# SYNTHESIS AND CHARACTERIZATION OF THE $MnO_2/Al_2O_3$ CATALYST APPLIED FOR TREATMENT OF ORGANIC DYES IN WASTE WATER

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ABSTRACT

In this study, $MnO_2/Al_2O_3$ catalysts were synthesized from manganese acetate and aluminum hydroxide by the sol-gel method at room temperature, followed by thermal treatment at 300°C. The characterization of the product was performed by X-ray diffraction (XRD), energy dispersive analysis of X-rays (EDX), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Brunauer-Emmett-Teller (BET). The ozonation of methylene blue (MB) solution in the presence of $MnO_2/Al_2O_3$ catalyst was investigated in a laboratory scale batch reactor. The effect of pH solution (2-12), reaction time (0 - 60 minutes), and $MnO_2/Al_2O_3$ catalyst dosage (0 and 0.1 - 5 $g.L^{-1}$) on MB treatment was determined. The results showed that the reaction with the presence of catalyst required less time and improved the reduction level of MB compared to conventional ozonation. The optimal pH and catalyst dosage values were 8 and 1 $g.L^{-1}$, respectively. For textile dyeing wastewater treatment, the catalytic ozonation decreased the color scale from 7693.89 Pt-Co to 28.40 Pt-Co and COD from 387.60 $mg.L^{-1}$ to 52.35 $g.L^{-1}$. Therefore, the ozonation with $MnO_2/Al_2O_3$ catalysts can be considered as effective and feasible for treating the textile dyeing wastewater.

Keywords: Metal oxide, $MnO_2/Al_2O_3$, Methylene blue, organic dyes, ozonation

## Tổng hợp và đặc tính của xúc tác $Mno_2/Al_2O_3$ ứng dụng xử lý thuốc nhuộm hữu cơ trong nước thải

TÓM TẮT

Trong nghiên cứu này, xúc tác $MnO_2/Al_2O_3$ được tổng hợp từ mangan axetat và nhôm hydroxit bằng phương pháp sol-gel ở nhiệt độ thường, sau đó được nung ở 300°C. Các đặc trưng cấu trúc sản phẩm được đo bằng phương pháp nhiễu xạ tia X (XRD), phổ tán xạ năng lượng điện tử (EDX), kính hiển vi điện tử quét (SEM), kính hiển vi điện tử truyền qua (TEM), diện tích bề mặt riêng (BET). Phản ứng ozon hóa chất màu xanh metylen (MB) được khảo sát trong phòng thí nghiệm. Nghiên cứu ảnh hưởng của pH trong khoảng 2 - 12, ảnh hưởng của thời gian phản ứng từ 0 - 60 phút, ảnh hưởng của hàm lượng xúc tác từ 0 - 5 g/l đến khả năng xử lý MB. Kết quả cho thấy các phản ứng có xúc tác $MnO_2/Al_2O_3$ thời gian phản ứng xảy ra nhanh hơn, hiệu quả tốt hơn so với phản ứng ozon hóa thông thường. Ở pH = 8, hàm lượng xúc tác 1g/l cho kết quả xử lý tốt nhất. Kết quả xử lý của xúc tác với mẫu nước thải dệt nhuộm cho kết quả độ màu giảm từ 7693,89 Pt-Co xuống còn 28,40 Pt-Co và hàm lượng COD giảm từ 387,60 mg/l xuống 52,35 mg/l. Do vậy phản ứng ozon hóa chất hữu cơ với xúc tác $MnO_2/Al_2O_3$ là một phương pháp có hiệu quả để xử lý chất hữu cơ trong nước thải dệt nhuộm.

Từ khóa: Oxit kim loại, $MnO_2/Al_2O_3$, xanh metylen, nước thải dệt nhuộm, ozon hóa.

