The Catalytic Activity Of Manganosite MnO/Activated Carbon For Photo-Degradation Of Synthetic Dye

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Abstract. Photocatalytic degradation of organic dye such as methylene blue (MB) has been on focused various research interest due to environmental impact. In this study, the composite manganosite MnO/activated carbon was synthesized by a facile one-pot of sol-gel method through the reaction between potassium permanganate, glucose and commercial activated carbon. The XRD result revealed the presence of rock-salt manganosite MnO in the composite. The catalytic studies were performed under different solution pH, different catalyst concentration and various initial MB concentrations. The result indicated that the catalyst is very effective for the degradation of MB at the basic condition (pH 9 and p11). The degradation of MB in an acidic environment, however, is much less than that of basic condition. In addition, an increase in initial MB concentration caused a decrease in MB degradation due to the saturation of the active sites of the catalyst. The maximum degradation of MB was 98.86 % achieved at pH 11, the initial MB concentration of 50 ppm, and the catalyst concentration of 35 mg.

1 Introduction

Photocatalysis is considered as a versatile technology for environmental remediation, hydrogen production, and energy harvesting [1]. Photocatalytic materials are highly effective and efficient for environmental treatment only if high photocatalytic activity is achieved with the appropriate robustness, reusability, and reliability for industrial investments. Therefore, a wide range of synthetic methods have been developed to accomplish that goal and various materials have been tested for environmental remediation.

Manganese oxides are obiquitous in environmental settings that act as an oxidating agent to degrade organic compounds into smaller ones. Manganese oxides exist in nature in various forms, such as tunnel or layer MnO_2, rock-salt manganosite MnO, and hausmanite Mn_2O_3. The tunnel or layer structures occur depending upon the arrangement of MnO_6 octahedral units, which result in the formation of 1x1, 2x1, 2x2, and 3x3 tunnels [2,3]. Many manganese oxides have been succesfully synthesized by various synthetic method, such as sol-gel [4-7], solid-state [3], precipitation [8-11], reflux [12] and hydrothermal [13]. Manganese oxides exist in nature as mixed valences Mn ($Mn^{2+}/Mn^{3+}/Mn^{4+}$) that could facilitate redox reaction. The presence of Mn^{3+} ion or oxygen vacancy in the framework of manganese oxide may

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cause defect in the material.This defect is an important factor for reducing the band gap of a material, thus accesible for visible region. The presence of a defect also helps to reduce charged recombination of e^- and hole, which is very important for high photocatalytic activity. The presence of other cations such as transition metals in manganese oxides enhances the degradation rates of dyes. [4-7 and 14]. Another strategy to improve catalytic activity could be conducted by formation of a composite. A composite is very useful to avoid the agglomeration of the catalyst and facilitates the electron transfer in a catalytic reaction. In the current study, the composite manganese oxide MnO/AC was prepared using a facile, one-pot using sol gel method and was then applied as a heterogeneous photocatalyst for the degradation of MB. The synthesis of MnO/AC catalyst has been reported by previous studies,

2 Experiment Section

2.1 Synthesis Composite MnO-Activated Carbon

The synthesis of the composite MnO/Activated Carbon, the mol ratio of $KMnO_4$:glucose was 2:3, which was then mixed with the Activated Carbon to form a gel after several minutes. The gel was washed with distilled deinoized water several times and heated at 105°C for 12 hours. The product is then calcined at 700 °C for 2 hours. The product washed HCl and distilled water and the final product was dried at 110°C to generate the composite manganosite MnO/AC. The as-synthesized composites were finally characterized by X-ray powder diffraction (XRD) and Surface Area Analyzer.

2.2 Photocatalityc Activity

The photocatalytic reaction for the degradation of MB was carried out in a glass beaker and about 100 mL MB dye solution 50 ppm was added with a 35 mg composite MnO-carbon activated catalyst. The resulting suspension was then continuously stirred with the aid of a magnetic stirrer for 60 min to achieve adsorption/desorption equilibrium. The UV light irradiation with at wavelength of 365 nm was applied to the suspension. At given time intervals of 10, 20, 30, 40, 50, 60, 90, 100, 110 and 120 min, the 8 mL of the mixture was pipetted into a volumetric flask and transferred into a tube for centrifugation at 2000 rpm for 10 min to settle the catalyst particles. The residual concentration of the MB in the solution at different times was determined using UV spectroscopy.

3 Results and Discuccion

3.1 Synthesis of composite Mno- carbon activated

The XRD patterns of pure manganosite MnO, commercial AC and MnO/AC are shown in Fig 1. The typical XRD pattern for AC appears at $2\theta = 33.15°$ and 49.98°, whereas the rock-salt manganese oxide manganosite MnO appears at 2θ=34.88°; 40.56°; 58.64°; 70.24° and 73.82° which correspond to the diffraction planes of (111), (200), (220), (311), and (222), respectively. The XRD pattern of a single MnO manganosite displayed sharp peaks, reflecting high crystallinity of MnO. For the composite MnO /AC, the intense peaks due to the MnO phase at reflection planes (111) and (200), however, reduced dramatically, indicating less concentration of MnO exists in the composite. The less intense peaks of MnO disappeared completely, which was also reported by previous studies [16].

