Optimization of Fenton process for refinery wastewater biodegradability augmentation

Syukriyah Ishak and Amirhossein Malakahmad[†]

Civil Engineering Department, Faculty of Engineering, Universiti Teknologi PETRONAS, 31750 Tronoh, Perak, Malaysia
(*Received 2 October 2012 • accepted 1 January 2013*)

Abstract−The Fenton process was used to increase the biodegradability of refinery wastewater. Initially, effects of reaction time, H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios were investigated and biodegradability of wastewater was determined in terms of the BOD_5/COD ratio. Preliminary results showed that the Fenton process was able to improve wastewater biodegradability from 0.27 to 0.43. Subsequently, the process was optimized by using response surface methodology based on a five-level central composite design. Adequacy and significance of results were analyzed in analysis of variance. The quadratic model was found to be significant to give less than 0.05 probability of error. The model was fit with data based on insignificant of lack-of-fit test at values of 0.93. The high R^2 and Adj.R^2 (0.95 and 0.91) indicates satisfactory adjustment of quadratic model to experimental data. Based on optimized conditions, wastewater biodegradability improved to 0.44 via H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios of 2.8 and 4 within 71 minutes reaction time.

Key words: Advanced Oxidation Process, Recalcitrant Discharges, BOD_5/COD Ratio

INTRODUCTION

Petroleum refining industries utilize large quantities of water and generate large volumes of effluent containing hydrocarbons, phenol and dissolved minerals. Approximately 246-341 L of water is being consumed in processing a barrel of crude oil [1]. Discharge of untreated petroleum refining wastewater into water bodies results in environmental and human health effects due to release of toxic contaminants. High exposure for long periods to these compounds can cause leukemia and tumors in multiple organs. Phenol and dissolved minerals are also toxic to aquatic life and lead to liver, lung, kidney and vascular system infection [2]. Therefore, refinery discharges have to be sufficiently treated for their quality to meet the established regulations [3]. Selection of the right treatment method for any discharge depends greatly on its characteristics. Among the available treatment methods, the application of biological processes is gradually gaining momentum as they are cost-effective alternative of conventional techniques [4]. However, the majority of industrial discharges, including petroleum refinery, have low biodegradability and thus cannot be treated directly using biological treatment methods [5]. The application of an appropriate pretreatment process before biological decontamination will reduce toxicity of the wastewater and shorten the acclimatization duration in biological system.

Advanced oxidation process (AOP) is an attractive pretreatment method to improve the biodegradability of various industrial discharges [6-8]. AOP is a chemical oxidation process that is able to generate and use hydroxyl free radicals (•OH) as strong oxidant. Its application reduces the COD load and contaminants levels in wastewater [9,10] and generates fewer toxic effluents. AOP also improves the biodegradability of wastewater by forming intermediates similar to the metabolic pathway substances [11]. The Fenton process is one of the promising alternative oxidation methods due to its cost
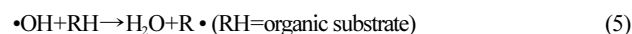
efficiency, simplicity of operation, leaving no residue, and stability to treat a range of substances. It is the combination of oxidation and coagulation reaction to reduce toxicity and COD using hydrogen peroxide and ferrous sulfate. The oxidation mechanism by the Fenton process is due to the hydroxyl radical generation in an acidic solution by the catalytic decomposition of hydrogen peroxide [12]. The Fenton reaction is shown in Eqs. (1)-(10). At acidic pH it leads to the production of ferric ion and hydroxyl radical:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} \cdot OH + OH^- \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightleftarrows Fe\text{-}OOH^{2+} + H^+ \rightleftarrows \cdot H_2O + H^+ \tag{2}$$

Hydroxyl radicals may be scavenged by reaction with another Fe^{2+} or with H_2O_2:

$$\cdot OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \tag{3}$$

$$\cdot OH + H_2O_2 \rightleftarrows HO_2 \cdot + H_2O \tag{4}$$

Hydroxyl radicals may react with organic and starting a chain reaction:

$$\cdot OH + RH \rightarrow H_2O + R \cdot (RH = \text{organic substrate}) \tag{5}$$

$$R \cdot + O_2 \rightarrow ROO \cdot \rightarrow \text{products of degradation} \tag{6}$$

Ferrous ion and radicals are produced during the reactions:

$$H_2O_2 + Fe^{3+} \rightleftarrows H^+ + FeOOH^{2+} \tag{7}$$

$$FeOOH^{2+} \rightarrow HO_2 \cdot + Fe^{2+} \tag{8}$$

$$HO_2 \cdot + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \tag{9}$$

$$HO_2 \cdot + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+ \tag{10}$$

As long as the process involves several intermediate reactions and adjustment of operational factors such as pH and concentration of the reagents, process optimization by statistical analysis would be favorable. Response surface methodology (RSM) is a useful tool to evaluate the significance of variables and their interactions, build models and reduce the number of experiments trials [13]. RSM con-

[†]To whom correspondence should be addressed.
E-mail: amirhossein@petronas.com.my, amirhossein76@gmail.com

sists of a group of mathematical and statistical techniques based on the fit of empirical models to the experimental data obtained in relation to experimental design such as central composite design (CCD). Adequacy of the proposed model is revealed by checking tests provided by analysis of variance (ANOVA) [14,15]. Many researchers have investigated the application of the Fenton process for pretreatment of industrial discharges [15-19]. We investigated the Fenton process for improvement of petroleum wastewater biodegradability. Operational parameters condition for maximum biodegradability and less usage of the chemicals was optimized using response surface methodology.

