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Contributed Paper

Synergistic Catalytic Action of Fe^0, Fe^{2+} and Fe^{3+} in Fenton Reaction for Methyl Orange Decolorization

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ABSTRACT

Fenton and Fenton-like reactions are well known to be a very effective method in the removal of many hazardous organic pollutants. The reactions are activated by the mixtures of hydrogen peroxide (H_2O_2) and catalysts (metal iron; Fe^0, Fe^{2+} and Fe^{3+}) to generate hydroxyl free radical ($OH^{\bullet}$), which is a strong oxidizing agent in the acidic pH range of 2.5 - 3.0. This study aimed to observe a synergistic catalytic action on Fenton and Fenton-like reactions with a combination of catalysts for Methyl Orange decolorization using experimental methodology *via* multilevel factorial design. It was revealed that efficiency of decolorization from a synergistic catalytic action was higher than the reactions with either Fe^0, Fe^{2+} or Fe^{3+} alone on Methyl Orange decolorization. In the mixtures with Fe^0, Fe^{2+}, and H_2O_2 at pH 3 within 10 min, efficiencies of Methyl Orange removal with initial concentration of 75 mg/l were 84 and 99 % when the reaction systems were added with 10 mg/l of each synergistic catalyst and 25 and 50 mg/l of H_2O_2 with the rate of decolorization of 6.69 and 7.47 mg/l/min, respectively.

Keywords: decolorization, Fenton reaction, Fenton-like reaction, Methyl Orange, synergistic catalysis

1. INTRODUCTION

Azo dyes are widely used in textile dying, printing, cosmetic and other processes. The azo dyes are characterized by azo group consisting of two nitrogen atoms with azo bond (-N=N-) and substituted with the stabilized strong electron azo-group. Their biodegradation products after the azo bond breaking down are sulfonated and/or unsulfonated aromatic amines. Azo dyes show their potential of toxic, carcinogenic and mutagenic agents for humans and environments [1-5]. The azo dye contaminated wastewaters were generally treated by chemical, physical and biological methods [6]. The traditional treatments such as activated carbon adsorption, membrane filtration, coagulation/flocculation, electrolysis, and microorganisms were also reported [7]. Advanced Oxidation Processes (AOP's) like Fenton reaction and Fenton-like reaction was used worldwide for azo dye decolorization. The main advantage was the complete destruction of contaminants to harmless compounds, for example, CO_2, water and inorganic salts. Fenton and Fenton-like reactions are oxidation processes which

generate $OH^{\bullet}$ and it can be generated by the inter-reaction of H_2O_2 with iron powder (Fe^0) and/or ferrous (Fe^{2+}) and/or ferric irons (Fe^{3+}) according to Equations 1 - 3 [2, 7-9]. The $OH^{\bullet}$ can attack and initiate the oxidation of organic pollutant molecule (R) by several degradation mechanisms as shown in Equations 4 - 6 [10, 11].

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O \quad (1)$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^- \quad (2)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^{\bullet} + H^+ \quad (3)$$
$$OH^{\bullet} + RH \rightarrow H_2O + R^{\bullet} \quad (4)$$
$$R^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + R^+ \quad (5)$$
$$R^{\bullet} + H_2O_2 \rightarrow ROH + R^+ \quad (6)$$

Several processes of AOP's are being used to decolorize azo dyes. For example, the catalytic and non-catalytic ozonation of Congo Red were investigated and showed high efficiency of color removal with 60-90% of COD reduction [12]. Modified Fenton reactions were catalyzed by zero-valent iron (Fe^0) or ferric iron (Fe^{3+}) and they widely were investigated to degrade many hazardous organic compounds [11]. The modified Fenton reaction using zero-valent iron and H_2O_2 process was used to decolorization of commercial azo dyes, such as Acid Red 18 [13], Reactive Red 120, Direct Blue 160, and Acid Blue 40. [14] The pH optimum for Fenton and modified Fenton reactions for azo dyes decolorization were usually reported in the acidic range (pH 2.5-3.0) [11, 15-17], in particular the decolorization of Methyl Orange using mesoporous Fe_2O_3/SiO_2 at an initial pH 2.93 [18].

Fenton reaction is catalyzed by either ferrous iron or ferric iron or zero-valent iron. They were used to eliminate several types of harmful organic compounds [1, 8, 11]. The objective of this study was to investigate an improvement of decolorization rate by using an interaction of a synergistic catalytic action on Fenton and Fenton-like reactions. The experimental methodology *via* multilevel factorial design was applied to Methyl Orange decolorization with a combination of three levels of metal ions (Fe^0, Fe^{2+} and Fe^{3+}) and two levels of H_2O_2 concentration.

