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Optimization and kinetic study of Fenton treated industrial wastewater using response surface method

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In this study, wastewater from food industry has been treated in terms of chemical oxygen demand (COD) removal using Fenton process under response surface methodology (RSM). The effect of four independent variables such as reaction time, pH, HP/Fe molar ratio and H_2O_2 /wastewater volume ratio (mL/L) are studied on the COD of wastewater. Experimental data are optimized using Box Behnken design (BBD). The optimum conditions are experimentally found at reaction time of 22.30 min, pH of 3.22, HP/Fe molar ratio of 5 and H_2O_2/wastewater (mL/L) of 2.64, for COD removal of 80.1%. The kinetic study is undertaken at different initial COD concentrations of 1920, 2304, 2688, 3072 and 3840 mg/L. The overall kinetics can be described by second order followed by zero order rate equation. The rate constant for second order is found to be 6×10^{-5} L/mg min and for zero order was found to be 2.5 mg/L min.

Keywords: COD, Fenton process, Kinetics, Optimization, RSM, Wastewater treatment

Introduction

The Fenton reaction was discovered by H. J. H. Fenton in 1894 and reported the activation of hydrogen peroxide by ferrous (Fe^{2+}) salts to oxidize tartaric acid[1]. In recent past Fenton reaction was utilized effectively for treatment and removal of many hazardous organic materials from wastewater[2,3] The hydroxyl radical generated during Fenton reaction has second highest oxidizing potential of 2.80 V preceded by fluorine. In the Fenton process the hydroxyl radical is generated at ambient temperature and pressure which avoids requirement of the complex reactor systems. The rapid reaction between ferrous salt and hydrogen peroxide and subsequent generation of hydroxyl radical are completed in shortest reaction time among all other advanced oxidation processes[4]. Fenton process uses reagents like ferrous salts and hydrogen peroxide which are moderately reactive, cheap and easy to handle. This makes the process practically viable and cost effective. Owing to high mineralization efficiency, Fenton process can transform organic pollutants into nontoxic carbon dioxide. In Fenton process soluble ferrous salts are used shows highest reaction efficiency because the mass transfer limitation between the active reagents[4]. The Fenton process has substantially employed for the treatment of diverse wastewaters from textile industries[5], winery industries[6], olive oil industries[7], paper and pulp industries[8] as well as from refinery and fuel terminals[9]. Iron catalyst used in Fenton process has several advantages like it is abundantly available, it has high environmental compatibility and low toxicity, highly reactive in both species, Fe^{2+}, Fe^{3+} respectively, low commercial cost. In the Fenton process formation of reactive hydroxyl ions is highly dependent on pH. The optimum pH range for the homogeneous Fenton process was found to be around 2 to 4. In case of heterogeneous Fenton process there is a wider range of pH is available[10]. The molar ratio of H_2O_2/Fe_2^{+} and volume ratio of H_2O_2/WW plays crucial role in removing chemical oxygen demand (COD) of wastewater (WW)[11]. The optimum value of ferrous salts to hydrogen peroxide ratio is usually 1:5 wt/wt[12]. With increase in ferrous ion concentration rate of degradation increases initially, after reaching optimum level[13–16]. Further increase in concentration leads to increased total dissolved solids in the effluent streams which is not permitted[17]. In deciding overall efficiency of degradation, concentration of hydrogen peroxide plays important role. However, excess amount of hydrogen peroxide contributes to COD and acts as scavenger for reactive hydroxyl ions[13]. Thus, the dosage of the hydrogen peroxide should be optimized such that entire amount should be utilized. The proposed mechanism for Fenton process found in literature suggests that it is quite complex[16,18–21], still

there is general agreement that the limiting step is hydroxyl ion formation from the following reaction[22–24].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^* \quad \ldots (1)$$

The Fe(II) is regenerated slowly from the reaction between Fe(III) and hydrogen peroxide

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{-}OOH^{2+} + H^+ \quad \ldots (2)$$

$$Fe\text{-}OOH^{2+} \rightarrow HO_2^* + Fe^{2+} \quad \ldots (3)$$

$$Fe^{3+} + HO_2^* \leftrightarrow Fe^{2+} + O_2 + H^+ \quad \ldots (4)$$

The organic substrates from the wastewater are attacked by OH* species formed from reaction (Eq. 1). There is numerous competitive reactions that also occur but the following reactions adversely affects the oxidation process[15,25].