## 1. INTRODUCTION

Dyes and organic compounds are widely used in industry and daily life. A large amount of these compounds is released into wastewater causing serious environmental problems, especially organic pollution ( Serano *et al.*, 2015; Pulit-Prociak *et al.*, 2016). Dyes are synthetic aromatic compounds used to colorize products of many different industries, including textiles,

tanneries, pharmaceuticals, pulp and paper, paint, plastics, food and electroplating ( Zhou *et al.*, 2017). Dyes can be classified into cationic, anionic and non-ionic dyes. In natural condition, dyes can be converted to toxic or carcinogenic compounds ( Bhatt *et al.*, 2013; Ratna *et al.*, 2012).

Methylene blue (MB), known as methylthioninium chloride, has been widely used in biology and chemistry and can serve as a good model for cationic dyes in environmental study (Zong *et al.*, 2013; *Rahman et al.*, 2012). It is a heterocyclic aromatic chemical compound with the chemical formula of $C_{16}H_{18}N_3SCl$. Structural formula of MB is shown in Fig. 1.

Ozonation is one of the oxidation processes used for industrial wastewater treatment in which ozone molecules break down recalcitrant and toxic organic compounds into smaller molecules. The ozonation reaction is accomplished through two pathways: direct ozone oxidation and indirect free hydroxyl radical oxidation in the surface of catalysts ( Khuntia *et al.*, 2016) among which the latter appears to be more effective to treat various types of organic compounds. Many catalysts including metals, metal ions and metal oxides have been used for enhancing the activation of ozonation process such as homogenous metal ions (Fe (II), Fe(III), Cu(II), Mn(II), Co(II), carbon aerogel, nano Fe, Fe/MgO, $TiO_2$ and $MnO_2$ ( Khuntia *et al.*, 2016; Nawaz *et al.,* 2016; Tan *et al.*, 2017). Among these, $MnO_2$ is one of the catalysts attracting the most attentions. There are also several investigations to improve $MnO_2$ catalytic activity by combination it with other materials ( Khuntia *et al.*, 2016; Nawaz *et al.*, 2016; Tan *et al.,* 2017).

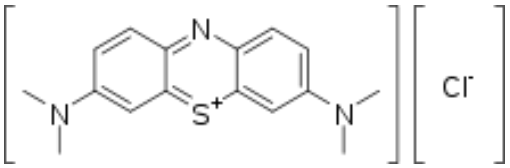



**Fig. 1. Structural formula of methylene blue**

**Table 1. Experimental steps and conditions**

| Experiment | Conditions | | | |
|---|---|---|---|---|
| | $C_{MB}$ (mg/L) | $C_{catalyst}$ (g/L) | pH | Time (min) |
| Effect of pH | 300 | 1 | 2 - 12 | 30 |
| Effect of catalyst concentration | 300 | 0 - 5 | 8 | 0 - 60 |

In this study, the heterogeneous catalyst $MnO_2/Al_2O_3$ was synthesized and used as the reactive support and free-radical initiator for ozonation the organic compounds in textile dyes. Especially, $Al_2O_3$ was introduced to the catalyst in order to increase the surface area of the materials and, therefore, increase the catalytic activity of the sample.

## 2. MATERIALS AND METHODS

### 2.1. Synthesis of $MnO_2/Al_2O_3$ catalyst

$MnO_2/Al_2O_3$ catalyst was synthesized by hydrothermal method. 44 g NaOH was dissolved in 100ml of deionized water by magnetic stirring. 21 g $Al(OH)_3$ was heated with continuously stirring and then added to the NaOH solution to form a precursor solution. The solution was concentrated and dried at 200°C for 6h. Afterwards, $Mn(CH_3COOH)_2$ was added with Mn:Al molar ratio = 1.5:1. The sample was continuously stirred, concentrated and calcined at 300°C for 3h. Finally, the sample was washed with deionized water and then thoroughly dried at 105°C for 4h.

