



Effects of Operating Parameters on Photocatalytic Degradation of Methylene Blue or Phenol on Supported Titanium-Based Catalysts

ABDULFATAH S. MUHAMMAD¹, JAMIL T. NASER^{2,*}, ILHAM KIRM² and BABA Y. JIBRIL^{2,*}

¹Department of Chemistry Bayero University, P.M.B. 3011, Kano, Nigeria

²Petroleum and Chemical Engineering Department, Sultan Qaboos University, P.O. Box 33, Al Khoud, PC 123, Muscat, Oman

*Corresponding authors: Fax: +968 24141354; Tel: +968 24141347; E-mail: naserj@squ.edu.om; baba@squ.edu.om

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Photocatalytic decompositions of both methylene blue and phenol in aqueous solutions were conducted separately on titanium-based catalysts. The catalysts were prepared using impregnation method on different supports (SiO₂, Al₂O₃ or ZSM-5) and titanium precursors (TiO₂ or TiCl₄). They were tested in visible light or UV irradiations of different wavelengths (254 and 365 nm). The physico-chemical characteristics of the catalysts were obtained using BET, XRD, FTIR and TGA. The supports surface areas and porosities showed insignificant decrease after impregnation with the active components. The diffraction patterns showed strong peaks that are assigned to titania anatase phase and weaker peak that indicated low concentration of rutile phase. Irrespective of the support, FTIR showed broad peaks of Ti-O-Ti linkages in TiO₂ particles. The catalysts were found to be active in decomposition of either methylene blue or phenol from aqueous solutions. For both methylene blue and phenol, the removal trend is TiO₂/SiO₂<TiO₂/Al₂O₃<<TiO₂/ZSM-5.

Keywords: Phenol, Methylene blue, Photocatalysis, Titania, Precursors, Supports.

INTRODUCTION

Photocatalytic degradation is of interest due to its efficient removal of organic pollutants. Ultimately, using effective catalysts; UV from the sunlight could be employed to convert undesired organic compounds into CO₂, water and inorganic minerals. In the last three decades, there have been extensive studies to shed more light on the reaction mechanism in both homogeneous and heterogeneous systems, in attempt to improve efficiency^{1,2}. Heterogeneous photocatalysis is favored due to easier removal of catalysts and its possible recycling. The reaction mechanism involves generation of strong radicals such as hydroxyl group by the UV irradiation³⁻⁵. Incidence photons of energies higher than the band gap of the underlying semiconductor such as titanium oxide leads to photo-excitations. This results in movement of electrons (e⁻) into the conduction band of the metals with corresponding holes (h⁺) in the valence band. The electrons interact with the dissolved or adsorbed oxygen to produce superoxide radical ions O₂⁻. These take place in chain reactions with the pollutant that lead to the final products. Alternatively, the electron-hole pair may recombine; thus, rendering ineffective the earlier photo-excitations⁵.

Improving the efficiency of photodegradation process requires further understanding of several important factors.

These include (i) the role of titania phases as active components of the catalysts, (ii) the active component-support interactions, (iii) effect of photon energy in its penetration depth and generation of radicals and (iv) the role of adsorption on the effectiveness of solid catalysts. Some of these have already been explored⁵⁻¹⁰. Several precursors such as sulphates or chlorides are used to produce titanium oxides of different surface properties¹¹. Surface groups such as OH, Ti-O-C and C-H were observed. This leads to different degrees of adsorption of organic pollutants and facilitate their decompositions. Surface groups may arise due to different phases of different degrees of crystallinity. Part of the roles of support is to serve as a nucleating agent^{12,13}. Therefore, heterogeneous nucleation of titania depends on the nature of the nucleation sites on the supports. These in turn depend on the acid-base character and population of high-energy sites. It was reported that doping of boron (> 0.5 wt %) led to amorphous TiO₂ while in the absence of dopant, anatase was obtained^{10,14}. Dopant and impurities also inhibited grain growth and facilitate anatase to rutile transformations¹⁰.

In the anatase form, TiO₂ has a band width of 3.2 eV. Therefore, it is only active upon irradiation with ultraviolet light (λ < 387). Catalysts that will ultimately use direct visible light for the reactions are being designed with transition metals dopants¹⁵⁻¹⁷ and substitution of non-metal atoms such as sulfur,

nitrogen for oxygen in the TiO₂ ionic lattice¹⁸. It has been demonstrated in theoretical calculations that substitutions with rare earth elements lead to decrease in the band gap compared with pure TiO₂¹⁹. Apart from modification of the catalysts, photons of different intensities and wavelengths may be employed. A recent study compared decomposition of a series of phenolic compound using both UV1 ($\lambda = 254$ nm) or UV2 (λ of both 254 and 185 nm). The latter was found to be more effective in terms of pollutant decomposition⁶. Interestingly, the reaction mechanism was also different depending on the wavelength^{6,20}. This means that multipurpose catalysts may be designed so that photons of different wavelengths and intensities could be employed on the same catalyst for decomposition of different pollutants.

