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Preparation of TiO_2/Aluminium Pillared Montmorillonite and its Application for Methylene Blue Photodegradation under UV Illumination

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Abstract: The photocatalytic degradation of methylene blue by TiO_2 dispersed in aluminium pillared montmorillonite (TiO_2/Al_2O_3-Montmorillonite) catalyst under UV light illumination has been investigated. Purpose of the research is to study the effect of titania dispersion onto the aluminium pillared montmorillonite matrix to the photocatalysis activity. The variation of methylene blue concentration in impregnation process was designed in order to obtain the reaction constant data as reaction rate indicator as well as adsorption process. Results of the research show that upon irradiation with UV light the methylene blue degradation is significantly changed compared to adsorption process. The role of titania dispersion was indicated by the upsurge of methylene blue decomposition rate in photocatalytic system significantly relative to the matrix use.

Key words: Photocatalysis · Aluminium pillared clays · Impregnation · Adsorption

INTRODUCTION

Some industries which use dyes and pigments generated wastewater, high in colour and pigments exists and over 7 x 10^5 tones are produced annually world wide and some of these discharged into rivers are harmful to the aquatic life. Dyes often contain elements such as nitrogen, chlorine or sulphur. The oxidation products of these molecules may be more toxic than the parent molecules. Many of the dyes are, however, difficult to remove, as they are stable to light and heat and are biologically non-degradable [1].

Most of the methods that have been studied have focused on producing clean water suitable for recycling. There are many possible methods for removing of dyes, including adsorption, ozonation, Fenton's oxidation, electrochemical treatment, coagulation/flocculation, biological treatment and photodegradation. Each method has limitation and specific to the certain conditions. For example, the adsorption process can be effective in the low concentration of contaminant and adsorbent regeneration can be a new problem. Ozonisation, Fenton's oxidation and coagulation/flocculation need chemicals that make the processes highly expensive and need some further steps for clean technology [2]. Photodegradation, however, is a method having a capacious prospect to generate clean environment. Basic principle of this process is oxidation/reduction of organic material by light and is activated using a photocatalyst. The main advantage of this process is complete mineralization of organic compounds, to CO_2 and H_2O, which are less toxic in environment and photocatalyst can be reused due to less surface deactivation compared to the adsorption process [3-4]. Titania, TiO_2, is known to be one of the most effective photocatalysts because of its nontoxicity, low cost and high photocatalytic activities, etc. Its band gap energy ($Eg = 3.2$ eV) can be activated by UV light provided from a lamp or sunlight. However, the use of titania in bulk form such as in powder or slurry makes its loss activity rapidly. Titania incorporated/dispersed onto the inorganic matrix is a technique to overcome this problem. Clay is a kind of inorganic matrix with some advantages to improve the activity such as its high surface area. Metal oxide dispersion in clay structure for pillarization process can form the material of pillared interlayered clays (PILCs). This synthesis technique has been studied in the past years. PILCs constitute one of the families of new microporous materials developed by molecular engineering and prepared by a multi-step synthesis process which involves: (i) preparation of bulky

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inorganic polyoxocations by polymerisation of cations of some metallic elements; (ii) exchange of the exchangeable charge balancing cations of smectitic clays by these polyoxocations, forming intercalated solids; (iii) stabilisation of the intercalated solids by calcination. These metal oxide clusters, called pillars, are inserted between the clay layers, maintaining them apart for a relatively large distance thus avoiding their collapse and developing a porous network with molecular range dimensions [5-6].

In the case of titania pillarization, synthesis step is facing to several problems regarding to the titania stability at low pHs. In addition, low pH will destroy clay structure. As an alternative method for titania supported material preparation, titania dispersion onto aluminium pillared clays is the interest. The easy synthesis in aluminium-pillared clays and its stability can alleviate the problem of titania dispersion and also provide higher surface area [7-8].