2. MATERIALS AND METHODS

2.1 Reagents

Methyl Orange (Color Index 13025), hydrogen peroxide (H_2O_2 30% w/w) and sulfuric acid (H_2SO_4) were provided by Merck Chemicals International. Iron powder high purity, Iron (II) sulphate heptahydrate ($FeSO_4.7H_2O$) and iron (III) chloride anhydrous ($FeCl_3$) were provided by Fisher Scientific as laboratory reagent. The solutions were prepared by dissolving reagent with distilled water.

2.2 Experimental procedures

The pH level of 1 L aqueous solution of 75 mg/l of Methyl Orange was adjusted to 3.0 using sulfuric acid (H_2SO_4) prior to addition into a 2 L Erlenmeyer flask with controlled temperature at 30°C and stirring by a magnetic stirrer at 250 rpm. Synergistic catalysis action comprised a mixture of Fe^0, Fe^{2+} and Fe^{3+} was added into the Methyl Orange solution with concentrations and formula as shown in Tables 1. After that, H_2O_2 was added to initiate reaction. Samples were taken out from the flask every 5 min for 30 min. As Fenton and Fenton-like reactions were stopped instantaneously by adjusting the reaction mixture to pH 7 before subsequent analysis [19]. All reactions in each treatment were performed in triplicate.

2.3 Analytical methods

The Methyl Orange concentrations were measured by spectrophotometer (Genesys 10UV, Thermo Spectronic, Krackeler Scientific, USA) at l_{464} nm using the respective

molar extinction coefficients of the azo dyes and all data were measured in triplicate [20, 21]. Decolorization rate and decolorization removal (%) were calculated by Equations 7 and 8, respectively.

$$\text{Decolorization rate} = (C_{dye,t} - C_{dye,0}) / (t_0 - t_t) \quad (7)$$

$$\text{Decolorization removal (\%)} = (1 - C_{dye,t} / C_{dye,0}) \times 100\ \% \quad (8)$$

where $C_{dye,0}$ and $C_{dye,t}$ are the initial concentrations of Methyl Orange and the final concentration of Methyl Orange at the reaction time of 10 and 30 min, respectively.

2.4 Experimental design

Multilevel factorial design was used in this study. The main and interaction effects between operational parameters in the Methyl Orange decolorization using Fenton and Fenton-like reactions were investigated. The parameters coded as *A* (Fe^0), *B* (Fe^{2+}), *C* (Fe^{3+}), and *D* (H_2O_2) were designed as indicated by selected factors. The *A*, *B* and *C* were investigated at three levels (3^3) at low (0 mg/l), middle (5 mg/l) and high (10 mg/l). The *D* was investigated at two levels (2^1) at low (5 mg/l) and high (50 mg/l) levels. This factorial design resulted in 54 runs of experiment with all possible combinations of *A*, *B*, *C* and *D*. Design and analysis of factorial experiments were carried out by Statgraphics Centurion version 16.1 program.

3. RESULTS AND DISCUSSION

The experiments were designed using factorial methodology to investigate interaction of mixtures of three catalysts (*A* (Fe^0), *B* (Fe^{2+}), *C* (Fe^{3+})) and *D* (H_2O_2). High rate of decolorization was observed in the first 10 min due to high levels of catalysts and reactants in the systems, after that the rate gradually decreased until it was stable at 30 min. The average actual values from experiments and predicted values from mathematical model (Equation 9) and efficiencies of decolorization at 10 and 30 min were also shown in Table 1. The interaction of the catalysts in which had *p*-value less than 0.05 indicated significant term with 95% confidence level and the Equation 9 was simplified as shown in Equation 10.

$$\text{Decolorization rate} = 2.312 + 0.014A + 0.635B + 0.427C + 0.009D + 0.008A^2 - 0.045AB + 0.050AC + 0.010AD - 0.060B^2 + 0.046BC - 0.001BD - 0.058C^2 - 0.004CD + 0.003AB^2 - 0.0005ABC + \mathbf{0.0019ABD} + 0.0015AC^2 - \mathbf{0.0028ACD} - 0.0024BC^2 + 0.0009BCD \quad (9)$$

$$\text{Decolorization rate} = 2.312 + 0.014A + 0.635B + 0.427C - 0.045AB - 0.060B^2 - 0.059C^2 + \mathbf{0.0019ABD} - \mathbf{0.0028ACD} \quad (10)$$

The rates of Methyl Orange decolorization were used to estimate mathematic equation for the Analysis of Variance (ANOVA). Various statistic data (standard error of estimate, sum of squares of the error, *F* statistic and *p*-value) were examined, as shown in Table 2. Determination of suitability of regression model was important for the data analysis.