It has been generally recognized that the present of surface defects are important for initiating the photocatalytic reactions^{21,22}. This is also directly associated with populations of hydroxyl group, surface oxygen and impurities in the catalyst. In this study, titanium oxide-based catalysts of different supports and titanium precursors were prepared and tested for decompositions of both facile (methylene blue) and refractory (phenol) pollutants under visible light or UV of different wavelengths ($\lambda = 254$ and 325 nm). Three supports of different acidities -SiO₂, Al₂O₃ and H-form of ZSM-5 were used as supports. On each 5 wt % TiO₂ was deposited either using suspension of commercial TiO₂ in water or equivalent amount of TiCl₄ solution in ethanol. Different degrees of decompositions were observed. Our objective was to determine how active component-support interactions and change in phases due to different titanium sources affect the degree of photocatalytic degradation. This will give useful insight toward improving efficiency of photocatalytic degradation especially when different organic compounds are considered under both visible light and UV of different wavelengths.

EXPERIMENTAL

Catalyst preparation: In the experimental part of this work, the following reagent grade chemicals were used: titanium dioxide powder, titanium(IV) chloride, phenol crystals, aluminum oxide active neutral (BDH chemicals limited, Poole, England), methylene blue, ethanol, silicon dioxide (Sigma Aldrich, Germany) and ZSM-5 (Zeolyst International). All chemicals were used without further purification. Two sets of catalysts were prepared by impregnating titania on alumina, silica or zeolite. The first set was prepared using suspension of titanium oxide in water. Measured amounts of TiO₂ to obtain 5 wt % active component on each of the supports were used. In each case, the suspension of titanium was mixed with the support and continuously stirred while evaporating water at about 70 °C. The remaining solid was further dried at 110 °C overnight. The solid was then calcined in air at 500 °C for 1 h. The second set was prepared in a similar manner using solution of TiCl₄ in ethanol instead of TiO₂ suspension. In the subsequent discussions, the catalysts are referred to as TiSi1, TiSi2, TiAl1, TiAl2, TiZ1 and TiZ2. The numbers 1 and 2 indicate TiO₂ and TiCl₄, respectively as the sources of the active component precursors, while the Si, Al and Z indicate the supports-silica, alumina and ZSM-5, respectively.

Catalysts characterization: The catalysts were characterized by X-ray diffraction using a Philips PW1710 powder diffraction with CuK α radiation (40 % KV, 40 mA) at a scan rate (2 θ) of 0.02/s. The Brunauer-Emmett-Teller (BET) surface area and total pore volume were measured using Quantachrome Autosorb-1 nitrogen adsorption apparatus. All samples were degassed at 300 °C for 4 h prior to the measurement. The FTIR spectra of samples in KBr matrix were obtained using Perkin Elmer FTIR spectrum 2000 spectrometer. Mass and energy changes profiles were observed using thermogravimetric analyser SDT 2960, at a heating rate of 10 °/min until maximum temperature of 1000 °C.

Adsorption and photo degradation: The photo catalytic activities of the prepared catalysts were evaluated in a Chromato-vue C-70G viewing system reactor (Ultra violet products, Inc., San Gabriel, CA, USA). At the top portion, it is fitted with visible light and UV lamps which emitted UV light at 254 or 365 nm. The reactions were conducted using dissolved oxygen. At room temperature, solubility of oxygen from air is about 8 mg/L. Therefore, the reactor content was vigorously stirred so that oxygen is continuously replenished to maintain its level in the reaction mixture. This also kept the catalyst particles dispersed. Physical adsorption (in the absence of light, later referred to as "no light" or NL) and photo degradation with artificial visible light (VL) or UV light at 254 or 365 nm were performed at room temperature and neutral pH conditions for 1 h. For the decomposition tests, 50 mg of each catalyst was placed in 250 mL beaker containing 150 mL aqueous solution (30 ppm) of either methylene blue or phenol. A 5 mL aliquot was sampled at 15 min intervals. It was centrifuged for 90 min at 1000 rpm. Prior to the analysis, the supernatant was filtered using a millipore membrane filter (0.45 μ m). The change in compositions of the compounds were measured at the respective wavelength for maximum absorbance (methylene blue at $\lambda_{\max} = 665$ nm and phenol at $\lambda_{\max} = 268.4$ nm) using a UV-visible Spectrometer, Perkin Elmer, USA.

RESULTS AND DISCUSSION

The surface areas and total pore volumes for all prepared catalysts are shown in Table-1. Bare supports areas are 469.7, 111.9 and 0.3 m²/g for ZSM-5, Al₂O₃ and SiO₂, respectively. The pore volumes follow similar trends. When the active component was impregnated, no significant changes in surface areas were observed. Due to the titania low concentration, there were no strong effects on either the porosity or physical adsorption sites on the catalysts. Fig. 1 shows the XRD profile of the samples. Anatase phase of titania was observed at 2 θ angle of 26 on all samples^{23,24}. The phases in Al₂O₃ are maintained after impregnation of titania. In addition to anatase, phases evolved at 2 θ angle of 29 (Ti-ZSM5) and 36 (Ti-SiO₂). Due to heat treatment at 500 °C, new solid solution could be developed²⁵. FTIR spectra of the samples are shown in Fig. 2. Bands at 3429 and 1630 cm⁻¹ are assigned to surface adsorbed water and hydroxyl group²⁶. In both ZSM-5 and Ti/ZSM-5, the peak at 1102 cm⁻¹ is assigned to stretching vibration of Si(Al)-O in tetrahedral²⁷ Si(Al)O₄. Broad bands in 1000-500 cm⁻¹ region are attributed to Ti-O-Ti linkages in TiO₂. Higher

