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Nanotitania-Activated Carbon with Enhanced Photocatalytic Activity: A Comparison Between Suspended and Immobilized Catalyst for Turquoise Blue Removal

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The present study aims to synthesize nanoTiO_2-AC and evaluate its property and photocatalytic activity using 254nm UV lamp in suspended system and as immobilized catalyst for the color removal of Turquoise blue dye solution. NanoTiO_2-AC is synthesized via the sol-gel method and calcined at 400^0C. Various ratio (1:10, 2:10 and 3:10) of weight AC / volume of TiO_2 sol were investigated. NanoTiO_2-AC is immobilized in glass plates using Polyethylene glycol (PEG) as binder. Powder and immobilized catalysts were characterized using BET, SEM-EDX, TGA, FTIR and XRD techniques. The effect of initial dye concentration, initial solution pH, catalyst loading and AC loading were investigated. SEM images confirmed the uniform distribution of nanoTiO_2 attached on the surface of AC. Immobilized 1:10 AC/nanoTiO_2 has lower surface area compared to powder 1:10 AC/nanoTiO_2. Increasing the AC loading in AC/nanoTiO_2 increases the dye adsorption in the composite catalyst to as much as 9%. The initial rate of color removal is faster in suspended catalyst compared to immobilized catalyst. In general, suspended catalyst is more efficient than immobilized catalyst. Further, PEG as a binder can be used to immobilize AC/TiO_2 in glass with considerable stability.

Keyword: Photocatalysis, Nanotitania-Activated Carbon, Suspended and Immobilized Catalyst

INTRODUCTION

Several studies have been done to degrade dyes by photocatalysis (Baran *et al.*, 2008; Behnajahdy *et al.,* 2007). Photocatalytic dye degradation is believed to take place according to the following mechanism. When a catalyst is exposed to UV irradiation, electrons are promoted from valence band to the conduction band. As a result, electron- hole pair is produced. Electrons in the conduction band (e^{-}_{cb}) and electron hole in the valence band (h^{+}_{vb}) can migrate to the catalyst surface where they can enter in a redox reaction with other species present on the surface. In most cases, h^{+}_{vb} can react with surface bound water to produce OH• radicals, whereas e^{-}_{cb} can react with O_2 to produce superoxide radical anion of oxygen (O2•). $OH^{\bullet}$ and $O2^{\bullet}$ will then react with the dye to form other species and is responsible for dye degradation (Rauf and Ashraf, 2009).

In photocatalysis, titania (TiO_2) is a very well known, well researched and widely used material due to its high photosensitivity, non toxicity, strong oxidizing power and long term stability. However, bulk TiO_2 has low surface area and less adsorption property which limits its performance in photocatalysis. This can be addressed by synthesizing nano-sized TiO_2 and impregnating with activated carbon (AC) to improve its adsorption property. Sol-gel process is a novel technique for the preparation of nanocrystalline TiO_2. This method was demonstrated by Venkatachalam *et al.* (2007) who produced nanocrystalline TiO_2 with higher activity over Degussa P-25. To further enhance adsorption of pollutant in nano-TiO_2, it is desirable to use AC with high surface area to act as carrier of TiO_2 powders. Araña *et al.* (2003) reported the effect of mixing TiO_2 with different portions of AC in an aqueous suspension with continuous stirring. TEM studies showed a perfect TiO_2 particle distribution on the AC surface in catalyst with lower AC contents. Results of the study also showed that AC not only exerts a synergistic effect when combined with TiO_2 but also modifies the catalyst characteristics. Other methods to synthesize AC/TiO_2 include the work of Liu *et al.* (2007) who produced AC/TiO_2 by mixing AC with TiO_2 sol previously prepared by sol-gel using Tetrabutylorthotitanate, diethanolamine, ethanol and H_2O. Wang *et al.,* (2007) also synthesized AC/TiO_2 by modified sol-gel procedure using $Ti(OC_3H_7)_4$, ethyl alcohol and nitric acid where certain amount of AC was added into the solution under stirring until a carbon contained gel was formed. The xerogel was ground into fine powder, dried and calcined to obtain the composite catalyst. Ao *et al.,* (2008) produced AC/TiO_2 film by adding AC with TiO_2 sol prepared using $Ti(OBu)_4$, PrOH, nitric acid and H_2O; and the suspending solution became the sol for coating films. Results of their investigations showed that AC has a significant effect on TiO_2 activity. Aside from AC's well developed structure, high surface area and strong adsorption capacity (Liu *et al.*, 2007), low cost is another important advantage of using this material as a support. Moreover, immobilized catalyst addresses the problem on the recovery of the material for reuse. From Han *et al.* (2009), the process of sedimentation, centrifugation and filtration to recover the catalyst after use is time consuming and small particle catalysts penetrate filtration materials and clog filter membranes.

