

Degradation of methylene blue: Optimization of operating condition through a statistical technique and environmental estimate of the treated wastewater

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Abstract

FeO_x-MoO₃-P₂O₅ ($x = 1$ or 1.5) composite catalyst was prepared by solid reaction method and characterized by X-ray diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). Its catalytic activities on degradation of a heteropolyaromatic dye, methylene blue (MB), were also investigated under mild condition. In order to determine the optimum operating condition, the orthogonal experiments were devised. And the results revealed that initial concentration of MB was the key factor that affected the decoloration, while the catalysts dose has an insignificant effect. Environmental estimation was also done and the results showed that the treated wastewater have little influence on plant growth and could totally be applied to irrigation.

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1. Introduction

Nowadays the textile processing industries are available in developing countries, so large volume of wastewater generated from the textile processing industries contains suspended solids, un-reacted dyestuffs (color) and other auxiliary chemicals. Even small amount of dye in water (example $10\text{--}20\text{ mg L}^{-1}$) is highly visible, the water transparency and the gas solubility of water bodies are affected as well [1]. In addition, some dyes can be considered carcinogens or mutagens [2] and they may also contain various heavy metals that breach environmental standards.

Many studies have been carried out on the treatment of wastewater, including biological treatment [3], wet oxidation [4], ozone treatment [5] and chemical coagulation [6]. However, in the biological processes, the lignin and its derivatives show high stability to degradation [7] and the inhibition potential of phenolics and the presence of other organic and inorganic is a major drawback of the process [8]. Wet oxidation (catalytic and non-catalytic) has been found to reduce COD in a large extent.

However, the energy requirement and the use of high-pressure reactors and associated equipment make the wet air oxidation of large volume of wastewater unviable and uneconomical [9]. Hence, it is necessary to made attempts to find a new kind of catalyst which works not only under mild condition but also less of consumption.

Composite catalyst has attracted many researchers' attention, because synergetic effect was induced by a strong interphase interaction between the support and the supported materials, such as, the iron oxide carbon composite catalyst (Fe-C) used in catalytic debromination process [10]; multi-walled carbon nanotubes-TiO₂ composite catalysts [11] applied in visible light photodegradation of phenol; Mn-Ce-O composite catalyst showed high activity in terms of total oxidation of EG as well as total organic carbon reductions (up to 99.3%) [12]. Al-Zn composite catalyst on the degradation of Poly vinyl chloride-containing polymer mixtures [13]; raschig rings-Fe₂O₃ composite catalyst for degradation of 4-chlorophenol and Orange II under daylight irradiation [14]; Fe₂O₃-CeO₂-TiO₂/g-Al₂O₃ composite catalyst for degradation of methyl orange azo dye [15]. The high activity and versatility of the composite catalyst make them very promising candidates as potential industrial

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catalysts. While no mixed-valent composite catalyst has been studied in catalytic process.

For the degradation experiments, many factors affect the degradation efficiency, such pH, the concentration of wastewater, scavenging agents, anions, catalyst dosage and reaction temperature, etc. To optimize design of an existing process, it is necessary to identify which factors have the greatest influence and which values produce the most consistent performance. Experimenting with design variables – one at a time or by trial and error – until a first feasible design is found is a common approach to process optimization. However, this approach can lead to a very long and expensive time span for completing the design process. A technique for laying out the experiments when multiple factors are involved is popularly known as the factorial design of experiments. This method helps researchers to determine possible combinations of factors and to identify the best combination. Since it is extremely costly to run a number of experiments to test all combinations, application of a full factorial design of experiments is restricted when many factors and levels are studied. A commonly applied statistical method, Taguchi experimental design [16–18] and analysis of variance (ANOVA), where only a fraction of the combination of variables were considered, but covered a wide range of operating conditions; it was appropriate for this optimization problem, can be used to analyze results of the experiments on the response and to determine how much variation quality influencing factors contribute. A significant amount of research has been conducted on experiments for identifying the optimum operation condition using the Taguchi method and the orthogonal experiment design. Lin et al. employed orthogonal collocation method to solve the kinetic model [19]. Jian et al. [20] studied on separation of polyethyleneglycol by orthogonal array of the design of experiments.

