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Synthesis and characterizations of manganese oxide-modified titanium dioxide photocatalyst for degradation of palm oil mill effluent

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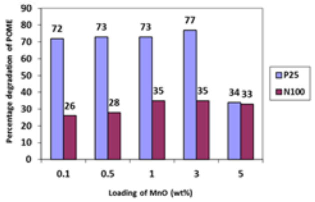
GRAPHICAL ABSTRACT



Percentage degradation of POME using P25 and N100 by impregnation method

ABSTRACT

In this research the effect of the different amount of MnO loading on commecial TiO_2 (P25) were investigated using two methods of preparation which are co-precipitation and impregnation methods. P25-MnO prepared by impregnation method showed an impressive photocatalytic performance in the degradation of Palm Oil Mill Effluent (POME) which was monitored by UV-Vis spectroscopy, compared to P25-MnO prepared by co-precipitation method. The photocatalytic activity were found maximum for 3 wt.% MnO loading on P25. The XRD of P25-MnO composites showed the presence of anatase and rutile phases while Fourier transform infrared spectroscopy spectra exihibed Ti-O-Ti bond streching mode of TiO_2 appeared below 800 cm^{-1}. Diffuse reflectance ultraviolet-visible spectroscopy (DR-UV Vis) of the P25-MnO composit gave maximum absorption spectra at 273 nm while fluorescence spectroscopy shown the emmision band at 421 and 469 nm when excited at 221 nm. The morphology of the best sample, P25-MnO (3wt%) synthesised using impregnation method characterized using Field Emission Scanning Electron Microscope (FESEM) exhibited various size of irregular granulated particles in the nano range size between 40 to 55 nm while energy dispersive X-Ray (EDX) spectroscopy proved the presence of Ti, Mn and O. The highest photocatalytic degradation activity recorded was 77% performed by P25-MnO (3wt%) catalyst synthesised using impregnation method. Study show that the method of preparation of the MnO loaded P25 has an effect into producing an active catalyst for degradation of POME.

Keywords: *TiO_2, Manganese, impregnation, co-precipitation, palm oil mill effluent.*

1. INTRODUCTION

Titanium dioxide (TiO_2) have a band gap of ~3 eV [1]. Because of its wide band gap, it exhibit a fast rate of electron hole recombination. This drawback retard the photocatalytic reaction to occur and resulting to no photocatalytic degradation take place [2]. Previous researches suggested that modification of TiO_2 with metal can minimize the rate of recombination and improve the photocatalytic activities of TiO_2 [3]. One of the metal that has been reported to show great potential is Manganese. Manganese oxide (MnO) catalysed the oxidation reaction since it was able to enhance the degradation of hydrogen peroxide that led to the acceleration of the oxidation reaction [4]. In a research, Mn reduced the rate of electron-hole recombination of the ZnO, which led to the improved the photocatalytic process in the degradation of organic dyes [5]. In this study, palm oil mill effluent (POME) has been chosen as a model of organic pollutants. Discharged POME that has not been treated have high organic content which could lead to eutrophication effect that might be activated by the algae in the water source. Photocatalytic reaction would be one of the most suitable processes since it involves minimum requirement of energy for degradation of organic pollutant. In this research, TiO_2 modified with MnO was synthesised using two methods which are impregnation method and co-precipitation method with different MnO loading.

2. EXPERIMENTAL

Synthesised composites, TiO_2 were characterized by X-ray diffraction (XRD, Bruker AXS Diffracplus release 2000) in the 2θ range of 20 to 60°, the Fourier transform infrared spectroscopy (FTIR, Thermo Scientific, Nicolet iS50), range from 4000 - 400 cm^{-1}, Diffuse reflectance ultraviolet-visible spectroscopy (DR UV-Vis, UV 2600, Shimadzu), .fluorescence spectroscopy (FP-8500, JASCO), Field Emission Scanning Electron Microscopy (FESEM, JEM-2100) at an accelerating voltage of 200 kV and Ultraviolet visible spectroscopy (UV Vis, UV 2600, Shimadzu) with Xe-Hg as te light source.