The quality of the model was expressed in terms of the R^2 value. The R^2 indicated that the model fitted at 90.12% of the variability in Methyl Orange decolorization. The adjusted R^2 statistic, which was more suitable for comparing models with different numbers of independent variables, was 80.62%. The normal probability plot of the decolorization in the model (Equation 9) was shown in Figure 1. It showed that the distribution of the residuals for the response suitably follows the fitted normal distribution.

Table 1. Experimental design, experimental results and theoretically predicted values for methyl orange decolorization using Fenton and Fenton-like reactions.

Standard order	Fe^0 (mg/l)	Fe^{2+} (mg/l)	Fe^{3+} (mg/l)	H_2O_2 (mg/l)	Decolorization		
					rate (mg/l/min) at the first 10 min	10 min (%)	30 min (%)
1	0	0	0	25	2.591	1.82	10.45
2	5	0	0	25	3.679	23.58	87.43
3	10	0	0	25	5.605	62.09	96.57
4	0	5	0	25	5.082	51.64	88.78
5	5	5	0	25	4.918	48.36	86.30
6	10	5	0	25	5.873	67.46	98.36
7	0	10	0	25	3.619	22.39	81.85
8	5	10	0	25	4.396	37.91	85.85
9	10	10	0	25	6.687	83.73	98.78
10	0	0	5	25	3.530	20.60	59.70
11	5	0	5	25	4.873	47.46	92.39
12	10	0	5	25	6.234	74.69	98.39
13	0	5	5	25	6.330	76.60	90.12
14	5	5	5	25	6.524	80.48	97.07
15	10	5	5	25	7.193	93.85	98.90
16	0	10	5	25	6.203	74.06	82.12
17	5	10	5	25	7.221	94.42	97.70
18	10	10	5	25	7.348	96.96	99.28
19	0	0	10	25	3.008	10.15	18.81
20	5	0	10	25	4.381	37.61	84.78
21	10	0	10	25	7.091	91.82	98.96
22	0	5	10	25	4.455	39.01	60.60
23	5	5	10	25	7.000	90.00	97.13
24	10	5	10	25	7.284	95.67	98.99
25	0	10	10	25	5.485	59.70	69.55
26	5	10	10	25	6.908	88.15	97.49
27	10	10	10	25	7.287	95.73	98.99
28	0	0	0	50	2.858	7.16	8.66
29	5	0	0	50	5.739	64.78	90.87
30	10	0	0	50	7.445	98.90	99.40
31	0	5	0	50	4.097	31.94	40.90
32	5	5	0	50	6.239	74.78	97.22
33	10	5	0	50	7.464	99.28	99.40
34	0	10	0	50	7.406	98.12	98.63
35	5	10	0	50	5.112	52.24	96.84
36	10	10	0	50	7.469	99.37	99.28

Table 1. Continued

Standard order	Fe^0 (mg/l)	Fe^{2+} (mg/l)	Fe^{3+} (mg/l)	H_2O_2 (mg/l)	Decolorization		
					rate (mg/l/min) at the first 10 min	10 min (%)	30 min (%)
37	0	0	5	50	2.843	6.87	11.04
38	5	0	5	50	6.821	86.42	98.72
39	10	0	5	50	7.443	98.87	98.40
40	0	5	5	50	6.370	77.40	82.78
41	5	5	5	50	7.293	95.85	99.19
42	10	5	5	50	7.461	99.22	99.31
43	0	10	5	50	7.372	97.43	97.79
44	5	10	5	50	7.205	94.09	98.57
45	10	10	5	50	7.451	99.01	99.25
46	0	0	10	50	5.440	58.81	82.42
47	5	0	10	50	6.554	81.07	97.88
48	10	0	10	50	7.360	97.19	99.10
49	0	5	10	50	7.443	98.87	99.01
50	5	5	10	50	7.297	95.94	99.28
51	10	5	10	50	7.445	98.90	99.13
52	0	10	10	50	7.418	98.36	99.49
53	5	10	10	50	7.439	98.78	99.25
54	10	10	10	50	7.464	99.28	99.40

Table 2. Analysis of variance for Methyl Orange decolorization rate.