In this paper, mixed-valent $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ ($x=1$ or 1.5) composite catalyst was prepared by a solid reaction, and this catalyst shows a high activity to decolor MB under mild condition. To find the optimum operation condition, effects of four operating parameters (pH, the initial concentration of methylene blue, the amount of catalysts and temperature) were studied using Taguchi experimental design [16–18]. Another objective is to test the effect of treated wastewater on environment.

2. Experimental

2.1. Materials

All chemicals used in the experiment were analytically grade and used without further purification.

Certain concentration of MB represented the dyes.

2.2. Preparation of catalyst

The catalyst $\text{Fe}_2\text{O}_3\text{-MoO}_3\text{-P}_2\text{O}_5$ was prepared by a solid reaction. $\text{Fe}(\text{OH})_3$, $(\text{NH}_4)_3\text{H}_4[\text{P}(\text{Mo}_2\text{O}_7)_6]\cdot 0.5\text{H}_2\text{O}$ were mixed in relevant proportions. After careful grinding, the mixture was put into a crucible and heated at 300°C for 6 h under air atmosphere. This treatment resulted in decomposition of ammonium

molybdophosphate and $\text{Fe}(\text{OH})_3$. And then this compound was calcined at 650°C for 4 h to obtain $\text{Fe}_2\text{O}_3\text{-MoO}_3\text{-P}_2\text{O}_5$ catalyst.

$\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ ($x=1$ or 1.5) was also prepared by a solid reaction using $\text{Fe}(\text{OH})_3$, $(\text{NH}_4)_3\text{H}_4[\text{P}(\text{Mo}_2\text{O}_7)_6]\cdot 0.5\text{H}_2\text{O}$ and starch. Appropriate amounts of each reagent were used to obtain (starch)/ $(\text{Fe}(\text{OH})_3 + (\text{NH}_4)_3\text{H}_4[\text{P}(\text{Mo}_2\text{O}_7)_6]\cdot 0.5\text{H}_2\text{O})$ weight ratio of 4% and 25%, respectively, in the raw stuff. Starch served as reductant, and Fe^{3+} in the $\text{Fe}(\text{OH})_3$ was reduced to Fe^{2+} in the calcination process. The others step was the same as $\text{Fe}_2\text{O}_3\text{-MoO}_3\text{-P}_2\text{O}_5$.

2.3. Analytical method

Five cubic centimeter samples were taken at regular intervals without addition of fresh liquid, and then were filtrated to the UV–vis detection. The maximum absorbency visible wavelength was detected and used as color removal index. Color removal ratio was calculated as follows:

$$R_{\text{color}}(\%) = \frac{\text{Abs}_0^{\lambda_{\text{max}}} - \text{Abs}^{\lambda_{\text{max}}}}{\text{Abs}_0^{\lambda_{\text{max}}}} \times 100\% \quad (1)$$

Where, $\text{Abs}^{\lambda_{\text{max}}}$ was the maximum value of absorbency at the maximum absorbency visible wavelength, $\text{Abs}_0^{\lambda_{\text{max}}}$ was the absorbency of the initial solution. Color was analyzed by a double beam UV–vis spectrophotometer (UV-7504, China). The chemical oxygen demand (COD) was chosen as the parameter by which to evaluate the process of oxidation and was determined according to standard methods [21]. The pH of the solution was measured using an Orion 290 pH meter. X-ray diffraction (XRD) measurements of the catalyst powder were recorded using D/Max-3c (Janpan Rigalcu) diffractometer equipped with Ni filtered Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Bragg's angles between 20° and 30° were collected at a rate of 1° min^{-1} . X-ray photoelectron spectroscopy (XPS) was carried out to analyze chemical state of surface elements for the catalysts. PHI ESCA 5700 instrument, with a Al $K\alpha$ X-ray source (1486.6 eV) and pass energy of 29.5 eV operating at a pressure of 9.33×10^{-11} kPa, was used. An IR spectrometer, model IR Eouinx55 (Germany) was used for sample IR spectrometer analysis. Total organic carbon (TOC) and total inorganic carbon (TIC) analysis was carried out by means of a Shimadzu TOC-5000A total organic carbon analyzer.

2.4. Degradation of methylene blue

The degradation of methylene blue synthetic wastewater was performed in a glass reactor with a capacity of 150 ml equipped with a magnetic stirrer and a heat-exchanger. The reaction was conducted at 25, 30, 35 and 40°C and atmospheric pressure for 30 min. After the degradation reaction, the wastewater was drained to get the used catalysts.