### 2.2. Characterization of $MnO_2/Al_2O_3$ catalyst

The crystalline structure of $MnO_2/Al_2O_3$ catalyst was analyzed by X-ray diffraction (XRD) technique using a Bruker B8 Advance X-ray powder diffractometer. The elemental composition was determined by Energy dispersive analysis of X-rays (EDX, Varian Vista Ax). The size and morphology of materials were examined using scanning electron microscopy (SEM, Hitachi S-4800FEG) and transmission electron microscopy (TEM, Philips Tecnai G220 S-TWIN). The surface area and pore distributions of the material sample were

determined by a Beckman Coulter SA3100 surface area analyzer based on the nitrogen adsorption-desorption isotherm at the temperature of liquid nitrogen (-196°C)

### 2.3. Catalytic ozone degradation of MB

300 mg methylene blue were dissolved in 1000 mL of deionized water to form the solution of MB 300 mg/L. Ozone was produced by an ozonizer (A-Ozone Sachben S5, VietNam) supplied with oxygen (2scfm). The ozone in the inlet gas stream was analyzed by iodometric titration and was found to be 1.83 $g.h^{-1}$.

100 ml of MB 300 mg/L were carried out in 500 ml glass beakers at room temperature (25°C). Then $MnO_2/Al_2O_3$ was added as the catalysts and ozone was supplied in the stirring condition 100 rounds per minute.

The concentration of MB was determined using an UV-VIS Spectro 2550 spectrophotometer at its maximum absorbance wavelength of 660nm. The color removal in each experiment was calculated from the difference of initial (before reaction) and final (after reaction) concentrations of MB. COD was measured by the standard method of potassium dichromate oxidation (TCVN 6491:1999) in Department of Chemistry, Faculty of Environment, VietNam National University of Argicuture (VNUA).

To ensure the reproducibility of data, each experiment was conducted in duplicate and the average of the two measurements was reported.

### 2.4. Catalytic ozone degradation of textile dyeing wastewater

Textile dyeing wastewater samples were taken at the exhaust outlet of a textile dyeing unit in Nam Thanh factory, Hung Ha, Thai Binh, Vietnam in August 26th, 2016. The composition, characteristics of wastewater samples are presented in table 2.

To examine the $MnO_2/Al_2O_3$ catalytic activity, 100 ml of textile dyeing wastewater were placed in 500 ml glass beakers. Then, 0.1 g $MnO_2/Al_2O_3$ was added and ozone was supplied in the stirring condition.

**Table 2. Characteristics of textile dyeing wastewater samples**

| Parameter | Unit | Result |
|---|---|---|
| pH | - | 7.6 |
| COD | mg/L | 387.60 |
| $BOD_5$ | mg/L | 162.15 |
| Total N | mg/L | 18.2 |
| Total P | mg/L | 4.0 |
| Color scale | Pt-Co | 7693.89 |

**Table 3. Characteristics of the catalyst**

| Parameters | $S_{BET}$ ($m^2/g$) | Pore volume ($cm^3/g$) | Pore size (nm) |
|---|---|---|---|
| Catalyst $MnO_2/Al_2O_3$ | 216.74 | 0.294 | 5.4442 |
| $MnO_2$ (F. Nawaz *et al.*, 2016) | 81.8 | 0.242 | - |

The concentration of the textile dye in the wastewater and treated samples were determined using an UV-VIS Spectro 2550 spectrophotometer at the absorbance wavelength of 455 nm based on a standard curve of Pt-Co standard solutions.

## 3. RESULTS AND DISCUSSION

### 3.1. Catalyst characterization

The surface area and the total pore volume of the catalyst were 216.74 $m^2.g^{-1}$ and 0.294 cm3.$g^{-1}$, respectively. It is obvious that the surface area of the synthesized material was very high compared to other reports (Nawaz et al., 2016; Tan et al., 2017; Jalali et al., 2016). This property of the material can be due to the role of $Al_2O_3$ that is highly porous present in the sample.

In Figure 2a, the phase composition was investigated by XRD, with observed diffraction peaks at about 2θ = 25.5°; 35°; 38°; 43°; 52.5° and 57° which were related to the presence of $Al_2O_3$. The weak peaks around 2θ = 17°; 28°; 37°; 43°; 55°; 57° can be assigned to the presence of $MnO_x$. Among the peaks, the peaks at 28°, 37°, and 55° were characterized for pyrolusite crystals of $MnO_2$ ( Arene et al., 2007).

