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ORIGINAL RESEARCH PAPER

Polluting potential of post-Fenton products in landfill leachate treatment

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ABSTRACT: Fenton process, as one of the most conventional advanced oxidation processes, is widely used in the treatment of specific wastewaters, especially landfill leachate. In current study, the main target was to evaluate some neglected aspects of Fenton process in operational applications. Thus, three novel responses were introduced.Mass removal efficiencyevaluates overall recalcitrant destruction by establishing organics mass balance pre- and post-Fenton treatment. This differentiates itfrom conventional chemical oxygen demand removal, since mass removal efficiency basically considers the whole mixture and not only the supernatant. The mass content ratio response provides a measure to evaluate the remaining organics in the sludge. Therefore, a borderline mode considering these limitations leads to best feasible field operations. It was found that mass content ratiofor effluent reacted conversely to the sludge in response to coagulation. By increasing the coagulant dosage, coagulation improved and the sludge ratio increased in result. For the mass removal efficiency response, it seemed that appropriate balance of the oxidation/coagulation had considerable role through Fe^{2+} dosage and $[H_2O_2]/[Fe^{2+}]$ ratio. Finally, by including further conventional parameters such as sludge quantity, the best operational conditions (X_1 = 5.7, X_2 = 16, X_3 = 207 mM) were optimized by response surface methodology to 27.4% and 14.4% for sludge and effluent mass content ratio, respectively, and 58.1% for mass removal efficiency.The results were in good agreement with determination coefficient (R^2) of 0.94–0.97, prediction R^2 of 0.80–0.93 and coefficient of variation less than 10.

KEYWORDS: *Feasibility assessment; Coefficient of variation (CV);Fenton oxidation; Mass removal efficiency (MRE);Response surface methodology (RSM); Sludge generation.*

INTRODUCTION

Leachate production is still the main environmental concern in landfilling of solid waste.Now, it is well-proved fact that even small amount of leachate infiltration into groundwater or surface water can pollute a large volume of water resources. Leachate can induce different environmental impacts such as severe contamination of surface and groundwater, significant variations of soil properties, biodiversity disorder, and genotoxic disturbances (De *et al.,* 2016; Emenike *et al.*, 2012). To reduce such risks and due to recalcitrant nature of the leachate, a train of treatment methods is usually applied before any leachate discharge to the environment (Kamaruddin *et al.,* 2014; Wiszniowski *et al.*, 2006). Among the classical combination of biological/chemical methods, application of advanced oxidation processes (AOPs) as pre- or post-biological treatments is proved to be efficient (Van Aken *et al.*, 2011; Wang *et al.*, 2003).

Fenton, generally as the most cost-effective and most common used oxidation process, consists of H_2O_2 as a oxidant and $FeSO_4$ as catalyst. Recently, some comprehensive studies have reviewed the applications of Fenton and Fenton-related processes as a part of landfill leachate treatment (Bashir *et al.*,

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2012; Deng and Englehardt, 2006; Nidheesh and Gandhimathi, 2012; Pouran *et al.*, 2015; Umar *et al.*, 2010). The mechanism of Fenton process including generation of reactive hydroxyl radicals ($OH^{\bullet}$), oxidation of recalcitrant substances, and formation of stable ferric hydroxo complexes is found in detail in literature (Ciotti *et al.*, 2009; Ghatak, 2013; Neyens and Baeyens, 2003; Pignatello *et al.*, 2006). However, the net reaction occurring in Fenton is shown in Eq. 1.

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \quad (1)$$

Compared to other AOPs, Fenton process has some advantages including high efficiency in recalcitrant removal, lower costs and simplicity in operation, non-toxicity of reagents, and no specific energy consumption. However, the excessive generated sludge is the main problem encountered (Benatti *et al.*, 2006; Cañizares *et al.*, 2009; Kilic *et al.*, 2014). The variable factors influencing Fenton efficiency (though not with equal importance) include reaction pH, coagulation pH, dosages and mole ratio of Fenton reagents, initial concentration of target pollutant, reaction time and temperature.