2.5. Environmental estimate

The experiment of environmental estimate of treated wastewater was conducted in laboratory, in a climate controlled model greenhouse with a heating system and an evaporative cooling

system. The set point minimum and maximum temperatures in the greenhouse were 15 and 20 °C. The minimum day and maximum night relative humidities were 60% and 90%, respectively. The plants were planted 2 cm apart and the irrigation was supplied once a day at 8:00 a.m. Samples were collected sixth per 2 h a day from 8:00 a.m. to 18:00 p.m., including the soil and leaf blade. The amount of chlorophyll a and b were determined by a spectrophotometer at wavelengths of 645 and 663 nm, according to Mackinney's equation [22].

3. Results and discussion

3.1. Properties of catalyst

3.1.1. X-ray diffraction

Fig. 1 shows XRD spectra for $\text{Fe}_2\text{O}_3\text{-MoO}_3\text{-P}_2\text{O}_5$ (0% starch) and $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ ($x = 1$ or 1.5) and (25% starch). It can also be seen from Fig. 1 that the line width slightly increased with an increasing of starch dose.

The size of the crystallites can also be estimated with the help of Scherrer equation:

$$D = \frac{0.941\lambda}{\beta \cos \theta} \quad (2)$$

where D is the average grain size, λ is the X-ray wavelength (0.15406 nm), θ and β are the diffraction angles and full-width at half-maximum (FWHM, in radian) of an observed peak, respectively [23]. The calculated average particle sizes (D) were found to be 93.26 nm for as synthesized with 0% starch dose and 25.396 nm with 25% starch dose. Thus, the crystal size becomes smaller with increasing of starch dose, which were consisted with the theory that the grain size decreased with the line width increasing.

3.1.2. XPS

The XPS analysis mainly reflects the component and chemical elementary state of the surface and the inferior surface of

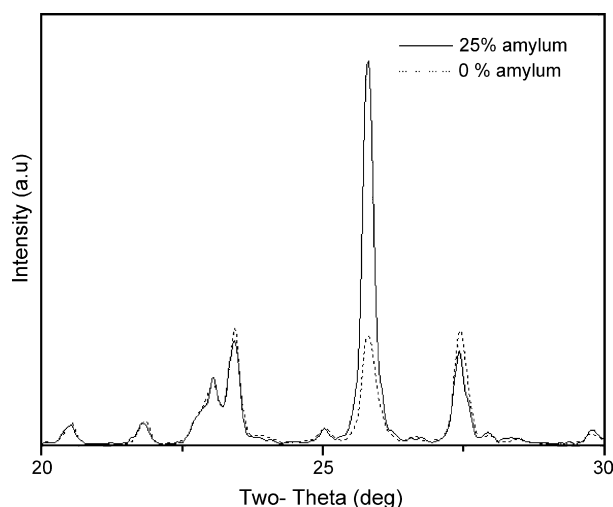


Fig. 1. XRD patterns of $\text{Fe}_2\text{O}_3\text{-MoO}_3\text{-P}_2\text{O}_5$ (0% starch) and $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ ($x = 1$ or 1.5) and (25% starch).

samples. $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ (25% starch) catalyst power (before and after reaction) were dried in vacuo and tested by XPS. Fe 2p peak (Fig. 2a before reaction) has been deconvoluted to two different valent components (Fe^{3+} and Fe^{2+}) and the ratio of two atoms was 73.89:26.11 (molar ratio), indicating that iron was the mixture of Fe^{2+} and Fe^{3+} before reaction. Compared to that Fe^{3+} occupied 100% in the raw material, indicating Fe^{3+} was partly reduced to Fe^{2+} due to starch's deoxidizing in calcination process. After reaction the ratio of $\text{Fe}^{3+}:\text{Fe}^{2+}$ (49.60:50.40) (Fig. 2b) was different from that of before reaction, indicating that $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ (25% starch) has good catalytic activity, thus also illustrating that Fe^{3+} or Fe^{2+} occupied a half, respectively in catalytic cycle processing.