The EDX analysis reveals mass fraction of the elements in the catalyst sample. Figure 2b shows that the catalysts consisted of 32.90% manganese and 13.22% aluminum. It can be inferred that the sample composed of 51% $MnO_2$ and 25% $Al_2O_3$ corresponding to the ratio of Mn:Al at initial formula. The remaining composition of the sample was assigned to be sodium carbonate formed from the reaction of $CO_2$ in the atmosphere and the excess NaOH during the synthesis.

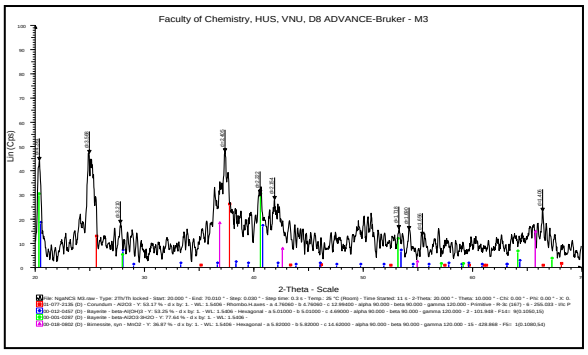
Typical SEM and TEM images of the catalyst are shown in figure 2c and 2d. The catalyst particles with the average sizes of 30nm (shown in SEM image) were highly fractional (as seen in TEM image). This property accounts for the exceptional high surface area of the sample.

### 3.2. Ozonation of methylene blue with $MnO_2/Al_2O_3$ catalysts

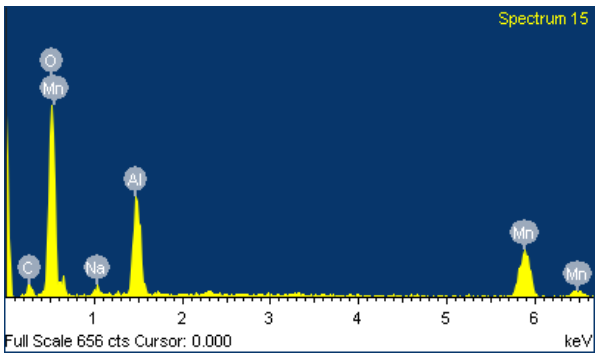
#### *3.2.1. Effect of pH solution*

The pH of the solution plays an important role in the contaminant degradation mechanism during an oxidation process. Therefore, the effect of initial pH of the dye solutions on degradation was studied at pH values ranging from 2 to 12. Figure 3 shows the removal percentages of MB under different pH conditions.

As seen in Figure 3, the percentage of MB removal at an acidic pH of 2 was 96.4% and decreased to 90% when pH was increased to 6 and then the percentage of MB removal increase when pH increase to 12. At pH = 8, the treatment efficiency has reached 98%. It reached a maximum value of 99.7% at pH 10.




(a)

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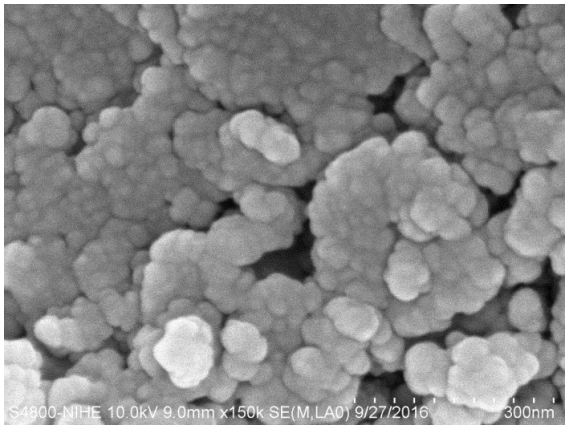
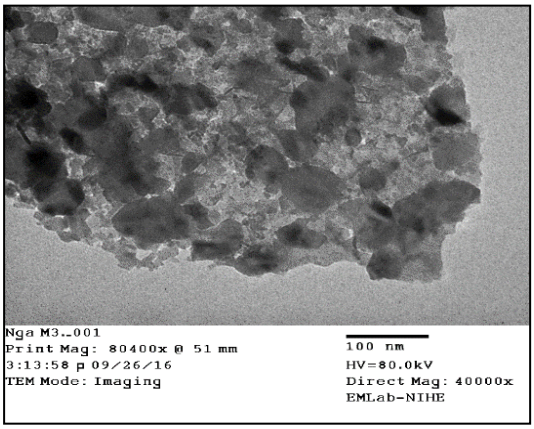



