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## $\beta$ -MnO<sub>2</sub> ACTIVATION OF PEROXYMONOSULFATE FOR CATALYTIC PHENOL DEGRADATION IN AQUEOUS SOLUTIONS

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### Abstract

$\beta$ -MnO<sub>2</sub> was prepared and used to activate peroxymonosulphate for degradation of aqueous phenol. The sample was characterized by N<sub>2</sub> adsorption, X-ray diffraction (XRD), scanning electron microscopy (SEM). The catalyst is highly effective in heterogeneous activation of PMS to produce sulfate radicals for phenol degradation compared with homogeneous oxidation.  $\beta$ -MnO<sub>2</sub> could completely remove phenol in 30 min at the conditions of 25 ppm phenol, 0.4 g/L catalyst, 2 g/L PMS, and 25 °C. A pseudo first order model would fit to phenol degradation kinetics and activation energy was obtained as 38.2 kJ/mol.

*Keywords:* manganese catalysts, AOPs, treatment, phenol degradation, oxone

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### Introduction

Worldwide attention to the problem of clean water is increasing day by day. This is because of the need for clean water increased along with the increase in population and economy, as a result demands for fresh water also continuously growing [1]. The main concern in this case is not due to depletion of fresh water, but the damage done by industrial and human activities. Thus, water is the most pressing challenges such as health, agriculture, energy and urbanization [2].

Water resources available today are not as abundant as it seems, because only a very limited amount of available water resources can be used without any treatment. Only a small portion of the total amount of fresh water is about 0.26% which can be used for human purposes, located in lakes, reservoirs and rivers [3]. Based on the use of fresh water, agriculture is the biggest user at around 70% of the total fresh water, followed by industry 25% and 5% domestic [4]. In most cases, the main contaminants originating from agriculture is the increased use of pesticides (insecticides and herbicides) [5], while the industry as a by-product of their activities [6]. In order to manage environmental pollution, many countries have designed environmental regulations containing guidelines regarding the maximum threshold allowed for a variety of toxic organics that can be disposed of in the environment, for instance 0.01 mg/L for Indonesian wastewater [7, 8]. However, even with the strict regulations of the water resources are still a major problem. Therefore, it is important to develop a waste treatment technology that can destroy pollutants into non-toxic compound or biodegradable end products.

The most promising method for degradation of organic pollutants in wastewater is advanced oxidation processes (AOPs). AOPs are based on generation and utilization of hydroxyl radicals (OH•), as reactive species. That have a high standard oxidation potential and react non selectively [9, 10]. Heterogeneous catalytic oxidation systems have several advantages such as easily recovery and reuse of the catalysts [11]. Currently, sulphate radicals (SO<sub>4</sub><sup>-•</sup>) produced by peroxymonosulfate have been proposed as an alternative to hydroxyl radical for organic degradation due to has the higher oxidizing potential (1.82 V) than that of H<sub>2</sub>O<sub>2</sub> (1.76 V). In this research, we investigate the  $\beta$ -MnO<sub>2</sub> catalysts for heterogeneous activation of sulphate

radicals for chemical mineralizing of phenol in the solution. This catalyst will be an alternative catalyst in AOPs process.