The XRD pattern of MnO, Mno-Activated carbon and activated carbon are shown in fig 1. The composite are typical Manganosite with 2θ value of 34.88°; 40.56°; 58.64° and 73.82° coresponding to the reflection planes (111), (200), (220) and (222).

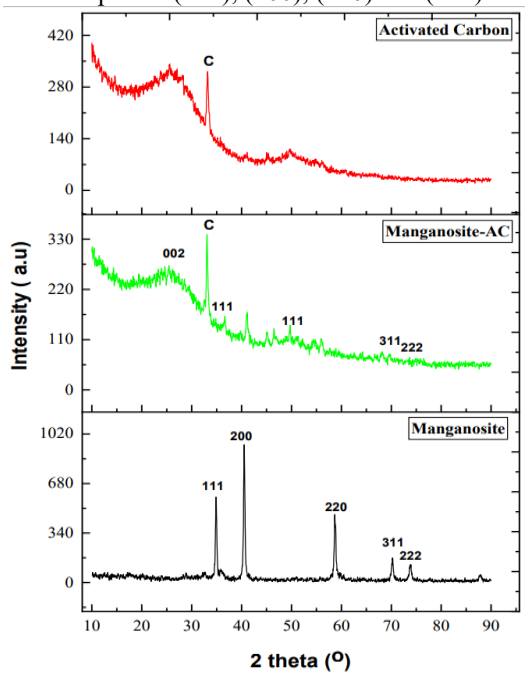

Fig. 1. XRD of Manganosite MnO, composite Manganosite MnO/AC, and Activated carbon AC

The surface areas and pore volumes of MnO, MnO/AC and AC are shown in table 1. The surface area of the composite increased significantly compared to that of MnO, which is about a 47-fold increase in surface area compared to MnO. This high surface area is highly important in a catalytic reaction since the adsorption process is an important step and occurs prior to the catalytic reaction in heterogeneous catalysis.

Table 1. BET value and Crystal Size of MnO, MnO/AC and AC

No	Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Crystal Size (nm)
1	MnO	14.158	-	31.542
2	MnO/AC	667.260	0.167	44.366
3	Activated Carbon	590.759	0.148	-

3.2 Photocalytic Activity

The effect of solution pH on the degradation of MB is shown in Figure 2. The degradation of MB by the composite MnO/AC depends significantly on solution pH. At high acidic condition (pH 3), the degradation of MB reached 81.85% at 110 minute of reaction time. In a moderately acidic environment (pH 5.8), the degradation of MB increased and reached 92.54% at the same reaction time. Further increase to neutral condition (pH 7), the degradation of MB also increased steadily to 95.93% at 110 minutes of reaction time. The increase in the degradation of MB also took place in the basic condition (pH 9 and 11) as shown in Fig 2. Photocatalytic reaction strongly depends on the adsoption of an adsorbate

on the surface of an adsorbent since the adsorption, process is an important step in photocatalytic reaction.

Nguyen T [15] reported the increase in MB degradation in rising solution pH on the surface of copper-doped TiO_2. The zeta potential of copper-doped TiO_2 is zero at pH 6-6.5, indicating that at basic condition (pH>7), the zeta potential of the material is minus. Since MB has positive charge, there is strong electrostatic attraction, leading to strong adsorption between the material with MB. A similar situation could occur with for the photo-degradation of MB by the composite MnO/AC. Most manganese oxides have the zero zeta potential below neutral pH, thus high degradation of MB took place at basic environment [16]. Interestingly, in acidic condition (pH 3), the degradation of MB by the composite reached 81.85% at 100 minutes of reaction time. At acidic condition, some of the MnO particles in the composite may dissolve into the solution as Mn^{2+} ions. This would reduce the availability of active sites in the composite, decreasing the degradation of MB.