3.2. Degradation of methylene blue

In order to enhance the catalytic performance, different mass starch was added into the raw material that was precursors of $\text{Fe}_2\text{O}_3\text{-MoO}_3\text{-P}_2\text{O}_5$ to obtain $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ ($x = 1$ or 1.5). Activities of these catalysts were exhibited in Fig. 3. The presence of starch in the raw material led to an amazing increase in catalytic activity. The catalytic activity followed the decreasing order of 25% > 4% > 0%. The reaction time for the 98% of decoloration and 85% of COD removal was as short as about 30 min for 25 wt.% starch addition, while the decomposition percent was 84% for 4% starch within the same time and 45.47% for 0% starch. It can be concluded that an appropriate amount of starch introduced into the raw material well contributing to degradation, which was maybe due to the existence of Fe^{2+} species: Fe^{2+} accounted for 26.11% in the whole ion species for 25 wt.% starch in $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ ($x = 1$ or 1.5), while no Fe^{2+} was detected in 0% starch $\text{Fe}_2\text{O}_3\text{-MoO}_3\text{-P}_2\text{O}_5$. This result maybe indicates that Fe^{2+} was favor of the initiation stage of catalytic cycle.

It can be seen from Fig. 4 that two major absorbance peaks of methylene blue can be seen at 291 and 663 nm, due to benzene ring and heteropolyaromatic linkage. These two absorbance peaks became weaker and weaker in intensity as the treatment time prolong. After 30 min, these two peaks almost totally disappeared, which indicated the benzene ring and heteropolyaromatic linkage of methylene blue were almost destroyed.

The IR spectra in the region 2000–500 cm^{-1} of methylene blue before and after treatment shows in Fig. 5. Characteristic infrared absorption peaks of MB [24,25] were at 1600 cm^{-1} (ring stretch), 1390 cm^{-1} (C=N) and 1335 cm^{-1} ($-\text{CH}_3$ symmetric deformation). The disappearance of these peaks after treatment for 30 min indicated the total destruction of the aromatic part of a dye molecule, C=N bond in heteropolyaromatic linkage and $-\text{CH}_3$ structure. The disappearance of peaks between 1030 and 1230 cm^{-1} indicated the total destruction of C–N.

Moreover, the appearance of two new peaks at 1638, 1388 cm^{-1} , due to asymmetric stretching of N=O bond, N–O stretching vibration and N–H bonding vibration, respectively, indicated the production of intermediates in the degradation process and more aliphatic and inorganic species were produced.