In this paper, we present the results in the synthesis of titania dispersed onto aluminium pillared montmorillonite and its use as a photocatalyst in methylene blue photodegradation. Study on kinetics of degradation process is reported.

EXPERIMENT

Materials: Chemicals with analytical grade of $TiOCl_2$, $AlCl_3.6H_2O$, NaOH and methylene blue (structure as presented in Fig.1) were supplied by E.Merck.

Experimental Procedure: The method of preparation of the aluminium oxide pillared montmorillonite consists of aluminium polyoxocation intercalation followed by calcination at the temperature of 500°C. Titania dispersion onto the aluminium pillared montmorillonite was enganged by impregnation method with titanium oxide chloride precursor at the theoretic concentration of 1% titanium. Physicochemical characters of materials were studied by XRD measurement (XRD Shimadzu X 6000), surface area analysis (Quantachrom Autosorb-1) and diffuse reflectance UV-visible spectrophotometer (JASCO V 670).

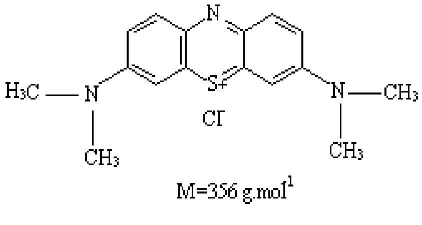

Fig. 1: Methtylene blue structure

Photodegradation of methylene blue was performed in a pyrex glass photoreactor with a volume of 250 mL. Four lamps as UV light source were powered at 10 volts and λ = 356 nm. Two sets of lamps were placed on the top and others were placed beside the reactor. An electrical magnetic stirrer with magnetic bar was used continuously so that TiO_2/Al_2O_3-Montmorillonite can be uniformly dispersed in the solution when the sample was decomposed by UV light. Methylene blue concentration after the treatments was analyzed by UV-visible spectrophotometer (Shimadzu U 2080) at the wavelength of 630 nm.

RESULTS AND DISCUSSION

Material Characterizations: Physicochemical character of TiO_2/Al_2O_3-Montmorillonite compared to the raw montmorillonite sample were studied by XRD, surface area analyzer and diffuse reflectance UV-visible. XRD patterns of the materials are depicted in Fig. 2. Reflections of natural montmorillonite (NM) show the significant characteristic peaks at 2θ = 6.30° (d= 14.47 ?) and 2θ = 19.91° (d= 4.45) with the valuable intensity and other reflections at 2θ=20.18°, 23.57° and 26.57°. The reflection at 2θ = 5.92° is correlated to the d_{001} basal spacing of smectitic clay structure. Other reflections corresponding to the impurities minerals of quartz and crystoballite are also identified. Specific alteration to the montmorillonite reflection was observed, which shows a shift of d_{001} to the lower angle after pillarization and titania dispersion. The d_{001} reflection of TiO_2/Al_2O_3-Montmorillonite is at 5.80° implying a larger d_{001} value resulted from aluminium oxide pillarization.

However, the d_{001} peak of TiO_2/Al_2O_3-Montmorillonite is much broader than that of NM clay and Al_2O_3-Montmorillonite indicating that there is decreasing in the crystalinity. This effect can be attributed to the titania dispersion process.

This analysis can be confirmed by surface area analysis as shown in Fig. 3. The adsorption desorption isotherm in Fig.3 is in agreement with the XRD analysis. The dispersion of titania contributes to a significant decrease in the specific surface area of Al_2O_3-Montmorillonite and thus the adsorption. The specific surface area of materials is presented in Table 1.