In current study, the response surface methodology (RSM) was used as a statistical method for modeling the behavior of introduced responses. In the traditional optimization approach, the effect of a variable is tested while the other variables are kept constant. Then, by repeating and narrowing the range of each variable, the optimal conditions are achieved. As a result, the variables interactions are neglected and simultaneous optimizations is difficult if even possible. To avoid such drawbacks, RSM is an useful method for design, derivation of multivariate regression models, multi-response optimizations with minimum experimental tests (Aravind *et al.,* 2016; Myers *et al.*, 2016). Though some studies have recently pointed to the Fenton and RSM applicationsin landfill leachate treatment(Ghanbarzadeh Lak *et al.*, 2012; Li *et al.*, 2010; Zhang *et al.*, 2009), all the responses were assigned to the conventional purposes (i.e. COD, color and turbidity removals). Thus, the evaluation of post-treatment remains and Fenton by-products is just limited to the quantity of generated sludge (Amiri and Sabour, 2014; Wu *et al.*, 2010b). Therefore, the pollution loading remained in the sludge and the overall mass reduction of organics (in the post-treatment supernatant/sludge as a whole) are not presented elsewhere. Both are potentially qualitative targets that are applicable for analysis of Fenton in aforementioned field concerns respect to the undesirable remains and its management. From an operational point of view, due to handling difficulties, the concentration of Fenton by-products in the sludge is not necessarily the best feasible mode. In this study, the performance of Fenton treatment was evaluated to predict the pollution remained in the form of sludge. In addition, by establishing a mass balance of organics in pre- and post-treatment samples, the state of organics removal from supernatant and possible accumulation in the sludge was investigated.

In all cases, RSM was used for the data analysis and final optimizations. The considered variables were pH, $[H_2O_2]$ to $[Fe^{2+}]$ ratio and $[Fe^{2+}]$ dosage. Therefore, the present study aims; 1) to determine the organic content of the final sludge and effluent, where the mass content ratio (MCR) of the final to initial samples were considered as the response with MCR_S and MCR_E for the sludge and effluent, respectively, 2) to estimate the operational success in the form of the mass removal efficiency (MRE) based on the total target mass present in the post- and pre-treatment samples, 3) to derive the quadratic regression models for each response and then to depict the three dimensional response surfaces and find the optimum conditions, and 4) to optimize these introduced responses in addition to the three additional responses based on the overlay plot. Thus, in the last step, six responses including COD removal, sludge quantity, sludge/effluent organic content, and organic mass removal were optimized simultaneously and their joint optimum area was determined. The study experiments was carried out in laboratory of K.N.Toosi University of Technology in Iran in 2015.

MATERIALS AND METHODS

The leachate samples were collected from the leachate ponds of Aradkooh Landfill site in Tehran, Iran. The leachate was sampled from 3 different points and were transferred in 20 L containers and preserved at 4 ˚C in accordance with standard methods. The characteristics of leachate are presented in Table 1.

Table 1: Sampled raw leachate characteristics

Parameter (unit)	Range	Mean
pH	7.05 - 7.24	7.17
COD (mg/L)	11,230 - 11,290	11,250
BOD_5 (mg/L)	2,780 - 2,860	2,810
Turbidity (FAU)	122 - 125	124

All chemicals were obtained from Merck Company, Germany. The experiments were conducted in one L. glass beakers (reactors) in atmospheric pressure and ambient temperature (25 ± 2 ˚C). At first, 400 ml of leachate sample was added to the reactor and the mixing started after initial pH adjustment. The pH was controlled by Martini pH-meter and addition of 1 M sulfuric acid and 10 M sodium hydroxide solution throughout each experiment.

Based on the previous study (Amiri and Sabour, 2014), the mixing was carried out by Jar-test device adjusted to 175 and 30 rpm for rapid and slow mixing, respectively. The rapid mixing stage started by addition of designed amount of reagents: first, the powdered ferrous sulfate ($FeSO_4.7H_2O$) and then hydrogen peroxide (H_2O_2, 30% w/w). After 30 min of reaction time, pH was first adjusted to neutral value of 7 and then to coagulation pH of 8. Then, the mixture was mixed slowly for 20 min.After the flocculation stage, 100 ml of mixture was transferred to graduated glass cylinder for final measurement. Then, the samples were left aside for sedimentation and the settled sludge volume was recorded. Finally, two samples were taken from two phase of the supernatant and the sludge. The COD was analyzed by Lovibond test vials with Lovibond spectrophotometer.