2.1. Chemicals and materials

Four commercial TiO_2 were used in this study, which were P25 TiO_2 (99.5%, Evonik Industries), P90 TiO_2 (99.5%, Evonik Industries), Hombikat UV100 TiO_2 (99%, Sachtleben Chemie) and Hombikat N100 TiO_2 (98%, Sachtleben Chemie). In order to prepare the TiO_2-MnO composites, manganese(III) acetylacetonate ($Mn(C_5H_7O_2)_3$, 99%, Sigma Aldrich) and ethanol (C_2H_6O, Score Scientific) were used. For photocatalytic removal of POME, POME and double distilled water was used in this study

2.2. Sample preparation

In impregnation method, various TiO_2-MnO composites were prepared with various MnO contents of 0.1, 0.5, 1, 3 and 5 mol%. Since P25 and N100 showed better activity than other investigated commercial TiO_2, these two types of TiO_2 were modified with the MnO. The composites were labelled as P25-MnO IM (x) or N100-MnO IM (x), with x shows the MnO content. For the typical synthesis of P25-MnO IM (0.1), manganese(III) acetylacetonate (0.005 g) were dissolved in ethanol (40 mL) as a solvent. After all the Mn dissolved, P25 (1 g) was added slowly into the solution and sonicated for 5 min. The mixture was then stirred and dried at 60-80 ^{o}C in an oil bath until the solvent was evaporated. Then, the dried sample was calcined at 300 ^{o}C for 4 h. The similar steps were used to prepare other series of P25-MnO IM (x) and N100-MnO IM (x) composites.

In co-precipitation method, certain amount of the manganese(III) acetylacetonate (x : 0.1, 0.5, 1, and 5 mol%) will be dissolved in 30 ml ethanol under stirring condition. The P25 or N100 TiO_2 (1 g) will be added onto the solution. The co-precipitation process will be carried out by dropping the sodium hydroxide (NaOH) solution and the mixture will be continuously stirred for 1 h. The precipitate sample will be filtered and washed with ethanol. Later, the product will be dried at 100 °C for 1 h. Finally, the obtained solid will be then calcined at 300 °C for 4 hours. The samples were labelled as P25-MnO CP (x) or N100-MnO CP (x), which x shows the loading of manganese oxide.

2.3. Preparation of standard solution and calibration curve of POME

A stock solution of 100 % POME was prepared using the pre-treated POME, which was collected from final pond at Palm Oil Mill. Three standard solutions of POME were prepared with five different concentrations of 1, 2, 3, 4 and 5%. The calibration curve of the POME solution was obtained by measuring the absorbance of the standard solutions by using a UV-Vis spectroscopy, taking the absorbance peak at 265 nm.

2.4. Absorption of POME in dark condition

Photocatalyst (50 mg) was dispersed in a 100 mL beaker containing 50 mL of POME (5 %). The beaker was placed in a closed box and dark condition was set up to ensure that there was no activation by light occurred on the system. In order to determine the duration time for the photocatalyst to achieve equilibrium of absorption, the dark reaction condition was conducted for 3 h continuously. After each time, the photocatalyst was separated from the solution and the concentration of POME solution was measured by using UV Vis spectroscopy.

Photocatalytic removal of POME

The photocatalytic removal of POME is conducted on the photocatalyst (50 mg) that is dispersed in 100 mL jacketed-beaker containing 50 mL of POME (5 %). Then, the beaker is placed on the stirring plate in closed box for 1 h to let adsorption-desorption equilibrium be reached. The reaction is carried out over 15 hours under UV light irradiation. After reaction, the photocatalyst is separated from the solution. The concentration of the solution is then measured by the UV-Vis spectroscopy to determine the removal of POME.

3. RESULTS AND DISCUSSION

Synthesised composites photocatalyst P25-MnO were characterized using XRD, FTIR, DR UV-Vis, fluorescence spectroscopy and FESEM. Photocatalytic activity of POME was measured by UV Vis spectroscopy. P25-MnO with different loading prepared by impregnation method shows high photocatalytic activity in the degradation of POME.

3.1. Characterizations of TiO_2 P25-MnO composites synthesised using impregnation method.

In figure 1, XRD patterns exhibited strong diffraction peaks at 25°, 39° and 55° indicating TiO_2 in the rutile phase. In figure 2, no change was observed on the FTIR spectra when the amount of MnO loading increased on the TiO_2 composites. This is maybe due to the small amount of MnO added onto the TiO_2. All composite samples gave the Ti-O-Ti bond streching mode of TiO_2 below 800 cm^{-1} and surface adsorbed water molecule around 3400 and 1600 cm^{-1}.

