Characterization of fabricated MnO$_2$-amberlite photocatalyst by FTIR, XRD and SEM for alizarin removal

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Abstract. This study investigates the characterizations of fabricated MnO$_2$-amberlite using for alizarin photocatalytic degradation. Mixtures of fabricated MnO$_2$-amberlite were magnetically stirred for 6-, 12-, 18-, 24-, and 30h, respectively. Some functional groups of amberlite like C-O, C-C and N-H were eliminated after doping with MnO$_2$ as shown by FTIR (Fourier Transform Infrared) spectra in the range of 1600 – 900 cm$^{-1}$, change in crystalline structures due to linkage of MnO$_2$ with amberlite was observed at 20 of 25$^\circ$ in the XRD (X-ray diffraction) analysis, and change in surface morphology due to MnO$_2$ doping in amberlite was investigated in SEM (Scanning electron microscope) examination. Since alizarin is a harmful material causing environmental problem, this preliminary study found that the 18h-stirred fabricated MnO$_2$-amberlite showed the best photocatalytic properties, which enabled to degrade 23.4% alizarin under 1h UV exposure without heating.

1. Introduction

Nowadays the development of catalysts has taken greater interest especially in purification of wastewater for human health reason. Among the environmental catalysts, MnO$_2$ photocatalyst is the most promising one due to thermocatalytic activity for the decomposition of organic pollutant in wastewater [1]. Several publications reported MnO$_2$ as photocatalyst for dyestuff degradation [2 – 5]. As we have known advance oxidation process is associated with free radicals generated by irradiation of UV and/or visible light on semiconducting material such as MnO$_2$, which are responsible for the decomposition of organic compound and changed it into harmless products such as CO$_2$ and H$_2$O. The utilization of photocatalyst has attracted great interest due to its simple, low cost, and friendly environmental technology.

Amberlite or resin has largely used as solid phase adsorbent for removing contaminants in aqueous solution. Previous investigations reported amberlite used for extracting selected heavy metals (copper, cadmium and lead) from dairy cow’s milk, and fractionized amberlite for removing boron from water, as well as amberlite XAD 7 for extracting bismuth (III) from hydrochloric acid solution [6-8]. In addition, several sensors have used modified amberlite as immobilized matrix [9-11]. The utilization of amberlite as strong acid cationic exchanger has attracted considerable interest due to its stability and low cost. As resin produced by many plant particularly woody plants made resin in greater utility. Industrial effluents contain various chemicals including synthetic dyes, which are carcinogenic in nature. Several dyes decompose aerobically and anaerobically yielding the formation of carcinogenic compounds. Alizarin or mordant red is known as an organic compound, which is largely used as dye
in textile industries yielding environmental problems. Roopaei et al. [12] used hematite (Fe$_2$O$_3$)/NiS photocatalyst to degrade alizarin in aqueous solution on account of chemical stability and environmental friendliness, however, this study used MnO$_2$ immobilized in amberlite, which is more stable and has broader band gap for alizarin photocatalytic degradation. Different stirring times (6h, 12h, 18h, 24h and 30h) of MnO$_2$ and amberlite solution mixture followed by calcinations was used for the synthesis of MnO$_2$-amberlite. The mixture of MnO$_2$-amberlite and alizarin solution was exposed to UV light at 265 nm to degrade alizarin. Characterization study of MnO$_2$-amberlite photocatalyst by FTIR, XRD and SEM was investigated.

2. Experimental

2.1 Materials
All chemicals were purchased and used without further purification. Deion distilled water was used throughout the experiments. MnO$_2$ (Merck OHG, 99.5 %) for the synthesis of photocatalyst, amberlite IRA 400 (Sigma Aldrich GmbH, ≥ 95%) for immobilized matrix, and alizarin for assayed dyestuff (Fluka Chemie, 99%) were used in this study.

