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## Article

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## Investigation of important parameters for Photo-Fenton degradation of methyl orange over Fe/TiO<sub>2</sub> catalyst

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### Abstract

Methyl orange (MO) is an intensely colored compound used in dyeing and printing textile, which contaminates the effluent. Photo-Fenton reaction is one of the advanced oxidation processes (AOPs) which can treat the pollutant to the green products and small molecules. Photo-Fenton process using Fe/TiO<sub>2</sub> catalyst was applied to decolorization of methyl orange. The Fe/TiO<sub>2</sub> catalyst was prepared by using dry impregnation method. Plackett–Burman Full Factorial was applied to identify the significant parameters in methyl orange decolorization. Six factors (i.e. Fe/TiO<sub>2</sub> catalyst concentration, initial H<sub>2</sub>O<sub>2</sub> concentration, initial MO concentration, pH, stirring speed, and light intensity) influencing methyl orange decolorization were investigated. The results showed that the regression model for parameter screening was well-fitted with the experiment data, supported by the high R<sup>2</sup> of 0.95. The results also showed that Fe/TiO<sub>2</sub> catalyst dosage, H<sub>2</sub>O<sub>2</sub> concentration, initial MO concentration, stirring speed, and light intensity were the significant effects ( $P < 0.05$ ) rather than pH. The assumption means a lot in engineering design involving with the confounding multifactor. It could be seen from the conclusion that Plackett–Burman Full Factorial is a suitable tool for screening a large number of parameters, when the complicating interactions of these parameters are involved. Therefore, the key parameters can be found and properly engineered; thus warranting the treatment efficiency and minimizing the cost.

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**Keywords:** Photo-Fenton process; Methyl orange; Fe/TiO<sub>2</sub> catalyst; Plackett–Burman Full Factorial Design

### 1. Introduction

Methyl orange (MO) is an intensely colored compound used in dyeing and printing textile, which is non-degradable, toxic, and carcinogenic. Therefore, MO contaminated in wastewater must be worried and should be treated before being discharged into the environment. The difference wastewater treatment such as physical, chemical, and biological treatments have been applied to the synthetic dyed wastewater. However, chemical

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oxidation method is considered as promising technology because of result in complete degradation of organic pollutants. It is effective for a wide range of organics and environment-friendly.

Advanced oxidation processes (AOPs) is one of chemical methods which can treat the pollutant to green products and small molecules. Fenton oxidation reaction is one of AOPs which can effectively eliminate the organic compounds in wastewater since it is a strong oxidation potential at the mild reaction conditions and easy to operate. However, light irradiation can help improve the catalytic activity of the system. Photo-Fenton reaction, the hydroxyl radical generated using  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$  system is an important process. The ferrous ions are dissolved in water which was used as a catalyst in  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$  system [1]. This system is called “homogeneous photo-Fenton process”. However, homogeneous Photo-Fenton process has some disadvantages. The separation and reuse of iron ions after the reaction are rather difficult. Thus, heterogeneous catalyst used in Photo-Fenton process was interesting because it is easier to separate after the reaction than the homogeneous catalyst. In addition, a process by which titanium dioxide ( $\text{TiO}_2$ ) is arranged as photocatalyst is one of AOPs commonly used in environmental remediation of water and air. Also, it is possible to use the energy from the light source in the Photo-Fenton process.  $\text{TiO}_2$  has been commonly applied as a photocatalyst in a variety of applications because of its low toxicity, high photoactivity, chemical stability, self-cleaning ability, narrow band gap, and low cost. The adsorption and photocatalytic reaction constitute the main mechanisms of reaction in the photocatalytic process. Thus,  $\text{TiO}_2$  is a catalyst supported to increase the adsorption rate which is beneficial to the overall photocatalytic process [2].

Therefore, scanning experiments were used aiming to classify the significant parameters that provide large impacts on the response. Plackett–Burman is one of the full factorial designs that is usually employed to assess the relative importance of the investigative factors, in which there are no interaction effects between the different effective parameters in the range of consideration, and each parameter is established at both high and low levels [3]. In this condition, one or two relative important parameters are identified. Nevertheless, this was rarely studied before. Therefore, in this research, we used Plackett–Burman Full Factorial Design to screen the parameters affecting the efficiency of the Photo-Fenton oxidation reaction. In the Photo-Fenton oxidation reaction, many parameters affect the organic removal efficiency including light intensity, pH, initial concentration of the sample, catalyst loading, hydrogen peroxide, and stirring speed [4,5]. These factors were optimized to increase the organic removal efficiency.