TABLE-1
SURFACE AREAS, TOTAL PORE
VOLUMES AND NAMES OF THE CATALYSTS

	Surface area, (m ² /g)	Total pore volume, (cm ³ /g)	
Supports			
SiO ₂	0.249	7.8E-05	
Al ₂ O ₃	111.9	0.03169	
ZSM-5	469.7	0.157	
Catalysts			
(Precursor/support)			
TiCl ₄ /SiO ₂	5.882	0.001671	
TiCl ₄ /Al ₂ O ₃	113.1	0.03199	
TiCl ₄ /ZSM-5	430.3	0.147	
Catalysts' precursors, supports and names as used in the text			
(Precursor/support)	Name	(Precursor/support)	Name
TiO ₂ /SiO ₂	TiSi1	TiCl ₄ /SiO ₂	TiSi2
TiO ₂ /Al ₂ O ₃	TiAl1	TiCl ₄ /Al ₂ O ₃	TiAl2
TiO ₂ /ZSM-5	TiZ1	TiCl ₄ /ZSM-5	TiZ2

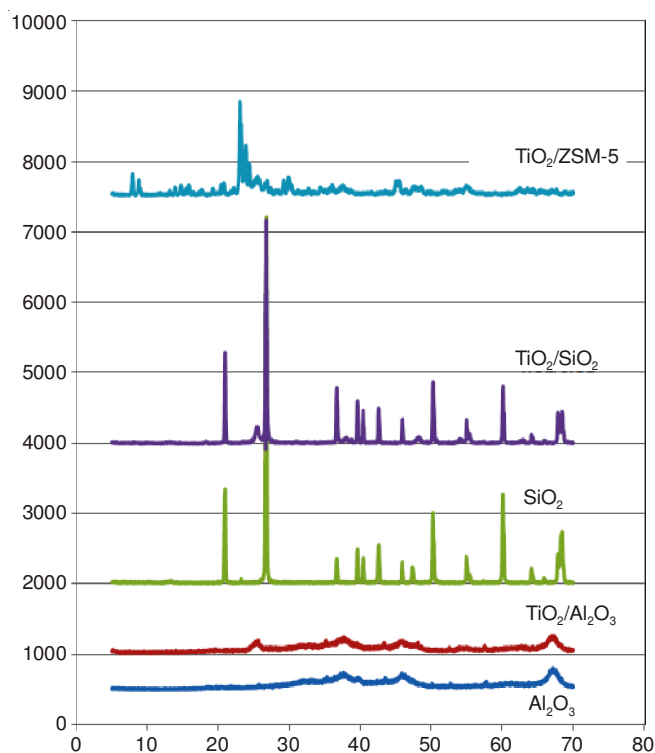


Fig. 1. XRD profile of the catalysts

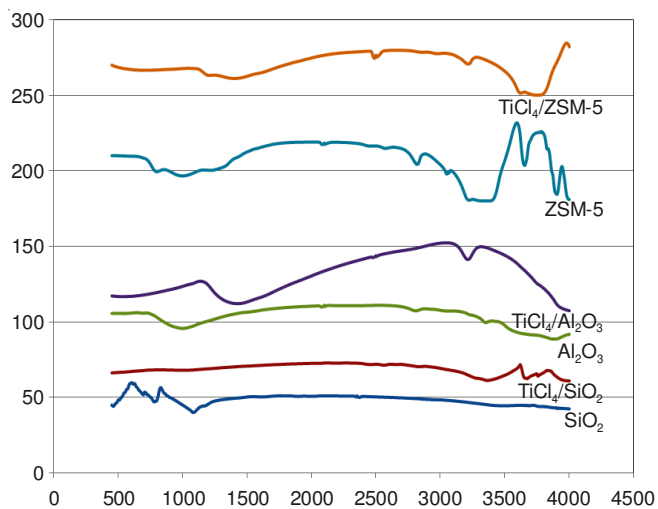


Fig. 2. FTIR profile of the catalysts

population of -OH on the Ti-sample indicates the present of additional adsorption sites on the catalyst compared with bare supports.

The catalysts were tested in photocatalytic decompositions of methylene or phenol in aqueous solutions. The test using a facile (methylene blue) or a refractory (phenol) organic compound may indicate the different nature of the catalytic activities of the sample. This in turn indicate the effects of support, precursors and UV intensities on the species decomposition. It may exhibit different removal profile at different light wavelengths and irradiation times. Fig. 3a,b) shows the methylene blue removal for two catalysts (TiSi1 and TiSi2) from two different precursors. For the control experiment in a dark room (No light-NL), the removal due to physical adsorption of methylene blue on TiSi1 was only about 15 % after 1 h. For the combination of both physical adsorption and UV decomposition, 30 % removal was obtained in the presence of ultraviolet irradiation of different wavelength (UV254 and UV365). Although there is no significant difference between experiments in the dark room (NL) and visible light (VL), the presence of UV increases both the decomposition after 1 h and the rate of the decompositions.