$$Fe^{2+} + OH^* \rightarrow Fe^{3+} + OH^- \quad \ldots (5)$$

$$H_2O_2 + OH^* \rightarrow HO_2^* + H_2O \quad \ldots (6)$$

In the literature, most of the exploration of the Fenton process was done with the help of synthetic wastewater. In the recent past studies of Fenton process with real wastewater are gaining importance. In the field of food wastewater biological processes are dominant and Fenton process was rarely explored in this field. This work is an effort to evaluate the efficiency of Fenton process for COD removal of food wastewater. In the present study real wastewater from local food industry was treated with Fenton process. The effect of independent process parameters such as reaction time, H_2O_2/Fe^{2+} molar ratio, H_2O_2/WW volume ratio and pH of the wastewater on the COD removal of food wastewater is considered, as well as the optimization of these parameters are done and validated by experimentation. For better understanding of the process, a detailed kinetic study was performed using predetermined optimized condition on the batch level.

Experimental Section

Materials and method

The food wastewater was collected from local food industry. The wastewater sample was acidified and stored at 4°C before experimental analysis. The characteristics of the wastewater are colour: aquamarine, initial COD: 5993 mg/L, pH: 6.89 and TDS: 1.475 ppt.

The wastewater was first filtered to remove floating impurities and then coagulated with $FeSO_4$ 98% pure of Fisher Scientific. A known quantity of $FeSO_4$ was added to the 200 mL sample of wastewater, it was mixed for one minute at 150 rpm and for two minutes at 50 rpm. The sample was left undisturbed for 30 min. The supernatant from the coagulated wastewater was filtered again and used for further experimentation. A reactor consisting of a 150 mL was stirred using a magnetic stirrer as shown in Fig. 1. In each experimental run 100 mL of wastewater with pH adjusted to desired value with the help of sulfuric acid (0.1 N) or sodium hydroxide (0.1 N) required amount of iron salt ($FeSO_4.7H_2O$ Merck grade) and hydrogen peroxide (about 50% W/W of Fisher Scientific) were added to reactor. The pH meter of Labtronics India was used to measure pH values. After completion of a run, the COD of the sample was determined by dichromate closed reflux method as per the standard method 5220-C (Standard methods for examination of water and wastewater 21st edition 2005). Block digester of Hach, USA model DRB 200 was used for digestion process. For kinetic study five samples were made from coagulated sample. The coagulated sample was diluted with distilled water and five samples of COD concentrations of 1920, 2304, 2688, 3072 and 3840 mg/L were made. With optimum dose of molar ratio of H_2O_2/Fe^{2+}, volume ratio of H_2O_2/WW and pH the reaction was carried out for 25 min and in an interval of 5 min the sample was removed and COD was determined by the above mentioned method.

Statistically guided experimental design

In the present experimental work, experimental runs were designed with the help of Box Benhken design (BBD). Effect of reaction time, molar ratio of

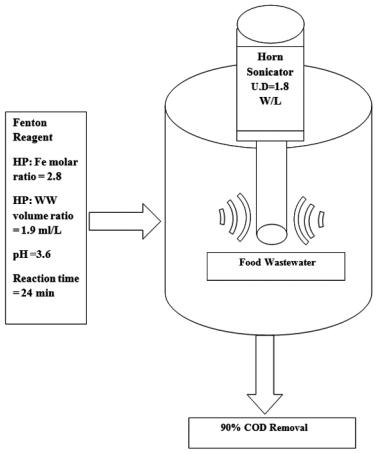

Fig. 1 — Schematic diagram of experimental set up

H_2O_2/Fe^{2+}, volume ratio of H_2O_2/WW and pH of the wastewater on the COD removal of wastewater were studied. Table 1 shows the different levels of process parameters. Optimization by conventional methods demands large number of experiments, time and material. The statistical experimental design comes over the shortcomings of the conventional optimization; it minimizes the number of experiments[26]. The response surface methodology (RSM) is an effective tool in optimizing and statistically analyzing the experimental data[27]. In optimization using RSM several parameters can consider simultaneously[28], it is also useful in establishing relationship between controllable input and response variable[29]. BBD facilitates to estimate linear, quadratic and interactive effects of the independent input parameters. BBD has crucial role in building the experimental design and determining lack of fit of the model. It's worthwhile to note that RSM will not help to understand reaction mechanism in the experiment but to study optimum level of independent variables to maximize COD removal. Three levels of four independent parameters yields twenty-seven experimental runs by BBD as shown in the Table 2.