## Experimental Methods

All chemicals were obtained from Sigma-Aldrich. Synthesis of  $\beta$ - $\text{MnO}_2$  followed the hydrothermal method with some modifications based on the redox reactions of  $\text{Mn}^{2+}$  ions with persulphate [12], this method . Typically,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (0.008 mol) and an equal amount of ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) were put into distilled water at room temperature to form a homogeneous solution, which was then transferred into a 40 mL Teflon-lined stainless steel autoclave, sealed and maintained at 140 °C temperatures for 12 h. After the reaction was completed, the resulting solid product was filtered, washed with distilled water to remove ions possibly remnant in the final products, and finally dried in air. The crystal structure of the synthesized materials was characterized by an X-ray diffractometer (XRD, Bruker D8 Advance) equipped with  $\text{Cu K}\alpha$  radiation at accelerating voltage and current of 40 kV and 40 mA, respectively. The particle morphology was examined from scanning electron microscopy (SEM) obtained using a JEOL JEM1010 electron microscope. The particle surface area and pore size measurement were carried out by  $\text{N}_2$  adsorption analysis at -196 °C using a Micromeritics AS-1. Samples were degassed at 200 °C for 24 h prior to adsorption analysis. The surface area and pore size distribution were obtained by the BET and BJH methods. Phenol degradation tests were carried out at 30 °C in 1 L glass vessel with 500 mL containing 25, 50, 75 and 100 mg/L of phenolic solutions with a constant stirring of 400 rpm. Firstly, a catalyst at varying amounts (0.2-0.40 g) was added into the phenol solution for a while, then oxone ( $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ , PMS) was added into the solution at 1.2-2.4 g/L. At certain time, water sample (1 mL) was withdrawn into a HPLC vial, 0.5 mL of pure methanol was then injected into the vial to quench the reaction. The concentration of phenol was analyzed using a Varian HPLC with a UV detector set at  $\lambda = 270$  nm. A C-18 column was used to separate the organics while the mobile phase with a flow rate of 1.5 mL/min was made of 30%  $\text{CH}_3\text{CN}$  and 70% water. For the recycle tests of the catalyst, after each run, the catalyst was obtained by filtration and thoroughly washed with distilled water several times, then dried at 80 °C for 2 h.

## Result and Discussion

### a. Characterization of $\beta$ - $\text{MnO}_2$ catalyst.

Fig. 1 shows the XRD patterns of  $\beta$ - $\text{MnO}_2$ . The diffraction peaks in Fig. 1 match well with those from the JCPDS card (24-0735) for  $\beta$ - $\text{MnO}_2$ . Figure 2 shows SEM images of the  $\beta$ - $\text{MnO}_2$  samples. As can be seen,  $\beta$ - $\text{MnO}_2$  was observed to be as nanorods with diameters 5-100 nm and lengths ranging between 0.4 and 1.2  $\mu\text{m}$ . From  $\text{N}_2$  adsorption/desorption and pore size distribution of  $\beta$ - $\text{MnO}_2$ , the sample has surface area 194  $\text{m}^2/\text{g}$ , pore volume 0.238  $\text{cm}^3/\text{g}$  and pore radius 1.89  $\text{\AA}$ , which means it is a mesoporous material.