EXPERIMENTAL

1. Sampling and Wastewater Characterizations

Samples were collected from the mud trap unit of a local refinery plant and then transported to the laboratory and stored in a cool room at 4 °C. Sampling was carried out before the oil skimming process to keep the originality of the produced industrial influent prior to any treatment. Analyses were done according to standard method for the examination of water and wastewater [20] and HACH. Each experiment was tested in triplicate and the standard deviation was measured accordingly (Eq. (11)).

$$\sigma = \{\sum [(x_1 - x_2)^2]/n\}^{1/2} \qquad (11)$$

Where σ is standard deviation, Σ is sum of, x_1 is individual value in data set, x_2 is means of all values in the data set and n is number of values in the data set. The petroleum refinery wastewater characteristic is shown in Table 1.

The BOD of refinery wastewater is commonly lower than that from municipal wastewater due to the presence of materials which are not easily biodegradable [21]. The higher COD concentration in the characterized refinery wastewater is due to existence of some compounds such as phenols and sulfide. Due to low BOD and high COD concentrations, the wastewater is considered as a low biodegradability wastewater [22]. Rather than that high concentration of some contaminants such as oil and grease and BTEX implies that the petroleum wastewater requires pretreatment before application of any biological decontamination.

2. Chemicals and Samples Preparation

Hydrogen peroxide, H_2O_2 (35%, w/w solution), ferrous sulfate heptahydrate, $FeSO_4 \cdot 7H_2O$ and sulfuric acid, H_2SO_4 (95-98%) were purchased from R&M Marketing, Essex, U.K. Sodium hydroxide, NaOH (Analytical grade, 46-48%) was purchased from Merck, Germany. H_2O_2 and $FeSO_4 \cdot 7H_2O$ were used for advanced oxidation process. H_2SO_4 and NaOH were utilized for pH adjustment.

3. Experimental Procedures

Experiments were conducted using jar test apparatus (VELP-Scientifica, Model JLT6, Italy) with solution volume of 500 mL. Samples were filtered through filter paper (Whatman, No.1) and set to pH 3 using H_2SO_4 to promote oxidation reaction. $FeSO_4 \cdot 7H_2O$ and H_2O_2 (35%, w/w solution) were added into the solution accordingly. The Fenton process was initiated by adding H_2O_2 into the solution. The solution was continuously mixed at 100 rpm. After a certain time, pH was increased to 10 using NaOH to promote coagulation and precipitation that occurred due to decomposition of H_2O_2 and deactivation of ferrous catalyst with the formation of ferric hydroxo complexes. The solution settled over night and was filtered to remove excess flocculates. pH of solution was decreased to range of 6.5 to 7.5 that is suitable for future implementation of biological treatment. COD and BOD_5 analyses were carried out to check the biodegradability improvement of the samples.

Preliminary analysis was divided into three sets of experiments to determine most favorable reaction time, H_2O_2/COD and H_2O_2/Fe^{2+}. The initial experiment was carried out by varying the reaction time in 20, 40, 60, 80, 100 and 120 minutes. Other operating conditions were fixed at H_2O_2/COD 2 : 1 and H_2O_2/Fe^{2+} 5 : 1. Based on the confirmed result from the initial experiment, the subsequent variations were done in terms of H_2O_2/COD molar ratios of 2, 4, 6, 8, 10 and 12 and H_2O_2/Fe^{2+} molar ratios of 5, 10, 15, 20, 25 and 30. Results were analyzed based on biodegradability improvement in terms of BOD_5/COD ratio.

4. Experimental Design and Mathematical Modeling

The design expert software was used for the statistical design of experiments and data analysis. The central composite design (CCD) and response surface methodology (RSM) were applied to optimize the three main operating variables: H_2O_2/COD (A), H_2O_2/Fe^{2+} (B) and reaction time (C) for optimum biodegradability augmentation via BOD_5/COD ratio improvement in refinery wastewater. The operational and process factors (H_2O_2/COD, H_2O_2/Fe^{2+} and reaction time) were introduced with the most significant impact, which were considered as the system variables, and BOD_5/COD ratio was calculated as the process response. The design consisted of 2^k factorial points expanded by 2k axial points and a center point, where k is the number of variables. The coded values for operating variables (A, B and C) were set at five levels: $-\alpha$ (minimum), 1, 0 (central), +1, and $+\alpha$ (maximum). Accordingly, 20 experiments (2^k+2k+6) were conducted with 15 experiments organized in a factorial design (includ-

Table 1. Petroleum refinery wastewater characteristics

Parameters	Range	Average
COD	744-1673	1209
BOD_5	205-448	327
pH	7.50-9.41	8.46
Turbidity	402-419	411
Color	3400-3650	3525
Nitrate	3.30-4.90	4.10
TSS	280-340	310
Alkalinity	133-138	136
Ammonia nitrogen	40-45	43
Oil and grease	48-97	73
Phosphorus	1.67-1.73	1.70
TOC	184-217	201
Phenol	1.16-1.44	1.30
Sulphide	14-17	16
Sulphate	40-50	45
TKN	82-95	89
Benzene	33.31-34.36	33.85
Toluene	38.58-41.08	39.83
Ethylbenzene	1.80-1.90	1.85
Xylene	30.03-33.04	31.54