Analysis of variance was used to determine regression coefficients and their effects within the confidence interval of 95%. COD removal was considered as response variable and was calculated by the equation

%COD removal = (CODI – CODF/CODI) ×100, where CODI and CODF are initial and final COD, respectively.

Table 1 — Levels of different process variables in coded and uncoded form

Independent variable	Levels of variables in design		
	-1	0	1
Reaction time (min)	10	20	30
Molar ratio H_2O_2/Fe^{2+}	0.5	2.75	5
Volume ratio H_2O_2/WW (ml/L)	0.5	1.75	3
pH	2	3.5	5

Table 2 — Box Behnken design matrix with experimental and predicted COD removal

S. N.	Reaction time (min)	pH	HP:Fe (Molar ratio)	HP:WW (ml/L)	% COD Removal	
					Observed	Predicted
1	10	2	2.75	1.75	38.85	39
2	30	2	2.75	1.75	57.76	58
3	10	5	2.75	1.75	37.67	37
4	30	5	2.75	1.75	46.56	46
5	20	3.5	0.5	0.5	54.97	54
6	20	3.5	5	0.5	59.14	59
7	20	3.5	0.5	3	69.30	69
8	20	3.5	5	3	79.46	80
9	10	3.5	2.75	0.5	38.47	38
10	30	3.5	2.75	0.5	56.37	52
11	10	3.5	2.75	3	59.80	61
12	30	3.5	2.75	3	69.69	70
13	20	2	0.5	1.75	53.61	54
14	20	5	0.5	1.75	48.92	50
15	20	2	5	1.75	62.27	58
16	20	5	5	1.75	54.58	54
17	10	3.5	0.5	1.75	51.43	51
18	30	3.5	0.5	1.75	69.33	70
19	10	3.5	5	1.75	62.60	63
20	30	3.5	5	1.75	72.49	74
21	20	2	2.75	0.5	39.40	46
22	20	5	2.75	0.5	37.21	39
23	20	2	2.75	3	60.72	60
24	20	5	2.75	3	50.53	50
25	20	3.5	2.75	1.75	71.93	70
26	20	3.5	2.75	1.75	71.93	72
27	20	3.5	2.75	1.75	71.93	74

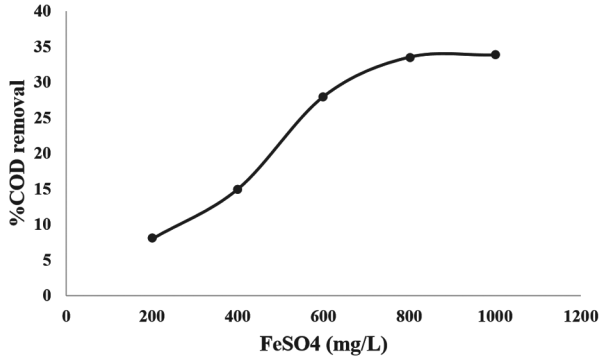

Fig. 2 — Effect of $FeSO_4$ dosage on COD removal

Regression analysis was performed to estimate the response function as second order polynomial:

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum \sum_{i=1}^{3} \beta_{ij} X_i X_j \quad \ldots (7)$$

Where Y is predicted response, βi, βii, and βij are the coefficients estimated by the regression for liner, quadratic and cross-product effects of X1, X2, X3 and X4 respectively on the response. The parameters of the response equation and analysis of variance (ANOVA) were evaluated using MINITAB 16.

Results and Discussions

In the coagulation with $FeSO_4$, the dosage of $FeSO_4$ (mg/L) varied from 200 mg/L to 1000 mg/L, Fig. 2 shows % removal of COD with increasing dosage of $FeSO_4$, it was observed that, from 200 mg/L to 800 mg/L there was significant COD removal, after that negligible COD removal was observed. Initial COD of wastewater was 5993 mg/L and after coagulation it was found to 3840 mg/L, nearly 36% COD removal was observed.

Regression model based on ANOVA

The following equation presents BBD model for % COD removal obtained from the software. Eq. (8) shows relation between response variable and input parameters.

% COD Removal = -124.849 + 5.324A +59.496B +2.309C +28.173 D -0.088A2 -7.963B2 +0.165C2-4.507D2 -0.167A×B -0.089A×C – 0.160A×D -0.222B×C – 1.067 B×D +0.533 C×D ... (8)

Where A, B, C and D are reaction time, pH, H_2O_2/Fe^{2+} molar ratio, and volume ratio of H_2O_2 to wastewater (mL/L) respectively. Observed and predicted data (from Eq. 2) are shown in Table 2. The normal probability plot of residuals is shown in the Fig. 3, it shows that observed data follows normal distribution and there is a straight line pattern. The predicted data is shown in Fig. 4 for COD removal, according to this plot there is good agreement between the observed and predicted data. Therefore, the quadratic model in Eq. (8) is suitable for %COD removal.