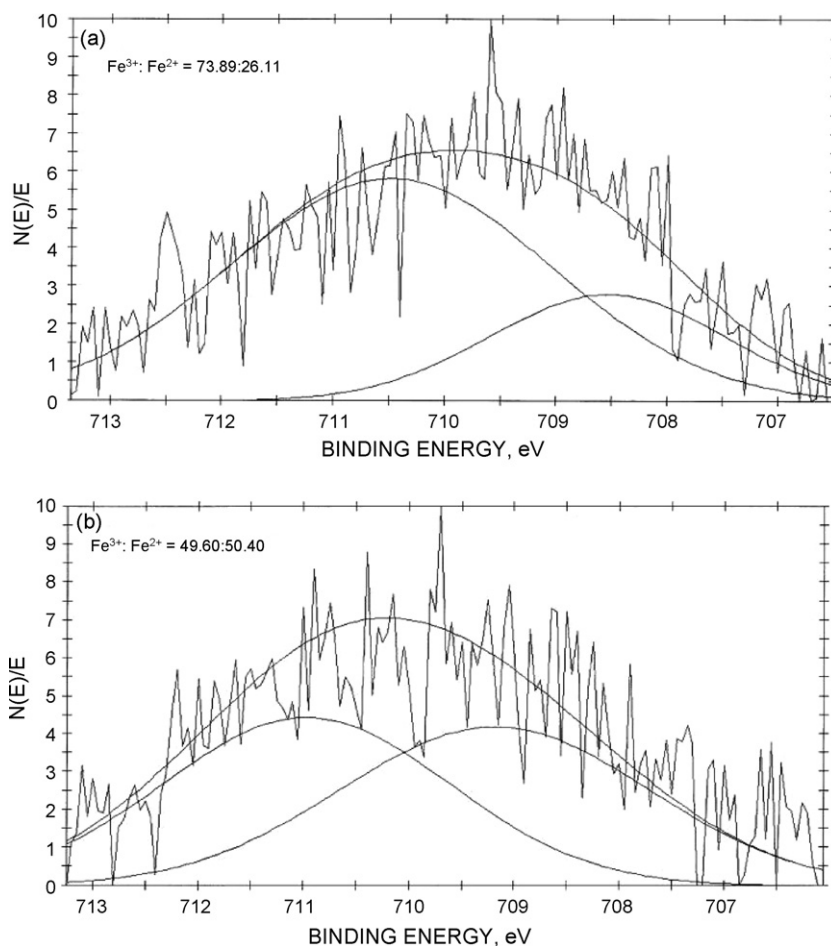


Fig. 2. XPS of Fe 2p in FeO_x-MoO₃-P₂O₅ (25% starch) before (a) and after (b) reaction.

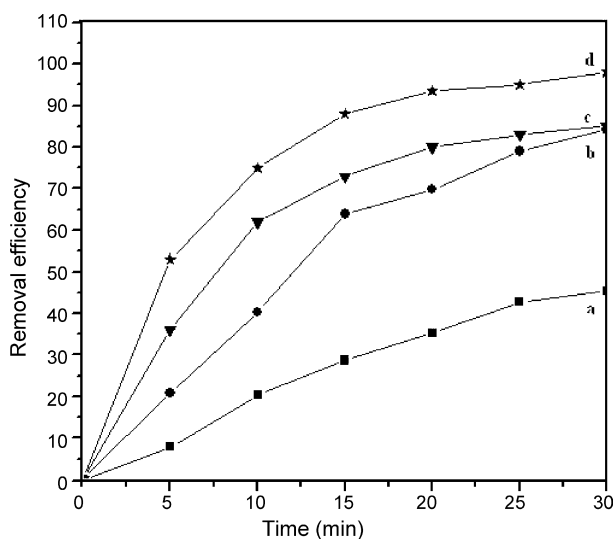


Fig. 3. Removal efficiency of 0.3 g L⁻¹ of MB with different catalyst (a) decolorization with Fe₂O₃-MoO₃-P₂O₅ (0% starch); (b) decolorization efficiency with FeO_x-MoO₃-P₂O₅ (4% starch); (c) COD removal efficiency with FeO_x-MoO₃-P₂O₅ (25% starch); (d) decolorization efficiency with FeO_x-MoO₃-P₂O₅ (25% starch).

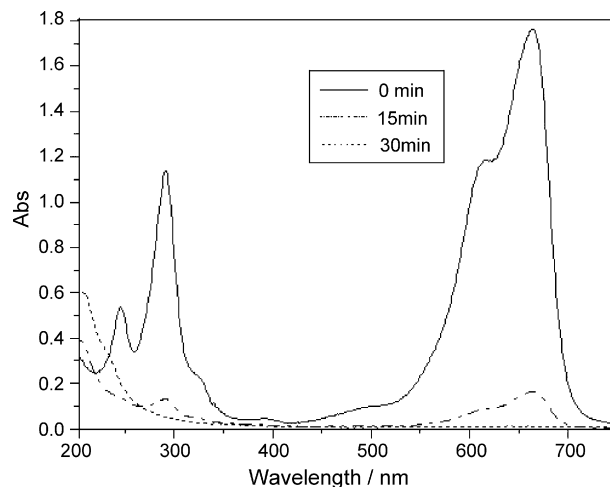


Fig. 4. UV-vis spectra of MB with different time.

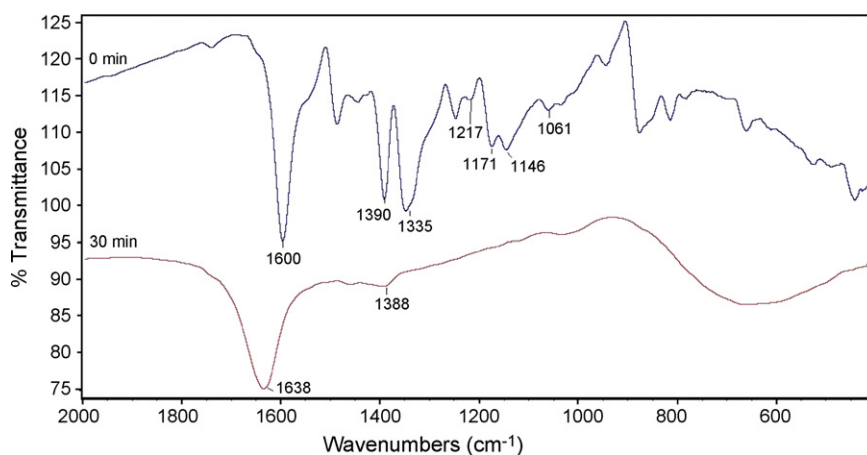


Fig. 5. Changes of MB in FT-IR spectra during degradation.