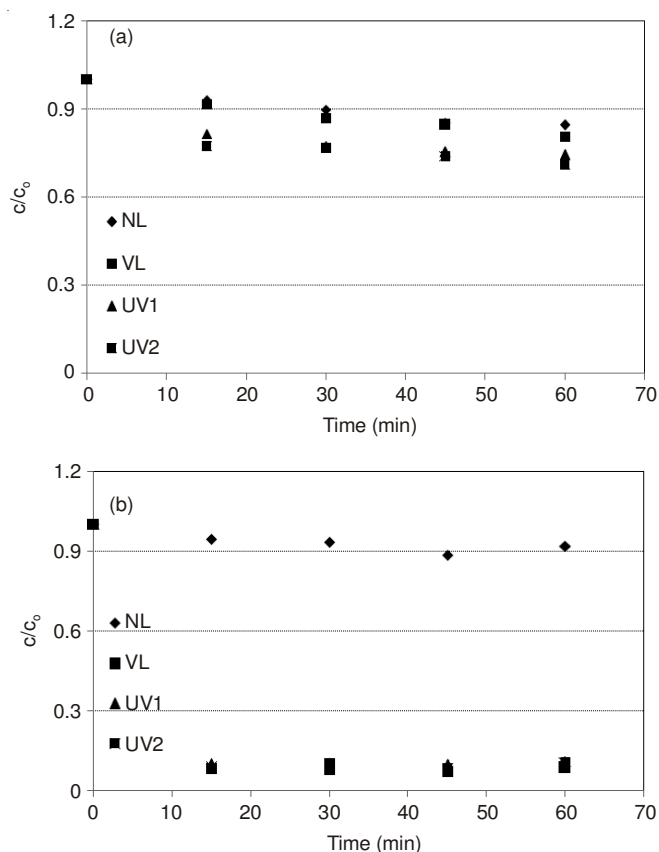


Fig. 3. Methylene blue removal with time using visible light and ultraviolet on catalysts of different precursors; (a) TiSi1 and (b) TiSi2

This observation was more pronounced when TiSi2-a catalyst of different precursor (TiCl₄) was used. Less physical adsorption (8 %) was observed, indicating a change in the nature of sites. The difference in the degree of the physical adsorption depends on the structure of the catalysts due to active components interaction with the support^{28,29}. In turn,

this determines its electrostatic interactions with the reactants. It also affects the photon penetration depth and removal of electron from the titanium atom in the catalyst matrix. Under VL or UV irradiation, there was significant increase in both methylene blue decomposition rate and its ultimate removal (90 %) after 1 h on TiSi2. This implies increase in the chemisorption sites that led to a better catalytic removal. The significant difference between the performances of TiSi1 and TiSi2 is associated with the change in precursor that may develop surface defects. This enhances catalytic activity. It is well known that the photocatalytic reaction mechanism involves hydroxyl, which interacts with electron holes to generate radicals. Electron-hole recombination decreases the effectiveness of the catalysts⁵. Chlorine in the precursor may form interstitial site defect in the Ti-O-Ti ionic lattice. This enhances photocatalytic activities. In a previous report, doping with halogens such as fluorine or iodine has been demonstrated to enhance photocatalytic reactions^{30,31}. Similarly, carbon coating or impurity will be in the sample due to the use of ethanol as a solvent. The presence of carbon is known to improve the photocatalytic activities of Ti-based catalyst³²⁻³⁴. Therefore, the higher activity of TiCl₄-based sample is associated with the presence of chlorine or carbon sites.

In addition, change of support from SiO₂ to a more acidic Al₂O₃ led to higher removal of methylene blue (Fig. 4a,b). About 60 % removal was observed on TiAl1 using UV365. Again, there was further improvement on TiAl2. Further comparison shows that the more acidic samples TiZ1 and TiZ2 are most

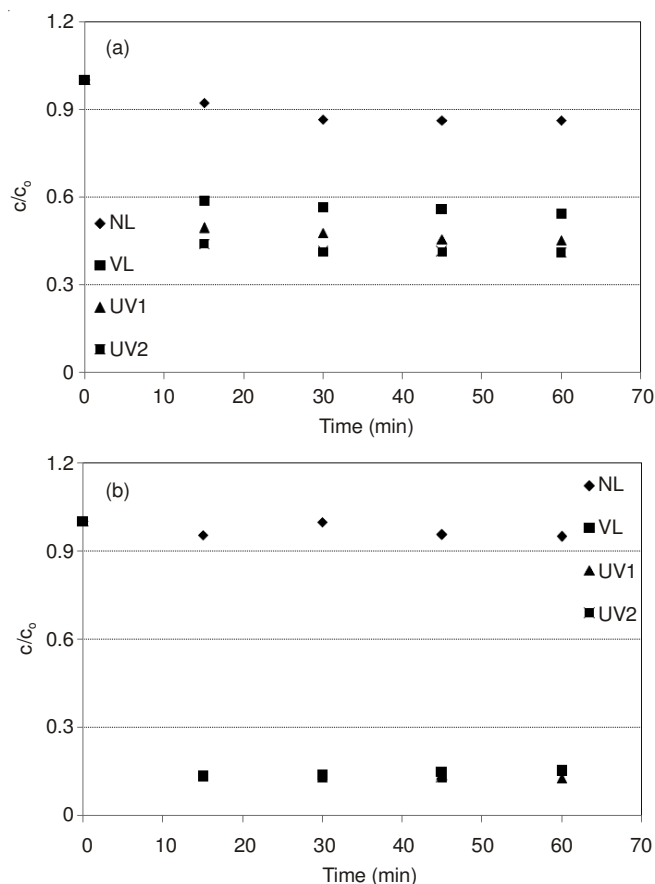


Fig. 4. Methylene blue removal with time using visible light and ultraviolet on catalysts of different precursors; (a) TiAl1 and (b) TiAl2

effective in removal of methylene blue. As high as 89 % was achieved using UV365 (Figs. 3a vs. 4a). However, TiAl2 shows lower removal than TiSi2. Furthermore, the sample on more acidic support TiZ1 and TiZ2 are more effective in the methylene blue removal (Fig. 5a,b). The highest methylene blue removal of 89 % was achieved. However, there are significant differences in the methylene blue removal between TiZ1 and TiZ2 despite differences in their precursors. This suggests that although different supports increase the rate of methylene blue removal based on their respective acid-base characters; the observed effects of titanium precursor depend on the nature of the support.