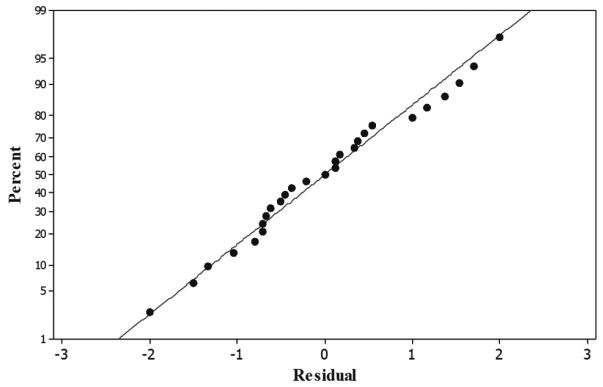

Fig. 3 — Normal probability vs. residual values for COD removal

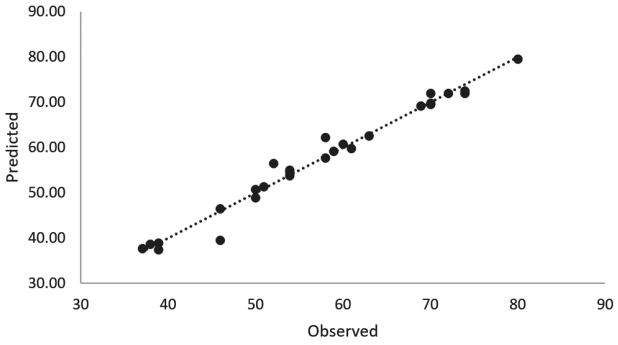

Fig. 4 — Predicted vs. observed data

Table 3 — The ANOVA for % COD removal

Variables	Values
Press	125.04
%R-Squared	99.34
%Adj R-Squared	98.56
%Pred. R-Squared	96.88
F-Value	128.51
P-Value	0.0001
Lack of fit (p -value)	0.833

ANOVA Analysis

According to analysis of variance, the terms in the quadratic model having p value lesser than 0.05 are significant for confidence interval of 95%. All the linear effect terms, A, B, C, and D in Eq. (2) are significant. The square or quadratic effects are significant for A^2, B^2 and D^2. The significant interactive effects are BC and BD. As shown the Table 3, quality of the fitted model in relation with its

capacity to predict response variable was evaluated on the basis of the determination coefficients R^2 and R^2 adj. their values show that Eq. (8), can explain 99.34% variation in the observed data. R^2 adj. is more rigorous parameter to determine the quality of model; it increases only when the new term improves the model more than would be expected by chance, in case of %COD removal its value is sufficiently high that is 98.56%. The predicted R^2 indicates the capability of regression model to predict the response for new observation. In this work predicted R^2 is 96.88%. Values of R^2, R^2 adj. and predicted R^2 near to one indicate model validation[30]. The predicted residual error sum of squares (PRESS) is used to assess predictive ability of the model; the low PRESS value is generally good for the proper model. Lack of fit can occur when several abnormally large residual results from fitting the model, it may also occur due to omission of important quadratic or interactive from the model. Insignificant lack of fit in this work indicates there are no evidences that model does not fit data.