In this research, Photo-Fenton oxidation reaction was applied to determine the degradation of the azo dye methyl orange in experimental wastewater using  $\text{Fe}/\text{TiO}_2$  catalyst under the selected reaction conditions of  $\text{Fe}/\text{TiO}_2$  dosage, MO concentration, hydrogen peroxide concentration, pH, light intensity, and stirring speed. Plackett–Burman Full Factorial was applied to screen the important parameters

## 2. Experimental

### 2.1. Preparation of $\text{Fe}/\text{TiO}_2$ catalyst

$\text{Fe}/\text{TiO}_2$  catalyst was prepared by dry impregnation method. For preparation of  $\text{Fe}/\text{TiO}_2$  catalyst, 10%wt of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution was dropped into  $\text{TiO}_2$  (P-25). After that, the sample was dried at 100 °C for 12 h and calcined under the nitrogen atmosphere at 400 °C for 5 h (the heating rate was set to 2 °C/min). The crystal phase of  $\text{Fe}/\text{TiO}_2$  catalyst was studied by X-ray diffraction. X-ray diffraction was examined by a Bruker Advanced D8 Instrument coupled with  $\text{Cu-K}\alpha$  radiation at the room temperature.

### 2.2. Important-parameter screening designs

The Plackett–Burman Full Factorial Design (FFD) was applied to study the effects of the parameters on MO degradation using Photo-Fenton oxidation reaction over  $\text{Fe}/\text{TiO}_2$  catalyst. Two levels Plackett–Burman FFD with six parameters were applied to screen the important parameters for MO degradation. Six parameters were  $\text{Fe}/\text{TiO}_2$  catalyst dosage (300–500 ppm:  $X_1$ ),  $\text{H}_2\text{O}_2$  concentration (60–200 ppm:  $X_2$ ), initial MO concentration (200–250 ppm:  $X_3$ ), pH (3–7:  $X_4$ ), stirring speed (250–500 rpm:  $X_5$ ), and light intensity (54–108w:  $X_6$ ). The statistical analysis of each parameters at 95% significance level were estimated using the MINITAB software (version 16.0, Minitab Inc., State College, PA). These parameters were screened to estimate the effects of percent MO degradation which was identified as the response (Y, %) and can be calculated follow Eq. (1);

$$Y = \frac{(C_0 - C_i)}{C_0} \times 100\% \quad (1)$$

where  $C_0$  and  $C_i$  are the initial MO concentration and the MO concentration at a certain time, respectively. The experimental was run 2 replications, which was obtained 24 experimental runs as shown in Table 1.

**Table 1.** Plackett–Burman design for screening of Photo-Fenton oxidation reaction parameters.

Run order	Fe/TiO <sub>2</sub> concentration (ppm)	H <sub>2</sub> O <sub>2</sub> concentration (ppm)	Initial MO concentration (ppm)	pH	Stirring (rpm)	Light intensive (w)	%MO degradation
1	300	200	250	3	500	54	79.4
2	300	200	250	3	500	54	79.4
3	300	200	250	7	250	108	85.4
4	300	60	200	7	500	108	80.33
5	500	60	200	3	500	108	78.54
6	300	60	200	3	250	54	65.25
7	300	60	250	7	500	54	68.68
8	500	60	250	7	250	108	62.84
9	500	200	250	3	500	108	84.14
10	300	200	250	7	250	108	85.4
11	300	60	250	7	500	54	70.33
12	300	60	200	3	250	54	66.25
13	500	200	200	7	250	54	78.54
14	500	200	200	7	250	54	78.54
15	500	60	250	3	250	54	60.54
16	300	200	200	3	250	108	84.63
17	300	60	200	7	500	108	84.4
18	500	60	200	3	500	108	69.25
19	500	60	250	7	250	108	62.84
20	300	200	200	3	250	108	84.63
21	500	200	200	7	500	54	85.16
22	500	200	250	3	500	108	91.29
23	500	60	250	3	250	54	60.54
24	500	200	200	7	500	54	85.16

### 2.3. Photo-Fenton reaction experiment

The stock MO solutions containing 200 and 250 ppm were prepared. The Photo-Fenton oxidation reaction was tested in photo-box with 6 UV lamp 18 W. The Photo-Fenton oxidation reaction was run 20 min for each batch at the room temperature. The sample was kept and analyzed by UV–Vis spectrophotometer (Agilent 8453) at the wavelength of 465 nm