All the units are in mg/L, except turbidity (NTU), color (Pt Co) and pH

Table 2. Experimental conditions and results of central composite design

Run	H_2O_2/COD	H_2O_2/Fe^{2+}	Reaction time
1	1.0 (−1)	3(−1)	40(−1)
2	3.0 (1)	3(−1)	40(−1)
3	1.0(−1)	7(1)	40(−1)
4	2.0(0)	5(0)	60(0)
5	3.0(1)	7(1)	40(−1)
6	1.0(−1)	3(−1)	80(1)
7	2.0(0)	5(0)	60(0)
8	3.0(1)	3(−1)	80(1)
9	1.0(−1)	7(1)	80(1)
10	1.0(1)	7(1)	80(1)
11	2.0(0)	5(0)	60(0)
12	0.3(−1.682)	5(0)	60(0)
13	3.7(1.682)	5(0)	60(0)
14	2.0(0)	2(−1.682)	60(0)
15	2.0(0)	5(0)	60(0)
16	2.0(0)	8(1.682)	60(0)
17	2.0(0)	5(0)	26(−1.682)
18	2.0(0)	5(0)	60(0)
19	2.0(0)	5(0)	94(1.682)
20	2.0(0)	5(0)	60(0)

ing 8 factorial points, 6 axial points and 1 center point) and the remaining 5 involving the replication of the central point to get a good estimate of the experimental error. Repetition experiments were carried out followed by order of runs as shown in Table 2.

The relationship between the response, input and the equation model for predicting the optimal variables were identified using the following:

$$\eta = f(x_1, x_2, \ldots, x_n) + \varepsilon \qquad (12)$$

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j}^{k} \sum_{j} \beta_{ij} X_i X_j + \cdots + e \qquad (13)$$

Where η is the response, f is the unknown function of response, x_1, x_2, $\cdots$ x_n are the independent variables, n is the number of independent variables and ε is statistical error that represents the other sources of variability not accounted for f, i is the linear coefficient, j is the quadratic coefficient, β is the regression coefficient, k is the number of factors studied and optimized in the experiment, and e is the random error [23].

The quality of the fit polynomial model was expressed by the coefficient of determination R^2, and its statistical significance was checked by Fisher's F-test in the same program. Model terms were evaluated by the P-value (probability) with 95% confidence level. Three-dimensional plots were obtained for biodegradability augmentation based on effects of the three variables at five levels.

RESULTS AND DISCUSSION

1. Preliminary Analyses of Fenton Process
1-1. Effect of Reaction Time
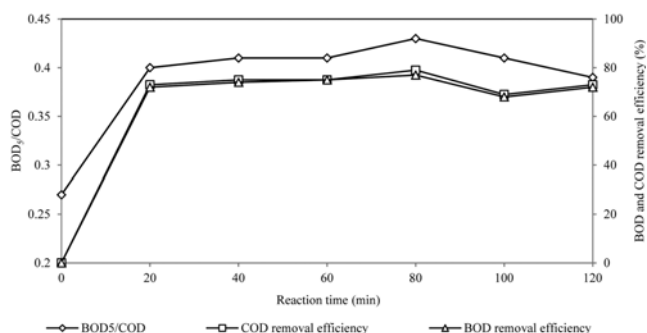Reaction time for the Fenton process was varied in the range of

Fig. 1. Effect of reaction time on biodegradability and COD and BOD removal efficiency.

20-120 min at constant initial COD (52 mM). Other operating conditions were fixed at H_2O_2/COD molar ratio 2 and H_2O_2/Fe^{2+} molar ratio 5. As shown in Fig. 1, at reaction time 20, 40, 60, 80, 100 and 120, the BOD_5/COD ratios were 0.40, 0.41, 0.41, 0.43, 0.41 and 0.39, COD removal efficiency was 73, 75, 75, 79, 69 and 73%, and BOD removal efficiency was 72, 74, 75, 77, 68 and 72%, respectively. In terms of maximum biodegradability, the best reaction time was 80 min with BOD_5/COD 0.43, 79% COD and 77% BOD removal efficiency. Almost similar reaction range was reported by treatment of petroleum refinery sour water (55% of dissolved organic content (DOC) removal) [24] and coking wastewater (44-50% and 95% of COD and total phenol removal, respectively) [25]. Interestingly, in the first 20 minutes of the Fenton reaction, more than 90% of COD and BOD removal was achieved. Also, a reasonable BOD_5/COD ratio of 0.40 was attained within 20 minutes. This finding is of special interest in the industrial application of Fenton's reagent, because it permits a significant biodegradability improvement and pollution reduction in a very short period of time. Short oxidation times are also reported by other authors [26,27].

1-2. Effect of H_2O_2/COD Molar Ratio
Initial H_2O_2 concentration was varied in the range 104-625 mM at constant initial COD (52 mM). Other operating conditions were fixed at reaction time 80 minutes and H_2O_2/Fe^{2+} molar ratio 5. At H_2O_2/COD molar ratios 2, 4, 6, 8, 10 and 12, the BOD_5/COD ratios were 0.43, 0.40, 0.37, 0.30, 0.34 and 0.39. COD removal efficiency was found to be 79, 82, 82, 88, 90 and 90% and BOD removal efficiency was 77, 82, 83, 90, 91 and 90% respectively (Fig. 2). Generally, increasing of H_2O_2 concentration will generate more
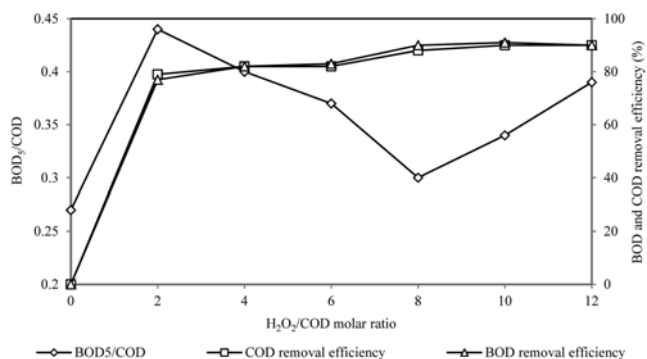