In this study, the design of experiments and data analysis were performed by central composite design (CCD) coupled with RSM. In Table 2 the variables coded values in the experiments are presented. The performance of Fenton process was evaluated in terms of the proposed responses of MCR_S, MCR_E and MRE calculated through the Eqs. 2 and 3.

$$\text{Mass content ratio (MCR)} = \frac{\text{remaining organic mass in sludge or effluent (gCOD)}}{\text{influent organic mass (gCOD)}}\% \quad (2)$$

$$\text{Mass removal efficiency (MRE)} = \frac{\text{total organics mass in sludge and effluent (gCOD)}}{\text{total organics mass in influent (gCOD)}}\% \quad (3)$$

The CCD consists of three parts: i) 2^k runs (in upper and lower levels), ii) 2 × k axial runs at the extremepoints of range and iii) 4 replicates at the center points. Here, k equals 3 as the number of variables. Therefore, 18 experiments were conducted in the experimental range. Each response was fitted to a mathematical model capable in prediction of the responses according to Eq. 4.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_i \sum_j \beta_{ij} X_i X_j \quad (4)$$

Where Y is the response, X is variable i in coded form,β_0 is the intercept constant, and β_{ij} is the interaction between factors i and j and β_i and β_{ii} are the first-order and second-order coefficients, respectively.

The analysis of variance (ANOVA) were used in analyzing mathematical models.The ANOVA conducted by Minitab Software and the three-dimensional response plots were prepared by a self-programmed MATLAB Software. The models fitness was evaluated by coefficient of determination in case of fitting and prediction. The significance of included terms was measured by F-test, and the final combinations of variables were selected based on P-value.

RESULTS AND DISCUSSION

Fitting mathematical models and statistical analysis

The experimental results including variables (X) and responses (Y) are showed in Table 3. It was expected that optimum conditions fall within the selected ranges of the variables: 2.3 to 5.7 for pH, 5 to 19 for $[H_2O_2]/[Fe^{2+}]$ mole ratio and 80 to 220 mM for $[Fe^{2+}]$. The considered responses were MCR_S, MCR_E and MRE as defined previously.To achieve the best mathematical models in terms of significant variables, the ANOVA was presented for responses. The terms found statistically significant (with P-value < 0.05 for Y_1– Y_2 and P-value < 0.15 for Y_3) were finally included in the models. The new ANOVA results of the reduced

Table 2: Designed values of variables in designed experiments.

Experimental variable (unit)	Symbol	Coded values				
		–1.73	–1	0	+1	+1.73
Initial pH	X_1	2.27	3	4	5	5.73
$[H_2O_2]/[Fe^{2+}]$ mole ratio	X_2	5.07	8	12	16	18.93
$[Fe^{2+}]$ (mM)	X_3	80.72	110	150	190	219.28

Table 3: The results of responses and design values.

Number	Variables						Responses		
	X_1		X_2		X_3		MCR_S	MCR_E	MRE
	Coded	Value	Coded	Value	Coded	Value	gCOD/gCOD		g/L
1	+1	5	+1	16	+1	190	29.03	17.14	53.83
2	–1	3	+1	16	+1	190	32.59	11.86	55.55
3	+1	5	–1	8	+1	190	42.54	18.96	38.50
4	–1	3	–1	8	+1	190	51.92	17.45	30.62
5	+1	5	+1	16	–1	110	16.37	47.60	36.04
6	–1	3	+1	16	–1	110	30.64	23.91	45.45
7	+1	5	–1	8	–1	110	30.20	45.43	24.37
8	–1	3	–1	8	–1	110	43.25	30.90	25.85
9	+1.73	5.73	0	12	0	150	22.86	22.84	54.30
10	–1.73	2.27	0	12	0	150	45.04	15.59	39.37
11	0	4	+1.73	18.93	0	150	34.05	17.16	48.80
12	0	4	–1.73	5.07	0	150	53.36	23.29	23.36
13	0	4	0	12	+1.73	219.28	34.47	18.66	46.88
14	0	4	0	12	–1.73	80.72	17.86	56.64	25.51
15	0	4	0	12	0	150	36.85	18.02	45.13
16	0	4	0	12	0	150	37.76	18.53	43.70
17	0	4	0	12	0	150	34.55	18.52	46.93
18	0	4	0	12	0	150	35.58	19.04	45.37

models are shown in Table 4. Consequently, the statistically approved models are presented in Table 5 including both variables and their interactions. The regression models were proved to be significant and adequate.