## 3. Results and discussion

### 3.1. Characterization of Fe/TiO<sub>2</sub> catalyst

Fe/TiO<sub>2</sub> catalyst was characterized by X-ray diffractometer to determine the degree of crystallinity and identify the metal ions, Fe(III), doped on TiO<sub>2</sub>. X-ray diffraction pattern of Fe/TiO<sub>2</sub> are shown in Fig. 1. Fig. 1(a) shows the X-ray diffraction pattern of TiO<sub>2</sub> (p-25) with 3 major peaks at  $2\theta = 25^\circ$ ,  $38^\circ$ ,  $48^\circ$ ,  $54^\circ$ ,  $55^\circ$ ,  $69^\circ$ , and  $70^\circ$  with  $d = 3.53$ , and  $3.91$  Å as a peak of anatase TiO<sub>2</sub> phase in accordance with anatase standard JCPDS (12–1276) at  $d = 3.520$  Å. Fig. 1(b) shows the X-ray diffraction pattern of Fe/TiO<sub>2</sub> catalyst indicating that Fe metal ions have been immobilized on the surface of TiO<sub>2</sub>.

### 3.2. Parameter screening

Fe/TiO<sub>2</sub> catalyst was selected to be used in Photo-Fenton oxidation reaction of MO degradation. It was found that a lot of parameters affecting the efficiency of the Photo-Fenton oxidation reaction are Fe/TiO<sub>2</sub> catalyst dosage, H<sub>2</sub>O<sub>2</sub> concentration, initial MO concentration, pH, stirring speed, and light intensity. The two-level Plackett–Burman FFD with six parameters and total of 24 experimental runs were carried out as shown in Table 1. The response

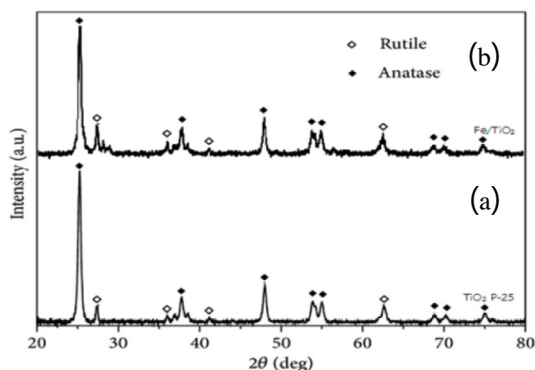


Fig. 1. XRD pattern of Fe/TiO<sub>2</sub> catalyst.

was chosen as the percentage of MO degradation. The response was found to range from 60.54 to 91.29% and the significant effect of each parameters on Y, % was estimated by normal probability plot of standardize effects, a pareto chart, main effect at 95% significance level using Minitab Version 17.0 Software.

Fig. 2 shows a normality plot of effect which was generated from the main effects of parameters. The results showed that are Fe/TiO<sub>2</sub> catalyst dosage, H<sub>2</sub>O<sub>2</sub> concentration, initial MO concentration, stirring speed, and light intensity are significant. It indicates that the standardized effect plots are placed far away from the straight line and have a non-zero mean.

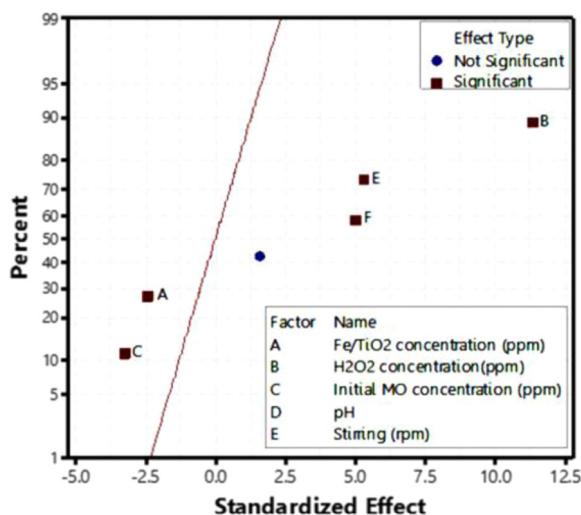


Fig. 2. Normal probability plot of standardized effect.

The pareto chart of effects as shown in Fig. 3 is applied to identify the important parameters. The estimated main effects were ranked according to their significance at P-value = 0.05 and showed that the most important effect was H<sub>2</sub>O<sub>2</sub> concentration, stirring speed, light intensity, initial MO concentration and Fe/TiO<sub>2</sub> catalyst dosage, respectively.