Table 1: Specific surface area of materials

Material	Specific surface area (m^2/g)
Natural Montmorillonite	59.88
Al_2O_3-Montmorillonite	183.09
TiO_2/Al_2O_3-Montmorillonite	79.24

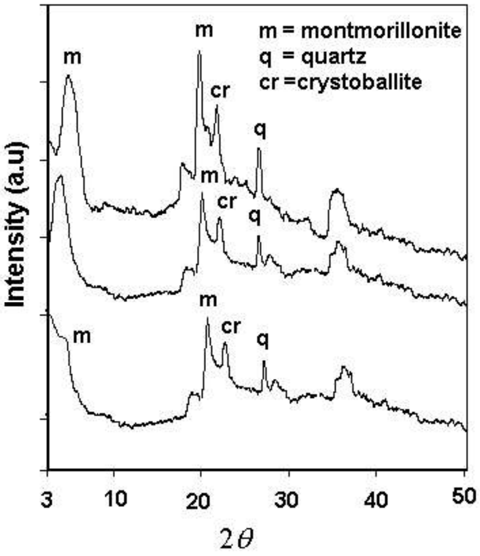

Fig. 2: XRD pattern (from top to down): Natural Montmorillonite, Al_2O_3-Montmorillonite and TiO_2/Al_2O_3-Montmorillonite

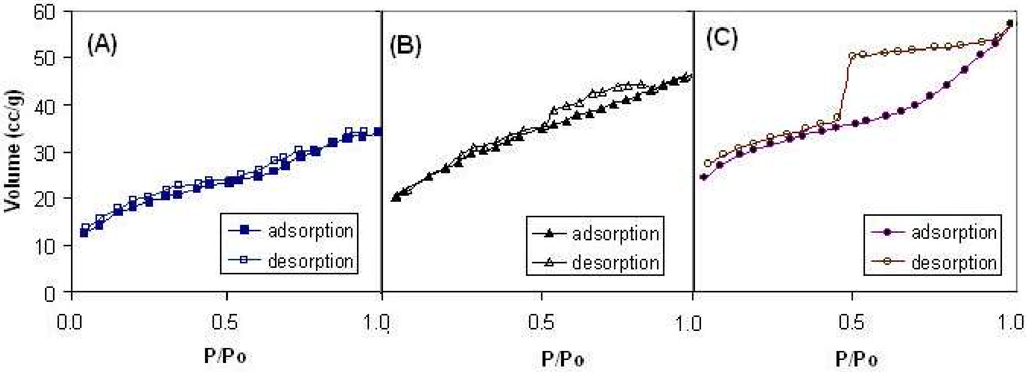

Fig. 3: Adsorption-desorption isotherm of (a) Natural montmorillonite (b) Al_2O_3-Montmorillonite and (c) TiO_2/Al_2O_3-Montmorillonite

The TiO_2/Al_2O_3-Montmorillonite exhibits a shape of type IV isotherm with a hysteresis of type H4 while NM and Al_2O_3-Montmorillonite show an isotherm of type I with lower adsorption volume. The differences in the isotherm type are evidence for the micropore-mesopore evolution in materials.

Figure 4 shows the UV-vis diffuse reflectance spectra of NM, Al_2O_3-Montmorillonite and TiO_2/Al_2O_3-Montmorillonite. Compared with the NM spectrum, the spectra of Al_2O_3-Montmorillonite and TiO_2/Al_2O_3-Montmorillonite show an absorption edge at about 400 nm shifted toward higher wavelength.

The shift of the absorption edge is more pronounced in the case of the titania formation in the aluminium pillared montmorilonite matrix by comparing spectra of Al_2O_3-montmorillonite with TiO_2/Al_2O_3-Montmorillonite. This indication is a representation of titania formation in the matrix. However, there is no clear explanation related to the significant shift of the comparison between the TiO_2/Al_2O_3-Montmorillonite spectrum and TiO_2 (E.Merck).

Photocatalytic Activity: In Figure 5, the kinetics of methylene blue degradation is presented by the relationship of abatment of MB concentration as a function of time. The adsorption and photodegradation results are compared. From these curves it can be concluded that the similar pattern is shown by the use of NM and TiO_2/Al_2O_3-Montmorillonite in photodegradation and adsorption treatments toward MB reduction.