The objective of this study is to synthesize nanoTiO_2/AC, determine its property and evaluate the photocatalytic activity of the catalyst using 254nm UV lamp in suspended system and as immobilized catalyst for the color removal of Turquoise blue dye solution. This study has a direct application with the textile industry partner who uses Turquoise blue dye in dyeing operation that generates effluent which is difficult to degrade using their present wastewater treatment system.

Turquoise blue dye ($C_{32}H_{16}N_8S_2O_6CuNa_2$), an azo dye with molecular structure shown in Fig. 1 is a direct dye which ranked next to acid dye in terms of persistency when subjected to photocatalytic treatment using JT. Baker TiO_2 (Gallo *et al.*, 2009). A study conducted by Liu *et al.* (2007) showed that fenton and photo-fenton processes have a satisfactory performance for the degradation of Turquoise blue dye.

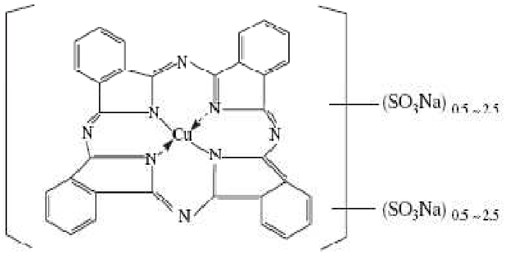


Fig. 1: Molecular structure of Turquoise blue dye (Liu *et al.,* 2007)

MATERIAL

Titanium (IV) isopropoxide (Sigma Aldrich) as a precursor and Glacial acetic acid (Ajax Finechem) as hydrolyzing agent were used in the synthesis of nanoTiO_2. AC used in the study is a granular activated coconut shell based carbon acquired from CarboKarn Co. Ltd. in Thailand. Turquoise blue dye was used as model pollutant. Also, PEG (MW= 10,000 g mol^{-1}) was used as binder in immobilizing the catalyst onto the glass plates.

EXPERIMENTAL

Synthesis of AC/nanoTiO_2

The nanoTiO_2 was synthesized by solgel following the procedure of Venkatachalam *et al.* (2007). AC was mixed with resulting sol at a ratio of 1:10, 2:10 and 3:10 (weight of AC: volume of sol). Aging was done at 70^0C for 12 hours. The gel produced was then dried at 100^0C, crushed into powder and calcined at 400^0C.

Immobilization of Catalyst

The catalyst was immobilized in glass plates (microscope slides, 75 mm x 25 mm x 1mm) via dip coating technique and fired in the furnace at 300 ^{0}C for 3 hours. The molar ratio of catalyst, binder and water mixture is 307:1:272 respectively.

Activity Testing

A 1-L capacity batch photocatalytic reactor was used (see Fig. 2) equipped with a 254nm wavelength and 100-Watt UV lamp (UVL-100HA, Riko) which irradiates the dye solution inside the reactor at an average light intensity of 0.7 mW cm^{-2} as measured by UVX-Digital Radiometer. The temperature of the dye solution is maintained at 32 ^{0}C by cooling water that passed in the sleeve of the UV lamp. Air was blown into the dye solution by an air pump at 100ml/s and stirring is maintained at 800 rpm.