Fig. 2. Effect of H_2O_2/COD on biodegradability and COD and BOD removal efficiency.
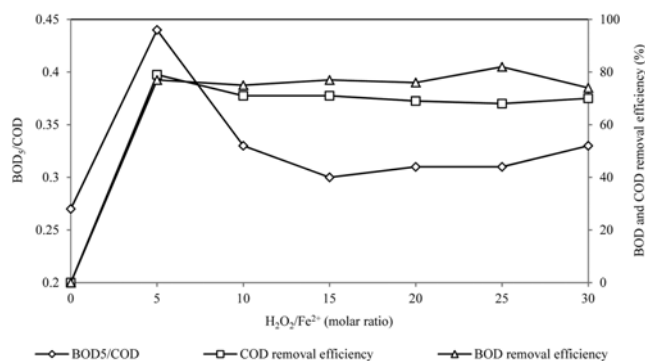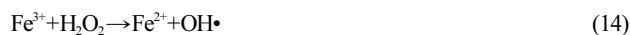
Fig. 3. Effect of H_2O_2/Fe^{2+} on biodegradability and COD and BOD removal efficiency.

hydroxyl radicals for better organic degradation [28]. However, at a certain limit, the complete organic removal could not be achieved even with higher than stoichiometric quantity of H_2O_2/COD and this led to decreasing the removal efficiency. COD and BOD removal kept increasing until H_2O_2/COD molar ratio 12. Biodegradability declined after H_2O_2/COD molar ratio 2. The achieved results are in agreement with those reported by other researchers [29,30]. Biodegradability declination may due to auto decomposition of H_2O_2 to oxygen and water and scavenging of $OH\bullet$ by H_2O_2. The excess H_2O_2 also reacts with ferric ions to form hydroperoxyl radicals [31].

1-3. Effect of H_2O_2/Fe^{2+} Molar Ratio

Fe (II) concentrations were varied in the range 3-21 mM at constant initial COD (52 mM). Other operating conditions were fixed consistent with achieved results in earlier steps. At H_2O_2/Fe^{2+} molar ratios 5, 10, 15, 20, 25 and 30, the BOD_5/COD ratios were 0.43, 0.33, 0.30, 0.31, 0.31 and 0.33 (Fig. 3). The best COD removal efficiency was found to be 79 at H_2O_2/Fe^{2+} molar ratio of 5. In terms of optimum biodegradability, the optimal H_2O_2/Fe^{2+} molar ratio was 5. Biodegradability decreased with increase of H_2O_2/Fe^{2+} molar ratio. However, COD and BOD removal efficiency increased at H_2O_2/Fe^{2+} molar ratio 5 and was considered steadily constant until it reached a molar ratio of 30.

Peroxide dose and iron concentration (Fe^{2+}) are important factors in the Fenton reaction [32]. Fe^{2+} concentration is important for the reaction kinetics while peroxide dose is for better degradation efficiency [33,34]. In this experiment, any increase in H_2O_2/Fe^{2+} molar ratio means less concentration of Fe^{2+}, which causes lower biodegradability. Lower H_2O_2/Fe^{2+} molar ratio causes a high removal of the target compound and formation of early intermediates [31]. Conversely, a higher dose of Fe^{2+} is more desirable for COD and BOD removal, which may generate more hydroxyl radicals for the degradation process [35]. Excessive formation of Fe^{2+} competes with the organic carbon for hydroxyl radicals when high Fe^{3+} concentration is used:

$$Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+OH\bullet \qquad (14)$$

$$Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+HO_2\bullet+H^+ \qquad (15)$$

$$Fe^{2+}+OH\bullet \rightarrow Fe^{3+}+OH^- \qquad (16)$$

2. Response Surface Methodology (RSM)

RSM has been applied to optimize the maximum biodegradability based on three operating variables (H_2O_2/COD, H_2O_2/Fe^{2+} and reaction time) of the Fenton process. The low and high ranges of those operating variables were chosen according to preliminary analysis (Table 2). The central composite design (CCD) allows the development of mathematical equations where predicted result (Y) was assessed as a function of H_2O_2/COD (A), H_2O_2/Fe^{2+} (B) and reaction time (C) and calculated as the sum of a constant, three first-order effects (terms in A, B, and C), three second-order effects (A^2, B^2 and C^2) and three interaction effects (AB, AC and BC). In RSM, adequacy and significance of results were analyzed and viewed in ANOVA. As shown in Table 3, the quadratic model was significant to give less than 0.05 of probability of error (P). Moreover, the model was fit with the data based on insignificant of lack of fit result at value 0.93. In addition, the high R^2 and Adj.R^2 (0.95 and 0.91) showed satisfactory adjustment of the quadratic model to the experimental data and high those values which are close to 1 indicate better estimation of regression equation which fits the sample data [36,37].

Adequate precision (AP) compares the range of the predicted values at the design points to the average prediction error. Ratios greater than 4 indicate adequate model discrimination and can be used to navigate the design space defined by the CCD [38]. In this study, the ratio of AP value was found to be 16.479, which is greater than 4 and considered a satisfactory result. The coefficient of variance (CV) as the ratio of estimate standard error to the mean value of the observed response defines reproducibility of the model. A model can be considered reproducible if its CV is not greater than 10% [39]. In this study, the model is reproducible since the CV is about 6.09%. A very high degree of precision and a good deal of reliability of the experimental values can be indicated by a low value of the coefficient of variation [40].

