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Wastewater treatment from shale gas operation by Fenton process: a statistical optimization

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ABSTRACT

In this study, the removal of chemical oxygen demand (COD), color and total phenol in the generated shale gas wastewater by Fenton process was investigated. As known, during shale rock extraction, a large volume of water is used. The fracturing fluid has different toxic chemicals and additives, and therefore, shale gas extraction may lead to adverse environmental impacts including deterioration of soil, water and air quality. The main purpose of this study was to investigate the mitigation of the adverse effects of wastewater produced during shale gas extraction. For this purpose, the central composite design and the response surface methodology were used to design and optimize the performance of the Fenton process parameters. Experimental data was analyzed by the analysis of variance identifying the mechanism of interaction between the process variables and the dependent variables. Laboratory studies and the results of optimized parameters denoted that the model prediction data overlap with the experimental study data, quite successfully. At the end of the study, high removal efficiencies were achieved under the optimum conditions for COD (68.20%), color (88.48%) and total phenol (92.65%) removal, by means of the Fenton processes.

Keywords: Wastewater; Shale gas extraction; Fenton oxidation; Optimization; Response surface methodology

1. Introduction

Apart from the physiological, safety and social needs, energy is one of the fundamental requirements for humans. This being the case, the distress of energy access brings along not only conflict and competition but also leads engineers to embark on new quests. In the last decade, global shale gas production is seen as an alternative potential energy. However, widespread concerns exist regarding possible environmental consequences of this development, especially impacts on water resources and generated wastewater.

Shale is an organic-rich and fine-grained sedimentary rock composed of mud and clay minerals [1]. Accumulation of sediments and their pressurized compaction constitute a thin layer of shale rock. Shale gas is a natural gas formed as a result of anaerobic degradation of the organic deposits and materials within shale formation [1]. Shale rock is impermeable which greatly inhibit gas migration and keep gas trapped within the rock [2].

1.1. Shale gas extraction

Shale gas extraction begins in Nagasaki 1945 by the detonation of atomic bombs in shale formations, which help to liberate natural gas successfully. As technology advanced, less dangerous extraction technologies were found, and gas exploitation became viable [3]. Seismic survey scans and images provided the discovery of prospective areas for highly productive shale gas reservoirs. Nowadays, advanced technologies, such as horizontal drilling, are applied in order to ensure maximum penetration in the rock and to achieve higher gas capacities. After drilling is completed, the process continues by applying hydraulic fracture that consists of the

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injection of a high volume of water in the horizontal well. This injection will ensure very high pressure exceeding rocks tensile and any other tectonic force leading to crack the rock and to form holes/fissures through the cement and the casing at different places in the well. Sand particles enter these holes and hold them open so shale gas will flow out the well [1].

High volumes of water (as high as 10 Km^3) is used during hydraulic fracturing. Water is usually mixed with different fracturing materials, such as proppants like quartz and ceramic which keep fractures open for a long time even after the pressure is released or biocides to inhibit any microbial activity reducing H_2S production risk which may contaminate extracted natural gas [1,2,4]. The addition of these fracturing materials generally would not exceed 1% (v/v). Depending on the rock structure, 10%–80% of hydraulic fracturing fluid may return to the surface, producing high volumes of wastewaters, which generates a major challenge, as it requires treatment before disposal or reuse [4].

1.2. Environmental risks

Due to the large volumes of water used during shale rock extraction and because of the toxic chemicals and additives found in the fracturing fluid, shale gas extraction may lead to undesired environmental effects, which may affect water and air quality, human health and plant life. Greenhouse gas emissions may also occur during shale rock fracturing process, which affects climate change [5]. In certain cases, due to the local geology, shale gas exploration may cause some low-intensity earthquakes [6]. Since environmental risks depend on the location, geology of the place and the duration of the process, a specific environmental assessment and regulation should be enforced accordingly [7].

1.3. Shale gas wastewater

During shale gas production, three different kinds of shale gas wastewater can be obtained: drilling muds, flowback and produced brine. Drilling muds generally used during drilling phase to lubricate and cool the drill. It is highly dense and clay-rich wastewater. However, the volume of drilling muds is relatively low compared with other types of wastewater. Wastewater, which quickly returns to surface during production, is known as flowback wastewater. It has a high TDS value, containing chemicals, hydrocarbons, metals, organic compounds and radionuclides [8]. The third wastewater type, named as produced brine, is the part of wastewater that takes longer time to return to the surface, after the well is started to operate. Therefore, produced brine tooks longer time in contact with shale formation. Therefore, TDS levels are extremely high, more than 100,000 mg/L with a higher concentration of chemicals and other additives [9].