Referring to Table 5, there is a significant fitness between proposed results and experimental data with high R^2 values (0.9425 to 0.9734) and also adjusted R^2 values (0.9023 to 0.9589). In better words,R^2 shows that how much of the variability of observed values is explained by the models. The predictive capability of the models was evaluated through prediction $R^2$and F-ratio. The more detailed concept of these indicators is presented elsewhere (Myers *et al.*, 2016). The prediction R^2 values vary from 0.7965 to 0.9206 and indicate that the models are strong in prediction of new experiments.

The ratio of regression F-value to the critical value read from the F-table is defined as F-ratio. For a model to be an appropriate predictor, this ratio should be 4 or more. Again, the ranges of 11.56 to 24.24 for F-ratios emphasize the acceptable prediction capability of the models.Another measure is the coefficient of variation (CV) that shows the variability relative to the mean. A model with smaller CV has predicted values closer to actual ones. Therefore, the low values of CV (6–11%) indicate the relative closeness of predictions to actual values. The plot of the predicted and actual values for the responses implies adequate agreement between observed data and those obtained from the models (Fig. 1).

Table 4: The results of ANOVA

MCR_S	SS	MS	F	P	t
Regression	1687.61	281.27	67.08	<0.001	
X_1	442.29	442.29	105.48	<0.001	-10.27
X_2	614.21	614.21	146.48	<0.001	-12.10
X_3	296.14	296.14	70.62	<0.001	8.40
X_2^2	162.72	104.20	24.85	<0.001	4.99
X_3^2	146.38	146.38	34.91	<0.001	-5.91
X_1X_3	25.87	25.87	6.17	0.030	2.48
Residual	46.12	4.19			
LoF	40.15	5.02	2.52	0.241	
PE	5.98	1.99			
Total	1733.74				
MCR_E	SS	MS	F	P	t
Regression	2572.48	514.5	75.28	<0.001	
X_1	236.78	236.78	34.65	<0.001	5.89
X_2	37.29	37.29	5.46	0.038	-2.34
X_3	1568.68	1568.68	229.53	<0.001	-15.15
X_3^2	606.21	606.21	88.7	<0.001	9.42
X_1X_3	123.52	123.52	18.07	0.001	-4.25
Residual	82.01	6.83			
LoF	81.49	9.05	51.88	0.004	
PE	0.52	0.17			
Total	2654.50				
MRE	SS	MS	F	P	t
Regression	1829.86	261.41	23.43	<0.001	
X_1	31.78	31.78	2.85	0.122	1.69
X_2	954.32	954.32	85.54	<0.001	9.25
X_3	501.65	501.65	44.97	<0.001	6.71
X_2^2	110.06	160.99	14.43	0.003	-3.80
X_3^2	157.28	157.28	14.1	0.004	-3.76
X_1X_2	38.43	38.43	3.45	0.093	-1.86
X_1X_3	36.33	36.33	3.26	0.101	1.81
Residual	111.56	11.16			
LoF	106.33	15.19	8.72	0.051	
PE	5.23	1.74			
Total	1941.42				

SS: sum of squares, MS: mean square, F: F-value, P: probability of error, t: t-value, LoF: lack of fit, PE: pure error.

Organic mass content ratio

Coagulation plays role in Fenton process through organics removal in form of the sludge.To imply the variables interactions and their influence on the response, the surface of X_1X_3 interaction was shown in Figs. 2. As it is evident in Fig. 2, the higher pH in combination with lower Fe^{2+} dosages led to MCR_S less than 20%. The clear curvatures of the 3-dimensional

Table 5: Statistical analysis of the models in terms of the coded factors

Response	Model	R^2	AdjR^2	Pre R^2	F-ratio	CV
MCR_S	$35.3 - 5.6X_1 - 6.6X_2 + 4.6X_3 + 2.7X_2^2 - 3.2X_3^2 + 1.8X_1X_3$	0.9734	0.9589	0.9187	21.68	6
MCR_E	$19.6 + 4.1X_1 - 1.6X_2 - 10.6X_3 + 6.3X_3^2 - 3.9X_1X_3$	0.9691	0.9562	0.9206	24.24	10
MRE	$45.7 + 1.5X_1 + 8.3X_2 + 6.0X_3 - 3.3X_2^2 - 3.3X_3^2 - 2.2X_1X_2 + 2.1X_1X_3$	0.9425	0.9023	0.7965	11.56	8