Fitting of the data to various models (linear, two factorial, quadratic and cubic) and their subsequent ANOVA presented that biodegradability augmentation of refinery wastewater was most suitably described with a quadratic polynomial model. Multiple regression coefficients of a second-order polynomial model describing refinery wastewater biodegradability augmentation are summarized in Table 4. The significance of each coefficient was determined by *F*-value and *P*-value. Corresponding *P*-values suggest that among the test variables used in this study A, B, A^2 and AB are significant model terms. Other model terms (with probability value larger than 0.05) were considered not significant according to Shahrezaei et al. [41]. To simplify the model, not significant terms (C, B^2, C^2, AC and BC)

Table 3. ANOVA results for response parameters

Response	Significant model terms	SD	R^2	Adj. R^2	Adeq. precision	CV	PRESS	*P*-value	*F*-value
Biodegradability augmentation	A, B, A^2, B^2, AB	0.023	0.95	0.91	16.479	6.09	0.025	<0.0001	0.93

R^2: determination coefficient, Adj. R^2: adjusted R^2, Adeq. precision: adequate precision, SD: standard deviation, CV: coefficient of variation, PRESS: predicted residual error sum of squares

Table 4. Estimated regression coefficients and corresponding to ANOVA results from the data of central composite design experiments before elimination of insignificant model terms

	Coefficient estimate	Sum of squares (SS)	Degree of freedom (DF)	Mean square (MS)	F-value	P-value	
Quadratic model	0.42	0.1	9	0.012	22.38	<0.0001	Significant
A	0.063	0.053	1	0.053	103.5	<0.0001	Significant
B	0.020	5.374E-003	1	5.374E-003	10.38	0.0092	Significant
C	−0.004	1.272E-005	1	1.272E-005	0.025	0.8786	Not significant
A^2	−0.050	0.036	1	0.036	68.57	<0.0001	Significant
B^2	−0.011	1.664E-003	1	1.664E-003	3.21	0.1033	Not significant
C^2	−0.003	4.266E-004	1	4.266E-004	0.82	0.3854	Not significant
AB	−0.034	9.112E-003	1	9.112E-003	17.60	0.0018	Significant
AC	−0.003	3.125E-004	1	3.125E-004	0.60	0.4552	Not significant
BC	−0.003	1.125E-004	1	1.125E-004	0.22	0.6511	Not significant
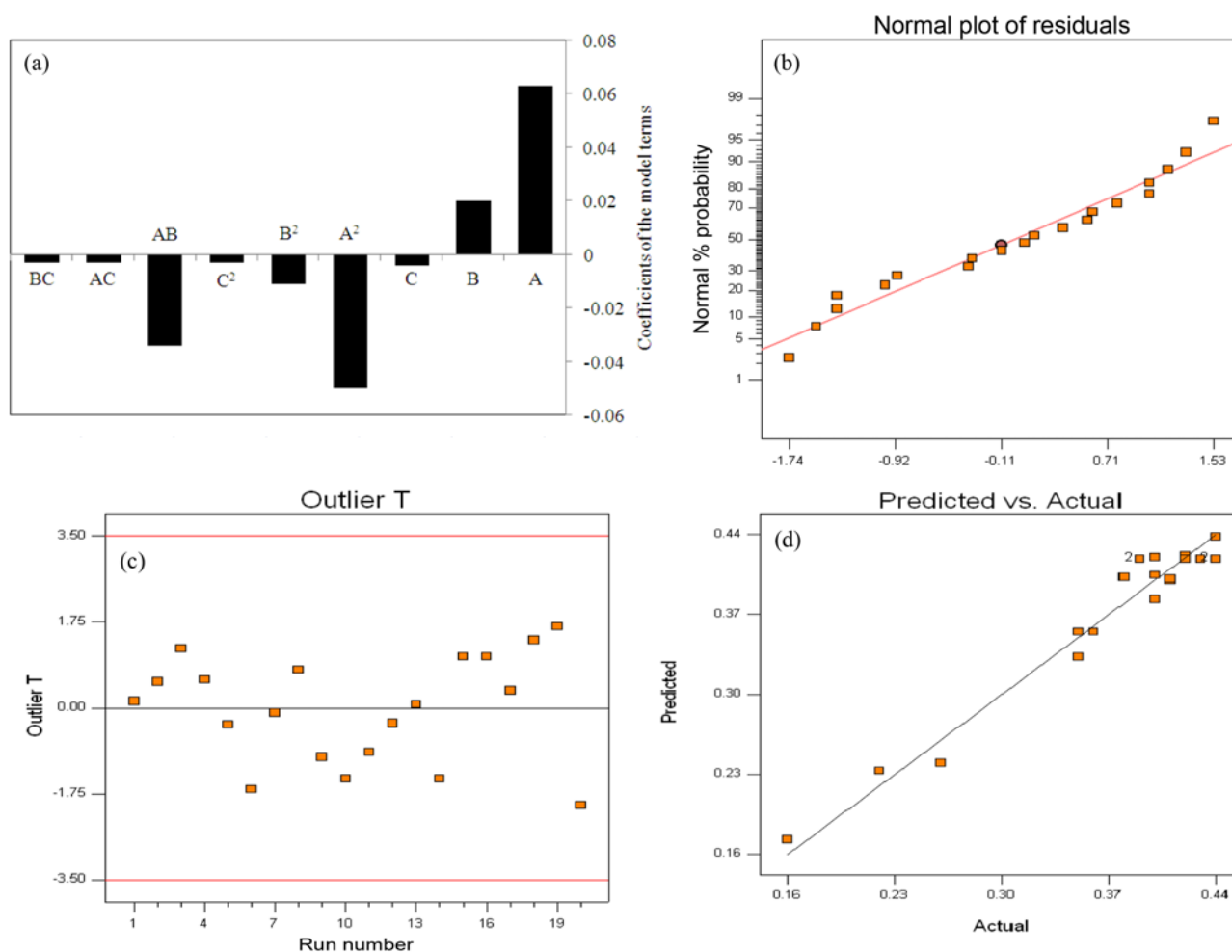
Fig. 4. (a) normalized coefficient of the model, (b) normal probability plot of residual, (c) plot of residual vs. predicted response and (d) predicted vs. actual values plot for refinery wastewater biodegradability augmentation.