As shown in Fig. 5(a), %removal of COD increases with increase in reaction time reaches maximum level and then decreases with increase in reaction time. It is evident from Table 2, that threefold increase in the and keeping pH, HP:Fe molar ratio and HP:WW ratio constant at 3.5, 5 and 1.75, respectively, 11% increment in the COD removal was observed. When the reaction time of increases from 10 to 20 min and pH increases from 2 to 3.5 at constant HP:Fe molar ratio of 2.75 and HP:WW volume ratio of 1.75 mL/L. However, further increase in pH to maximum level of 5 and reaction time of 30 min shows decrease in % COD removal which indicates presence of optimum level upto which % COD removal increases and further increase in pH and reaction time decreases COD removal. As shown in Table 2, increase in HP: WW volumetric ratio from 0.5 to 3 mL/L at constant pH of 3.5 and HP:Fe molar ratio of 0.5 shows 15% increment in COD removal for the reaction time of 20 min. However, keeping same levels of HP:Fe ratio and reaction time but elevated pH level of 5, the same increment in the HP:WW ratio shows 11% decrease in COD removal. Fig. 5(b) shows increment of 18% COD removal for 30 min reaction time, pH of 3.5, HP:Fe ratio of 2.75 when HP:WW ratio increases from 0.5 to 3 mL/L. The pH level when initially increased from 2 to 3.5 shows positive increment in % COD removal but further increment in pH up to 5 declinations in % COD removal. At lower pH level of 2 increment in HP:Fe ratio from, 0.5 to 5 the increment of 12% and at higher pH level of 5, only 5% enhancement in COD removal for same change in HP:Fe ratio with reaction time of 20 min and HP:WW ratio 1.75. As illustrated in Fig. 5(c), when pH and HP:Fe level increased simultaneously at constant reaction time of 20 min and HP:WW ratio of 1.75 mL/L , for pH changes from 2 to 3.5 and HP:Fe ratio from 0.5 to 2.75, 16% enhancement in COD removal was observed, however further increment in pH to 5 and HP:Fe ratio to 5 reduction of approximately 15% COD removal is shown. The peak in the Fig. 5(c) indicates increase and decrease in %COD removal with increment in HP:Fe ratio and pH levels. At reaction time of 10 min with increase in HP: WW ratio from 0.5 to 3ml/L with pH of 3.5 and HP:Fe ratio of 2.75, 23% COD removal was observed when the reaction time is tripled with same conditions and increment in HP:WW ratio 18% enhancement in COD removal was observed as shown in Table 2 and Fig. 5(d). By keeping pH and HP:Fe ratio at 3.5 and 2.75 and simultaneously increasing reaction time from 10 to 30 min and HP:WW ratio from 0.5 to 3mL/L, for the increment of 10 to 20 min and 0.5 to 1.75 mL/L of HP:WW ratio 32% enhancement in the COD removal was observed and further increase in time and HP:WW ratio has shown negligible changes in COD removal.

Fig. 5(e) shows the effect of HP:Fe molar ratio and reaction time on %COD removal. At low level of reaction time of 10 min and with increment of HP:Fe molar ratio from 0.5 to 5, COD removal of 12% was obtained. When the level of reaction time was at highest level of 30 min, for the same change in HP:Fe molar ratio only 4% of COD removal was observed. The pH and HP: WW ratio was held constant at 3.5 and 1.75 mL/L, respectively. When reaction time was varied from 10 min to 30 min, HP:Fe molar ratio was held constant at low of 0.5, pH and HP:WW ratio were held constant at 3.5 and 1.75 ml/L, respectively, positive change of 19% was observed in COD removal. For the same variation in reaction time at highest HP:Fe molar ratio of 5. COD removal was observed to change from 63% to 74%. As shown in Fig. 5(f), for simultaneous increment in HP:Fe ratio and HP:WW ratio from 0.5 to 2.75 and 0.5 to 3 mL/L, respectively. 16% increment in COD removal was observed and further increment in both ratio to