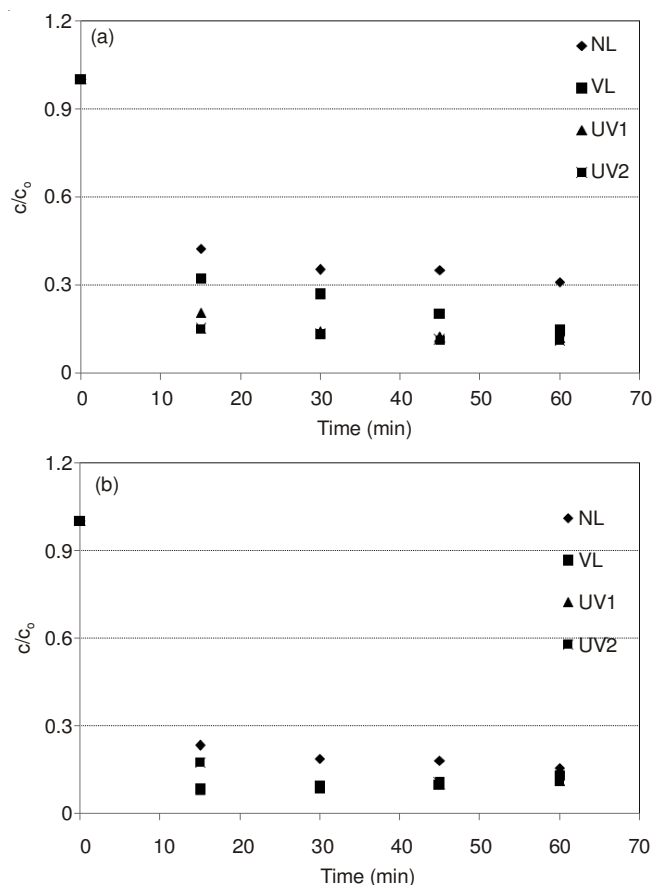


Fig. 5. Methylene blue removal with time using visible light and ultraviolet on catalysts of different precursors; (a) TiZ1 and (b) TiZ2

In the addition to methylene blue, phenol was considered. The phenol is a refractory compound. It may have different removal profile compared with a facile pollutant such as methylene blue. About 2 % phenol removal due to physical adsorption was observed (Fig. 6a). Highest removal of (13 %) was observed on TiSi1 using UV365. Still the source of titanium is important as the removal under UV irradiation was improved to 23 % on TiSi2 (Fig. 6b) under the same operating conditions. Change of the support to alumina exhibited better phenol removal with similar trend for sample from different precursor. The highest removal of 14 % was obtained under UV365 on TiAl1 (Fig. 7a). This change improved to 34 % for a different precursor-TiAl2 (Fig. 7b). The overall highest phenol removal of 44 % was exhibited by TiZ2. This is much higher than 14 % observed on TiZ1 (Fig. 8). Therefore, in

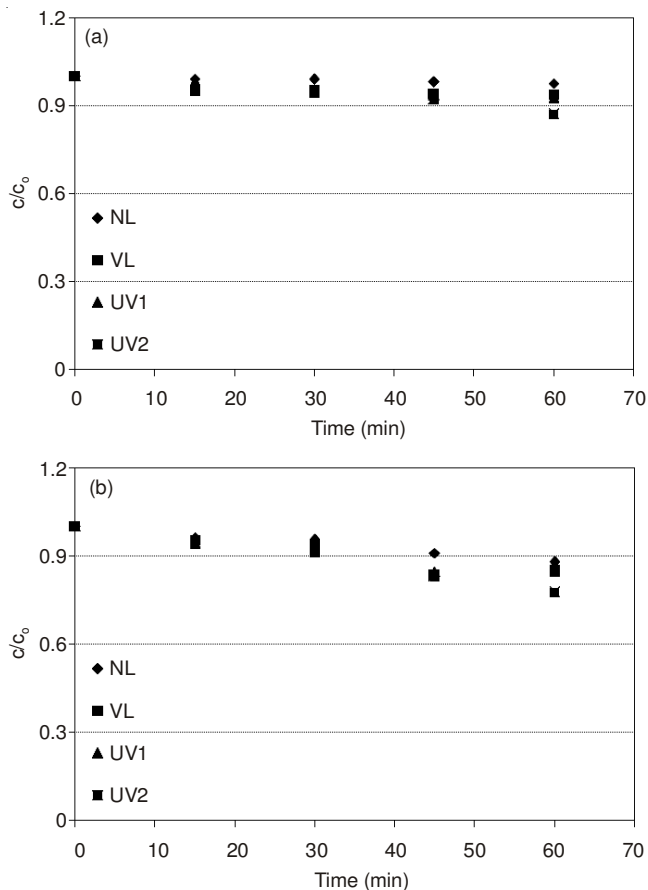


Fig. 6. Phenol removal with time using visible light and ultraviolet on catalysts of different precursors; (a) TiSi1 and (b) TiSi2