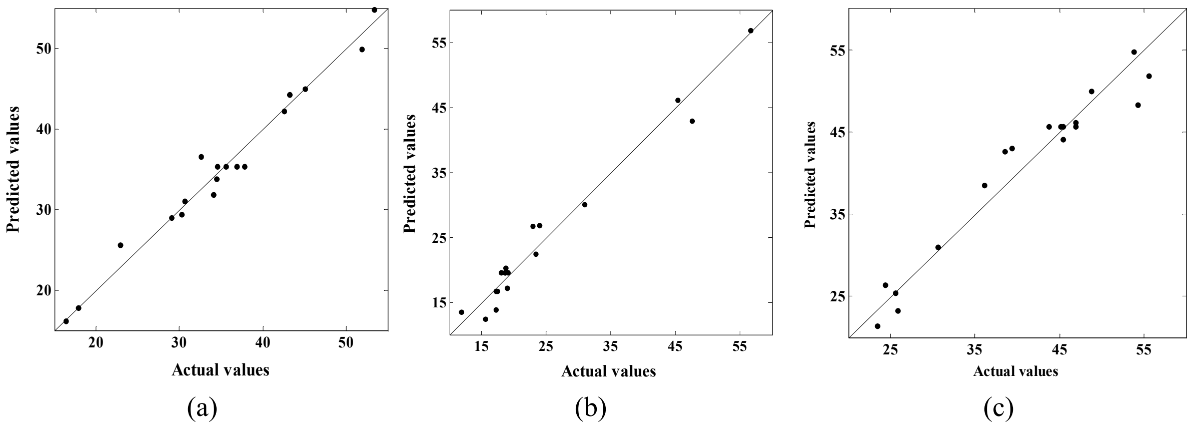

Fig. 1: Observed vs. modeled responses (a) MCR_S, (b) MCR_E, (c) MRE.

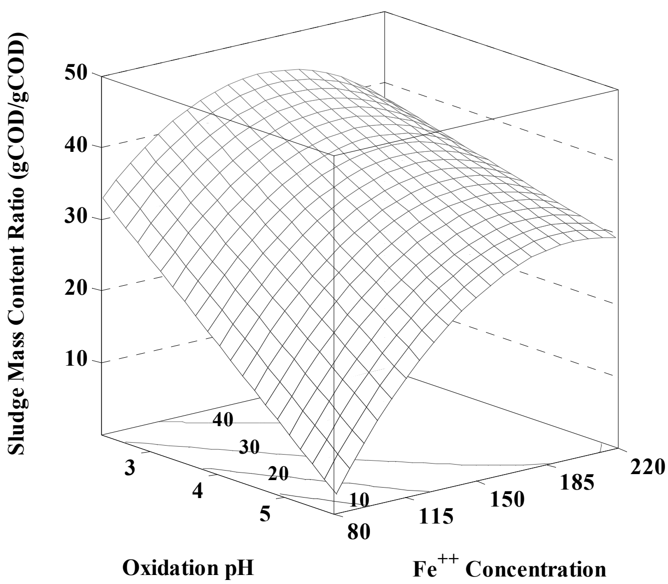

Fig. 2: MCR_S (Y_1). The response surface in terms of initial pH and Fe^{2+} dosage ($[H_2O_2]/[Fe^{2+}] = 12$)

Organic mass content ratio

Coagulation plays role in Fenton process through organics removal in form of the sludge.To imply the variables interactions and their influence on the response, the surface of X_1X_3 interaction was shown in Figs. 2. As it is evident in Fig. 2, the higher pH in combination with lower Fe^{2+} dosages led to MCR_S less than 20%. The clear curvatures of the 3-dimensional surface also confirms the significant interactions of the variables. This result could be due to the roles of the initial pH and $[H_2O_2]/[Fe^{2+}]$ ratio in oxidation that weaken the coagulation and subsequently the organics remained in the sludge. In addition, the lower coagulant dosage reduces the coagulation removal that causes less COD of the sludge.