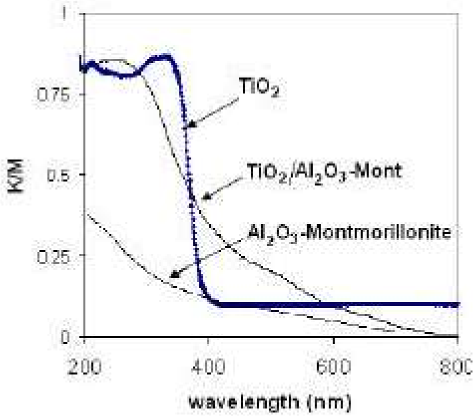

Fig. 4: Diffuse reflectance spectrum of TiO_2 (E.Merck), TiO_2/Al_2O_3-Montmorillonite and Al_2O_3-Montmorillonite

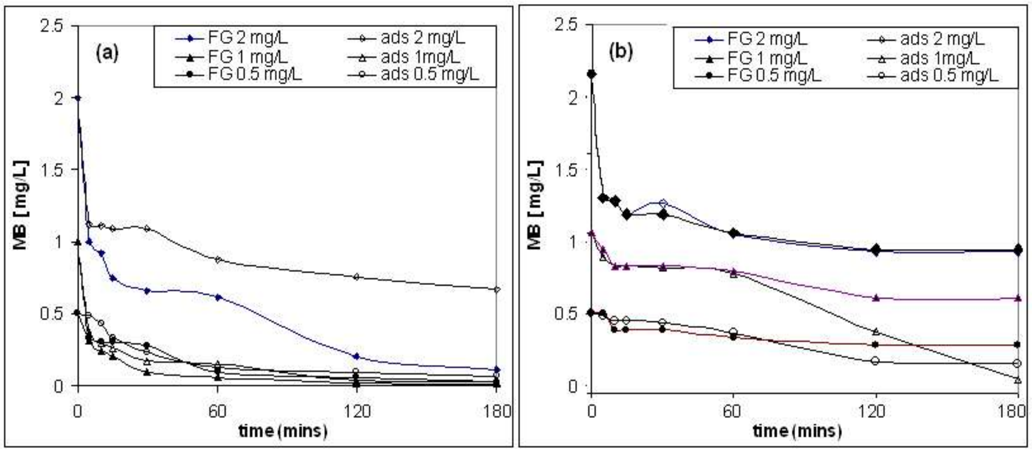

Fig. 5: MB concentration as function of time in photodegradation and adsorption by (a) TiO_2/Al_2O_3-Montmorillonite (b) Natural Montmorillonite- FG: photodegradation, ads: adsorption

The MB reduction gain stable in concentration at 30 mins of both treatments. It means that there was no effect of titania dispersion on the pattern of MB reduction. However, the MB reduction by photodegradation is slightly higher than that of adsorption process. The effect of MB initial concentration in the photodegradation process is presented in Figure 6. Simulation towards the data confirm that the photodegradation follows the pseudo-1st order reaction. The assumption of the pseudo-first order model was used in several studies to characterize the effect of different experimental conditions on the degradation rate [9,10]. Probing the Langmuir-Hinshelwood kinetic model for the MB photodegradation by TiO_2/Al_2O_3-Montmorillonite, curve of the reaction kinetics is depicted in Figure 6.

To more quantitatively evaluate the photocatalytic activity of material, the pseudo first order reaction as expressed by following equation:

$$-\frac{dC}{dt}=k.C$$

In which C is methylene blue concentration, t is time of reaction and k is pseudo first order constant.

The constants, *k,* can be obtained from the intercept and slope of the line formed when ln Co/Ct is plotted against time of reaction. The values of *k* derived by this model simulation is 4.24×10^{-3} M/s obtained by the initial reaction rate with different initial concentrations of MB, from 1.404×10^{-6} mol/l.s to $1.404.10^{-4}$ mol/l.s. This value is lower than the k value predicted for MB photodegradation by TiO_2 reported by Kalyavka *et al.* [7] and Kou and Ho [10]. However, the value is higher than that derived by the use of natural montmorillonite with 1.511×10^{-7} mol/l.s. The role of titania dispersion was indicated by the upsurge of methylene blue decomposition rate in photocatalytic system significantly relative to the matrix use.