1.4. Shale gas wastewater management

The shale gas wastewaters cannot be treated within municipal wastewater treatment facilities due to high levels of TDS [10]. Therefore, several methods are applied to manage shale gas wastewaters, such as industrial wastewater treatment plant discharge, disposal or underground injection, and reuse and recycling [11]. In particular, there are serious attempts in the aim to find profitable and useful treatment methods for impurities removal from flowback wastewaters in the USA [12–14]. Several objectives, such as disinfection, suspended particles and sand removal, dissolved gas removal, soluble organic removal, desalination, hardness removal and naturally occuring radioactive material removal, are mainly requested in the treatment of the flowback and produced water [15]. There are many treatment methods for all types of wastewater from gas production begining from the separate methods to the combined ones known as physical, chemical and biological methods [8,12].

Advanced treatment technologies can be successfully conducted for the treatment of shale gas wastewater. One of the most important advanced treatment methods is “the Fenton process” where iron and hydrogen peroxide are two major active chemicals determining operating cost and treatment efficiency [16]. During the Fenton reaction, hydrogen peroxide is catalyzed by ferrous ions to produce hydroxyl radicals (OH·), where the last is involved in the breakdown of organic matters in the wastewater [17]. Fenton treatment consists on the following stages: pH adjustment, oxidation reaction, neutralization, coagulation and solid–liquid separation [18]. The success of this process is affected by several parameters such as chemical dosages, strength of the wastewater and reaction pH [16].

In Fenton treatment, pH is an important parameter, and it controls the hydroxyl radicals production and the ferrous ions concentration in the solution [19]. An increase in the pH level causes the precipitation of iron ions (especially Fe^{3+}) leading to suppress the reformation of ferrous ions, showing that as pH increases, the generation of OH· decreases. Additionally, when the pH increases levels above than 5, hydrogen peroxide becomes unstable and decomposes into water and oxygen [20]. It was reported that there is a production of stable OH· with high oxidizing potential at pH values of 2–4 [21]. On the contrary, H_2O_2 is transformed to H_3O^{2+} instead of OH· by Fe^{2+} at pH values lower than 2. As a result, the reaction rate between H_2O_2 and Fe^{2+} declines to cause a deficiency in the removal efficiencies [20].

The purpose of this study is to investigate the treatment of shale gas wastewater by the Fenton process. The effects of operating parameters by the Fenton process on the chemical oxygen demand (COD), total phenol and color removal efficiencies were analyzed to determine the optimum operating conditions (i.e., H_2O_2/COD, H_2O_2/Fe^{+2} and initial pH). Optimizations of Fenton Process were carried out by the response surface methodology (RSM) approach using central composite design (CCD), which was used to develop a mathematical model to describe the effects and relationship of the studied parameters.

2. Materials and methods

2.1. Shale gas wastewater

The Southeast Anatolian Basin (southern Turkey) and the Thrace Basin (western Turkey) are two main shale basins in Turkey where effective gas and oil exploration is carried out by some international companies and by the Turkish National Petroleum Company. Furthermore, Turkey has two shale gas resources in the Sivas and Salt Lake basins. The exploitation of these two shale gas resources is really difficult due to the lack of reservoir data [22]. The total wet shale gas capacity is 23.6 trillion cubic feet in Turkey [23]. The samples used in the study were received from shale gas wastewater from the Southeast Anatolian Basin. For better and long-term preservation, collected samples were kept at 4°C before the experimental research. Characteristics of raw shale gas wastewater are given in Table 1.

2.2. Experimental setup and procedure

The schematic view of the experimental system is presented in Fig. 1. In the Fenton's oxidation process, $FeSO_4 \bullet 7H_2O$ was dissolved in pure water in order to prepare a stock solution of Fe^{2+} (10 g/L), and a H_2O_2 solution (35%) with a density of 1.13 kg/L was also used. 400 mL of wastewater was used for each experimental test. In the first step of Fenton's oxidation process, the pH of shale gas wastewater was adjusted to the desired value by the addition of sulfuric acid (6N) and sodium hydroxide (6N). The necessary amount of the $FeSO_4 \bullet 7H_2O$ was supplemented, and then the desired volume of H_2O_2 solutions was added initiating the Fenton reaction. After this step, rapid mixing is realized through a Jar Test Equipment at 200 rpm for 5 min. In each experimental run, the effluent sample was then gently stirred at 20 rpm for a reaction time of 90 min. For improved sludge settling rates, pH was adjusted to around 7.0 by adding NaOH solution, leading to the precipitation of residual Fe^{2+} ions. After pH adjustment, the sample was quietly settled for 60 min in a graduated settling column. After the settling process, about 200 mL of the supernatant was taken for further analysis such as COD, TOC and color analyses. Finally, for the elimination of the residual H_2O_2 from the supernatant to prevent any interference during COD measurement, the pH of supernatant samples was adjusted to 10 and mixed at 70°C for 10 min [24,25]. Only analytical grade chemicals were used during the study.