(c)




(d)

**Fig. 2. (a) XRD diagram, (b) EDX diagram, (c) SEM and (d) TEM image of the material**

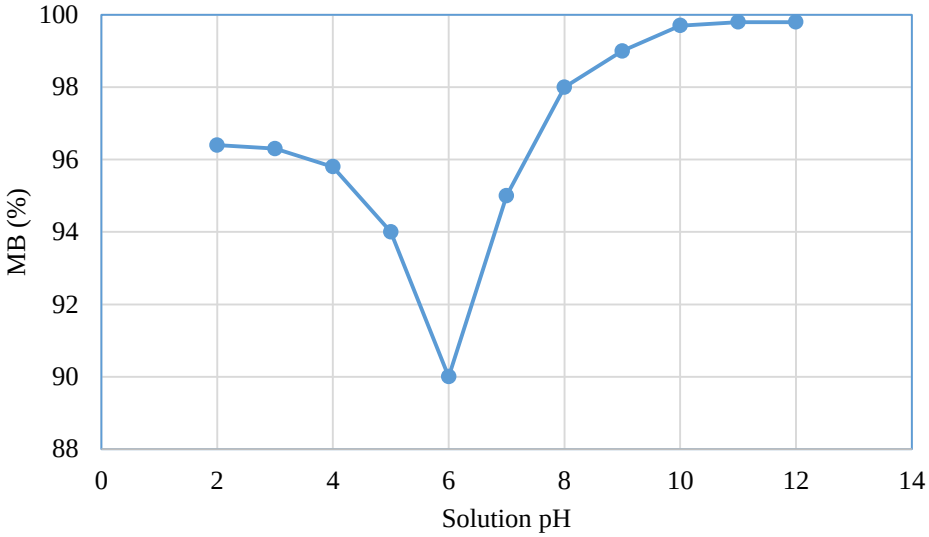



**Fig. 3. Effect of initial pH on degradation of MB**

The high percentage of MB removal at pH of 2 can be explained by the direct oxidation of MB molecules by ozone, which is the best performed at acidic pH. As described in literature ( Liu *et al.*, 2015), in acidic environment, ozone reacts with water to form radical $^*OH$ and then, the MB molecules are degraded by $^*OH$:

$$O_3 + H_2O \rightarrow 2HO^* + O_2$$

$$HO^* + MB \rightarrow [MB\text{-}OH]^{+*}$$

In alkaline condition, beside the direct oxidation of ozone, there is also the formation of radical $HOO^*$ that can reproduce $O_3$ molecules and makes the oxidation more effective:

$$O_3 + OH^- \rightarrow HOO^* + O_2^-$$

$$O_2 + HOO^* \rightarrow O_3 + {}^*OH$$ [29]

In our catalytic process, ozonation occurred indirectly by oxidation the metal oxide catalyst. Ozone reacted with manganese dioxide to form $O^{2-}$ and then $O^{2-}$ reaction with water to form $HOO^*$. In the next step, hydroxyl radical was created by the reaction of ozone with $HOO^*$. Finally $HO^*$ degraded MB molecules in solution

$$O_3 + Mn^{4+} \rightarrow O^{2-} + Mn^{6+} + O_2$$

$$O^{2-} + H_2O \rightarrow HOO^* + HO^-$$

$$O_3 + HOO^* \rightarrow HO^* + O_2$$

$$MB + HO^* \rightarrow [MB\text{-}OH]^{+*}$$

In the presence of $MnO_2/Al_2O_3$, ozone converted to its more active component ($O^{2-}$), this reacts with water faster than $O_3$ alone.