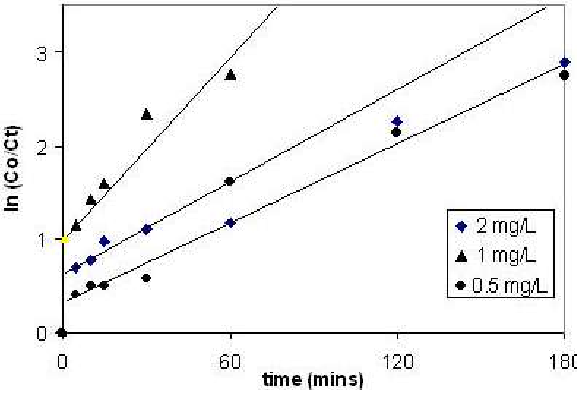

Fig. 6: Pseudo first order reaction of MB photodegradation by TiO_2/Al_2O_3-Montmorillonite

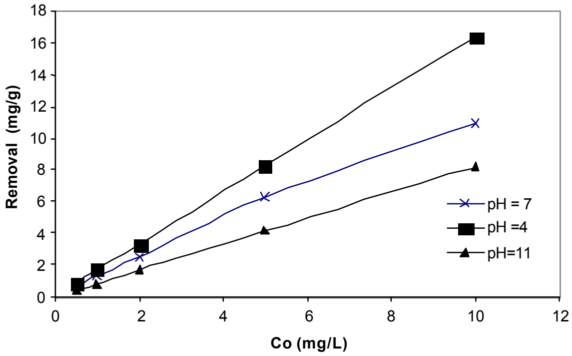

Fig 7. MB removal as a function of pH

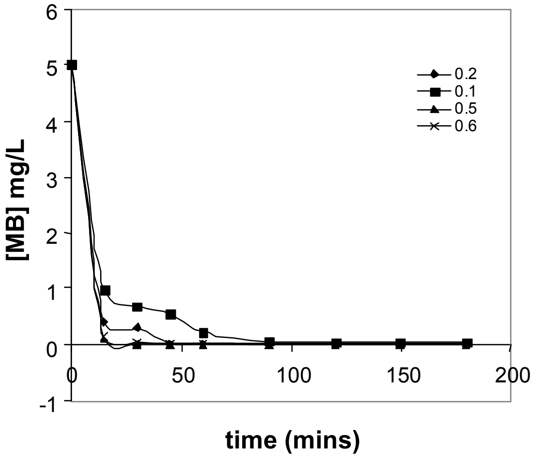

Fig. 8: Kinetics curves of MB degradation in varied catalyst dossage

Effect of pH: Figure 7 shows MB removal as the function of the pH of solution. It was found that the pH of solution affect to the MB removal. The better MB removal reached at pH of 4. This could be due to more cationic interaction within the lower pH and it increase the MB adsorption in surface. The adsorption capability play important role in photodegradation mechanism.

Table 2: Kinetic constant of MB degradation as function of catalyst dossage

Catalyst Dossage (g catalyst in 250 mL MB solution)	k (M/s)
0.1	1.89×10^{-3}
0.2	4.67×10^{-3}
0.5	5.90×10^{-3}
0.6	5.92×10^{-4}

Effect of Catalyst Dossage: The effect of catalyst dossage on the photocatalyst activity was studied by measure the mean of MB concentration in solution as function of reaction time. The varied amount of catalyst at the range of 0.1 to 0.6 g for 250 mL of MB solution were used to determine the kinetic constant of photodegradation reaction. The kinetic curve is presented in Fig. 8 and the kinetics constant values is tabulated in Table 2.