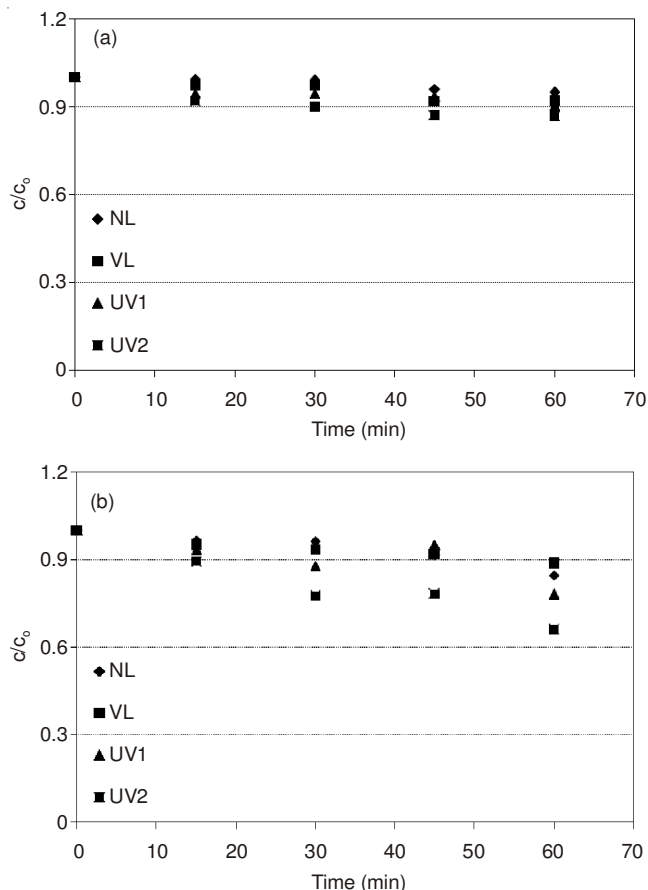


Fig. 8. Phenol removal with time using visible light and ultraviolet on catalysts of different precursors; (a) TiZ1 and (b) TiZ2

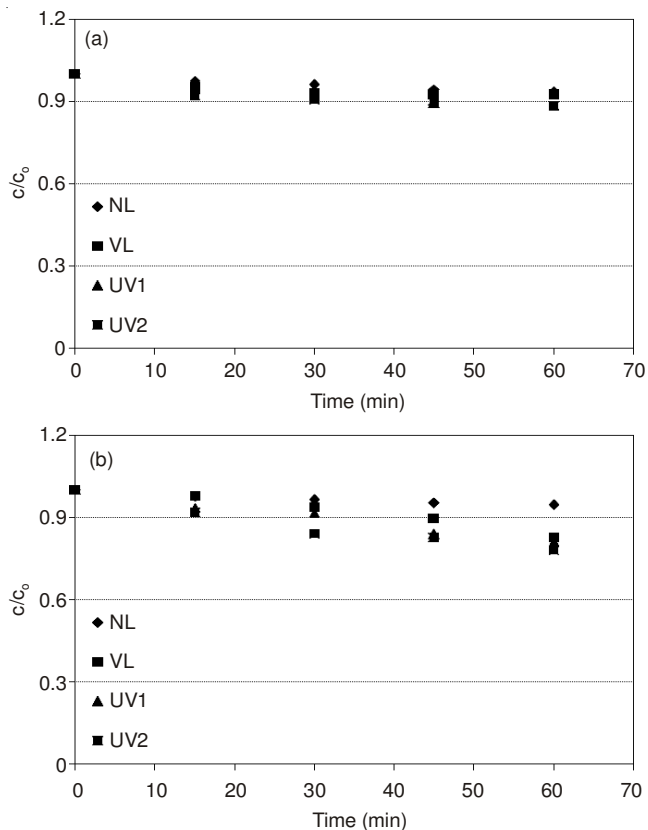


Fig. 7. Phenol removal with time using visible light and ultraviolet on catalysts of different precursors; (a) TiAl1 and (b) TiAl2

addition to the observation that depending on the nature of the support; the titanium precursor is important in determining the effectiveness of the photocatalyst, the nature of the compound being decomposed is important. Compounds with large molecular sizes may have strong adsorption or decomposes into adsorbed products. These block further adsorptions or limit penetration depth of UV photons. As observed in the case of methylene blue, the removal is dominated by the physical adsorption, thereby limiting the penetration of photons and rendering the subsequent catalytic decomposition insignificant.

The removals of both methylene blue and phenol reach equilibrium in about 1 h. The efficiencies of the catalysts were further compared at 15 min after the start of the removals as shown in Figs. 9 and 10. The data at shorted time may exhibit more pronounced effect of photocatalytic activities of the catalysts. In the absence of UV irradiation, TiSi1 shows the lowest methylene blue removal of 10.3 % (Fig. 9). For the other supports, it increased to 13.5 % for TiAl1 and 64.6 % for TiZ1. Under visible light, the removal was improved with similar trend -TiSi1 < TiAl1 < TiZ1. But the most significant increase (from 13.5 to 43.5 %) was observed on TiAl1, than on TiZ1 (64.5 to 73.2 %). Further removal improvement was obtained under UV irradiation. Again, more significant difference in the removal between UV irradiation of two different wavelengths was observed on TiAl1. Although irradiation with UV increased methylene blue removal; the effect of differences in the UV wavelength on removal is low.

