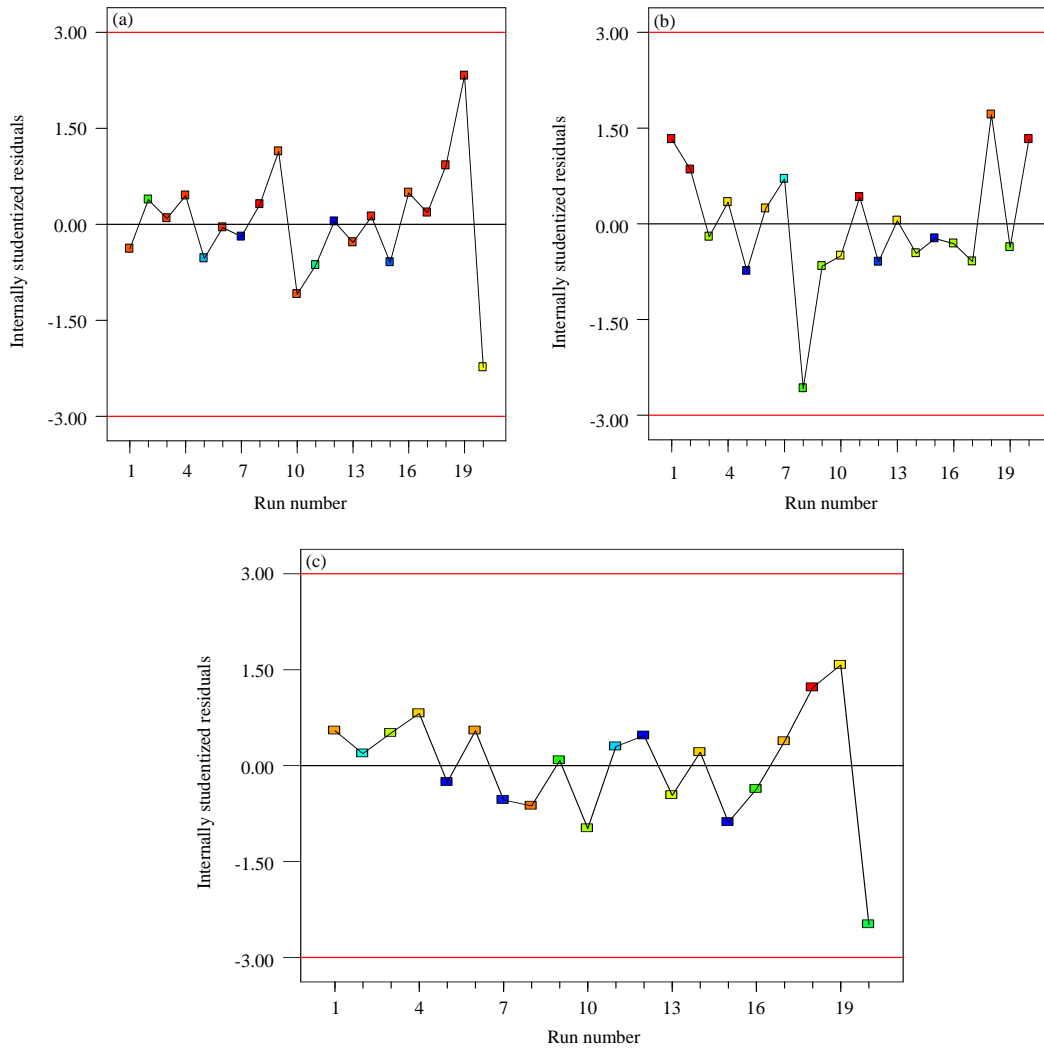
Fig. 3(a-c): Residuals versus Runs for (a) COD removal, (b) BOD_5 variation and (c) BOD_5/COD ratio

Figure 3 shows residuals versus runs for COD removal BOD_5 and BOD_5/COD variations. These plots can be used to study independence of residuals. If there were sinusoidal variations therefore, data independence would be acceptable (Amr *et al.*, 2013; Mason *et al.*, 2003). As shown in Fig. 3, there are no evidences for rejection of data independence hypothesis and this is concluded that selected model is suitable for data analysis.