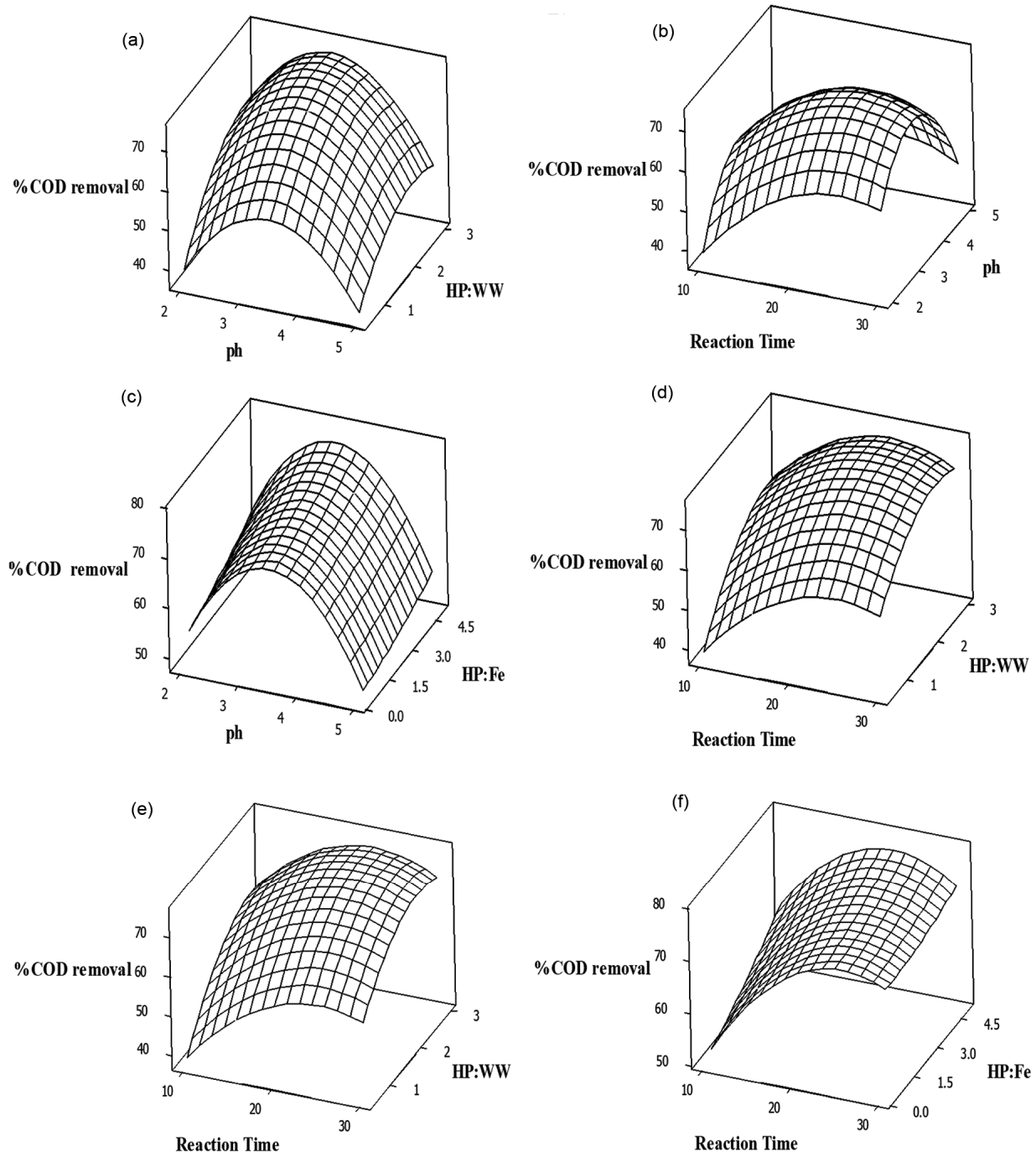

Fig. 5 — Three dimensional surface plots of %COD removal as function of (a) Reaction time and pH, (b) pH and HP: WW, (c) pH and HP:Fe, (d) Reaction time and HP:WW, (e) Reaction time and HP:Fe and (f) HP:Fe and HP:WW

highest level shows maximum COD removal of 80%. The reaction time and pH level was kept constant at 20 min and 3.5, respectively. The numerical prediction tool of MINITAB 16 was used to find the optimum conditions of the independent parameters for maximum COD removal. The optimum condition for the independent parameters for maximum COD removal of 80.91% were determined at reaction time of 22.32 min, pH value of 3.24, HP: Fe molar ratio of 5 and HP: WW volume ratio of 2.64. The peak area of three dimensional surfaces plots shown in Fig. 5 (a)-(f) corresponds to the maximum COD removal which

validates the optimum conditions for maximum COD removal. For experimental validation, the experimental run was carried out reaction time of 22.32 min, pH value of 3.24, HP:Fe molar ratio of 5 and HP:WW volume ratio of 2.64 ml/L. The maximum COD removal was found to be 80.10%.

Kinetic Study

The kinetic study for the Fenton treatment of food wastewater was conducted to determine the order of the reaction and reaction constant k. The optimum conditions obtained from the RSM were used in the kinetic study. For five different initial COD concentrations, 1920, 2304, 2688, 3072 and 3840 the effect of reaction time is shown in the Fig. 6(a). Departing from higher COD concentrations more significant decrease in COD was observed in first 15 min of the reaction and less pronounced decrease in last 10 min.

$$(-r) = kCn = -dC/dt \quad \ldots (9)$$

Eq. 9 shows mass balance on the batch reactor, where 'n' is the order of the reaction, k is reaction rate constant and (-r) indicates rate of consumption of COD.