Table 1
Characteristics of raw shale gas wastewater

Parameter	Mean value	Standard deviation
COD (mg/L)	7,715	50
TSS (mg/L)	750	40
TKN (mg/L)	28.70	2.5
NH_3-N (mg/L)	23.50	1.8
TP (mg/L)	0.50	0.05
Chloride (mg/L)	435	22.2
Color (Pt-Co)	4140	35
Total phenol	14.10	1.3
Cadmium (mg/L)	<0.001	–
Chrome (mg/L)	0.136	0.002
Copper (mg/L)	0.21	0.03
Iron (mg/L)	14.60	0.13
Nickel (mg/L)	0.028	0.011
Lead (mg/L)	0.009	0.0013
Zinc (mg/L)	0.041	0.001
Silver (mg/L)	<0.001	–
Conductivity (mS/cm)	107.1	3.12
pH	7.20	0.05

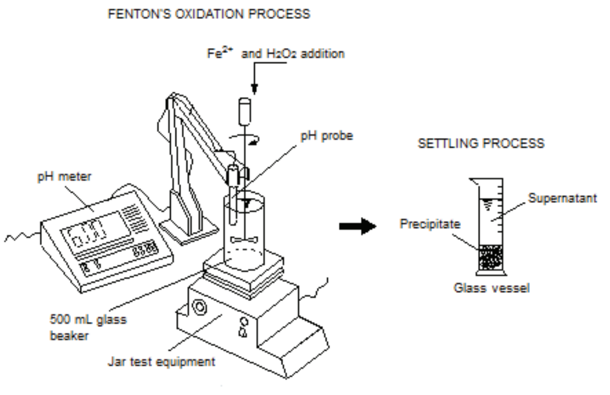

Fig. 1. A detailed schematic of the experimental setup.

2.3. Analytical methods

Open reflux titrimetric method was used for COD measurement (Standard Method 5220 B) due to high chloride concentration of shale gas wastewater. All other experimental analyses were performed according to the Standard Methods of the APHA [26]. The pH of the samples was determined by a pH meter (WTW series pH 720). A Merck spectroquant (model: NOVA 60) was used to measure color, and a multimeter instrument (Thermo Scientific ORION 5 STAR) was used to determine electrical conductivity.

2.4. Experimental design and statistical model

RSM is an effective method for the research of the relation between several variables and responses by varying them simultaneously and carrying out a limited number of laboratory experiments [27]. RSM is not only limited to the description of the system or process mechanisms but also gives interpretation and evaluation of relations existing between experimental studies and the observed results [28]. The CCD is an ideal design for sequential experimentation and allows a reasonable amount of information for testing the lack of fit while not involving an unusually large number of design points [26]. In this study, experimental design of the Fenton process for COD, color and total phenol removal from shale gas wastewater was performed through the use of the RSM. The CCD was used to create experiment sets, and the three independent operating variables: H_2O_2/COD rate (X_1), H_2O_2/Fe^{2+} rate (X_2) and pH (X_3), which were optimized by RSM. All data analysis and the statistical design of experiments were performed using Statgraphic Centurion IVI.I. COD (Y_1), color (Y_2) and total phenol (Y_3) removal efficiencies (%) were considered to be dependent factors. These responses was selected, as these parameters, namely the COD, color and total phenol, are encountered in shale gas wastewater in high concentrations.The other factor, affecting the selection process of the dependent factors, was the knowledge that they can be removed from the wastewater with high removal efficiencies by the Fenton Process.

Table 2 lists the level of the independent variables, and Table 3 shows three dependent responses (COD, color and total phenol removal efficiencies) for CCD with the coded values of the factors. Process performance was determined by analyzing the removal efficiencies of COD, color and total phenol.

$$Y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_{11}X_1^2 + \beta_{22}X_2^2 + \beta_{33}X_3^2 + \beta_{12}X_1X_2 + \beta_{13}X_1X_3 + \beta_{23}X_2X_3 \quad (1)$$

where Y is the dependent factor; X_1, X_2 and X_3 are independent factors. The Y was therefore correlated to the set of regression coefficients (β): the intercept (β_0), linear (β_1, β_2 and β_3), interaction (β_{12}, β_{13} and β_{23}) and quadratic coefficients (β_{11}, β_{22} and β_{33}).

The results were analyzed by using analysis of variance (ANOVA) by the Statgraphics Centurion software. The model terms were utilized based on the *p*-value (probability) with a 95% confidence level. The coefficient of determination R^2 and adjusted R^2 was used to evaluate the quality of the fit polynomial model, and the Fisher's *F*-test was used to check the model statistical significance in the same program. The respective contour of the three-dimensional (3D) plots were used to evalute the interaction between the two independent factors on the dependent variables.