Source	Estimate coefficient	Sum of squares	Df	Mean square	*F*-Ratio	*P*-Value
A:Fe^0	0.1395	2.7431	1	2.7431	6.25	0.0188
B:Fe^{2+}	0.6348	3.7173	1	3.7173	8.47	0.0072
C:Fe^{3+}	0.4274	4.9203	1	4.9203	11.21	0.0024
D:H_2O_2	0.0087	0.2080	1	0.2080	0.47	0.4971
AA	0.0084	$1.3653E^{-05}$	1	0.0000	0.00	0.9956
AB	-0.4471	9.0109	1	9.0109	20.53	0.0001
AC	0.0499	0.7377	1	0.7377	1.68	0.2058
AD	0.0099	0.5733	1	0.5733	1.31	0.2631
BB	-0.0598	3.1873	1	3.1873	7.26	0.0120
BC	0.0464	0.0812	1	0.0812	0.18	0.6706
BD	-0.000975	0.1508	1	0.1508	0.34	0.5626
CC	-0.0586	3.1322	1	3.1322	7.14	0.0126
CD	-0.0040	0.0048	1	0.0048	0.01	0.9173
AAB	0.0000	0.7389	1	0.7389	1.68	0.2055
AAC	0.0000	0.8906	1	0.8906	2.03	0.1658

Table 2. Continued

Source	Estimate coefficient	Sum of squares	Df	Mean square	*F*-Ratio	*P*-Value
AAD	0.0000	0.0469	1	0.0469	0.11	0.7463
ABB	0.0031	1.1821	1	1.1821	2.69	0.1124
ABC	-0.0005	0.0062	1	0.0062	0.01	0.9062
ABD	0.0019	2.1182	1	2.1182	4.83	0.0368
ACC	0.0015	0.2945	1	0.2945	0.67	0.4199
ACD	-0.0028	2.5945	1	2.5945	5.91	0.0220
BBC	0.0000	0.0225	1	0.0225	0.05	0.8225
BBD	0.0000	0.5623	1	0.5623	1.28	0.2677
BCC	-0.0024	0.7137	1	0.7137	1.63	0.2131
BCD	0.0009	0.4678	1	0.4678	1.07	0.3111
CCD	0.0000	1.5020	1	1.5020	3.42	0.0753
Total error		11.8516	27	0.4389		
Total (corr.)		120.0340	53			
Coefficient	2.3118					
R^2 = 90.12%, Adj-R^2 = 80.62%, Standard Error of Est. = 0.6625						

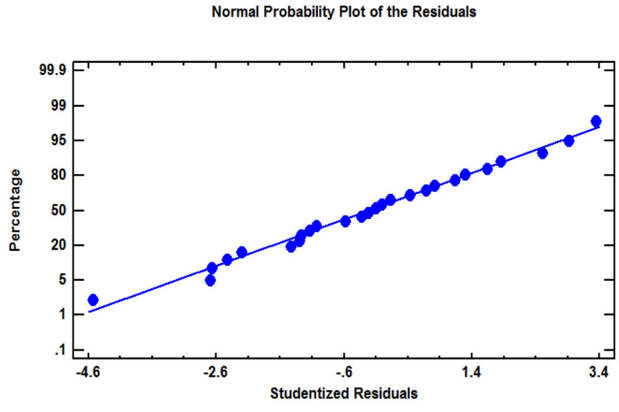

Figure 1. Normal probability plot for Methyl Orange decolorization in the model Equation 9.

From Table 2 in the standard orders of 19, 25, and 27 with 25 mg/l of H_2O_2, Methyl Orange decolorization rates were 3.008, 5.485 and 7.287 mg/l/min while in the standard orders of 46, 52 and 54 with 50 mg/l of H_2O_2, the rates were 5.440, 7.418 and 7.464 mg/l/min, respectively. In mixtures with the three catalysts, rates of decolorization with 25 and 50 mg/l of H_2O_2 were over 7 mg/l/min. It could be noted that H_2O_2 was saved about 50%. The high efficiency of synergistic catalysis could remove Methyl Orange up to 99% within 10 min in the treatment orders of 33, 36, 42, 45, and 54. However, Methyl Orange was decolorized about 40-75% within 10 min when only one catalyst was used in the reaction mixtures. Fenton and Fenton-like reactions using synergistic catalytic action were more efficient than using one catalyst alone [2]. Only an interaction in the mixture of Fe^0,