This phenomenon is in accordance with previous studies in which the sludge COD was widely attributed to the coagulation contribution and emphasize the effect of coagulant dosage (Fe^{2+}) on the organics removal due to coagulation (Kang and Hwang, 2000; Wu *et al.,* 2010a; Wu *et al.,* 2010b). However, the remained organics (as COD) in the final sludge cannot be attributed just to the coagulation, but rather to the both of oxidation and coagulation roles. To discuss in more detail, though there is an obvious relation between coagulation and the sludge organic content, but limiting the latter to the former is not a precise approach.In the case of organics remained in the effluent, there are some useful reviews regarding COD removal of the leachate treatment by Fenton (Deng and Englehardt, 2006; Umar *et al.,* 2010). Though they are mainly focused on the overall COD removal in pre- and post-treatment, the relative mass removal of the organics compared to initial leachate sample was not presented elsewhere. Naturally, the MCR_S response is different from the MCR_E. While the former develops a concept to evaluate the sludge organic loading, the latter correlates the effluent mass to the influent organics mass. Same as the MCR_S, the coagulation plays a significant role in the MCR_E response.As mentioned before, the coagulation depends strongly on coagulant dosage. Thus, MCR_S and MCR_E react conversely to the coagulation. While the Fe dosage had positive effect on MCR_S it had negative effect on MCR_E, i.e. increasing the Fe dosage led to reduction of MCR_E.The response surface depicted in Fig.3 emphasizes the above concept of dominant coagulation role, in which the increasing of coagulant dosage has led to reduction of MCR_E. Though the minor contribution of oxidation was probably due to less significant role of $[H_2O_2]/[Fe^{2+}]$ mole ratio that is clearly shown in Fig.3.

In the separate optimization of responses, the values of less than 10% was obtained for MCR_S in the 5.7of pH, $[H_2O_2]/[Fe^{2+}]$ higher than 16 and $[Fe^{2+}]$ less than 110 mM. However, the priority was devoted to the

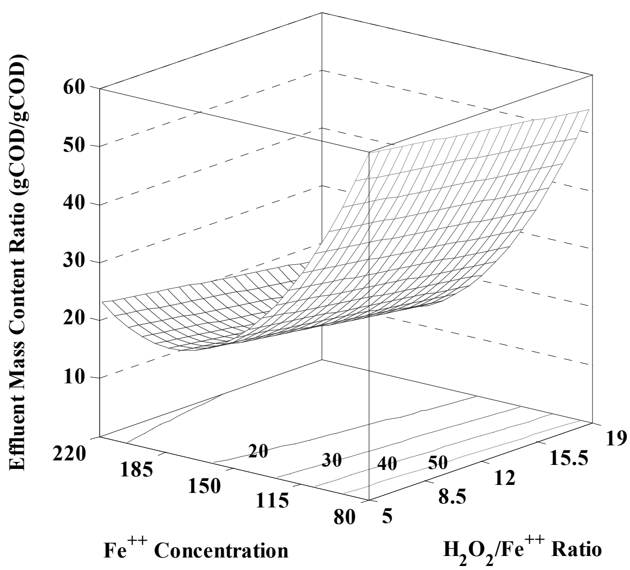

Fig. 3: MCR_E (Y_2). The response surface in terms of $[H_2O_2]/[Fe^{2+}]$ and Fe^{2+} dosage (pH = 4).

other considerations such as overall COD removal, sludge quantity and feasibility assessment. Thus, MCR_S was intended to be consistent with these more important responses. This urges the improvement of the oxidation (relative to coagulation) that leads to operational conditions with higher coagulant dosages. In the case of MCR_E optimization, the optimum conditions caused minimum MCR_E of 12.1% with initial pH 5.7, $[H_2O_2]/[Fe^{2+}]$ of 18.8 and Fe^{2+} dosage of 206 mM.

Overall mass removal efficiency

For the evaluation of the treatment, the previous studies are mostly focused on the organics removal in the supernatant compared to the initial sample (in terms of conventional COD removal). Thus, the success of Fenton process was mainly limited to the supernatant status, whereas the treatment as a whole is not mentioned elsewhere. Consequently, the sludge organic content on one hand, and the overall mass balance of organics (established pre- and post-Fenton) on the other are merged into a unique parameter, namely MRE. This response was introduced as percentage of organic content of supernatant plus sludge (in gCOD) per organic content of the leachate (in gCOD). In better words, the MRE reflects the Fenton actual potential in recalcitrant breakdown considering what remain after the treatment, not just the supernatant.The response surface shown in Fig. 4 confirms the expected peak of MRE within the considered range. This figure clearly depicts the variables interactions with a sudden increase due to the synergic effects occurred in higher levels of variables. This showed that appropriate balance in the oxidation/coagulation roles had led to distinguished peak in MRE response. Also, the curvature of the surface confirms the significant interaction of variables.