Table 2
Experimental factors of independent variables and their levels for Fenton process

Factors	Symbol	Factor level				
		–2	–1	0	1	2
pH	X_1	2	2.5	3	3.5	4
H_2O_2/COD (mg/mg)	X_2	0.4	0.8	1.2	1.6	2
H_2O_2/Fe^{+2} (mg/mg)	X_3	5	10	15	20	25

3. Result and discussion

3.1. Statistical analysis and optimization of the experimental condition

The experimental results from CCD were analyzed by a second-order (quadratic) polynomial response surface model. The regression models (Y_1 for COD, Y_2 for color and Y_3 for total phenol removal efficiencies) are presented in Eqs. (2)–(4), respectively:

$$Y_1, \% = -30{,}0257 + 34{,}5526X_1 + 51{,}068X_2 - 1{,}14181X_3 - 4{,}36773X_1X_1 + 0{,}60625X_1X_2 - 0{,}0805X_1X_3 - 18{,}8089X_2X_2 + 0{,}618125X_2X_3 - 0{,}000577273X_3X_3 \quad (2)$$

$$Y_2, \% = 24{,}9952 - 17{,}4192X_1 + 153{,}242X_2 - 1{,}33465X_3 + 2{,}64091X_1X_1 - 5{,}31875X_1X_2 + 0{,}6735X_1X_3 - 43{,}2095X_2X_2 - 0{,}893125X_2X_3 + 0{,}0117091X_3X_3 \quad (3)$$

$$Y_3, \% = 40{,}5718 + 34{,}7001X_1 + 11{,}0524X_2 - 0{,}655057X_3 - 5{,}25773X_1X_1 - 3{,}09375X_1X_2 + 0{,}2535X_1X_3 + 1{,}01136X_2X_2 - 0{,}210625X_2X_3 + 0{,}00177273X_3X_3 \quad (4)$$

Based on Eqs. (2)–(4), shale gas wastewater treatment removal efficiencies of COD, color and total phenol by the

Table 3
CCD for the study of three experimental variables for Fenton process and obtained results for COD, total phenol and color removal

Independent variables				Response 1		Response 2		Response 3	
Set	pH (X_1)	H_2O_2/ COD (X_2)	H_2O_2/ Fe^{+2} (X_3)	COD		Phenol		Color	
				Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
1	–1	–1	–1	54,01	50,5435	96,72	96,0422	86,75	79,7718
2	1	–1	–1	59,44	58,5697	98,59	99,256	85,82	80,678
3	–1	1	–1	61,99	61,4422	99,82	98,9535	99,85	101,621
4	1	1	–1	68,71	69,9535	99,84	99,6922	98,92	98,2718
5	–1	–1	1	44,75	41,8847	94,95	94,676	84,06	79,6305
6	1	–1	1	50,18	49,106	99,98	100,425	94,12	87,2718
7	–1	1	1	58,48	57,7285	96,99	95,9022	94,27	94,3343
8	1	1	1	63,59	65,4347	98,92	99,176	95,82	97,7205
9	–2	0	0	45,71	48,7147	89,38	90,6222	94,12	96,3676
10	2	0	0	65,83	64,4472	97,93	97,1097	97,83	100,66
11	0	–2	0	31,97	35,2972	99,23	98,9397	42,91	52,0701
12	0	2	0	64,23	62,5247	99,89	100,602	88,45	84,3676
13	0	0	–2	66,47	67,4797	99,94	100,242	94,43	97,3901
14	0	0	2	53,69	54,3022	98,24	98,3597	94,58	96,6976
15	0	0	0	60,4	60,9486	99,14	99,1236	95,98	95,873
16	0	0	0	60,72	60,9486	98,97	99,1236	94,5	95,873
17	0	0	0	61,11	60,9486	99,07	99,1236	94,85	95,873
18	0	0	0	62,34	60,9486	99,06	99,1236	95,2	95,873
19	0	0	0	60,4	60,9486	99,06	99,1236	95,05	95,873
20	0	0	0	59,1	60,9486	99,02	99,1236	94,58	95,873

Fenton process were calculated and summarized with the experimental results in Table 3. Coefficient analysis in Eqs. (2)–(4) indicated a synergistic effect for the positive sign coefficients, whereas an antogonistic effect for the negative ones [29].

Eq. (2) shows that the COD removal was positively affected by the individual operating variables, such as the H_2O_2/COD ratio and the initial pH of wastewater, whereas the H_2O_2/Fe^{2+} ratio affected the COD removal negatively. The color and total phenol removals were positively affected by H_2O_2/COD ratio, whereas H_2O_2/Fe^{2+} ratio affected the color and total phenol negatively.

Model satisfaction was determined from comparison of the prediced and actual values (Fig. 2) known as diganostic plots. The predicted vs. actual values plots of removal parameters are presented in Figs. 2(a)–(c) for COD, color and total phenol removal, respectively. As it can be seen from Fig. 2, the actual and predicted data from the models helped evaluating the Fenton process performance, which is, in turn, related well to COD, color and total phenol removal. The results showed that the prediction of experimental data is rather satisfactory.