DR UV-Vis spectra in Figure 3 shows that with the addition of MnO at high loading (5 mol%) the absorption peak was slightly shifted to longer wavelength and additional background absorption at visible region was also observed. This is in good agreement with the colour of the sample, which is grey. From the fluorescence spectra in Figure 4 below, emission band at 421 and 469 nm are observed. It can be seen that the emission band are decrease with the decrease of Mn loading. These emission peaks occur at larger wavelength in which the decrease in fluorescence emission may be attributed to the transfer of the electrons. The oxygen vacancies and surface hydroxyl groups are the sites for trapped electrons and holes. These trapped carriers which are captured by oxygen and hydroxyl groups contribute to the visible luminescence in these nanoparticles. Emission at 421 and 469 are due to the recombination of trapped electron-hole from the bonds in the TiO2 nanoparticles.

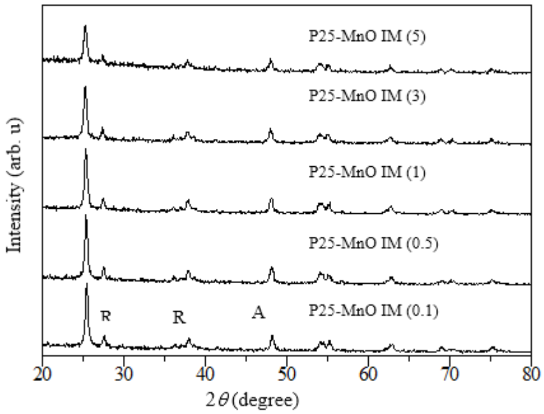


Figure 1 The XRD spectra of the P25-MnO composites prepared by using the impregnation method. A: Anatase, R: Rutile

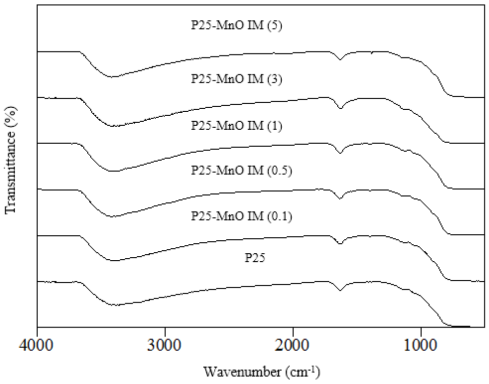


Figure 2 The FTIR spectra of the P25-MnO composites prepared by using the impregnation method.

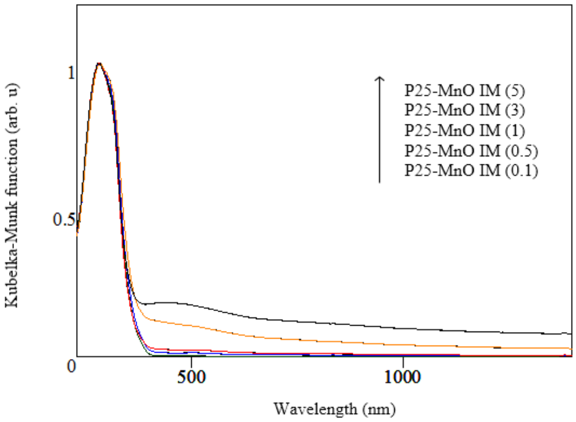


Figure 3 DR UV Vis spectra of P25-MnO synthesised using impregnation method

From the Figure 5 it can be seen that P25-MnO particles exist as aggregates of irregular granulated particles with with the majority of the nanocomposites particles in the nanorange size of 30 to 50 nm. This shows that P25 exhibit higher surface area and roughness. TiO_2 with larger surface area will give better photocatalytic activity which proven true as it give 77% percentage degradation with an optimum loading of 3wt%. Topographical and elemental imaging is possible at the same time. The dispersion of the Mn metal and O deposited on the TiO2 catalyst can also be characterized by the EDX mapping technique. EDX mapping is is a valuable tool to indicate the quality of the Mn dispersion. The electron beam is scanned pixel by pixel across a selected area of interest. The EDX spectrum shows the peaks of Ti, O and Mn indicates that these elementals composition present in the P25 TiO2 nanoparticles.