Optimization of operating conditions: In this study factors including the pH, H_2O_2/Fe^{2+} and oxidation time were selected in range and responses including COD removal, BOD_5 removal and BOD_5/COD ratio were selected as maximize. Results from numerical optimization showed that in pH = 3.3, H_2O_2/Fe^{2+} = 15.82 and oxidation time of 130 min, COD removal, BOD_5 and BOD_5/COD ratio variation were 93.1, 0.56 and 0.49%, respectively. In this condition desirability was 100% (Fig. 4). These results about pH were consistent with those of (Yoo *et al.*, 2001) but about H_2O_2/Fe^{2++}, results were not adapted to results of them (Yoo *et al.*, 2001).
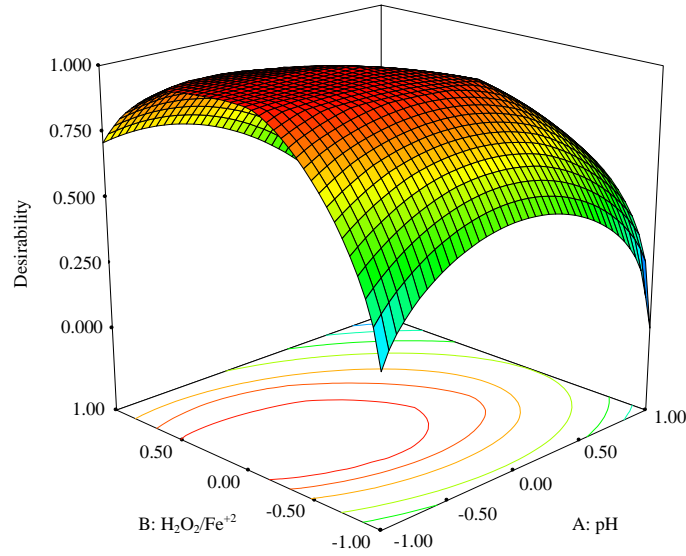
Fig. 4: Optimal conditions for COD removal, BOD_5 and BOD_5/COD variations

Table 6: Verification experiments at optimal conditions

| Parameters | Responses | | |
	COD removal (%)	BOD_5 variation (%)	BOD_5/COD ratio
Experimental value	92.1	572.2	0.481
Model response	93.1	568.0	0.49
Error	1	4.2	0.009
Standard deviation	±0.56	±1.2	±0.001

Five excess tests were performed at the optimum point to confirm adequacy and validity of optimization procedure. The results of these tests are given in Table 6. As shown in Table 6 results from experiments will agree to results from model. This agreement confirms accuracy and approach of model.

Response surface of quadratic models are given in Fig. 5-9. To determine effect of experimental parameters on process response, in optimal condition one parameter was selected at midrange and variation of the tow other parameters was evaluated. Results of response surface of quadratic model are given in Fig. 5.

Figure 5 shows contour plot and 3D plot of COD removal as a function of H_2O_2/Fe^{2+} ratio and pH at the oxidation time of 90 min it can be seen that pH significantly influenced the COD removal and the more pH from optimal point (3-3.5) the less COD removal achieved ($p<0.05$). This supports results reported in many previous studies which supported by Zhang *et al.* (2012), Ghafari *et al.* (2009) and Farrokhi *et al.* (2003).