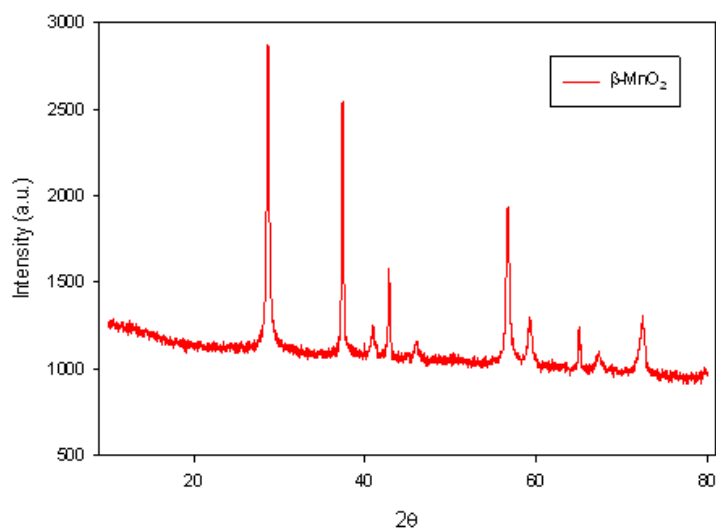


Figure 1. XRD patterns of  $\beta$ - $\text{MnO}_2$

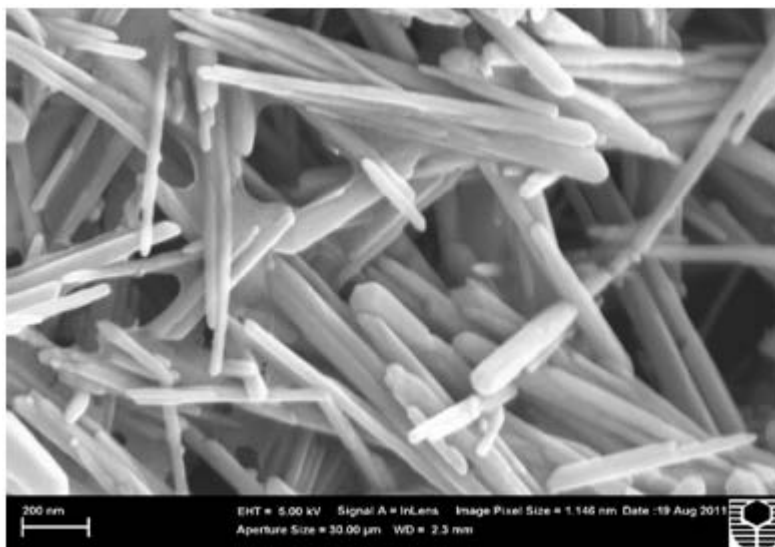
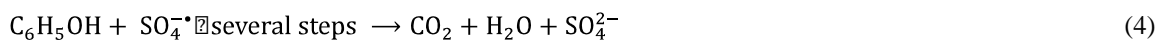


Figure 2. SEM images of various  $\beta$ - $MnO_2$  catalyst[13].

b. Phenol degradation on  $\beta$ - $MnO_2$  catalyst.

Fig. 3 shows the preliminary test of adsorption and catalytic oxidation of phenol using  $\beta$ - $MnO_2$  catalyst. The catalyst,  $\beta$ - $MnO_2$ , can adsorb phenol despite of low efficiency. From the figure, it also seen that phenol removal would not change significantly in the presence of oxone® without catalyst. In catalytic oxidation tests, phenol degradation would only occur when catalyst and oxidant were simultaneously presence in the solution.  $\beta$ - $MnO_2$  catalyst with oxone® in the heterogeneous system could degrade phenol up to 100% in 30 min. The high degradation rate was due to the activation of oxone® by  $\beta$ - $MnO_2$  catalyst to produce sulfate radicals. Compared with the efficiency of homogeneous oxidation,  $Mn^{2+}$ /oxone® system, the heterogeneous was found to be higher. The homogeneous system could degrade phenol up to 97% in 120 min. The reaction mechanism for heterogeneous phenol oxidation for  $\beta$ - $MnO_2$  catalysts can be proposed as below.