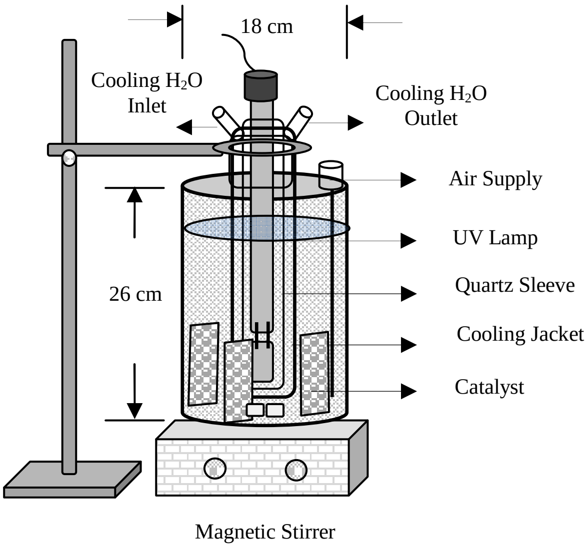


Fig. 2: Batch photocatalytic reactor

Effect of Operating Parameters

Effect of AC loading, initial dye concentration, initial solution pH, and catalyst loading were investigated in this study. Dark adsorption test was performed for Turquoise blue dye solution prior to activity testing to determine the color removal due to adsorption alone.

Stability Test of Immobilized Catalyst

The test on the stability of the catalyst in the glass plates is based on the weight difference of the catalyst before and after photocatalytic treatment. At the same time, the stability of nanoTiO_2 attached in the surface of AC was evaluated via SEM-EDX technique.

Analytical Techniques

Quantachrome Autosorb-1 was used for BET analysis. XRD (Rigaku Multiflex) and Scanning Electron Microscopy (Jeol JSM-5310) were used to determine structure properties and morphologies respectively. Nicolet – 6700 Thermoscientific was used for FTIR analysis and Thermogravimetric Analyzer (Rigaku Thermo Plus TG - 8120) was used to determine the percentage weight of AC in the composite catalyst. Dye concentration was measured using UV-Vis Spectrophotometer (Shimadzu UV Pharmaspec-1700) based on a calibration curve at the maximum absorbance of 605 nm. The percentage color removal was calculated using Equation (1).

$$\%Color\ Removal = \left[\frac{(C_0 - C)}{C_0}\right] x\ 100 \qquad (1)$$

Where :

C_0 = the initial dye concentration.

C = the final dye concentration.

RESULTS AND DISCUSSION

Characterization of Catalyst

BET results of powder catalyst (Table 1) showed that the BET surface area is shifted to higher values at higher AC loading. The reduction in pore volume of 2:10 AC/nanoTiO_2 maybe due to the nanoTiO_2 that agglomerate and partially blocked in pore entrances of AC. The average pore sizes of all catalysts are within the mesopore range (20- 500 Å). Well developed mesoporosity is necessary for the adsorption of solutes from solutions (Bandoz, 2006). Higher surface area for immobilized catalyst is expected due to the addition of PEG which is considered an effective template for the formation of nanoporous TiO_2 thin films (Chen *et al.*, 2008). However, the immobilized 1:10 AC/nanoTiO_2 significantly dropped its surface area to 537.0 m^2/g which is much lower than 747.8 m^2/g surface area of powder 1:10 AC/nanoTiO_2. This contrasting result can be ascribed to the linking up of pores between AC, TiO_2 and PEG and possible reduction of pore depth of the resulting catalyst (Bu *et al.*, 2005). Meanwhile, Table 2 shows that as AC loading increases, both %Ti and %O decreases and no contaminant is present on the catalyst. On the other hand, the percentage weight of AC in AC/nanoTiO_2 powder determined by TGA (Table 3) was close from their respective theoretical values which signify that error in sol-gel preparation is minimized.

SEM images of AC/nanoTiO_2 (see Fig 3) revealed a uniform distribution of nanoTiO_2 deposited at the surface of AC.

In immobilized catalyst, 1:10 AC/nanoTiO_2 was deposited in glass plates at 4.8 - 6.0 mg mm^{-2} with a film thickness of 472 μm (Fig 4).