The results of stability tests conducted to assess the catalytic activity of $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ (25% starch) catalyst through three consecutive experiments with the same catalyst load under the same reaction conditions. The results show that the catalytic activity kept in the successive runs, and the decolorization efficiency of 0.3 g L^{-1} of methylene blue in 30 min maintained from 98.67% for the first run to 98.4% for the third run. Fig. 6 indicated XPS spectra of $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ (25% starch) before (a) and after (b) reaction. Characteristic peak of element S can be seen faintly in curve b (after reaction), indicating that a little bit of sulfur was adsorbed on the surface of catalyst. The degradation products containing element N did not appear in curve b. Then, it can be concluded that the reason why the activity of $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ (25% starch) catalyst kept constant, maybe due to that few degradation intermediates of methylene blue containing N and S elements were adsorbed on the surface of catalyst and covered the active sites. It also can be concluded that the degradation of dye were mainly due to $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ (25% starch) catalysis rather than adsorption.

3.3. Analysis of the Taguchi experiment

The Taguchi method is generally used to optimize a process or product by a special design of orthogonal arrays. The experimental results are analyzed using the Response (R) and Analysis of Variance (ANOVA) to determine the optimal design parameters and estimate the contribution of each design parameter to a certain characteristic. R has a different meaning from that of in analytical chemistry. Usually, there are three categories of the characteristic in the analysis of R , viz. the-lower-the-better, the-

higher-the-better, and the-normal-the better. For all categories, a greater R is better. The optimal level of the design parameters is the level with the greatest R . ANOVA is a statistical analysis of the variance and gives information about which process parameter is statistically significant.

3.3.1. Analysis of experimental data

Each variable (each factor) was tested at four levels and the levels covered a broad range (Table 1). Fractional factorial design led to a total of 16 experimental runs listed in Table 2. The response from each experiment was symbolically indicated as $R_1, R_2, R_3, \dots, R_{16}$. The average response of each factor was computed at each level (K_{ij} where i represented a factor and j represented a level); for example, the average response in Factor A at Level-2 was computed as $(R_5 + R_6 + R_7 + R_8)/4$. The total mean K_{ij} for 16 experiments shows in Fig. 7. K_{ij} can give us the optimal levels of design parameters with the greatest K_{ij} . From Fig. 7, it can be seen that the A_1, B_4, C_2 and D_4 was the optimal combination of the parameter levels.

3.3.2. Analysis of variance

To investigate which design parameter can affect the decoloration of MB more significantly, an ANOVA was introduced. This was to be accomplished by separating the total variability of R response, which was measured by the sum of the squared deviations from the total mean R response, into contributions by each of the design parameters and the error. The total sum of square SS_T from the R_i can be calculated as [26]:

Table 1
Experimental variables: factors and levels

Level	Factors			
	A: pH	B: T ($^{\circ}\text{C}$)	C: Concentration (g L^{-1})	D: Catalysts dose (g L^{-1})
1	3	25	0.1	1
2	5	30	0.2	5
3	7	35	0.3	10
4	9	40	0.4	15

Table 2
Design matrix and measured response

Run no.	Design matrix				Response	Measured response variable MB removal (%)
	Factors					
	A	B	C	D		
1	1	1	1	1	R_1	31.61
2	1	2	2	2	R_2	60.26
3	1	3	3	3	R_3	82.63
4	1	4	4	4	R_4	98.65
5	2	1	2	3	R_5	91.38
6	2	2	1	4	R_6	81.39
7	2	3	4	1	R_7	3.79
8	2	4	3	2	R_8	79.47
9	3	1	3	4	R_9	74.22
10	3	2	4	3	R_{10}	12.05
11	3	3	1	2	R_{11}	56.89
12	3	4	2	1	R_{12}	88.42
13	4	1	4	2	R_{13}	0.60
14	4	2	3	1	R_{14}	9.80
15	4	3	2	4	R_{15}	98.42
16	4	4	1	3	R_{16}	6.00

$$SS_T = \sum_{i=1}^M R_i^2 - \frac{1}{m} \left[\sum_{i=1}^m R_i \right]^2 \quad (3)$$

where m is the number of the experiment. The sum of squares from the tested parameter SS_P can be calculated as:

$$SS_P = \frac{\sum_{j=1}^t (sR_j)^2}{t} - \frac{1}{m} \left[\sum_{i=1}^m R_i \right]^2 \quad (4)$$