It can be observed from the Fig. 6(b) that for different initial concentrations reaction rate is almost constant within first 15 min. The reaction rates were computed from linear decrease in each run for average COD concentration. The order of reaction was obtained from slope of the line 1.91 indicates that reaction proceeds with approximately second order rate kinetics. To confirm the order of reaction, in addition to differential method of data analysis, method of initial rates was employed. The straight line obtained from the representation of $\ln r = \ln(-dC/dt)$ $t = 0$ *vs*. $\ln C_0$ fig 6 E where C_0 is initial COD concentration with slope equal to 2. Similarly, analysis was employed for last 10 min, in this case slope of the line obtained was -0.12 as shown in the Fig. 6(c), indicating that in the last 10 min, reaction follows zero order kinetics. To determine kinetic constant, integral method was used. Integral method is most often when reaction order is known and kinetic constant is to be evaluated. Thus for second order reaction, putting n equal to 2 and integrating Eq. (1) we get

$$1/C - 1/C_0 = Kt \quad \ldots (10)$$

The data corresponding to Eq. (2) is shown in the Fig. 6(d), the apparent kinetic constant obtained from the data is 6×10^{-5} L/mg.min. For zero order kinetics, putting n equal to zero in Eq. (9) and integrating yields linear decrease of COD concentration with respect to time as shown in Fig. 6(a). The average apparent kinetic constant for zero order was found to be 2.5 mg/L min. The COD removal rate was faster in the initial 15 min of the reaction was due to rapid formation of hydroxyl radicals. In experiment, the large excess of hydrogen peroxide used as compared to ferrous ions (HP/Fe molar ratio of 5), which initially produces hydroxyl ions rapidly. In the last 10 min of the reaction most of the Fe(II) has been oxidized, Fe(III) reacts slowly with residual hydrogen peroxide to regenerate Fe(II) via formation of peroxo complexes and their slow decomposition (Reactions 3 and 4) to Fe(II). The slower removal rate in the last 10 min can be understood from reactions 3 and 4. Furthermore the decrease in hydroxyl species concentration and oxidation potential the media is due the formation of other radicals, especially perhydroxyl radicals through reactions 3 and 6.

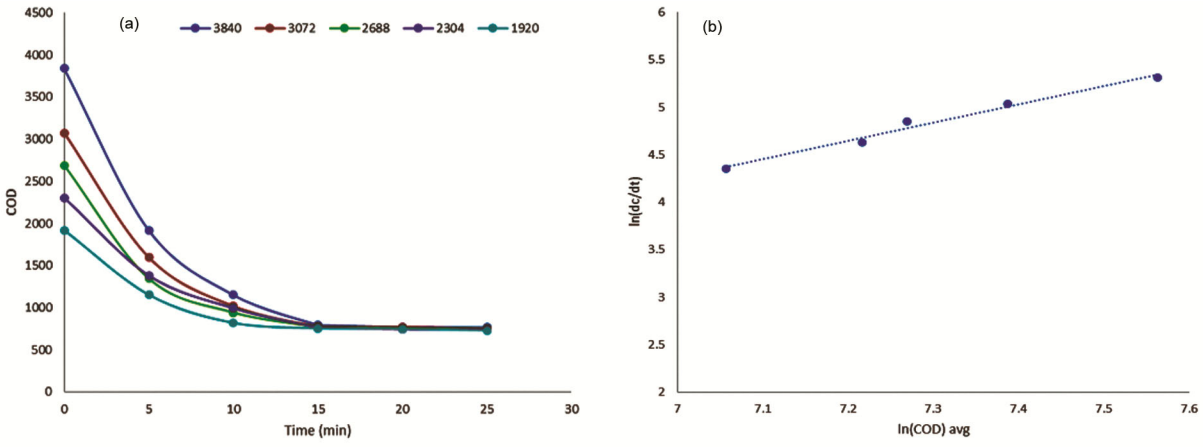

Fig. 6 (*Contd.*)