Graphical data was analyzed by ANOVA in order to determine how the process variables and the responses interacted. ANOVA results of the predicted response surface quadratic model for removal efficiencies of COD, color and total phenol are given in Tables 4–6. The probability value (Prob > *F*), the model *F* value and the adequate precision are the main indicators of the satisfactory and importance of the model used. Larger *F*-values indicate that the corresponding term is more significant. Moreover, in order to decide whether the *F*-value is large enough or not, the *p*-value, which is related to the *F*-value, could be used [30,31]. The values of Prob > *F* less than 0.05 showed that the model terms are significant, but if the values are greater than 0.1, the model terms are not significant [32–35]. The results from Tables 4–6 indicated that the ratio of mean square of the regression, owing to the residual error known as *F* values of regressions, was found to be adequate. According to the results from Tables 4–6, the model was found to be highly significant statistically, because the Prob > *F* values were found to be less than 0.0001 for the second-order polynomial fitting. For COD removal by the Fenton processes, the model *F* value was found to be 26.202 with the corresponding *p*-value of 0.00000844 and a high sum of squares value (Table 4) showing that the model was quiet significant and could appropriately clarify the relationship between the independent and the dependent variables. It was, thus, obvious to conclude that linear coefficients were more significant than interacting and quadratic coefficients. The pH values, H_2O_2/COD ratio and H_2O_2/Fe^{2+} had highly significant effects on COD removal, while the interaction effect between pH and other parameters on COD removal was insignificant. The pH value and the H_2O_2 dosage were the parameters having significant effects in quadratic parameters.

As can be seen from Table 5, the ANOVA results on the color removal by Fenton processes showed an *F* value of 9.85 and a quadratic model revealing the significancy of the model. According to the ANOVA table, the quadratic model indicated that only H_2O_2/COD ratio affected color removal highly (Table 5).

The ANOVA study on total phenol removal by Fenton process is presented in Table 6. The high significance of the model with the relationship between the response and independent variables for total phenol removal by Fenton processes is demonstrated by a model *F* value of 19.20 with a corresponding *p*-value of 0.0000356 and a high sum of squares value (106.380) (Table 6). As can be seen from Table 6, linear coefficients and quadratic coefficients, except X_2X_2, X_2X_3 and X_3X_3, have significant effects on total phenol removal.

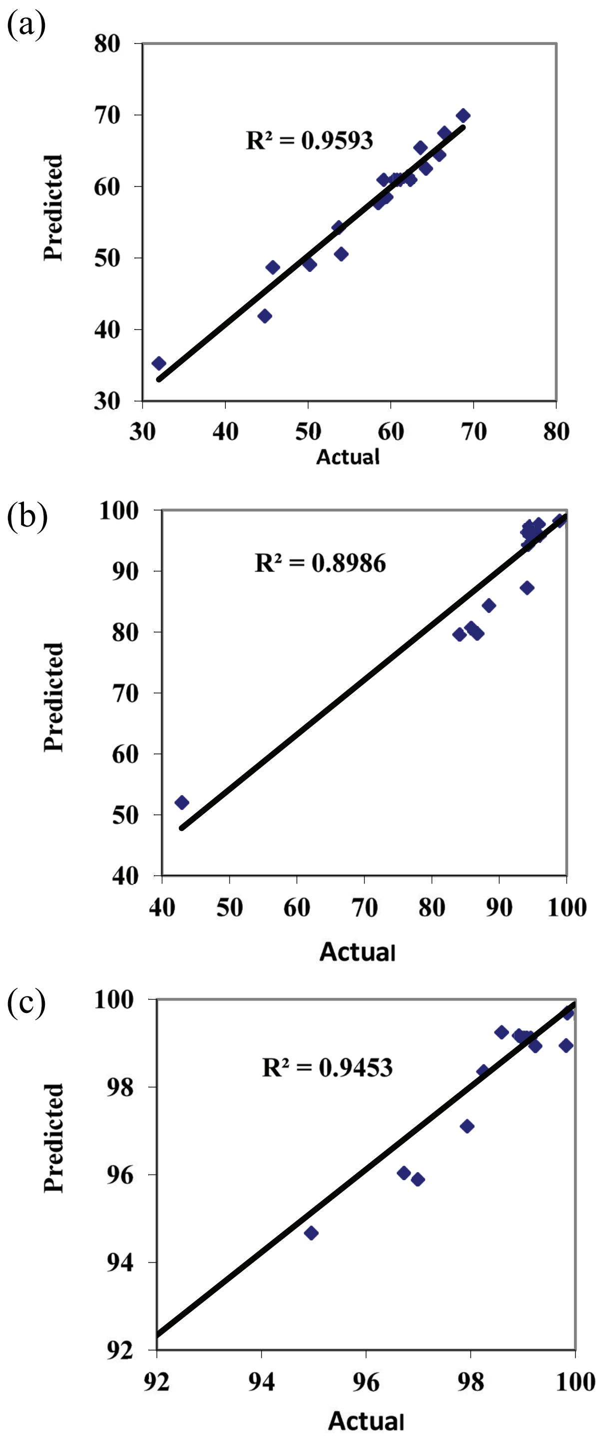

Fig. 2. Comparisons of predicted and actual values of COD (a), color (b) and total phenol (c) for Fenton process.