At the pH below optimum conditions COD was not reduced significantly by Fenton reagent because H_2O_2 was not decomposed by ferrous ion at the pH below optimal and so there would be no H_2O_2 decomposition, no hydroxyl radical generation. This fact proved by constant oxygen level (DO = 0.61 at the initial of reaction and DO = 0.73 at the end of reaction). Also hydrogen ions could be played a scavenging role for hydroxyl radical according to the following reaction (Barbusinski *et al.*, 2006):
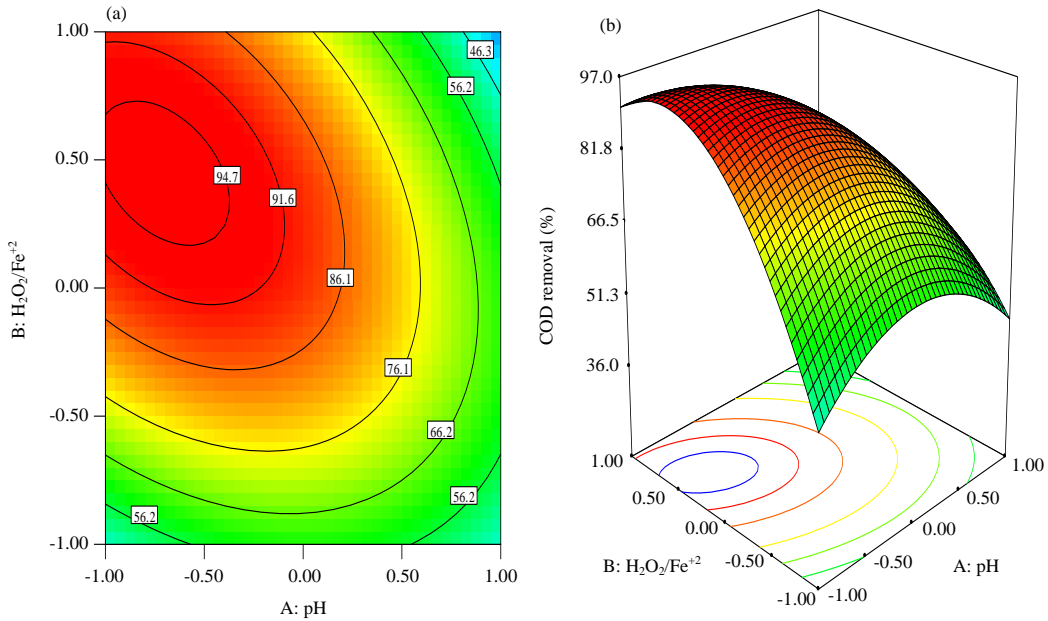
$$OH^{\bullet} + H^+ + e \rightarrow H_2O$$
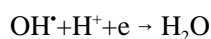
Fig. 5(a-b): (a) COD removal as a function of H_2O_2/Fe^{2+} ratio and (b) Counter plot and 3D plot of ph at the oxidation time of 90 min
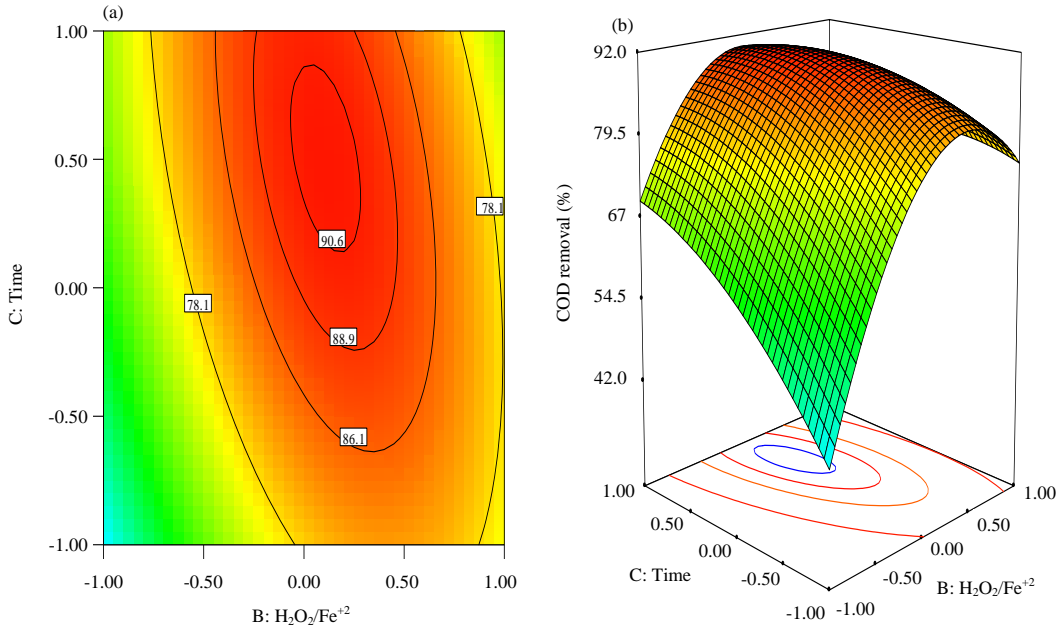