Table 1. BET Result

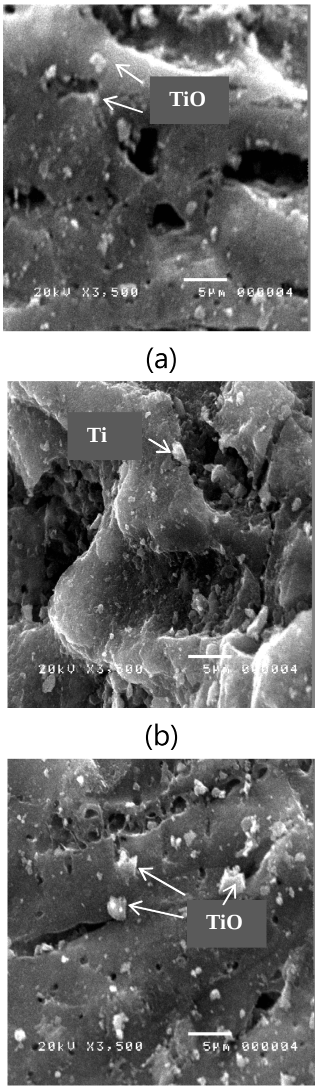
Catalyst	BET surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Pore size (Å)
NanoTiO_2	247.6	0.124	156.7
1:10 AC/NanoTiO_2 (immobilized)	537.0	0.221	68.23
1:10 AC/NanoTiO_2	747.8	0.412	57.91
2:10 AC/NanoTiO_2	837.2	0.393	65.44
3:10 AC/NanoTiO_2	851.1	0.499	56.28

Table 2. Percentage Elemental Composition

Catalyst	%C	%Ti	%O
NanoTiO_2	0	51.22	48.78
1:10 AC/NanoTiO_2	68.14	7.00	24.86
2:10 AC/NanoTiO_2	76.59	5.48	17.93
3:10 AC/NanoTiO_2	82.46	1.23	16.32

Table 3. Percentage weight of AC in AC/Nano TiO_2

Catalyst	% wt AC (Theoretical)	% wt AC (TGA data)
1:10 AC/NanoTiO_2	89.1	89.3
2:10 AC/NanoTiO_2	94.2	94.6
3:10 AC/NanoTiO_2	96.1	95.8



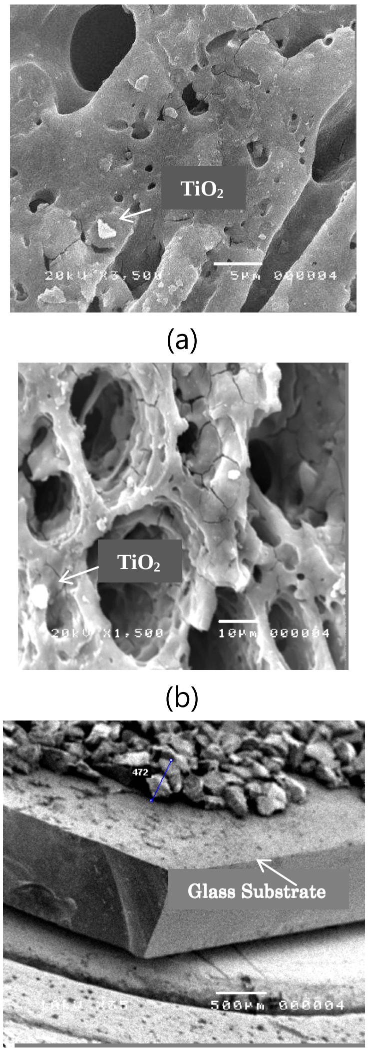
(a)

(b)

(c)

Fig. 3: SEM images of powder catalysts (a) 1:10 AC/TiO_2 (b) 2:10 AC/TiO_2, (c) 3:10 AC/TiO_2

The catalyst film produced was observed to be porous and contained cracks on the surface. This confirms the work of Sonawane *et al.* (2004) who reported that films prepared by the addition of PEG are porous in nature due to the decomposition of PEG during heat treatment.