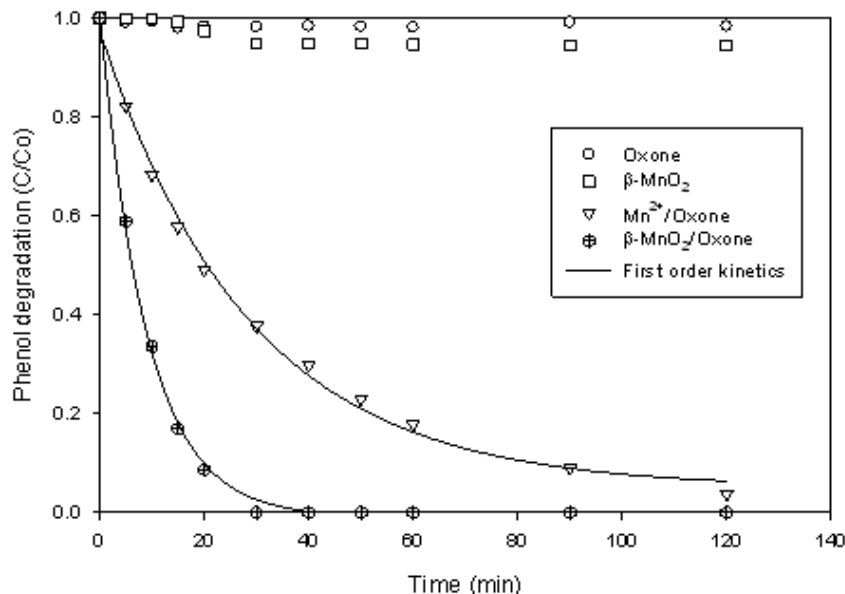


Figure 3. Phenol reduction with time in adsorption and catalytic oxidation. Reaction condition: [Phenol] = 25 ppm, catalyst = 0.4 g/L, oxone = 2 g/L, and T = 25 °C.

Effect of phenol concentration at 25-100 ppm on phenol degradation is presented in Figure 4. As can be seen, phenol degradation efficiency decreased with increasing initial phenol concentration. At 25 ppm, the 100% phenol removal could be achieved in 30 min while at phenol concentration of 50, 75 and 100 ppm, complete phenol removal could be achieved in 40, 50 and 60 min, respectively. Due to the amount of catalyst and oxone® is the same, to achieve 100% efficiency degradation requires a longer time, thus lowering the efficiency of phenol degradation.

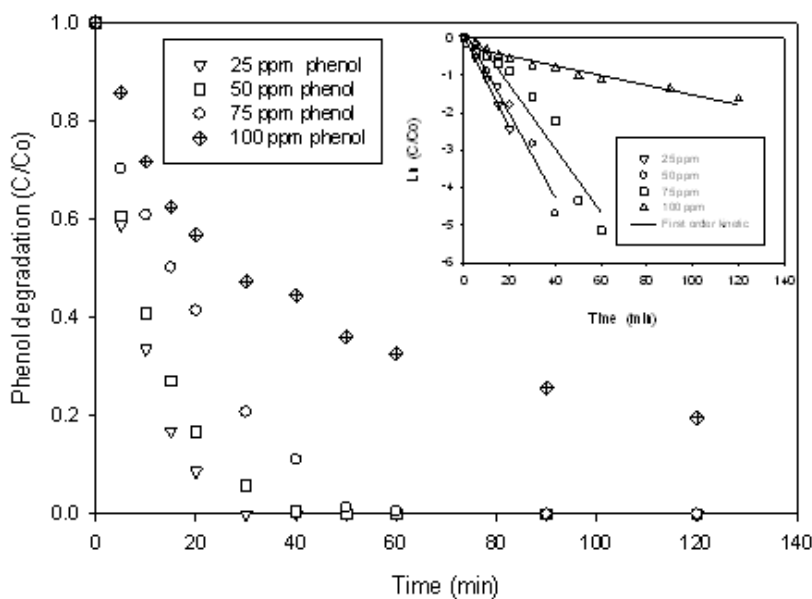


Figure 4. Effect of phenol concentration on phenol removal. Reaction condition: catalyst = 0.4 g/L, oxone = 2 g/L, and T = 25 °C.

In order to estimate the kinetic rates, a general pseudo first order kinetics for phenol degradation was employed, as shown in equation below.

$$\ln\left(\frac{C}{C_0}\right) = -k \cdot t \quad (5)$$

Where k is the apparent first order rate constant of phenol removal, C is the concentration of phenol at various time (t). C<sub>0</sub> is the initial phenol concentration. Using this model showed that ln(C/C<sub>0</sub>) versus time produced straight line for three different of concentration as shown in Figure 4 (in set). Base on regression coefficient, it is clear that phenol degradation followed the first order kinetic. The rate constant at varying phenol concentration is shown in Table. 1. As seen, rate constant will decrease as the concentration of phenol increase.