Fig. 6(a-b): Contour plot and 3D plot of (a) Oxidation time at the pH = 3.5 and (b) COD removal as a function of H_2O_2/Fe^{2+} ratio

When the pH reaches to above optimal the COD removal significantly decrease that it can be due to decrease dissolved fraction of iron, resulting relatively slow reaction between Fe^{2+} and H_2O_2. Furthermore the oxidation potential of hydroxyl radical will be decrease with increasing pH. This was consistent with other researchers report that Fenton oxidation had high removal efficiency at the pH = 3-3.5 (Farrokhi *et al.*, 2003; Ghafari *et al.*, 2009; Singh and Tang, 2013).
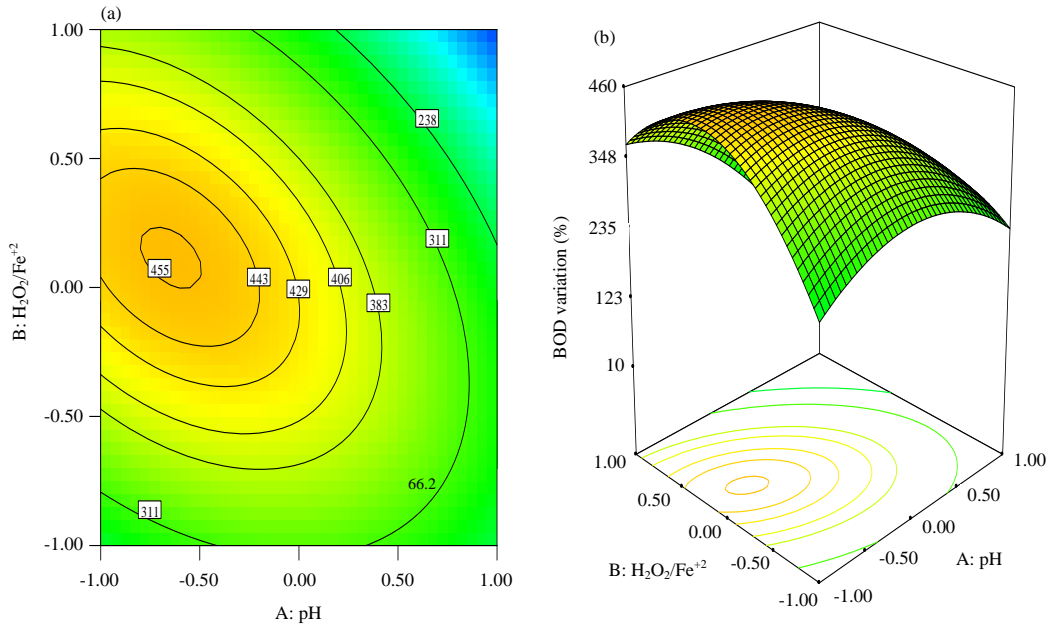
Fig. 7(a-b): (a) BOD$_5$ variation as a function of H$_2$O$_2$/Fe^{2+} and (b) pH at the oxidation time of 90 min
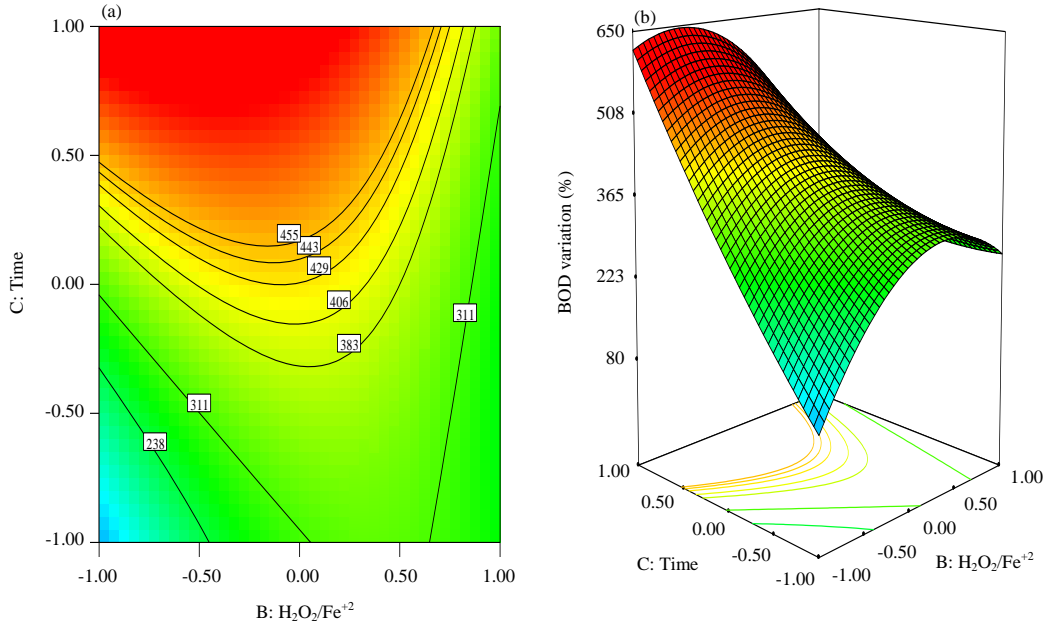