Fig. 4 shows the main effect plot describes the trend of all effects. Increase in H<sub>2</sub>O<sub>2</sub> concentration, stirring speed, and light intensity lead to increase in percent of MO degradation. The result was similar to Zhu et al. [6], which reported that the photo-generated electrons on the conduction band of TiO<sub>2</sub> could transfer to the surface of catalyst, which could inhibit the recombination of electron–hole pairs, leading to more efficient usage of holes on TiO<sub>2</sub>, and could accelerate the reduction of Fe(III) to Fe(II) on the surface, producing more efficient decomposition of H<sub>2</sub>O<sub>2</sub> and production of •OH. Additionally, OH<sup>−</sup> and H<sub>2</sub>O can be oxidized to •OH due to the lower redox potential of •OH/H<sub>2</sub>O (2.27 V vs. NHE) [7]. In addition, the conduction band of TiO<sub>2</sub> is more negative than the O<sub>2</sub>/O<sub>2</sub><sup>−</sup>

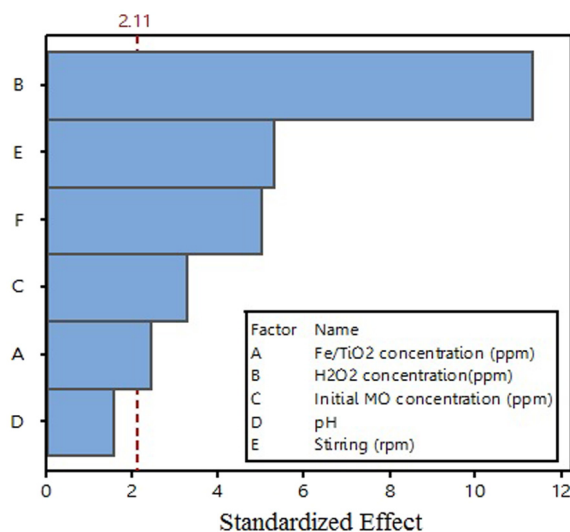


Fig. 3. Pareto chart for the main parameters effect.

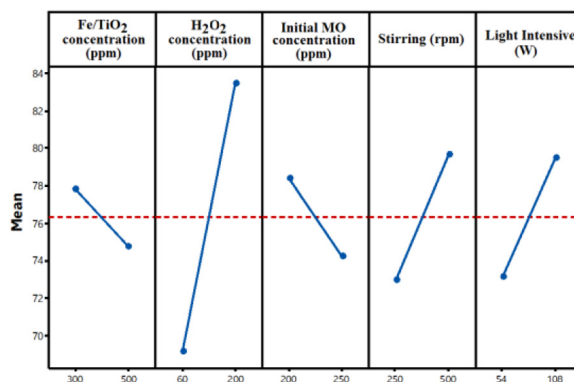


Fig. 4. Plot of main effect for % of MO degradation.

potential ( $-0.046$  V vs. NHE) [8], indicating that the photo-generated electrons can react with  $O_2$  to form  $O_2^-$  in the heterogeneous Fenton reaction. Both the  $\bullet OH$  and  $O_2^-$  could take part in the degradation of MO. As a result, the efficiency of MO degradation by Fe/TiO<sub>2</sub> catalyst can be enhanced over Fe<sup>2+</sup> (the conventional heterogeneous Fenton catalyst) and TiO<sub>2</sub> (the conventional semiconductor).

#### 4. Conclusion

MO was degraded by Photo-Fenton oxidation reaction using Fe/TiO<sub>2</sub> catalyst. It was found that a lot of parameters affecting the efficiency of the Photo-Fenton oxidation reaction are Fe/TiO<sub>2</sub> catalyst dosage, H<sub>2</sub>O<sub>2</sub> concentration, initial MO concentration, pH, stirring speed, and light intensity. Thus, two levels Plackett–Burman FFD was applied to screen the important parameters for MO degradation. The results showed that Fe/TiO<sub>2</sub> catalyst dosage, H<sub>2</sub>O<sub>2</sub> concentration, initial MO concentration, stirring speed, and light intensity are significant effects on MO degradation. The effects of parameter ranked were found that H<sub>2</sub>O<sub>2</sub> concentration and light intensity were the important parameters on MO degradation using Fe/TiO<sub>2</sub> catalyst since TiO<sub>2</sub> needs the energy to activate electron for produce the oxidizing agent. Thus, Plackett–Burman Full Factorial is a suitable tool for screening many parameters, when complicated interactions of these parameters are involved. Therefore, the key parameters can be found and properly engineered; thus the treatment efficiency is warranted, and the cost is minimized.

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