### *3.2.2. Effect of catalyst concentration on MB ozonation*

The effect of catalyst amounts on the rate of MB ozonation was tested for several initial $MnO_2/Al_2O_3$ catalyst amounts of 0, 0.5, 1, 2, 3, 4 and 5 g/L. The rate of MB ozonation increased by enhancing initial amount of $MnO_2/Al_2O_3$ catalyst as shown in Fig. 4.

The concentration of MB reduced quickly over reaction time. After 30 minutes, without catalyst, the degradation was influenced by the oxidation of ozone alone. The oxidation reaction MB run slowly, making it less effective in degrading MB with the balanced degradation percentage of 46,78%. Catalytic ozonation of MB in the presence of $MnO_2/Al_2O_3$ was much more effective. With the catalyst concentration 0.5 g/L the treatment efficiency was about 71.29% and the efficiency reached 100% when the catalyst concentration is about 1g/L. Higher concentrations of $MnO_2/Al_2O_3$ led to rather higher efficiencies but in a similar pattern to 1 g/L concentration. This fact indicates that 1 g/L was the optimum catalyst concentration for this ozonation.

### *3.2.3. Textile dyeing wastewater treatment by catalytic ozonation*

Figure 5 illustrates the difference between the 2 textile dyeing wastewater samples untreated and treated with catalytic ozonation. The untreated wastewater samples had high organic matter, COD of 387.60mg/L and color scale of 7693.89Pt-Co. All of the composition of textile dyeing wastewater has exceeded the National technical regulation on the effluent of textile industry (200 Pt-Co for color scale and 200 mg/L for COD) on the effluent of textile industry. After treatment with the catalytic ozonation, both parameters decreased significantly after 120 minutes (COD left was 52.35 mg/L and color scale left was 28.40 Pt-Co) and satisfied the National technical regulation on the effluent of textile industry (QCVN 13-MT:2015/BTNMT) (Fig. 6).