Fig. 8(a-b): (a) BOD$_5$ variation as a function of H$_2$O$_2$/Fe^{2+} and (b) Oxidation time at the pH = 3.5

As shown in Fig. 5, H$_2$O$_2$/Fe^{2+} ratio had similar effect on COD removal. At the optimal condition of H$_2$O$_2$/Fe^{2+} = 17.5, COD removal was 95% and above this ratio COD removal was decreased significantly. There is a transparent optimal zone in plot. This phenomenon could be explained by scavenging effect that occur in the presence of excess reagent (Amiri and Sabour, 2014). As shown in this plot the interactive effect of pH and H$_2$O$_2$/Fe^{2+} ratio is significant for COD removal. This result was consistent with previous studies that have indicated H$_2$O$_2$/Fe^{2+} ratio has an important role in Fenton oxidation efficiency (Lak *et al.*, 2012).
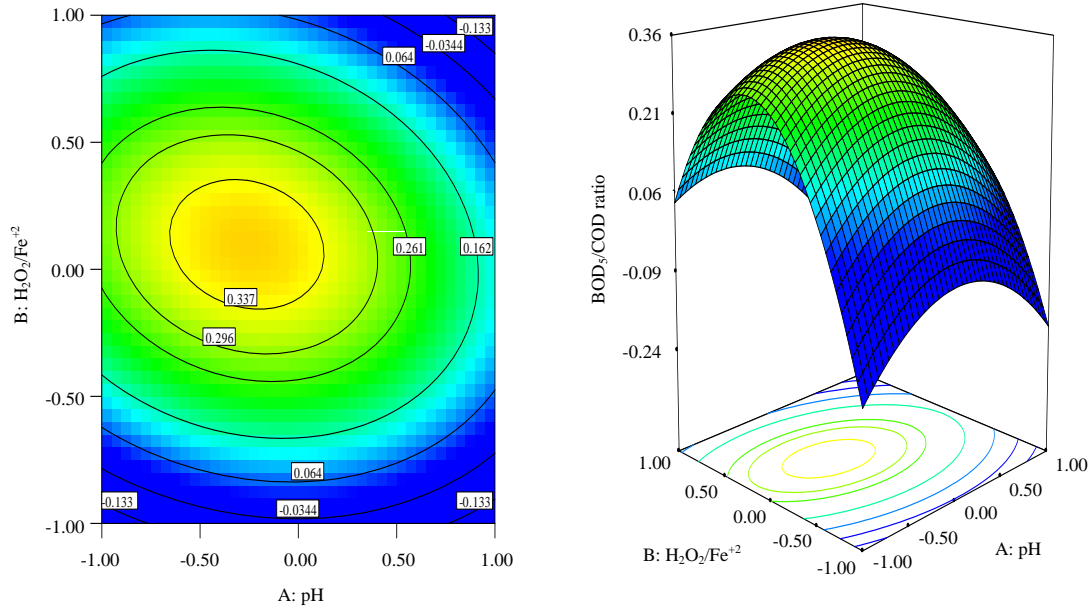
Fig. 9: BOD$_5$/COD variation as a function of H$_2$O$_2$/Fe^{2+} and pH at the oxidation time of 90 min