Table 1. Rate constant at different feed concentration of phenol

| Initial phenol concentration | Rate constant min <sup>-1</sup> | R <sup>2</sup> |
|------------------------------|---------------------------------|----------------|
| 25 ppm                       | 0.114                           | 0.99           |
| 50 ppm                       | 0.096                           | 0.96           |
| 75 ppm                       | 0.063                           | 0.90           |
| 100 ppm                      | 0.024                           | 0.83           |

Phenol removal efficiency is also affected by β-MnO<sub>2</sub> loading in the system as shown in Fig. 6. Higher β-MnO<sub>2</sub> loading in solution resulted in higher phenol degradation efficiency. At 0.2 g/L of β-MnO<sub>2</sub>, phenol degradation efficiency would achieve 100% in 90 min while at 0.3 and 0.4 g/L of catalyst loading, phenol degradation could be reached 100% within 30, 60min, respectively. The increased catalyst loading would enhance the active sites in solution for reaction with oxone® thus generating more the active sulfate radicals (SO<sub>4</sub><sup>-•</sup> and SO<sub>5</sub><sup>-•</sup>), resulting in an increase in the rate of phenol removal.

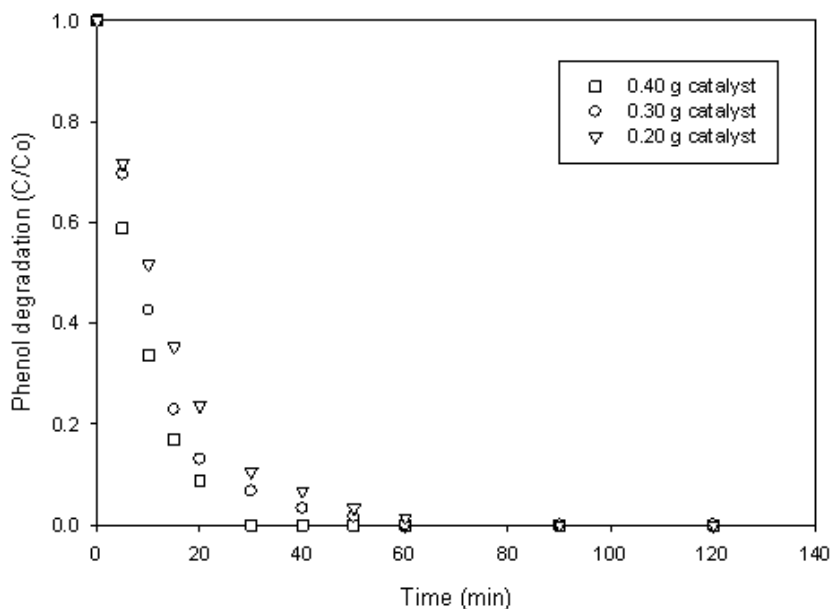


Figure 5. Effect of catalyst loading on phenol removal. Reaction condition: [phenol]= 25 ppm, oxone = 2 g/L, and T = 25 °C.

Figure 6 shows oxidation of phenol on  $\beta$ -MnO<sub>2</sub> with variety of oxidants. In general, the increased concentrations of oxone® in solution will increase phenol degradation. However the influence was not as significant as catalyst loading. At 1.2 g/L oxone®, complete phenol removal could be achieved in about 50 min while at 1.6 and 2.0 g/L of oxone® loading, phenol degradation could be reached 100% within 40 and 30 min, respectively. However, further increase in oxone® concentration at 2.4 g/L would decrease phenol degradation efficiency. Shukla et al. [14] studied the effect of concentration of oxone® with the Co-SBA-15 catalyst for removing phenols from aqueous solutions. They found that oxone® can reduce the rate of oxidation of phenol at oxone® increases from 2 to 4 g/L due to a higher concentration of oxone would consume the active SO<sub>4</sub><sup>-•</sup>, resulting in a lower degradation rate, according to the mechanism as follow.