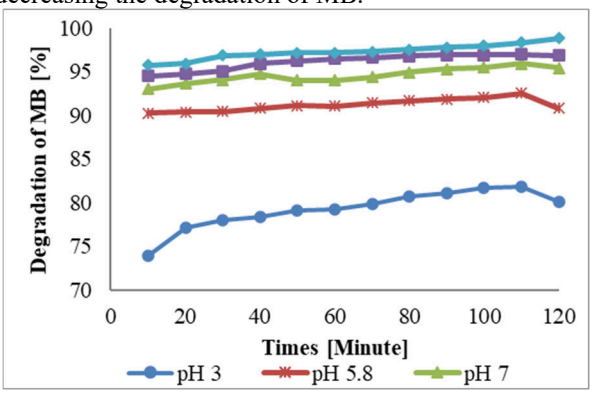

Fig. 2. Effect of pH on degradation MB

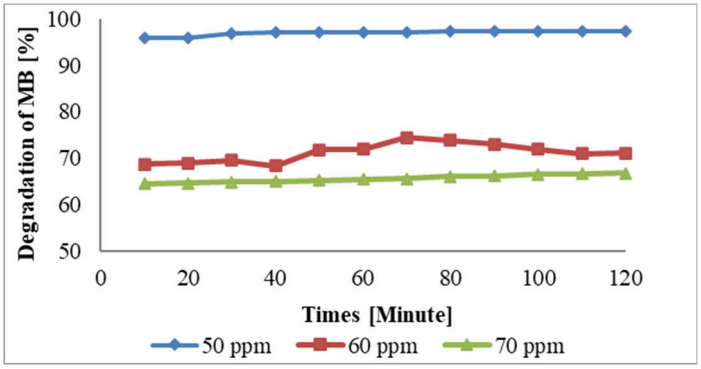

Fig. 3. The Effect of composite mass on the degradation of MB (initial MB concentration of 50 ppm with solution pH 11).

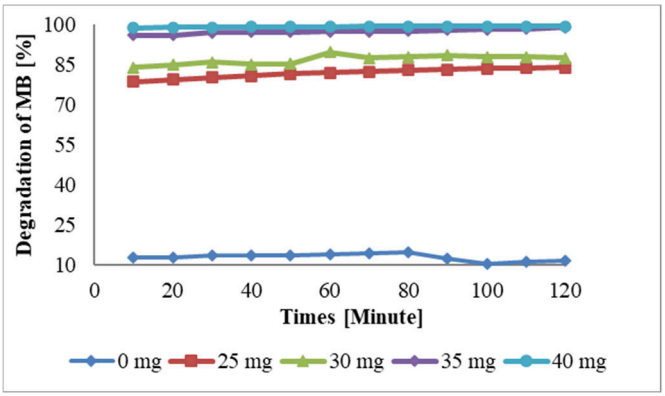

Fig. 4. Effect of MB concentration on degradation (50 ppm, pH 11 and 35 mg catalyst)

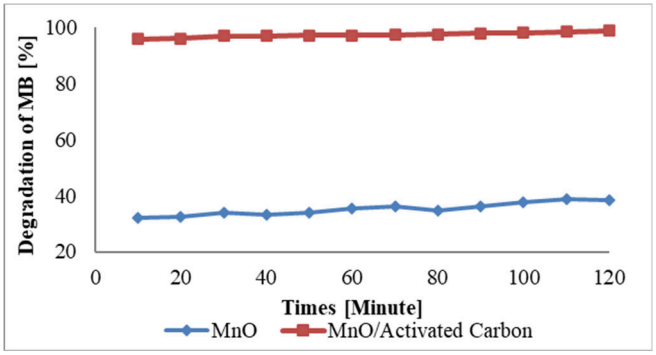

Fig. 5. Effect of catalyst on MB degradation (MB concentration 50 ppm, pH 11 and 35 mg catalyst).

The effect of composite mass on the degradation of MB is shown in Fig. 3. It is obvious that an increase in the composite mass leads to higher degradation of MB. At a low composite mass, there is a competition of MB molecules for the adsoption process on active sites of the composite surface, thus reducing the degradation of MB. At high amount of composites mass, more active sites available for the adsoption of MB on the composite surface. This leads to the higher degradation of MB by the composite as shown in Fig. 3. To study the effect of the initial concentration of MB on the degradation of the molecule by the MnO/AC, a series of different initial MB concentrations were prepared and tested with the solution pH of 11 and the amount of composites of 35 mg. The result indicated that an higher initial concentration of MB led to the lower degradation of MB. This result suggested that at high initial concentration of MB (70 ppm), fewer active sites on the composite are available for the adsorption of MB. This leads to a lower degradation of MB than that of low initial concentration of MB as shown in Fig. 4. Finally, to investigate the effect of the composite on the degradation of MB, the degradation of MB by the composite is compared to the control catalyst, namely MnO, without the addition of AC. The result is shown in Fig. 5, which clearly displays the efficient and effective composite for the degradation of MB.

4 Conclusion

The composite MnO/activated carbon has been successfully prepared by a simple, one-pot sol-gel method. The XRD result indicated the presence of manganosite MnO phase in the composite MnO/activated carbon. The BET surface area method indicated that the composite has a much higher surface area than MnO surface area. The photocatalytic reaction for

degradation methylene blue revealed that basic condition led to higher degradation of MB than that of an acidic condition. There is a strong correlation between high surface area of the composite with high degradation of MB. The composite is much more effective for the degradation of MB compared to a single MnO

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