(a)

(b)

(c)

Fig. 4: SEM images of immobilized 1:10 AC/TiO_2 a) 3500x magnification (b) 1,500x magnification and (c) cross - sectional view

Meanwhile, the presence of anatase crystal structure of TiO_2 in all catalysts was revealed in XRD results (see Fig. 5). TiO_2 with pure anatase structure has long been considered the most oxidative and has higher photocatalytic activity compared to other phases of TiO_2. It is commonly accepted that calcination at least 400 ^{0}C is required to obtain anatase TiO_2 powder (Ao *et al.*, 2008). The broad reflection of typically amorphous materials observed at 44.0 corresponds to micrographitic structure which is a typical characteristic of AC (Carpio *et al.*, 2005). Further, the average crystallite size was estimated by Scherrer's equation (Equation 2):

$$D = \frac{K\lambda/\beta}{cos\theta} \qquad (2)$$

Where,

D = the crystal size of the catalyst

λ = X-ray wavelength (1.54056 Å)

β = full width at half maximum (FWHM) of the catalyst

K = (0.9)

θ = diffraction angle

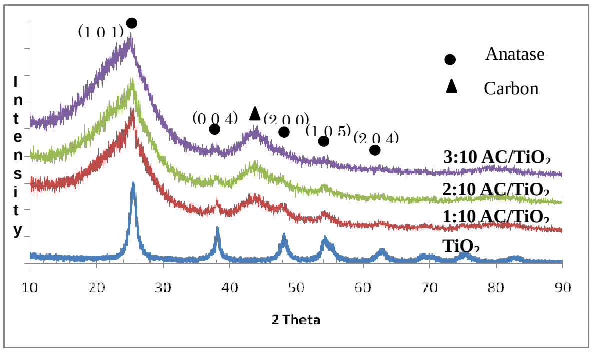


Fig. 5: XRD diffraction patterns of TiO_2 and AC/TiO_2

In the present study, crystallite sizes of TiO_2, 1:10 AC/TiO_2, 2:10 AC/TiO_2 and 3:10 AC/TiO_2 which are confirmed nanosize are 12.9 nm, 4.6 nm, 3.4 nm and 1.7 nm respectively. This result also explained why TiO_2 /AC produced by solgel has higher surface area than Degussa P-25 TiO_2 which is known to have particle size of 30 nm (Chen *et al.*, 2006).

In Fig 6, peak observed at 3600-3100

cm^{-1} is the stretching mode of OH and the narrow peaks at 1600-1400 cm^{-1} are the bending modes of hydroxyl groups. This indicates the basic surface characteristics of the catalyst.

The region below 800 cm-1 represents the stretching band of Ti-O. The center of OH vibration shifted towards lower wavenumbers as more AC is added to the composite catalyst. This vibration shift (inset in Fig. 6) is due to an increment of the positive charge of OH groups adsorbed on the surface of TiO_2 which altered the acid-base character of the hydroxyl groups present in catalyst. It further indicates that AC used to impregnate with TiO_2 is basic.

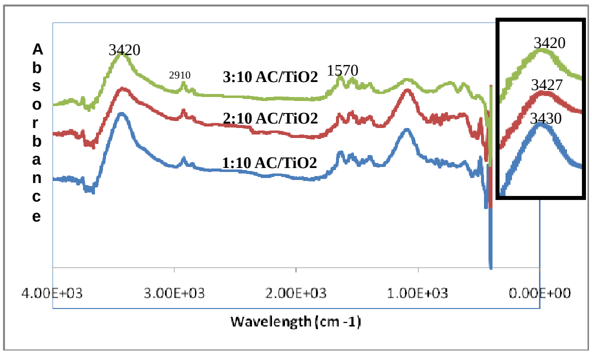


Fig. 6: FTIR spectra of AC/TiO_2

In general, results on characterization of composite AC/TiO_2 revealed similar findings with various researchers (Arana *et al.*, 2003 ; Liu *et al.*, 2007) that AC when combined with TiO_2 modifies the catalyst characteristics.

Dark Adsorption Test Result

At natural dye solution pH, adsorption of dye onto the nanoTiO_2 was increased from 2% to 9% when AC is added to as much as 3:10 wt of AC / volume of TiO_2 sol. There is low adsorption of dye molecules onto the catalyst surface since Turquoise blue dye is cationic which does not favor adsorption onto positively charged catalyst surface due to electrostatic repulsion. Adsorption of dye in suspended catalyst (Fig. 7) is comparable to the immobilized catalyst (Fig. 8). This indicates that the addition of PEG as binder has no significant effect on the adsorption capability of the catalyst.