Table 4
Analysis of variance for COD removal

Source	Sum of squares	Degrees of freedom	Mean square	F value	p-value	Remark
Model	1421.7840	9	157.976	26.202	0.00000844	Highly significant
X_1	247.5120	1	247.512	41.05	0.0001	Highly significant
X_2	741.3370	1	741.337	122.95	<0.0001	Highly significant
X_3	173.6470	1	173.647	28.80	0.0003	Significant
X_1X_1	29.9782	1	29.978	4.97	0.0499	Significant
X_1X_2	0.1176	1	0.118	0.02	0.8917	Not significant
X_1X_3	0.3240	1	0.324	0.05	0.8214	Not significant
X_2X_2	227.7110	1	227.711	37.76	0.0001	Highly significant
X_2X_3	12.2265	1	12.226	2.03	0.1849	Not significant
X_3X_3	0.0052	1	0.0052	0.00	0.9771	Not significant
Total error	60.2979	10	6.0298			
Total (corr.)	1,482.1200	19				

Note: R^2: 0.9593; adjusted R^2: 0.9227.

Table 5
Analysis of variance for color removal

Source	Sum of squares	Degrees of freedom	Mean square	F ratio	p-value	Remark
Model	2494.94	9	277.216	9.85	0.000673	Significant
X_1	18.4256	1	18.4256	0.65	0.4373	Not significant
X_2	1043.13	1	1043.13	37.06	0.0001	Highly significant
X_3	0.47956	1	0.47956	0.02	0.8987	Not significant
X_1X_1	10.9598	1	10.9598	0.39	0.5466	Not significant
X_1X_2	9.05251	1	9.05251	0.32	0.5831	Not significant
X_1X_3	22.6801	1	22.6801	0.81	0.3905	Not significant
X_2X_2	1201.75	1	1201.75	42.70	0.0001	Highly significant
X_2X_3	25.5255	1	25.5255	0.91	0.3634	Not significant
X_3X_3	2.15447	1	2.15447	0.08	0.7877	Not significant
Total error	281.452	10	28.1452			
Total (corr.)	2776.40	19				

Note: R^2: 0.8986; adjusted R^2: 0.8074.

Table 6
Analysis of variance for total phenol removal

Source	Sum of squares	Degrees of freedom	Mean square	F ratio	p value	Remark
Model	106.380	9	11.8203	19.20	0.0000356	Highly significant
X_1	42.0877	1	42.0877	68.37	<0.0001	Highly significant
X_2	2.76391	1	2.76391	4.49	0.0499	Significant
X_3	3.54381	1	3.54381	5.76	0.0374	Significant
X_1X_1	43.4401	1	43.4401	70.57	<0.0001	Highly significant
X_1X_2	3.06281	1	3.06281	4.98	0.0498	Significant
X_1X_3	3.21311	1	3.21311	5.22	0.0454	Significant
X_2X_2	0.65837	1	0.65837	1.07	0.3254	Not significant
X_2X_3	1.41961	1	1.41961	2.31	0.1598	Not significant
X_3X_3	0.04938	1	0.04938	0.08	0.7828	Not significant
Total error	6.15588	10	0.61559			
Total (corr.)	112.539	19				

Note: R^2: 0.9453; adjusted R^2: 0.8961.

The R^2 coefficient gave the proportion of the total variation in the response predicted by the model, indicating ratio of sum of squares due to regression to total sum of squares. For COD, color and total phenol removal, R^2 value of the models were found to be 0.9593, 0.8986 and 0.9453, respectively. The results indicated that only 4.0%, 10.1% and 5.5% of the variability in the response could not be explained by the models for COD, color and total phenol removal, respectively. Joglekar and May suggested that R^2 should be at least 0.80 for a good fit of a model [36]. Since all the determined R^2 values were higher than 80%, it was concluded that the determined R^2 values were adeuqate and the model fit was satisfactory.

In order to investigate the integrated effect of H_2O_2/COD, H_2O_2/Fe^{2+} and pH, the 3D plots response surface plots were plotted by means of RSM. The response surface plots are given in Figs. 3(a)–(c), 4(a)–(c) and 5(a)–(c). As can be seen in Figs. 4 and 5, the removal efficiencies of the color and the total phenol were much higher than the removal efficiency of COD during the Fenton process.