The highest value obtained in the optimization of the MRE response (Table 5) was 56.2% with initial 5.7 of pH, $[H_2O_2]/[Fe^{2+}]$ of 16.2 and Fe^{2+} dosage of 202 mM. In other words, Fenton treatment was success in destruction of 56% of the high molecular weight organics into smaller molecules either in the sludge or the effluent. However, it is interesting that two of the introduced responses were maximized in close optimum regions. This observation were consistent with the previous research (on the same originated leachate) in which the optimum COD removal and organics removal to sludge ratio (ORSR) were obtained in 5.7 of pH, $[H_2O_2]/[Fe^{2+}]$ of 17.7 and Fe^{2+}dosage of 195 mM. This shows that the achieved range in this study has close adjacency with other operational parameters studied previously. Thus, an overall optimization could be useful where all possible responses are present.

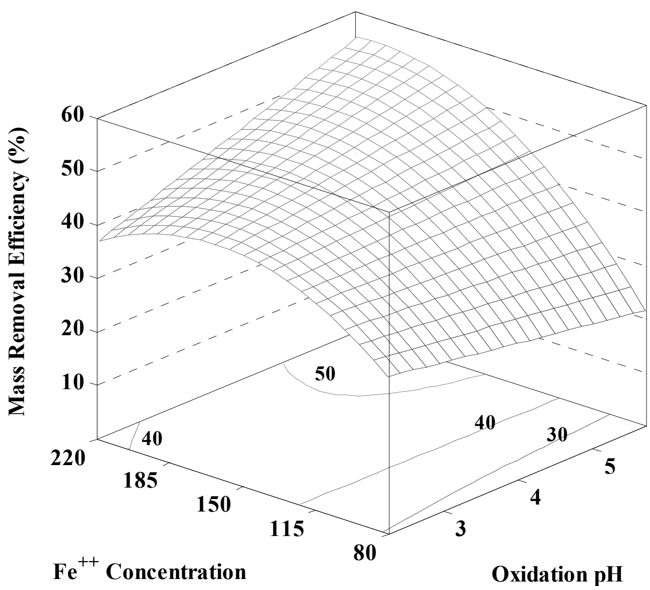

Fig. 4: MRE (Y_3). The response surface in terms of pH and Fe^{2+} dosage ($[H_2O_2]/[Fe^{2+}]$ = 12)

Table 6: Verification experiment in the joint simultaneous optimized conditions

Response	Limit	Observed value	Predicted value	Error (%)	Standard deviation (±%)
Y_1	< 27%	27.4	26.3	4.18	0.81
Y_2	< 13.5%	14.4	13.2	9.09	0.86
Y_3	> 56%	58.1	56.5	2.83	1.18
Y_4	> 70%	69.3	70.4	1.56	0.80
Y_5	< 2.5 (l/mole)	2.56	2.48	3.23	0.06
Y_6	> 15 (g/L)	14.7	15.1	2.65	0.28

Y_1: MCR_S, Y_2: MCR_E, Y_3: MRE, Y_4: COD removal, Y_5: SIR, Y_6: ORSR.

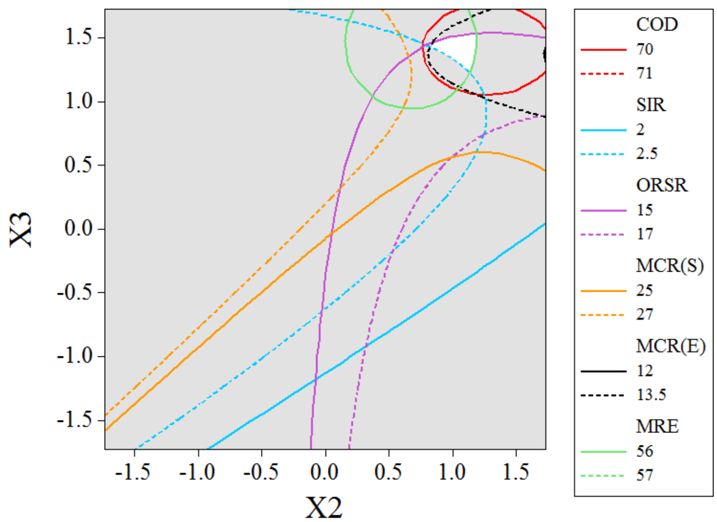

Fig. 5: The responses overlaying plot. The target areadisplayed in blank area and factors are in coded form (initial pH = 5.7)