It may be observed that H$_2$O$_2$ doses significantly influenced the degradation of COD and the maximum COD removal was obtained in the molar ratio of H$_2$O$_2$/Fe^{2+} of 17.5. Optimal molar ratio of H$_2$O$_2$/Fe^{2+} of 17.5 was not adapted to results of Yang Deng study which was 3 (Deng, 2007). It can be observed that COD removal efficiency dropped when H$_2$O$_2$/Fe^{2+} ratio increase from 17.5 to above. This is due to the scavenging effects of peroxide and Fe^{2+} on hydroxyl radicals according to the below reactions, respectively:

$$H_2O_2+OH^{\bullet} \rightarrow H_2O+HO_2\bullet$$

$$OH^{\bullet}+Fe^{2+} \rightarrow Fe^{3+}+OH^{-}$$
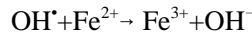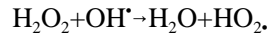
Interactive effects of oxidation time and H$_2$O$_2$/Fe^{2+} ratio at the constant pH of 3.5 are given in Fig. 6. it can be seen that COD removal will increase until H$_2$O$_2$/Fe^{2+} reached to 17.5 and oxidation time reached to 120 min in optimal condition COD removal efficiency was 92%. With attention to Fig. 6 after optimal zone there is a revers relationship between COD removal and H$_2$O$_2$/Fe^{2+} ratio and oxidation time. There is transparent lump in plot that shows interactive effect of independent variables (oxidation time and H$_2$O$_2$/Fe^{2+}) is significant. All p-values are given in Table 3.

Figure 7 indicates BOD$_5$ variation as a function of H$_2$O$_2$/Fe^{2+} and pH at the oxidation time of 90 min as shown in Fig. 7, the optimum condition for BOD$_5$ variation was pH = 3-3.5 and H$_2$O$_2$/Fe^{2+} = 17.5 as BOD$_5$ concentration was maximized. It can be seen clearly that interactive effect of pH and H$_2$O$_2$/Fe^{2+} on BOD$_5$ variation is significant. All P values are given in Table 3.

As shown in Fig. 8 BOD$_5$ will increase when oxidation time increase to 90 min, after this oxidation time BOD$_5$ will decrease with increasing the time.