Furthermore, once the physical removal of methylene blue reaches about 80 %, the UV irradiation turned out to be ineffective in providing additional removal. This implies that high physical adsorption leads to coverage of the titanium-phase from the photons, thereby hindering the catalytic reactions. This implies that although adsorption is important for enhancing heterogeneous photocatalytic reactions; the adsorption must be limited to avoid obstruction of photon from reaching the active sites adsorbents by the adsorbates.

This is further demonstrated using phenol (Fig. 10). There are limited physical adsorptions (0.9 - 4.5 %) on all samples. These were improved by irradiation with either visible light or UV of different wavelengths. This implies that irrespective of the energy of the photon, if it reaches the active sites, the titanium can be excited to generate radicals that lead to decomposition of the adsorbate. There is significant removal of phenol (22.5 %) on TiZ2.

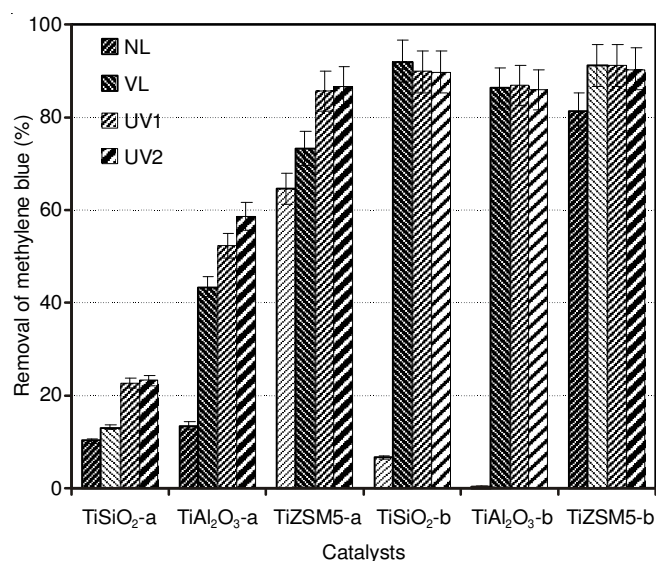


Fig. 9. Effects of catalysts supports and precursors on methylene blue removal after 15 min using visible light and ultraviolet of different wavelengths

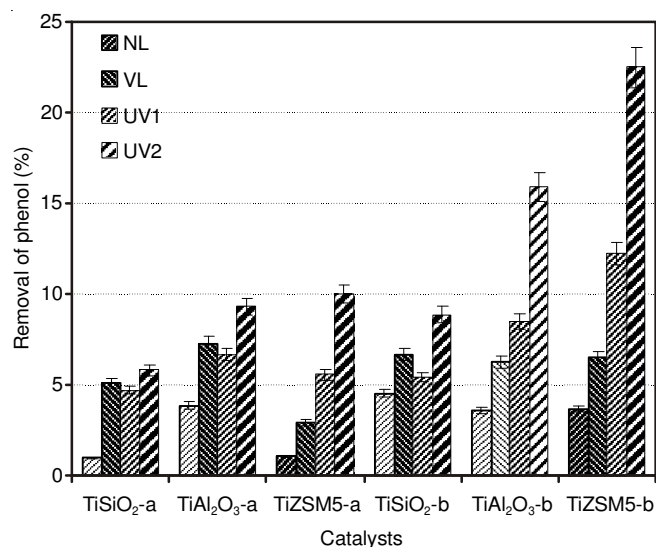


Fig. 10. Effects of catalysts supports and precursors on phenol removal after 15 min using visible light and ultraviolet of different wavelengths

The importance of the degree of physisorption and chemisorptions on the degradation of the compounds was further explored by evaluating the relevant kinetic parameters. The Langmuir-Hinshelwood model is useful for describing kinetics of heterogeneous photocatalytic reaction in aqueous systems^{35,36}. Based on the well known assumptions, the model relate rate of adsorption and/or reaction (r) with the concentration of the adsorbate (C) as follows:

$$r = -\frac{dC}{dt} = \frac{k_r K_{ad} C}{1 + K_{ad} C} \quad (1)$$

where k_r and K_{ad} are constants and indicating rates of reactions and adsorption, respectively. For systems with weak adsorption and/or low reactant concentrations, the equation can be modified and linearized as follows:

$$\ln\left(\frac{C}{C_0}\right) = -k_r K_{ad} t = -k_{app} t \quad (2)$$

where k_{app} is the apparent rate constant. Both the methylene blue and phenol data were fitted to eqn. 2. The model was found to be inadequate in describing the methylene blue removal data, indicative of strong adsorption. On the other hand, the phenol results give statistically acceptable regressions as shown in Table-2. In all cases, it shows very low reaction rate under dark condition. There are significant increases in the reaction rates with increase in the light wavelength. This indicates the dominant effect of phenol removal due to photocatalytic reaction rather than physical adsorption. The effect of precursor is also well pronounced. Samples prepared from TiCl₄ exhibited reaction rate about double compared with those from TiO₂.