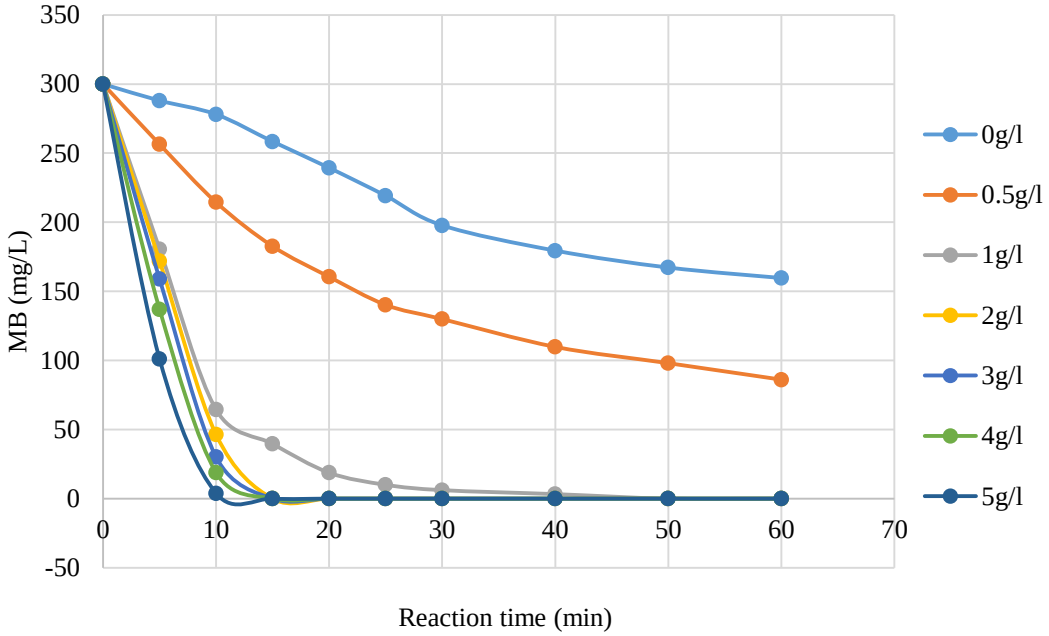



**Fig. 4. The effect of catalyst concentration on degradation of MB**

**Fig. 5. Textile dyeing wastewater (left) and catalytic ozonation treatment (right)**

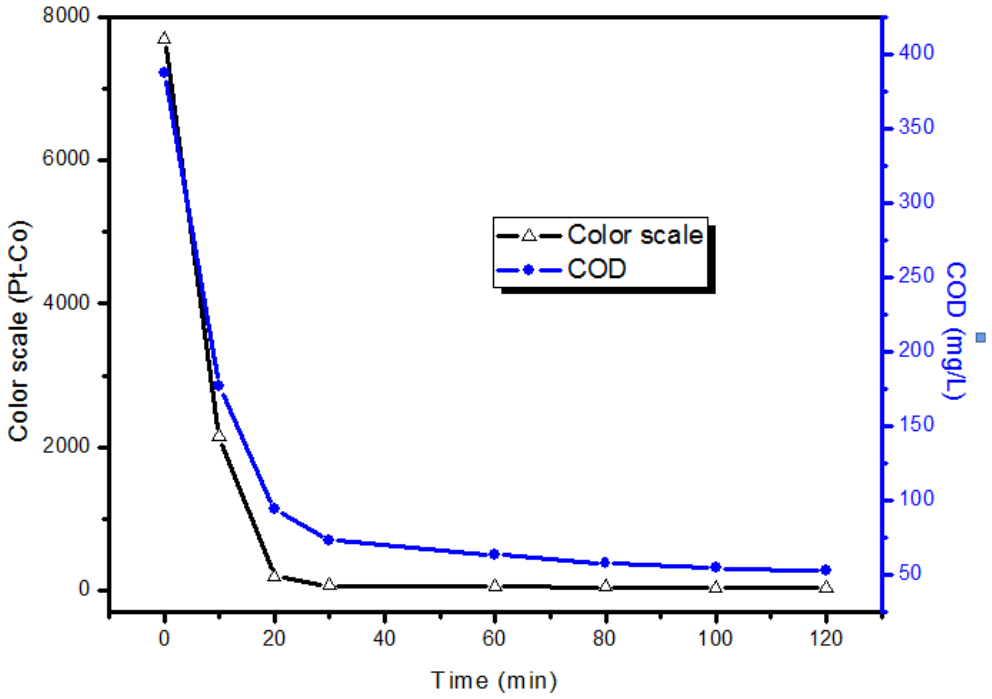



**Fig. 6. Changing in Color scale and COD of wastewater sample over time of treatment**

## 4. CONCLUSIONS

We have successfully synthesized $MnO_2/Al_2O_3$ catalyst by the sol-gel method. The nano particle catalyst has high surface area of 216.74 $m^2/g$ and high mesoporous with pore size of 5.4442 nm and pore volume of 0.294 $cm^3/g$. It has been proved to be a good catalyst for treatment of organic compounds in wastewaster. For MB 300 mg/L degradation, the catalyst shows lowest activity at neutral environment, pH = 6 (about 90%) and better activity in alkaline environment with the maximum of 99.7% achieved at pH 10. The optimum concentration of the catalyst was found to be 1 g/L.

Applying the ozonation with the $MnO_2/Al_2O_3$ catalyst at optimum conditions to treat actual textile dyeing wastewater samples, the organic compound present in the samples decreased from 387.60 mg/L to 52.35 mg/L and the color scale decreased from 7693.89 Pt-Co to 28.4 Pt-Co and satisfied the National technical regulation on the effluent of textile industry. This study confirms that $MnO_2/Al_2O_3$ can serve as an appropriate material for wastewater treatment.

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