Where, p represents one of the tested parameters, j is the level number of this parameter p , t is the number of levels for each parameter (here, $t = 4$), sR_j is the sum of the R response involving this parameter and level j , m is the number of the experiments. The total degree of freedom (d.f.) was

$$D_T = m - 1 \quad (5)$$

while the degree of freedom of the tested parameter was

$$D_P = t - 1 \quad (6)$$

The variance of the tested parameter was

$$V_P = \frac{SS_P}{D_P} \quad (7)$$

Then the F -value for each design parameter was simply the ratio of mean-of-square deviations to the mean of the squared error

$$F_P = \frac{V_P}{V_e} \quad (8)$$

The parameter with the bigger F_P gave the more significant effect on decoloration. Table 3 shows the result of ANOVA. It was found that concentration was the most significant parameter affecting the decoloration. This was due to the following reasons: the oxidant produced during decoloration processes collided with the dye molecule, which decolorized the MB molecule. However, the collision was non-selective, which resulted in an attack on intermediate products rather than on the chromophore of the initial dye molecule, which caused decreasing of the decoloration ratio. It was also can be seen in Table 3 that the change of the catalysts dose had an insignificant effect on the decoloration. The addition of more catalyst into the solution offered more reaction sites which were favorable to the decoloration reaction. It was observed that the order of the four factors' effect on decoloration was $C > D > A > B$.

Table 3
Results of the ANOVA analysis

Symbol	Parameter	d.f.	SS_P	V_P	F_P
A	pH	3	3828.8	1276.3	1.87
B	T	3	1728.1	576.0	0.85
C	Concentration	3	6916.7	2305.6	3.39
D	Catalysts dose	3	6590.0	2196.7	3.22
Error		3	2043.1	681.0	
Total		15	21106.7		

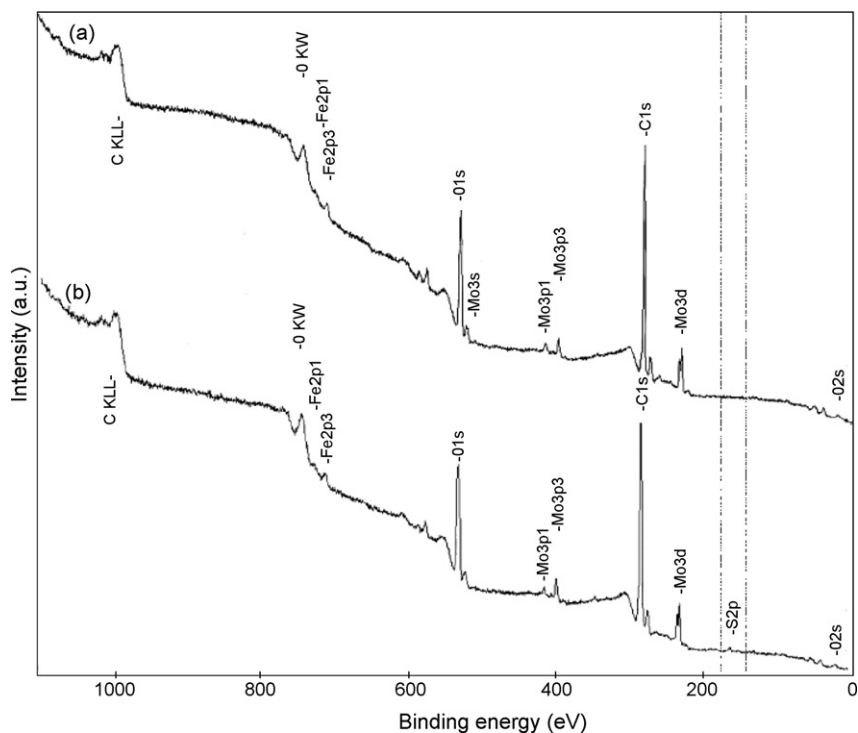


Fig. 6. Survey XPS spectra of FeOx-MoO₃-P₂O₅ (25% starch) catalyst before (a) and after (b) reaction.