Numerical optimization was used to designate the optimum process parameters for maximum removal efficiencies of COD, color and total phenol. Based on response

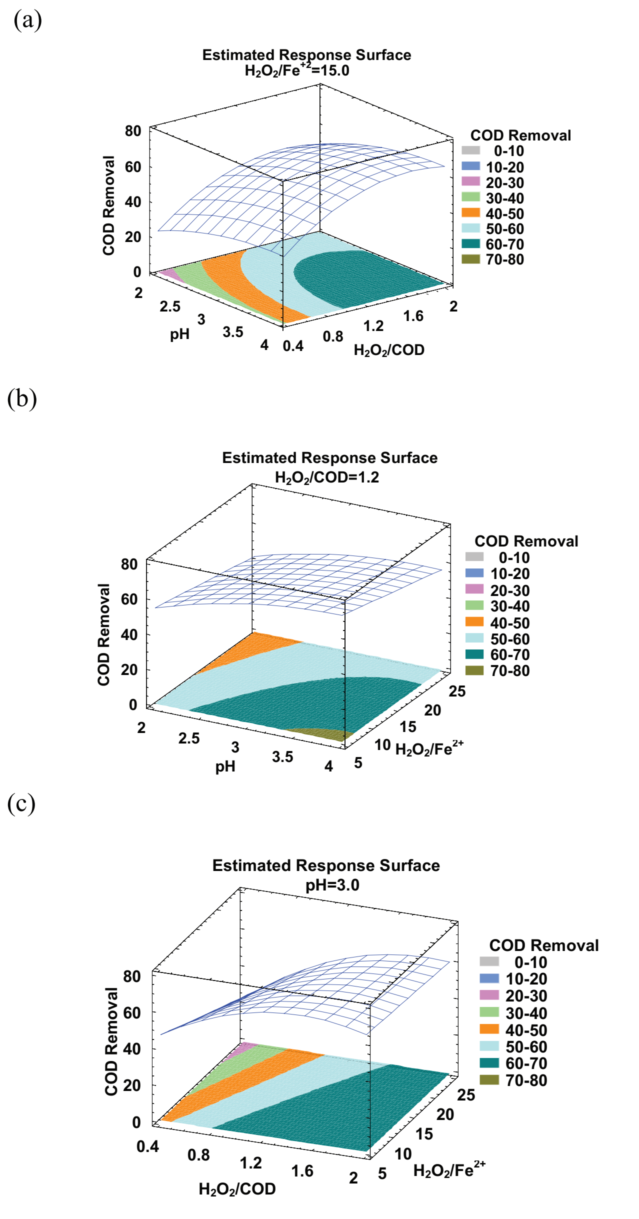

Fig. 3. Response surface graphs for the Fenton process of shale gas wastewater (a) effect of pH and H_2O_2/COD ratio, (b) effect of pH and H_2O_2/Fe^{2+} and (c) effect of H_2O_2/COD and H_2O_2/Fe^{2+} for COD removal.