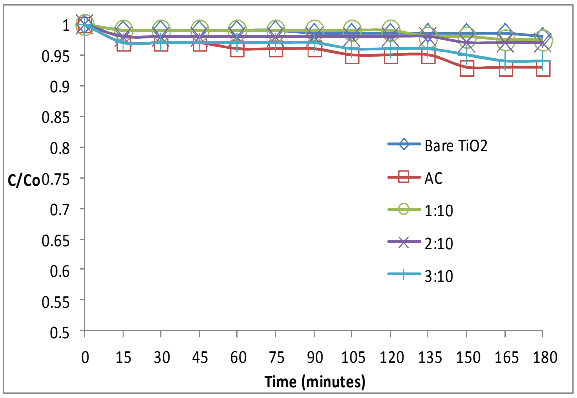


Fig. 7: Dark adsorption test using suspended catalyst (dye concentration: 20ppm, catalyst loading: 1g L^{-1}, pH = 6.3)

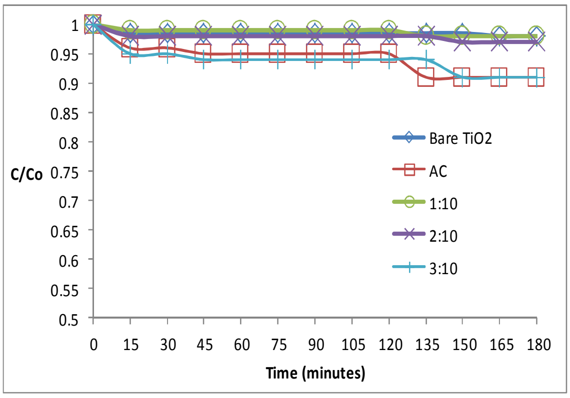


Fig. 8: Dark adsorption test using immobilized catalyst (dye concentration: 20ppm, catalyst loading: 1g L^{-1}, pH = 6.3)

Effect of AC Loading

Fig 9 shows that 1:10 AC/nanoTiO_2 exhibited the highest color removal as compared to 2:10 and 3:10 AC/nanoTiO_2 which implies that high TiO_2 content favors higher color removal over the addition of more AC to increase adsorption. This observation holds true for suspended and immobilized catalyst. The immediate transfer of dye particles onto the surface of suspended AC/nanoTiO_2 due to mixing resulted in higher initial rate of color removal compared to immobilized catalyst.

Effect of Initial Dye Concentration

In Fig 10, the color removal of Turquoise blue dye is favorable at 20 ppm initial dye concentration. The decrease in color removal at 40 ppm can be explained by an increase in the equilibrium adsorption of dye in the catalyst surface active sites thereby decreasing the competitive adsorption of OH• on the same sites, which means lower formation rate of OH• that is responsible in dye degradation. Also, when initial dye concentration is increased, the path length of photons entering the solution decreases resulting in lower photon adsorption on catalyst surface thus lowering the photocatalytic reaction rates. Efficiencies of suspended and immobilized catalysts are comparable at lower initial dye concentration. However, the immobilized catalyst outweighed the performance of suspended catalyst at high initial dye concentration. This can be the result of shielding effect that usually occurred in suspended catalyst which limits the penetration of light to the dye solution. These results are similar to the findings of Andronic and Duta (2008) who also conducted a comparative study on the influence of powder and catalyst films but using only TiO_2 in photodegradation of dyes.

Effect of Initial Solution pH

Fig. 11 shows that the color removal for Turquoise blue dye is favored at pH 3 indicating that as more dye particles is adsorbed onto the catalyst surface, more dye molecules is in contact with catalyst surface active sites for photocatalytic reaction. Lower but non-significant difference on the performance by immobilized catalyst compared to suspended catalyst maybe attributed to the lowering of surface area of the catalyst when attached to substrate. Higher initial rate of color removal for suspended catalyst can be due to the immediate contact of dye molecules onto the catalyst surface.