Therefore, the current study using heterogeneous catalyst for activation of oxone to generate sulfate radicals will have the same consequences.

Figure 7 shows the reduction of phenol concentration against time at various temperatures of 25-45 °C. As can be seen, the reaction temperature plays a significant role in phenol degradation. The rate of reaction would increase significantly with increased temperature. At temperature of 25 °C, degradation efficiency of phenol would reach 100% at 50 min. Further increase of 10 °C, complete phenol removal was achieved within 40 min while complete phenol degradation at temperature 45 °C would be achieved in 15 min. Based on first-order kinetic model of the reaction, the rate constant on temperature variation were obtained and the relationship was also found to follow the Arrhenius equation. The activation energies of  $\beta$ -MnO<sub>2</sub> was derived as 38.2 kJ/mol.

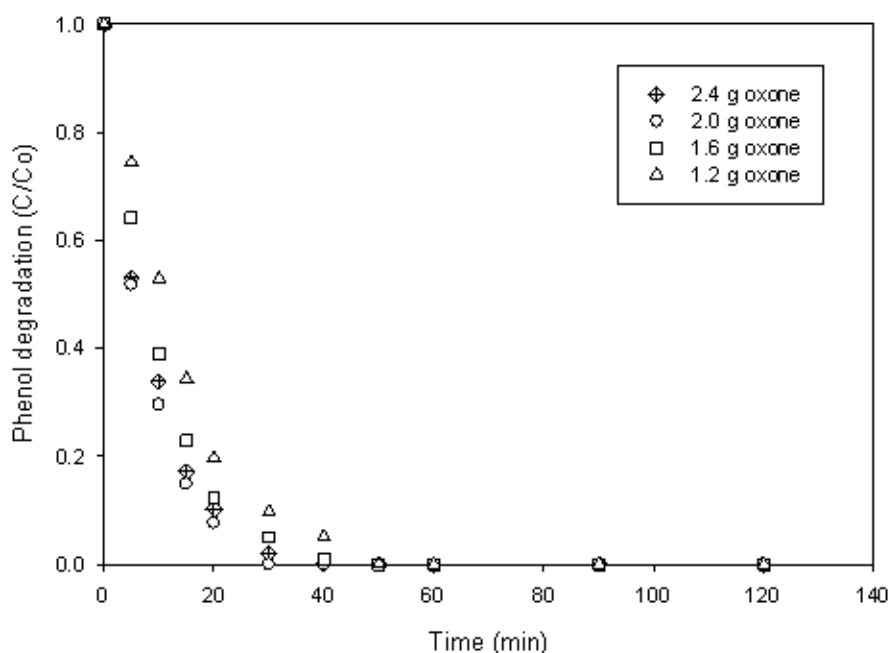


Figure 6. Effect of oxone concentration on phenol removal. Reaction condition: [phenol] = 25ppm, catalyst = 0.4 g/L, and T = 25 °C.