were eliminated. Coefficients of the model terms are listed in Table 4 and normalized coefficients are presented in Fig. 4(a). Normalized coefficients indicate effects of the terms on the response. The first-order effects of H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios and second-order effects of H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios produce the main effect on biodegradability improvement of refinery waste-

water.

The following regression equation is the empirical model in terms of coded factors for biodegradability augmentation.

$$Y = +0.42 + 0.063A + 0.020B − 0.050A^2 − 0.011B^2 − 0.034AB \qquad (17)$$

A second-order model, typical for response surface Eq. (13), in terms

of the coded variables X_i, was reduced to the form of Eq. (17) based on the experimental results describing the refinery wastewater biodegradability augmentation by Fenton process. From Table 4 and Eq. (17), the significant reaction parameters were (most to least significant): H_2O_2/COD molar ratio (0.063)>second-order effect of H_2O_2/COD molar ratio (−0.050)>interaction between H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios (−0.034)>H_2O_2/Fe^{2+} molar ratio (0.020) and second-order effect of H_2O_2/Fe^{2+} molar ratio (−0.011).

A diagnostic result interprets the fit of data based on graphs such as normal probability plot of residuals and outlier plot. If the residual plot approximately sets a straight line, the normality assumption is considered satisfied [36]. The major diagnostic plots (Fig. 4(b)-(d)) are used to verify the residual analysis of the response surface design, to ensure that the statistical assumptions fit the analysis data. Fig. 4(b) shows the normal probability of the residuals, to verify whether the standard deviations between the actual and the predicted response values follow a normal distribution [41]. Fig. 4(b) expresses the general impression of a normal distribution of underlying errors. The residuals fall near to a straight line, and therefore there is no clear indication of non-normality of experimental results. The plots of residual versus predicted responses are in Fig. 4(c). All points of experimental runs are scattered randomly within the constant range of residuals across the graph, i.e., within the horizontal lines at the point of ±1.75. This implies that the proposed models are adequate and that the constant variance assumption was confirmed [38]. Responses from experimental results also fitted well within an acceptable variance range when compared to the predicted values from respective empirical models (Fig. 4(d)).

The three-dimensional response surface plots for variables--$H_2O_2/$ COD molar ratio (A), H_2O_2/Fe^{2+} molar ratio (B) and reaction time minutes (C) on BOD_5/COD improvement-are shown in Fig. 5. In general, these plots show the interaction between each operating parameter. As illustrated in Fig. 5(a) BOD_5/COD is improved with increase of H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio. The addition of the hydroxyl radical to organic compounds found in refinery wastewater results in the production of a radical organic compound that can be oxidized further by ferrous iron to produce stable oxidized end product. Hydroxyl radical attack on the product is more rapid than on the parent compounds [42] and as long as the organic carbon is removed rapidly after degradation of petroleum hydrocarbons at the early stage of reaction, the longer duration does not produce any significant effect on biodegradation augmentation. It may be explained by the fact that the half-life of the hydroxyl free radicals is short and extension of reaction time does not improve degradation. This phenomenon can be observed in Fig. 5(b) and 5(c). The relationship between H_2O_2/COD molar ratio and reaction time in Fig. 5(b) indicates BOD_5/COD is improved only with increase of H_2O_2/COD molar ratio. The best result is obtained at H_2O_2/COD molar ratio of 2. A further increase in oxidant concentration does not improve the biodegradability. The observed fact can be explained by considering the oxidation of organic substances by hydrogen peroxide in the presence of Fe(II); according to Welling [43] when the $[H_2O_2]$ is much higher than $[Fe^{2+}]$ the share of following competing reactions increases and may reduce the available hydroxyl radicals:

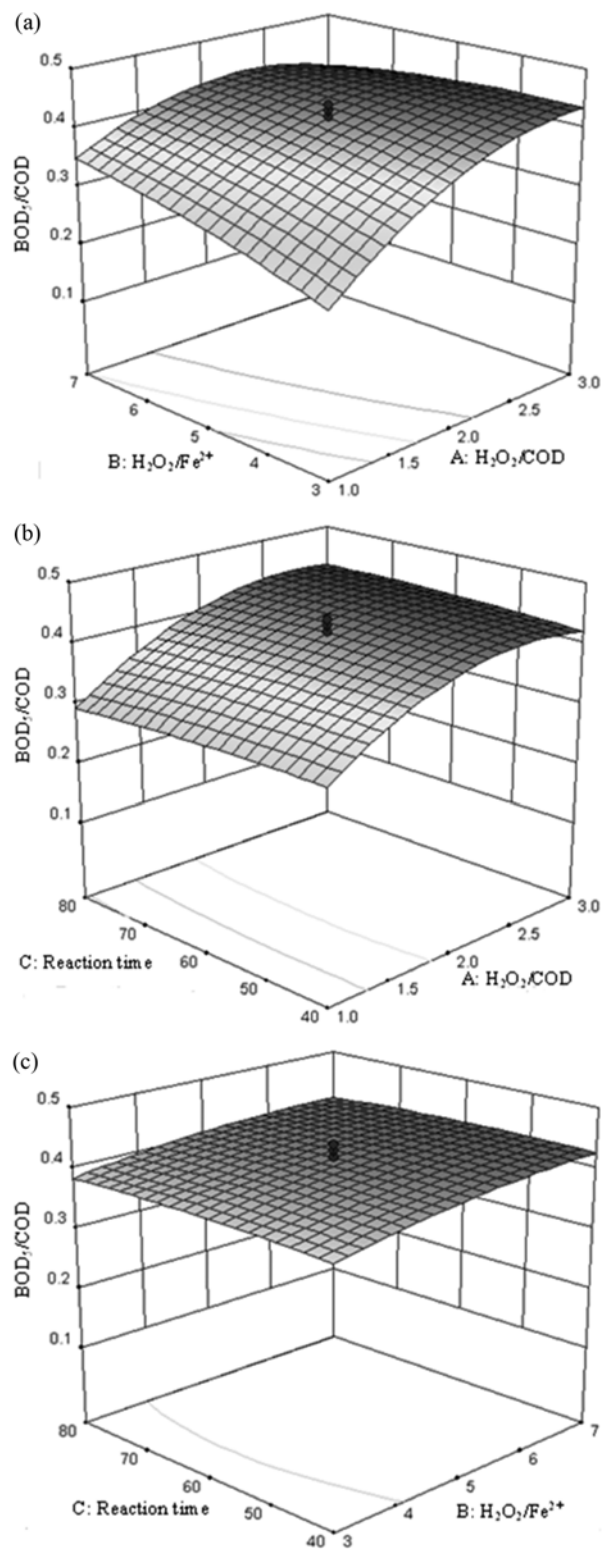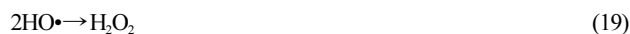$$HO\bullet + H_2O_2 \rightarrow H_2O + HO\bullet_2 \tag{18}$$

Fig. 5. (a) 3D plots of BOD_5/COD for the ratio H_2O_2/COD and $H_2O_2/$ Fe^{2+}, (b) 3D plots of BOD_5/COD for the ratio H_2O_2/COD and reaction time, (c) 3D plots of BOD_5/COD for the ratio $H_2O_2/$ Fe^{2+} and reaction time.

$$2HO\bullet \rightarrow H_2O_2 \tag{19}$$

The 3-D plot of H_2O_2/Fe^{2+} molar ratio and reaction time (Fig. 5(c))

indicates that increase of Fe (II) improves the biodegradability. But an optimum balance between [organic substances] and [Fe^{2+}] is vital to avoid any decrease in hydroxyl radical generation. It is better to maintain a lower value of the ratio of the catalyst to the concentration of the organic substances [28,31].

CONCLUSIONS

Application and optimization of the Fenton process to increase the biodegradability of real refinery wastewater was successful. The biodegradability in term of BOD_5/COD of the wastewater was increased from 0.27 to 0.44 after experimental and optimization phases. The partial oxidation was sufficient to render specific compounds to reduce their toxicity and make them more amenable to subsequent biological treatment. Optimization of the Fenton process through response surface methodology (RSM) indicates that the most favorable biodegradability is achievable at H_2O_2/COD ratio 2.8, H_2O_2/Fe^{2+} ratio 4 and reaction time within 71 minutes. More than 90% of COD and BOD removal efficiency was achieved during the first 20 minutes of the experiments. This early degradation of organic compounds is important for pretreatment of industrial discharges, as it can be accomplished quickly without a need for large treatment reactors. The quadratic regression model shows a satisfactory fit between the predicted and experimental values for BOD_5/COD ratio with R^2 0.95 and Adj. R^2 0.91. The outcome of this study is functional to recommend Fenton process as pretreatment of recalcitrant industrial discharges.

ACKNOWLEDGEMENT

NOMENCLATURE

Symbol
Adj. R^2 : adjusted R^2
ANOVA : analysis of variance
AP   : adequate precision
CCD : central composite design
CV   : coefficient of variance
DF   : degree of freedom
MS   : mean square
P   : probability of error
PRESS : predicted residual error sum of squares
SS   : sum of squares
β : regression coefficient
e   : random error
ε : statistical error
f   : unknown function of response
i   : linear coefficient
j   : quadratic coefficient
k   : number of factors studied and optimized in the experiment
n   : number of independent variables
n   : number of values in the data set
η : response

x_1 : individual value in data set
x_2 : values in data set
x_n : independent variable
σ : standard deviation
Σ : sum of