3.4. Environmental estimate

Many papers have studied environmental effect of the discharged pollutants from the pulp and paper industry, such as water, air and land [27,28]. Less information was available today concerning the effect of irrigation of secondary treated water on ecologies. In the present study, we investigated the effect of irrigation of treated methylene blue wastewater on the soil TOC/TIC changes and the amount of chlorophyll changes of clover.

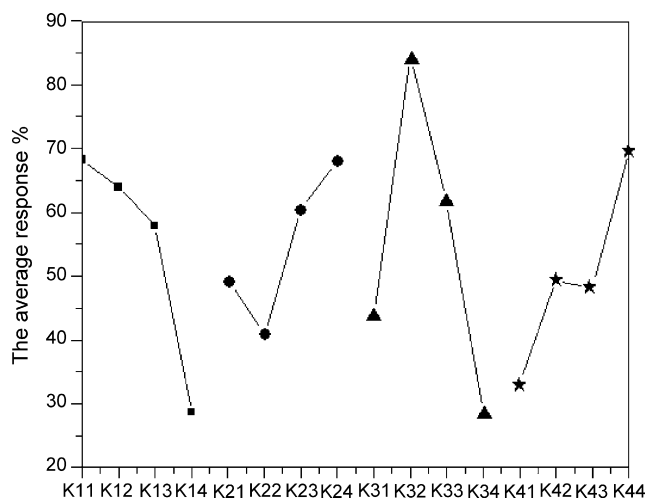


Fig. 7. Variation of mean response K_{ij} with the parameter level for each designed parameter. (■) Parameter A (pH), (●) parameter B (Temperature), (<▲) parameter C (Concentration) and (★) parameter D (Catalysts dose).

It can be seen from Fig. 8 that the treated wastewater has little effect on the content of chlorophyll, the overall chlorophyll content gradually increased when the treated wastewater was irrigated into the soil, and then the chlorophyll content reduced rapidly from 12:00 a.m. to 16:00 p.m., however, it was interesting to find its content gradually recovered to normal level at 18:00 p.m., which indicated that the treated wastewater could totally apply to irrigate. As the figure depicted, when the treated water was irrigated into the soil, the TOC and TIC increased at the beginning and decreased to average level gradually with the time gone, which was probably attributed to the absorption effect of plants' root.

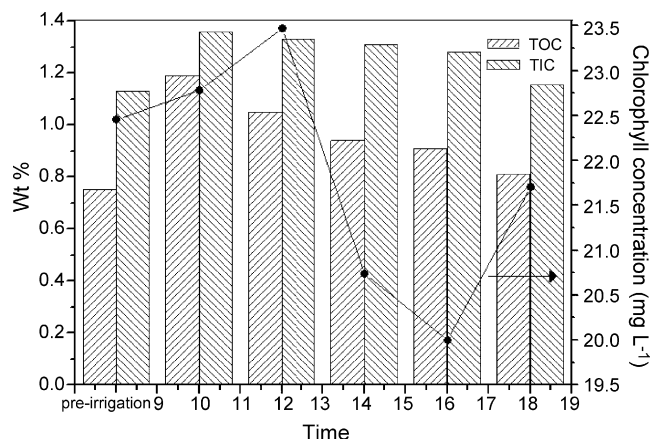


Fig. 8. Changes of TOC, TIC and chlorophyll concentration of clover as the function of time.

4. Conclusions

A study was conducted with $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ prepared by solid reaction method and employed as catalysts for degradation of methylene blue at mild condition. $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ exhibited an excellent catalytic activity under mild condition. The orthogonal experiments were devised to determine the optimum operating condition. The activity of catalyst increased with the increasing starch dose. 98% of color and 85% COD can be removed for 30 min by adding 13.3 g L^{-1} of $\text{FeO}_x\text{-MoO}_3\text{-P}_2\text{O}_5$ catalyst with 25 wt.% starch addition. Environmental estimate indicated that the treated wastewater have little influence on plant growth and could totally be applied to irrigation. Further studies on the treatment of actual dye wastewater would be further studied.

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