It is shown that the addition of catalyst has proven to increase the degradation rate within a range of concentrations. The kinetic constant is increased as the catalyst dossage increased. This could be attributed to the role of adsorption in the mechanism as well as the effect of pH. At the higher dossage, the greather amount of catalyst increase the adsorbent surface area within the range of 0.1 to 0.5 g per 250 mL of MB solution. However, the increase of catalyst dossage to 0.6 g does not followed by the increase of kinetic constant value. It indicate that the additional catalyst does not participate in the reaction and the reaction rate does not increase with growing catalyst load beyond a certain level. Photocatalysis activity may not dominantly occurs in in this condition due to the limitation of adsorptive capability improvement.

CONCLUSSION

Kinetic study of methylene blue degradation using TiO_2/Al_2O_3-Montmorillonite shows the effect of photocatalysis besides adsorption process by photocatalyst material. Simulation of the kinetic data reveals that methylene blue decomposition follows the pseudo 1st order reaction and by the Langmuir-Hinshelwood simulation, the value of rate constant is $1.87x10^{-6}$ mol/ls obtained by the initial reaction rate with different initial concentrations of MB, from 1.404×10^{-6} mol/l to $1.404.10^{-4}$ mol/l. Physicochemical character of TiO_2/Al_2O_3-Montmorillonite studied by diffuse reflectance UV-visible spectrophotometry, XRD and specific surface area analysis present the role of titania dispersion in the photocatalytic mechanism toward methylene blue decomposition.

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REFERENCES

1. Augugliaro, V., C. Baiocchi, B. Prevot, E.G. Lopez, V. Loddo, S. Malato, G. Marcýa, L. Palmisano, M. Pazzi and E. Pramauro, 2002. Azo-dyes photocatalytic degradation in aqueous suspension of TiO_2 under solar irradiation, Chemosphere, 49: 1223-1230.
2. Junbo, Z., M. Di1, Z. Hong, L. An, M. Jiao, M. Shengtian and L. Jianzhang, 2008, Photocatalytic decolorization of methyl orange solution with potassium peroxydisulfate, Cent. Eur. J. Chem., 6(2): 245-252.
3. Hussein, K., A. Alkhateeb and J. Ismail, 2008, Solar Photolysis and Photocatalytic Decolorization of Thymol Blue. E-Journal of Chemistry, 5(2): 243-250.
4. Fujishima, A., X. Zhang and D. Tyrk, 2007. Heterogeneous Photocataysis: From water photolysis to applications in Environmental Cleanup, Int. J. Hydrogen Ener., 32: 2664-2672.
5. Gil, A., S. Korili and M.A. Vicente, 2008. Recent Advances in the Control and Characterization of the Porous Structure of Pillared Clay Catalysts. Catalysis Reviews, 50: 153-221.
6. Kloprogge, J.T., 1998. Smectite and Porous Clay Catalyst, J. Por. Mat., 5: 5-51.
7. Yuan Peng, Yin Xiaolin, He Hongping, Yang Dan, Wang Linjiang and Zhu Jianxi, 2006, Investigation on the delaminated-pillared structure of TiO_2-PILC synthesized by $TiCl_4$ hydrolysis method., Micro. Meso. Mat., 93(1-3): 240-247.
8. Romero, A., F. Dorado, I. Asencio, P.B. García and J.L. Valverde, 2002. Titanium Pillared Clays: Synthesis And General Characterization., Clays, Miner., 12: 342-354.
9. Khalyavka, T.A., V.V. Shimanovskaya, V.V. Strelko, and E.I. Kapinus, 2001. Photocatalytic Activity of Titanium Dioxide in the Degradation of Methylene Blue and Tetrachlorofluorescein in Aqueous Solutions. Theoretical and Experimental Chemistry, 37(1): 58-62.
10. Kou, W.S. and P. Ho, 2001. Solar Photocatalytic Decolorization of Methylene Blue in Water, Chemosphere, 45: 77-83.