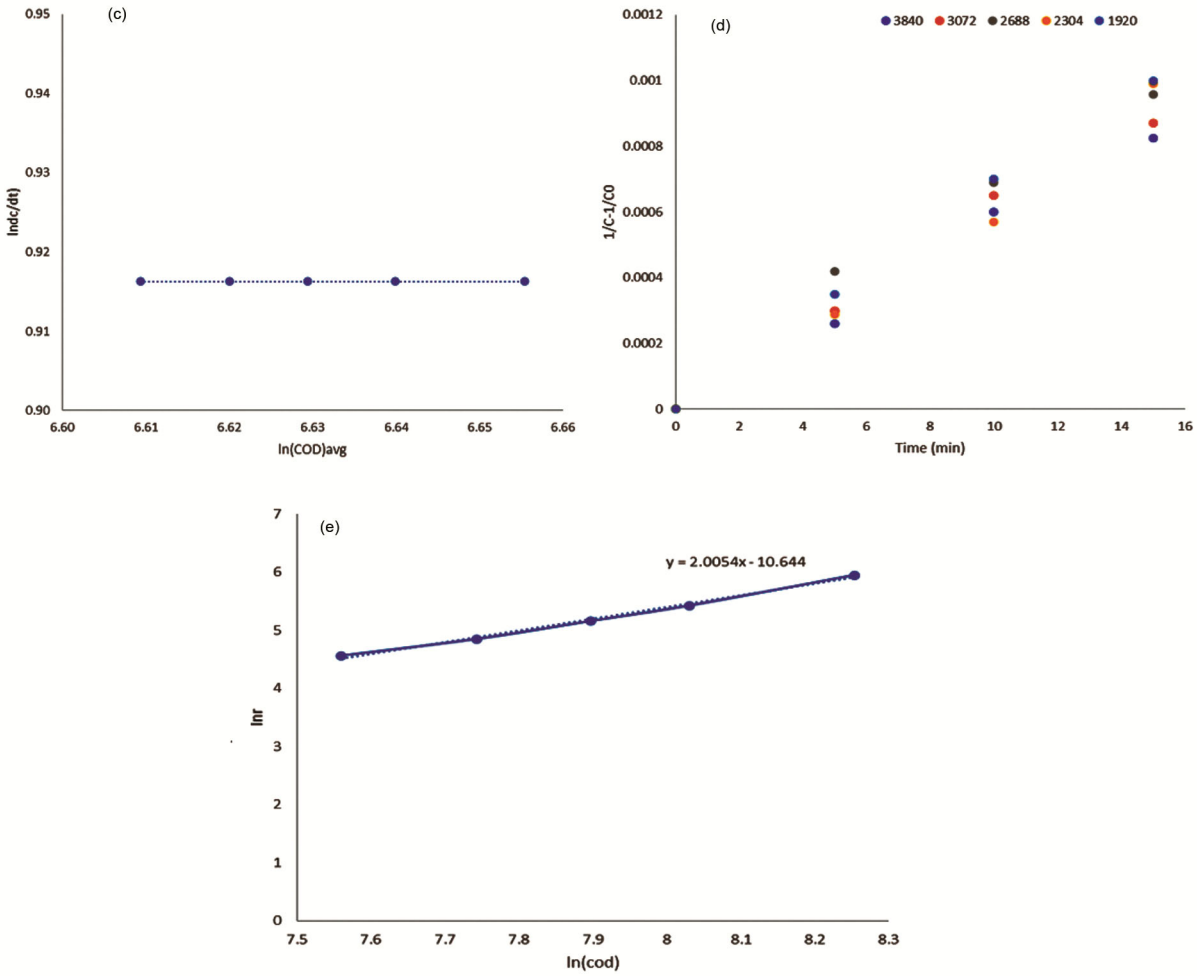

Fig. 6 — (a) Effect of time on different initial concentrations of COD, (b) Logarithm of reaction rate vs. logarithm of average COD for first 15 min, (c) Logarithm of reaction rate *vs*. logarithm of average COD for last 10 min, (d) Fitting of experimental data to second order reaction kinetic model for first minutes of reaction and (e) Method of initial rates for first 15 min of reaction

Conclusion

Response surface methodology combined with Box Behnken design of four independent variables and three levels of each variable were applied for treatment of real wastewater from food industry. The optimum conditions for maximum COD removal were obtained at reaction time of 22.32 min, pH of 3.24, H_2O_2/Fe_2^+ molar ratio of 5, H_2O_2/WW volume ratio of 2.64. The maximum% COD removals obtained statistically and experimentally were 80.91% and 80.10%, respectively. The second order polynomial equation was developed for COD removal. High values of R^2 = 99.34%, R^2 (Adj.) =98.56% and R^2 (Pred.) = 96.88% indicates the suitability of polynomial to predict COD removal. The lack of fit was found to be insignificant proposes the fitness of the model with confidence interval of 95%. For initial COD concentrations of 1920, 2304, 2688, 3072 and 3840, respectively, overall kinetics can be described in two parts. For initial 15 min second order kinetics was observed and for last 10 min follows zero order kinetics. The kinetic constants for second and zero order was found to be 6×10^{-5} L/mg.min and 2.5 mg/L.min, respectively.

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