TABLE-2
APPARENT REACTION RATE CONSTANT (k_{app} , min⁻¹)
FROM THE LANGMUIR-HINSHELWOOD MODEL
FOR DECOMPOSITION OF PHENOL

	TiSi1		TiSi2	
	k_{app}	R ²	k_{app}	R ²
NL	0.0000	0.9610	0.0020	0.9950
VL	0.0010	0.4990	0.0020	0.9870
UV1	0.0010	0.9680	0.0020	0.9300
UV2	0.0020	0.9220	0.0040	0.9760
	TiAl1		TiAl2	
	k_{app}	R ²	k_{app}	R ²
NL	0.0010	0.9520	0.0010	0.9150
VL	0.0010	0.6650	0.0020	0.9340
UV1	0.0020	0.9210	0.0030	0.9730
UV2	0.0020	0.6450	0.0040	0.9350
	TiZ1		TiZ2	
	k_{app}	R ²	k_{app}	R ²
NL	0.0000	0.9760	0.0020	0.8800
VL	0.0010	0.9460	0.0020	0.9370
UV1	0.0010	0.9790	0.0040	0.9970
UV2	0.0030	0.9870	0.0060	0.9360

NL = Experiment in dark room, No light, or NL, VL = Visible light, UV = Ultraviolet at 254 or 356

As indicated above, removal of methylene blue could not be described by Langmuir-Hinshelwood adsorption-reaction model, when adsorption was neglected. Therefore, the dominance of physical adsorption is evaluated. The physical

adsorption mechanism is explored using well known pseudo-first-order kinetic model of Lagergren and second order kinetics model. The first order is given as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

eqn. 3 may be integrated from initial condition at $t = 0$, when the amount adsorbed, $q_t = 0$ to time t and any value of q_t , gives

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (4)$$

where q_e is the amount adsorbed at equilibrium and k_1 is the rate constant for pseudo first-order adsorption (min^{-1}).

The second order model is represented as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

this can be rearranged as

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 dt \quad (6)$$

and in integrated form using the same condition as indicated in the case of first-order, gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

k_2 is the rate constant for second-order adsorption ($\text{g mol}^{-1} \text{min}^{-1}$). The data of methylene blue and phenol removals were fitted to both eqns. 3 and 5. The pseudo-second-order kinetic model was found to describe the data better (Table-3). Sample data for four catalysts are presented. At the conditions of the experiment, the k_2 values for methylene blue are one or two orders of magnitude higher than those for phenol. As expected, this implies much stronger adsorption of methylene blue than phenol. This hinders photon penetration. It renders photocatalytic

decomposition of methylene blue not as effective as in the case of phenol. Therefore, adsorbate-adsorbent (or organic compound-catalyst) pair selection is important for efficient chemisorptions that may lead to complete decomposition of organic compound from aqueous solution using heterogeneous photocatalysis.

Conclusion

Photocatalytic degradation of methylene blue and phenol has been investigated on titanium-based catalysts. The degree of removal of either of the compounds depended on the nature of the support upon which the active titanium is deposited. At about 15 min, the removal of methylene blue as well as phenol were further improved when the titanium precursor was changed. In addition, the effect of light wavelength varied on the nature of the catalysts. This is associated with different level of defect generations. The defects are important in limiting the electron-hole recombination known to hinder the reaction. Further, the degree of physical adsorption of the compound on the catalysts must be low for effective photolysis. The photocatalytic removal efficiency is lower in the case of methylene blue than phenol. This is due to its higher adsorption on the catalysts. Therefore, the phenol data was found to be well described by Langmuir-Hinshelwood reaction model, when the physical adsorption is assumed to be negligible. The reaction rate constant showed increase in reaction on the three supports; $\text{ZSM-5} > \text{Al}_2\text{O}_3 > \text{SiO}_2$. Also the value of the constant was higher for TiCl_4 as a source of titanium than for TiO_2 irrespective of the support. The removal of methylene blue was considered to be dominated by physical adsorption. Therefore, the adsorption mechanism was evaluated and found to be better described by pseudo-second-order adsorption rate. The decomposition and/or adsorption results showed that the degree of removal of either methylene blue or phenol depend on the nature of the support and the titanium precursor. The differences among the catalysts were associated with differences in the phase and the surface defects generated in the samples.

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Methylene blue	TiAl1		TiAl2	
	k_2	R^2	k_2	R^2
NL	0.1529	0.9910	0.1180	0.9880
VL	0.5474	0.9990	2.9697	1.0000
UV1	0.8108	0.9990	4.5238	1.0000
UV2	2.2951	1.0000	1.2532	0.9990
Methylene blue	TiZ1		TiZ2	
	k_2	R^2	k_2	R^2
NL	0.1925	0.9980	0.0630	0.9990
VL	1.6207	1.0000	0.5740	0.9990
UV1	1.5763	1.0000	1.1899	1.0000
UV2	2.7353	0.9990	2.7353	0.9990
Phenol	TiAl1		TiAl2	
	k_2	R^2	k_2	R^2
NL	0.0388	0.9660	0.0492	0.9840
VL	0.1592	0.9940	0.0018	0.9640
UV1	0.0447	0.9660	0.0217	0.8820
UV2	0.0982	0.9940	0.0384	0.9690
Phenol	TiZ1		TiZ2	
	k_2	R^2	k_2	R^2
NL	0.0007	0.0060	0.0096	0.6770
VL	0.0130	0.5910	0.0302	0.9400
UV1	0.0384	0.9480	0.0221	0.9280
UV2	0.1040	0.9930	0.0728	0.9160

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