Simultaneous optimization of possible responses

The main objective of a modeling process in the leachate treatment is to obtain an estimating structure in which the response behavior is predictable. Then, the optimization comes forward to provide the optimum conditions from the obtained data. When multiple responses are present, it is necessary to find a joint common range to reach the best possible results. Here, the overlaying plot proved to be a useful tool where all the responses are simultaneously met the reasonable limits in a single plot. Here, based on the limits defined in Table 6, the plot was depicted in Fig. 5 where the optimum area was distinguished in blank. To evaluate the practical aspects of the optimization, the three responses of the previous research (all with the same experimental procedure) were added to the responses introduced in this study. Hence, all the six defined responses, i.e. COD removal, sludge to iron ratio (SIR), ORSR, MCR_S, MCR_E, and MRE were included and optimized simultaneously. The values predicted by models were presented in Table 6.

To verify the quality of the models, an extra experiment was performed in the optimum area in Fig. 5 in 5.7 of pH, $[H_2O_2]/[Fe^{2+}]$ of 16 and Fe^{2+}dosage of 207 mM. The experimental results were compared with the predicted ones in Table 6. As can be seen, the models provide appropriate predictions with maximum value of 9.09% for errors and 1.18% for standard deviation. These results confirm the strong ability of the models in the prediction of new observations in the design range. In addition, the BOD_5/COD of effluent increased to 0.55, showing significant improvement in biodegradability of the effluent.Also,the effluent pH in the optimum conditions ranged in 7.5 to 8 that is a easy-to-handle value for post-Fenton adjustment.

CONCLUSION

Fenton oxidation process is among the most common methods in the treatment of recalcitrant wastewaters. In this field, most of the researches are limited to the experimental applications with conventional goals without considering operational aspects or feasibility assessment of field cases.For this purpose, three responses of MCR_S, MCR_E, and MRE were introduced for the Fenton treatment evaluation. The influences of initial pH, Fe^{2+} dosage and $[H_2O_2]/[Fe^{2+}]$ mole ratio were investigated using RSM to model the Fenton performance. For MCR_S (as a measure of organics remained in the sludge) it was observed that the more coagulation favored the higher MCR_S, whereas oxidation had the reverse effect. Thus Fe^{2+} dosage increased the MCR_S while $[H_2O_2]/[Fe^{2+}]$ ratio had reductive effect on the response. On the contrary, MCR_E reacted conversely to MCR_S.This meant that dominant coagulation swept organics from the supernatant and accumulated them in the sludge. In the MRE response, it seemed that appropriate balance of the oxidation/coagulation had considerable roles through $[Fe^{2+}]$ and $[H_2O_2]/[Fe^{2+}]$ mole ratio. In the simulatanousfinal optimization of the responses, the best conditions of pH 5.7, $[H_2O_2]/[Fe^{2+}]$ ratio 16 and $[Fe^{2+}]$ 207 mM led to 27.4%, 14.4%, and 58.1% for MCR_S, MCR_E and MRE responses, respectively, that were in good agreement with model predictions.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

ABBREVIATIONS

ANOVA	Analysis of variance
AOP	Advanced oxidation process
BOD	Biochemical oxygen demand (mg/L)
COD	Chemical oxygen demand (mg/L)
CV	Coefficient of variation (%)
F	F-value
k	Number of variables
LOF	Lack of fit
MCR	Mass content ratio (%)
MCR_E	Effluent mass content ratio (%)
MCR_S	Sludge mass content ratio (%)
MRE	Mass removal efficiency (%)
MS	Mean square
ORSR	Organics removal to sludge ratio (g/L)
P	Probability of error
PE	Pure error
PRESS	Predicted residual sum of squares
R^2	Coefficient of determination
$R^2_{adjusted}$	Adjusted coefficient of determination
$R^2_{prediction}$	Prediction coefficient of determination
RSM	Response surface methodology
SIR	Sludge to iron ratio (l/mole)
SS	Sum of squares
X or x	Coded value of variable
Y or y	Response

Greek letters

β_0	Intercept constant in response equation
β_i	First-order regression coefficient
β_{ii}	Second-order regression coefficient
β_{ij}	Interaction between factors i and j

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