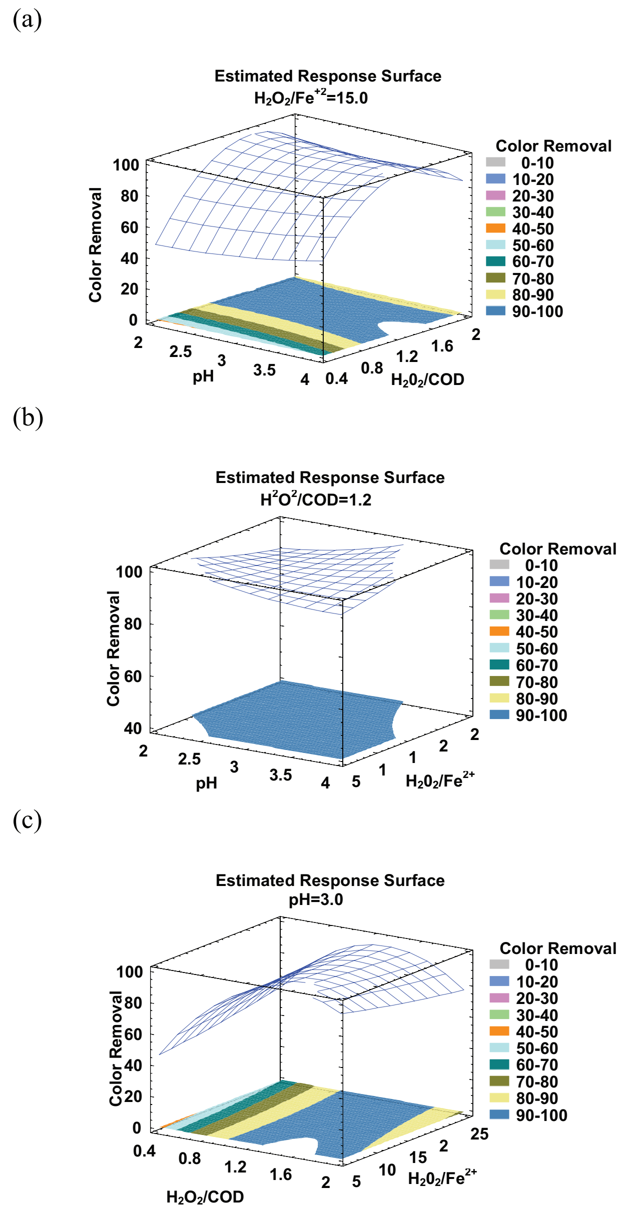

Fig. 4. Response surface graphs for the Fenton process of shale gas wastewater (a) effect of pH and H_2O_2/COD ratio, (b) effect of pH and H_2O_2/Fe^{+2} and (c) effect of H_2O_2/COD and H_2O_2/Fe^{2+} for color removal.

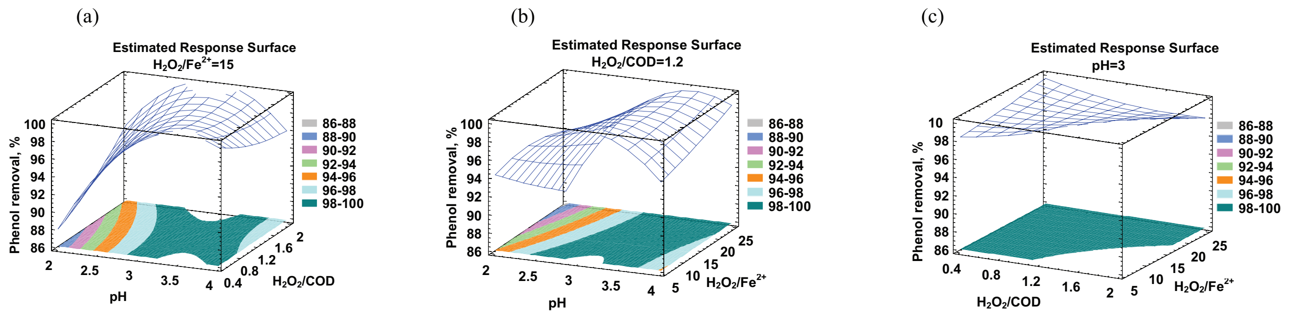

Fig. 5. Response surface graphs for the Fenton process of shale gas wastewater (a) effect of pH and H_2O_2/COD ratio, (b) effect of pH and H_2O_2/Fe^{2+} and (c) effect of H_2O_2/COD and H_2O_2/Fe^{2+} for total phenol removal.

Table 7
Optimum operating conditions of the process variables

Parameter	pH	H_2O_2/COD	H_2O_2/Fe^{2+}	Predicted removal efficiency	Experimental removal efficiency
COD	3.99	1.504	5.0	72.52	68.20
Color	4.0	1.509	5.02	99.99	88.48
Total phenol	2.84	2.0	5.05	99.99	92.65

surface and desirability functions, the optimum conditions for COD, color and total phenol removal efficiencies by the Fenton process were obtained (Table 7). In order to confirm the accuracy of the predicted models and the reliability of the optimum combination, additional experiments were carried out at optimum conditions. Table 7 shows the predicted removal efficiencies (COD: 72.57%, color: 99.9% and total phenol: 99.9%) according to the model under optimized operational conditions for shale gas wastewater. On the other hand, the results from the laboratory experiments were 68.20%, 88.48 % and 92.65% for COD, color and total phenol, respectively. Therefore, it can be said that the experimental values were found to agree well with the predicted ones.

4. Conclusions

The shale gas wastewater contains high levels of TDS (salinity) and other constituents, such as COD, color, total phenol and heavy metals, that require treatment. Therefore, in this study, the efficiency of Fenton process on shale gas wastewater treatment was investigated where the experimental conditions and the process performances were optimized and modeled by CCD and RSM. The quadratic model developed in this study showed the presence of a high correlation between experimental and predicted values. ANOVA showed high determination coefficients (R^2 > 0.80), ensuring a satisfactory adjustment of the second-order regression model with the experimental data. A COD removal value of 68.20% was obtained by the Fenton process, under optimal values of process parameters. However, it should be noted that the removal efficiencies for color and total phenol using the Fenton process under optimum conditions were 88.48% and 92.65%, respectively. The overall results indicated that the Fenton process is found to be a new and a powerful technique for shale gas wastewater treatment. The results also confirmed that RSM is a robust method for the optimization of the operational conditions of Fenton process particularly COD, color and total phenol removals from shale gas wastewater.

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