2.2 Methods

2.2.1 Synthesis of MnO$_2$-amberlite. About 15g amberlite was grinded to fine powder and dried in an oven at 98-99°C and then 0.500g dried amberlite was dissolved in 15 ml deion distilled water and stirred for 5h. 0.200g MnO$_2$ was added to amberlite solution and stirred vigorously with magnetic stirrer at different time (6-, 12-, 18-, 24-, and 30h), respectively. All MnO$_2$-amberlite solutions with respect to different stirring times were centrifuged at 3700 rpm for 15min. to obtain suspended solid, respectively. The MnO$_2$-amberlite products were dried in an oven at 98-99°C followed by calcination at 250°C for 5h, respectively.

2.2.2 Characterizations. The fabricated MnO$_2$-amberlite was characterized using the following instruments. The functional group of the MnO$_2$-amberlite was determined by FTIR (Perkin Elmer) with potassium bromide as the reference sample. The structural property of the fabricated MnO$_2$-amberlite was investigated by XRD (Siemens D5000) using CuKα radiation. The surface morphology of the fabricated MnO$_2$-amberlite was examined by SEM (Philips XL 40) using gold sputter (Polaron Division SEM coating system) to coat the material powder.

2.2.3 Photocatalytic degradation test. The catalytic degradation of alizarin by the fabricated MnO$_2$-amberlite was investigated by UV-Vis spectrometer (Perkin Elmer Lambda 25). Standard solutions of alizarin from 10 ppm to 50 ppm were prepared for calibration at 265 nm. A mixture of fabricated MnO$_2$-amberlite and alizarin solution of 50 ppm (part per million) placed in a bottle covered by aluminium foil was exposed to UV light at 265 nm for 1h stirring. The aluminium foil protects the sample from other contaminants.

3. Results and discussion

3.1 Functional group of the MnO$_2$-amberlite
The functional groups of the fabricated MnO$_2$-amberlite was determined by FTIR spectroscopy. As shown in Figure 1 (c), the peaks presence at 3421 cm$^{-1}$, 1614 cm$^{-1}$, 1488 cm$^{-1}$ and 1475 cm$^{-1}$ are corresponding with benzene sulphonig groups in cross-linked amberlite polymer. The pure amberlite shows the aromatic rings at 3022 cm$^{-1}$ and C-H stretching at 2921 cm$^{-1}$ (Figure 1c), while the N-H stretching at 3421 cm$^{-1}$ (Figure 1c) was getting weaker and showed at 3426 cm$^{-1}$ in Figure 1b due to MnO$_2$ doping in amberlite. Furthermore, the FTIR spectrum range of 1600 – 900 cm$^{-1}$ of pure
amberlite shows vibration of C-O and C-C stretching, and N-H bending in the amberlite polymer. When pure amberlite mixed and magnetically stirred with MnO₂, almost all of the functional groups initially present were eliminated due to mechanical effect and the inclusion of MnO₂ in the cross-linked polymer. The presence of remarkable peaks at 588 cm⁻¹ (Figure 1b) and 589 cm⁻¹ (Figure 1a) was due to the formation of Mn-O linkage in relation to tetrahedral and octahedral structure [13 – 15].

![FTIR spectra](image)

**Figure 1.** FTIR spectra of (a) 6h-stirred MnO₂-amberlite, (b) 18h-stirred MnO₂-amberlite, and (c) pure amberlite. KBr reference sample.

### 3.2 Structure of the MnO₂-amberlite

The structural property of the MnO₂-amberlite was investigated by the XRD. Figure 2 shows a peak cluster at 2θ of 25°, which forms unstable structure. It is apparent that the stirring action on the MnO₂-amberlite did not give meaningful effect on the crystalline structure of pure MnO₂. Previous work reported that the diffraction angles of 25°, 37° and 57° are corresponding with (211), (400) and (440) planes, respectively [15].