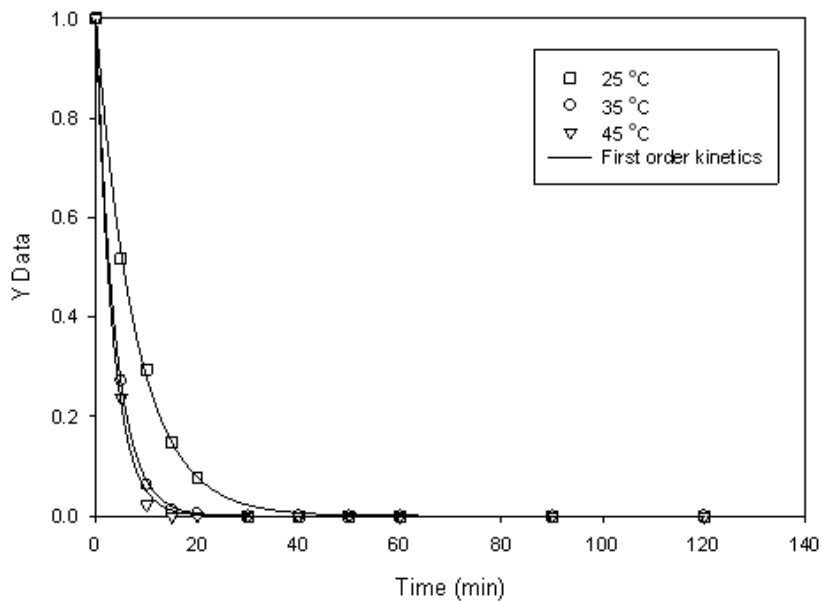


Figure 7. Effect of temperature on phenol removal. Reaction condition: [phenol] = 25 ppm, catalyst = 0.4 g/L, and oxone = 2 g/L.

Figure 8 presents the performance of  $\beta$ -MnO<sub>2</sub> in phenol degradation after catalyst recycling with filtration and water washing. As seen in the second use, phenol degradation profile is much similar to the first test. However, after third use, degradation efficiency of phenol only could reach 60 % in 30 min compared with 100% in the first use. This suggest that the activity of catalyst decreases due to the intermediate deposits on the catalyst surface.

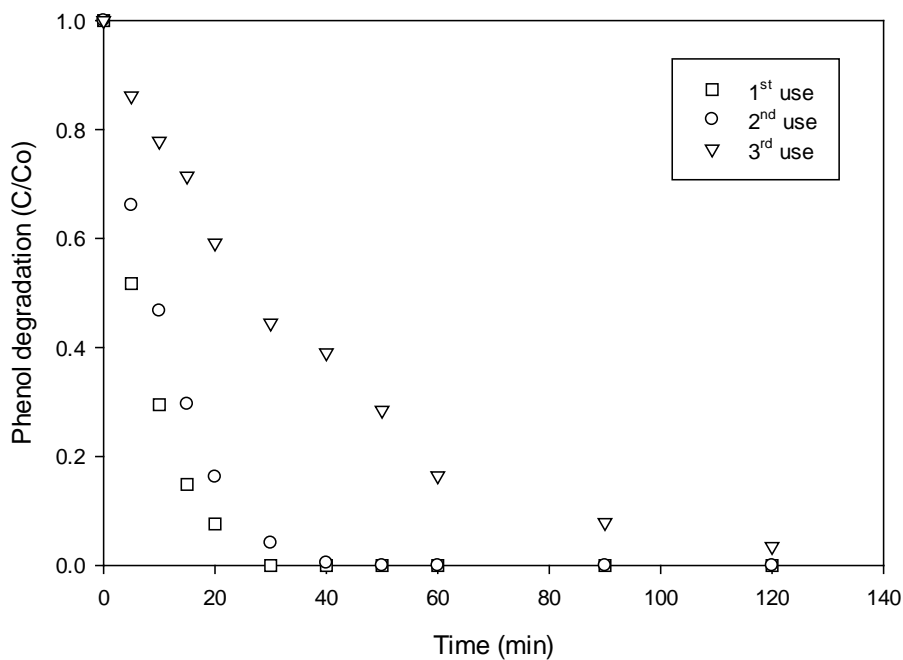


Figure 8. Degradation of phenol in multiple use of  $\beta$ -MnO<sub>2</sub> catalyst. Reaction condition: [phenol] = 25 ppm, catalyst = 0.4 g/L, and oxone = 2 g/L.

## Conclusion

There  $\beta$ -MnO<sub>2</sub> catalyst was successfully synthesized by a hydrothermal method. The particle shows as nanorods and it exhibits high activity in heterogeneous activation of oxone® for oxidation of phenol in water. The Kinetic studies showed that phenol degradation followed first order reaction and activation energy of the catalyst was obtained to be 38.2 kJ/mol. Phenol degradation on catalyst could be described by the first-order kinetics.

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