The study on biodegradability enhancement of mature leachate was the main objective of this research, therefore, the changes of BOD$_5$/COD ratio as biodegradability indicator was evaluated in the Fenton oxidation process in the optimal H$_2$O$_2$/Fe^{2+} molar ratio of 17 and different oxidation
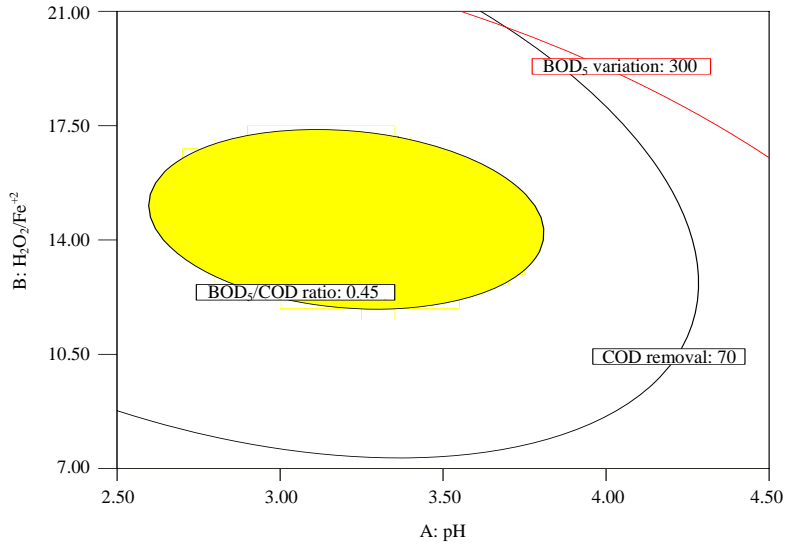
Fig. 10: Design expert overlay plot for optimal region using fenton reagent

time. As shown in Fig. 6, BOD_5/COD ratio increased with the time and the best BOD_5/COD ratio of 0.45 is achieved at the time of oxidation of 130 min. In comparison to the results of Derco *et al.* (2001), it is observed that Fenton oxidation is more efficient than ozonation for biodegradability enhancement of landfill leachate.

Derco results indicated that BOD_5/COD ratio increased from zero up to a maximum value of 0.21 using ozonation (Derco *et al.*, 2001). The BOD_5/COD ratio and COD removal efficiency are reached to above 0.35 and 80%, respectively that these observations are consistent with the shrawan study (Singh and Tang, 2013).

More biodegradability enhancement may be achieved at the longer oxidation time and the higher concentration of oxidation reagent (more than H_2O_2/COD ratio of 2.12), but it should be considered that it will be decrease the organic availability of leachate for the next biological treatment step and the cost of treatment will be strongly increased.

Figure 9 indicates 3D plot and contour plot of BOD_5/COD ratio variation as a function of pH and H_2O_2/Fe^{2+} ratio at the oxidation time of 90 min. It can be seen BOD_5/COD ratio will be increased when pH reached to 3.6, after this point BOD_5/COD ratio will be decreased. The similar influence was observed about H_2O_2/Fe^{2+} ratio, the maximal BOD_5/COD ratio was achieved at the H_2O_2/Fe^{2+} ratio of 17.5 and after this, it was decreased. There is a transparent zone about BOD_5/COD variation in these plots that show interactive influences of pH and H_2O_2/Fe^{2+} ratio on response surface are significant. Overlying the super imposing contour plots of response surfaces can be used to find optimum condition for all parameter (Montgomery, 2009). Graphical optimization shows the possible value of response levels in operative region as zone of fitness with optimization criteria as darker. Approximated selective response for each parameter as the minimum removable values that have overlying zone with other response was selected 70, 0.30 and 0.45% for COD removal and BOD_5 and BOD_5/COD ratio variation, respectively. These zones are near to points that have maximum values of removal efficiency and variations, therefore, a small zone will be selected as optimal zone.

Darker zone of Fig. 10 shows the optimum condition of Fenton oxidation for biodegradability enhancement of leachate. In this optimal condition it can be seen that oxidation time is 130 min,

pH = 3-3.5 and H_2O_2/Fe^{2++} ratio = 14-17. This is complies with the results of other study that report oxidation time of 120 and pH = 3.5 (Singh and Tang, 2013).

CONCLUSION

From this study it was concluded that mature landfill leachate biodegradability can be improved by Fenton oxidation process. In the optimal condition of Fenton oxidation as: H_2O_2/Fe^{2+} = 14-17, pH = 3-3.5 and oxidation time = 130 min, the BOD_5/COD ratio increased to 90 time greater than initial ratio (0.005-0.45).

Results from experiments will agree to results from model. This agreement confirms accuracy and approach of obtained model, therefore, it was concluded that response surface methodology can be used to optimize Fenton oxidation process for leachate treatment.

ACKNOWLEDGMENT

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