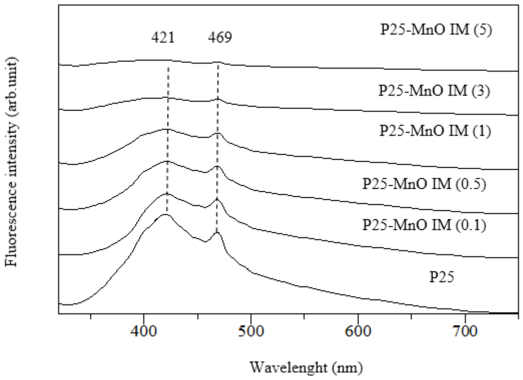


Figure 4 Fluoresecence spectra of P25-MnO synthesised using impregnation method

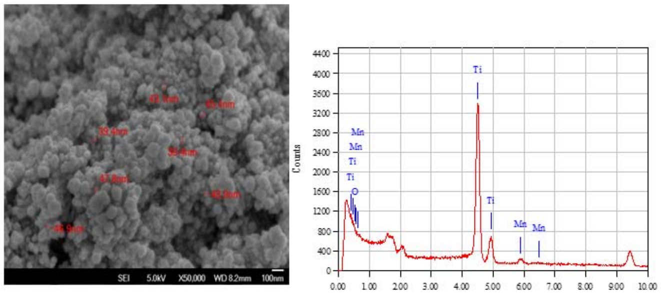


Figure 5 FESEM images of P25-MnO (3wt.%) synthesised using impregnation method.

3.2. Photocatalytic degradation of POME

From the figure below, it can be seen that P25 shows better catalytic activity compared to N100-MnO. This is might be due to N100 is very stable against the pollutant even with the presence of Mn metal deposited on the TiO_2 catalyst. The optimum catalyst loading enables the maximum photocatalytic activity while preventing the unnecessary excess use of applied catalyst.It was found that the optimum P25-MnO loading required is 3wt.% that yields maximum 77% percentage degradation prepared by impregnation method 54% percentage degradation was yields when it is prepared by co-precipitation method. The increase of photocatalytic activity with the increase of MnO loading from 0.1w1% to 3wt% might be because of the higher number of active sizes and more reactive radicals available for surface reaction. However the decrease in photocatalytic activity was observed at higher MnO loading which at 5wt%. This might be attributed to deactivation of activated molecules due to collisions with ground state molecules when catalyst concentration is increase.

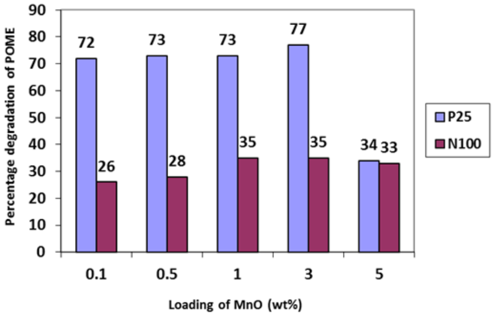


Figure 6 Percentage degradation of POME using P25 and N100 by impregnation method

4. CONCLUSION

Series of P25-MnO and N100-MnO composites have been prepared by the impregnation method and characterized by XRD, FTIR and DR UV-Vis and fluorescence spectroscopies. XRD patterns revealed that the P25 have both anatase and rutile phases, All composite samples gave similar functional groups to the unmodified TiO_2 samples. The DR UV-Vis spectroscopy revealed that the addition of MnO with high loading (5 mol%) slightly shifted the absorption edge of the TiO_2 to higher wavelength and gave additional absorption at visible light region. Fluorescence spectra show emission band at 421 and 469 nm are observed. It can be seen that the emission band are decrease with the decrease of Mn loading. P25-MnO particles exist as aggregates of irregular granulated particles with with the majority of the nanocomposites particles in the nanorange size of 30 to 50 nm. This shows that P25 exhibit higher surface area and roughness. Results of photocatalytic activities show that P25-MnO prepared by impregnation method gave maximum percentage degradation of 77%.

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