REFERENCES

1. A. Alva-Argáez, A. C. Kokossis and R. Smith, *Chem. Eng. J.*, **128**, 33 (2007).
2. M. Farhadiah, C. Vachelad, D. Duchez and C. Larroche, *J. Biotechnol.*, **99**, 5296 (2007).
3. United States Environmental Protection Agency, Technical Support Document for the 2004 Effluent Guidelines, Unites States (2008).
4. A. Malakahmad, A. Hasani, M. Eisakhani and M. H. Isa, *J. Hazard. Mater.*, **191**, 118 (2011).
5. C. S. D. Rodrigues, R. A. R. Boaventura and L. M. Madeira, *J. Adv. Oxid. Technol.*, **15**, 78 (2012).
6. J. C. Sin, S. M. Lam and A. R. Mohamed, *Korean J. Chem. Eng.*, **28**, 84 (2011).
7. N. Klamertha, L. Rizzoc, S. Malatoa, M. I. Maldonadoa, A. Agüera and A. R. Fernández-Alba, *Water Res.*, **44**, 545 (2010).
8. S. Baumgarten, H. FSchröder, C. Charwath, M. Lange, S. Beier and J. Pinnekamp, *Water Sci. Technol.*, **56**, 1 (2007).
9. I. Oller, S. Malato and J. A. Sánchez-Pérez, *Sci. Tot. Environ.*, **409**, 4141 (2011).
10. G. B. Tabrizi and M. Mehrvar, *J. Environ. Sci. Health (A)*, **39**, 3029 (2004).
11. D. F. Ollis, *Water Sci. Technol.*, **44**, 117 (2001).
12. S. Ledakowicz, M. Solecka and R. Zylla, *J. Biotechnol.*, **89**, 175 (2001).
13. A. Gürses, M. Yalc and C. Dgar, *Waste Manage.*, **22**, 491 (2002).
14. M. Ahmadi, F. Vahabzadeh, B. Bonakdarpour, E. Mofarrah and M. Mehranian, *J. Hazard. Mater.*, **123**, 187 (2005).
15. M. Ghanbarzadeh Lak, M. R. Sabour, A. Amiri and O. Rabbani, *Waste Manage.*, **32**, 1895 (2012).
16. J. Y. Park and I. H. Lee, *Korean J. Chem. Eng.*, **26**, 387 (2009).
17. P. Ghosh, L. K. Thakur, A. N. Samanta and S. Ray, *Korean J. Chem. Eng.*, **29**, 1203 (2012).
18. Y. Lee, S. Bae and W. Lee, *Korean J. Chem. Eng.*, **29**, 769 (2012).
19. B. Bianco, I. De Michelis and F. Vegliò, *J. Hazard. Mater.*, **186**, 1733 (2011).
20. APHA, *Standard methods for the examination of water and wastewater*, 21 Ed., A. W. W. Association, Ed. Washington D.C., Water Pollution Control Federation, USA (2005).
21. M. A. Zarooni and W. Elshorbagy, *J. Hazard. Mater.*, **136**, 398 (2006).
22. Metcalf & Eddy, *Wastewater engineering: Treatment and reuse*, McGraw-Hill Inc., New York (2003).
23. L. S. Villar and L. A. Escaleira, *Talanta*, **76**, 965 (2008).
24. A. Coelho, V. A. Castro, M. Dezotti and Jr. G. L. Sant' Anna, *J. Hazard. Mater.*, **137**, 178 (2006).
25. L. Chu, J. Wang, J. Dong, H. Liu and X. Sun, *Chemosphere*, **86**, 409 (2012).
26. N. S. S. Martínez, J. F. Fernández, X. F. Segura and A. S. Ferrer, *J. Hazard. Mater.*, **101**, 315 (2003).
27. A. Žgajnar Gotvajn and J. Zagorc-Konèan, *Acta Chim. Slov.*, **52**,

131 (2005).

28. Y. W. Kang and K. Y. Hwang, *Water Res.*, **34**, 2786 (2002).

29. E. G. Solozhenko, N. M. Soboleva and V. V. Goncharuk, *Water Res.*, **29**, 2206 (1995).

30. I. Casero, D. Sicilia, S. Rubio and D. Perez-Bendito, *Water Res.*, **31**, 1985 (1997).

31. E. C. Catalkaya and F. Kargi, *J. Hazard. Mater.*, **139**, 244 (2007).

32. J. Li, Z. Luan, L. Yu and Z. Ji, *Desalination*, **284**, 62 (2012).

33. V. Kavitha and K. Palanivelu, *Water Res.*, **39**, 3062 (2005).

34. E. M. Siedlecka and P. Stepnowski, *Pol. J. Environ. Stud.*, **14**, 823 (2005).

35. C. T. Benatti, C. R. G. Tavares and T. A. Guedes, *J. Environ. Manage.*, **80**, 66 (2006).

36. A. Ghalina, in Department of Robotics and Mechatronics, AGH-University of Science and Technology, Krakow, Poland (2009).

37. M. Y. Nordin, V. C. Venkatesh, S. Sharif, S. Elting and A. Abdullah, *J. Mater. Proc. Technol.*, **145**, 46 (2004).

38. Y. Mansouri, A. A. L. Zinatizadeh, P. Mohammadi, M. Irandoust, A. Akhbari and R. Davoodi, *Korean J. Chem. Eng.*, **29**, 891 (2012).

39. Q. Beg, V. Sahai and R. Gupta, *Process Biochem.*, **39**, 203 (2003).

40. A. Akhbari, A. A. L. Zinatizadeh, P. Mohammadi, M. Irandoust and Y. Mansouri, *Chem. Eng. J.*, **168**, 269 (2011).

41. F. Shahrezaei, Y. Mansouri, A. A. L. Zinatizadeh and A. Akhbari, *Powder Technol.*, **221**, 203 (2012).

42. R. J. Watts, M. D. Udell, P. A. Rauch and S. W. Leung, *Hazard. Waste Hazard. Mater.*, **7**, 335 (1990).

43. Ch. Welling, *Account. Chem. Res.*, **8**, 125 (1975).