Fe^{2+} and H_2O_2; *ABD* with p = 0.0368 gave positive to the response but in the mixture of Fe^0, Fe^{3+} and H_2O_2; *ACD* with p = 0.0220 significantly gave negative estimate coefficient at the 95% confidence level. In other words, the addition Fe^0, Fe^{2+} and H_2O_2 into azo dye containing wastewater could increase the decolorization rate. From Table 2 with ANOVA analysis, term of *AB*, however, gave negative estimate coefficient of -0.4471 with p value = 0.0001. Statistically, it is explained that the decolorization can perform well by using low level of *A* with high level of *B* or high level of *A* with low level of *B*. Practically, high rate of decolorization using Fenton and Fenton like reactions without addition of H_2O_2 cannot be occurred. So, in the mixture with high concentration of Fe^0, Fe^{2+} and H_2O_2; *ABD*, the decolorization rate increases. The synergistic catalytic reaction with Fe^0, Fe^{2+} and H_2O_2 generates higher level of $OH^{\bullet}$ than the reactions with either Fe^0, Fe^{2+} or Fe^{3+} alone. The synergistic effects were proved to enhance chemical reactions in a combination of two catalysts (TiO_2 and Fe^{3+}) with UV and H_2O_2 for degradation of phenol, benzoic acid and methanol. The system exhibited higher performance in oxidation over the systems with only one catalyst alone [22]. Moreover, synergistic effects on decolorization, degradation and mineralization were also investigated in ferrioxalate-Fenton/UV-A, ($Fe(C_2O_4)_3^{3-}/H_2O_2$/UV-A) and UV photo Fenton like oxidation ($UV/H_2O_2/Fe^{3+}$) [23, 24]

Oxidation by H_2O_2 alone is not very effective for Methyl Orange decolorization and the p-value of H_2O_2 alone was not significant with 0.4971 at 95% confidence level. In the treatment orders of 1 and 28, rates of decolorization with 25 and 50 mg/l of H_2O_2 alone were insignificantly different (2.591 and 2.858 mg/l/min). In fact, H_2O_2 plays an important co-chemical reagent in Fenton and Fenton like reactions, it needs to react with either Fe^0 or Fe^{2+} or Fe^{3+} to obtain high efficiency of decolorization. The systems with H_2O_2 and either valent iron (Fe^0 or Fe^{2+} or Fe^{3+}) could generate $OH^{\bullet}$ according to the Equations 1 - 3 and they were able to react with azo bonds [16, 25]. The increasing concentration of H_2O_2 increased $OH^{\bullet}$.

Table 3. Decolorization of azo dyes using Advanced Oxidation Processes (AOP's) - studies reported.

Dyes	Types of AOP's	Reaction Time (min)	pH	Decolorization (%)	References
Methyl orange (25.5 mg/l)	UV/H_2O_2	3	3.5	100	[29]
Methyl orange (200 mg/l)	Mesoporous Fe_2O_3/SiO_2	20	2.93	≥ 90	[18]
Methyl orange (100 mg/l)	Microwave assisted with Fenton catalytic	5	3.0	98.7	[30]
Methyl orange (20 mg/l)	Mesoporous TiO_2/UV	45	2.0	98	[31]
Methyl orange (75 mg/l)	Synergistic catalyst/ H_2O_2	10	3.0	99	This study
Reactive black 5 (100 mg/l)	Fe^{2+}/H_2O_2 Fe^{3+}/H_2O_2	480 480	2.5	99.8 99.5	[15]

Table 3. Continued

Dyes	Types of AOP's	Reaction Time (min)	pH	Decolorization (%)	References
Reactive black 5 (50 mg/l) Reactive blue 13 (50 mg/l) Acid orange 7 (50 mg/l)	Fe^{2+}/H_2O_2	30	3.0	95	[3]
Acid red 18 (100mg/l)	Fe^{0}/H_2O_2	15	3.0	99.9	[13]
Amido black 10B (50 mg/l)	Fe^{2+}/H_2O_2	60	3.5	99.25	[26]

Fenton oxidation process was widely used to degrade and decolorize the synthetic dyes such as Amido Black 10B [26], Basic Blue 41[27], Reactive Black 5 (RB5), Reactive Blue (RB13), Acid Orange [3] and Black Liquor [28]. Amido Black 10B with concentration of 50 mg/l was completely degraded using Fenton oxidation process within 60 min in the presence of 17 mg/l of H_2O_2 and 3.8 mg/l of Fe^{2+} [26]. Investigation of Methyl Orange decolorization using AOP's was represented in Table 3 such as UV/H_2O_2, mesoporous Fe_2O_3/SiO_2, microwave assisted with Fenton catalytic and mesoporous TiO_2/UV. In addition, pH and types of AOP's were important factors to cleavage the azo bonds. To sum up, synergic effect using a combination of catalysts could increase rate of chemical reaction [15].

CONCLUSIONS

This study demonstrated high efficiency of Methyl Orange decolorization using the synergistic catalytic actions using Fenton and Fenton-like reactions with the application of the experimental design *via* multilevel factorial design. From the analysis, the positive interaction effects in the mixture with Fe^0, Fe^{2+} and H_2O_2 increased the rate of decolorization within 10 min.

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