![XRD spectra](image)

**Figure 2.** XRD spectra of (a) pure MnO₂, (b) 6h-stirred MnO₂-amberlite, and (c) 18h-stirred MnO₂-amberlite (50 nA, 40 kV, and angular range of 20.80°).
3.3 Surface morphology of MnO$_2$-amberlite

The surface structure of the fabricated MnO$_2$-amberlite was examined by SEM. Theoretically, the longer stirring time yields finer particles, however, agglomeration of particles may occur during stirring process due to polarization and induction effects. Previous work reported manganese distribution on the ferrite surface were varied due to thermal effect [15-16], however, this study shows the particles distribution on the material surface due to mechanical effect. Figure 3 shows the SEM imaging of pure amberlite and fabricated MnO$_2$-amberlite at different stirring times.

3.4 Photocatalytic degradation of alizarin

The utilization of fabricated MnO$_2$-amberlite for photocatalytic degradation of alizarin was conducted by using UV-Vis spectrometer. Based on the surface adsorption test of BET (Brunauer Emmett Teller) (not shown), the 18h-stirred MnO$_2$-amberlite showed the largest surface area (65.11 m$^2$ g$^{-1}$ of 0.032g sample), which assumed to yield the best catalytic property in this study and therefore, this sample was used in the examination of degradation of alizarin. Based on the calibration curve of UV-Vis absorption at 265 nm the fabricated MnO$_2$-amberlite might degrade 23.4% of alizarin in aqueous solution under non heat condition and 6.8% of alizarin under heat condition.

![Figure 3. SEM imaging of pure amberlite and fabricated MnO$_2$-amberlite. 50 µm working distance. 500 x magnification. 25.0 kV.](image)

4. Conclusion

The study presented important features related to the characterization study of FTIR, XRD and SEM of fabricated MnO$_2$-amberlite, which gives meaningful information for photocatalytic degradation of alizarin. Some important functional groups were removed and replaced by remarkable peaks at 588 - 589 cm$^{-1}$ due to MnO$_2$ inclusion as shown in the study of FTIR spectra, however, the XRD
characterization at 2θ of 25° showed that amberlite matrix and stirring process did not give significant effect on the crystalline structure of pure MnO₂. The SEM imaging showed finer particle distribution on the material surface after MnO₂ mixed with amberlite under stirring process.

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References

[1] Qiliang J, Hiroshi A, Musashi F and Hiroaki T 2013 Catalysts 3 444
[2] Li S J, Ma Z, Wang L and Liu J Z 2008 Sci. China Series B: Chem. 51 179
[3] Lifang Z, Daiping H and Ping J 2009 Catalysis Commun. 10 1414
[4] Liu Y, Luo C, Sun J, Li H, Sun Z and Yan S 2015 J. Mater. Chem. A 3 5674
[5] Xue M, Huang L, Wang J O, Wang Y, Gao L, Zhu J and Zhou Z G 2008 Nanotechnol. 19 5604
[6] Hoque M I, Didarul A C, Holze R, Nakib C and Azam M S 2015 J.Environ.Chem.Engineer. 3 831
[7] Nawaf D, Victor K and Nidal H 2015 Desalination 370 1
[8] Navarro R, Ruiz P, Saucedo I and Guibal E 2014 Separation. Purifi. Tech. 135 268
[9] Moghaddam M K, Hellmann J and Lang W 2016 Procedia Engineer. 168 1110
[10] Bliznyuk V N, Duval C E, Apul O G, Seliman A F and DeVol T A 2015 Polymer 56 271
[11] Bairi A, Nithyadvisi N, Baiiri I, Garin A M and Garcia J A M 2017 Energy Build. 141 218
[12] Roopaeei H, Zohdi A R, Abbasi Z and Bazrafkan M 2014 Indian J Sci. Technol. 7 1882
[13] Pradeep A and Chandrasekaran G 2005 Mater. Lett. 60 371
[14] Pradeep A, Priyadharsini P and Chandrasekaran G 2008 J Magnetism & Magnetic Mater. 320 2774
[15] Hua T I and Sundari R 2012 Malaysian J. Fundamental Appl. Sci. 8 149
[16] Sundari R, Hua T I, Aziz M and Nizar U K 2014 Malaysian J. Anal. Sci. 18 485