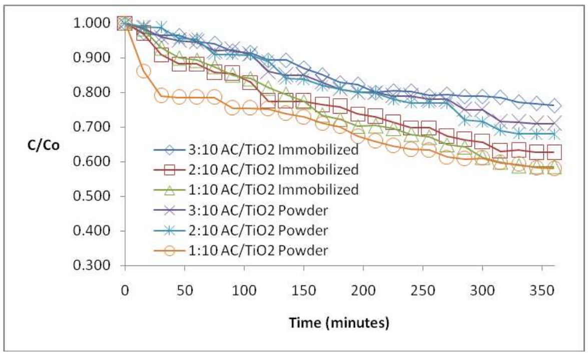


Fig. 9: Effect of AC loading (dye concentration: 20ppm, catalyst loading: 1g L^{-1}, pH = 6.3)

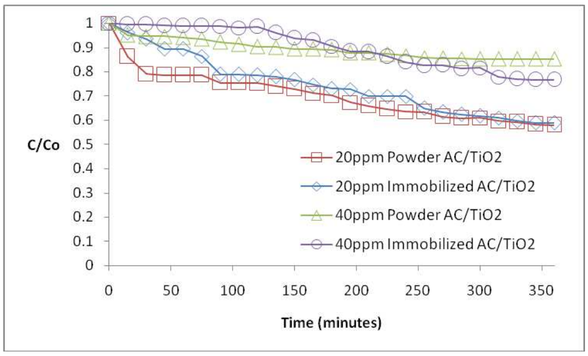


Fig. 10: Effect of initial dye concentration (AC loading: 1:10 AC/nanoTiO_2, catalyst loading: 1g/L, pH = 6.3)

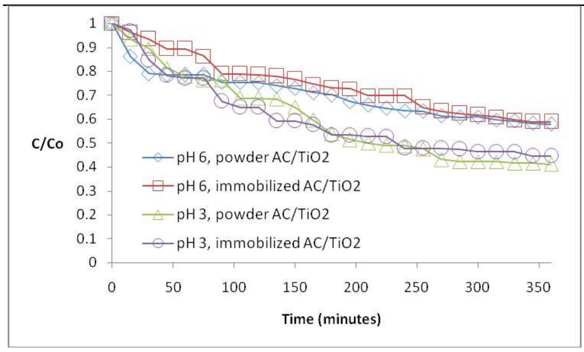


Fig. 11: Effect of initial solution pH (AC loading: 1:10 AC/nanoTiO_2, dye concentration: 20ppm, catalyst loading: 1g/L)

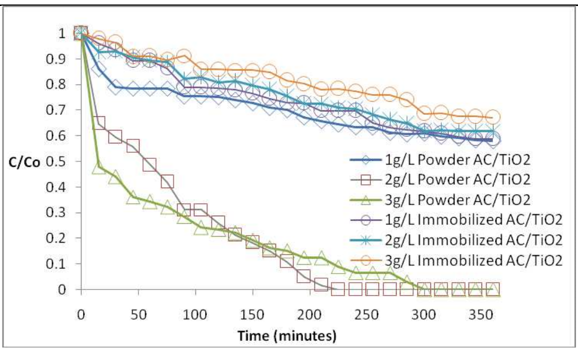


Fig. 12: Effect of catalyst loading (AC loading: 1:10 AC/nanoTiO_2, dye concentration: 20ppm, pH = 6.3)

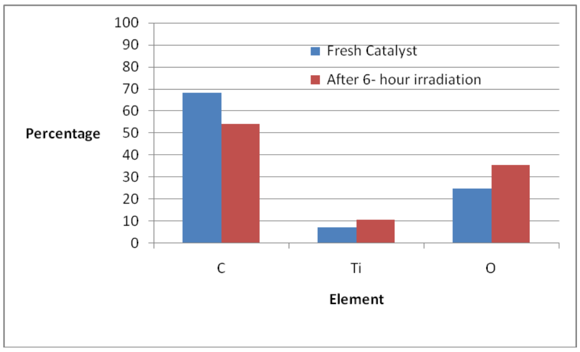


Fig. 13: Percentage elemental composition of fresh and used 1:10 AC/NanoTiO_2 immobilized catalyst

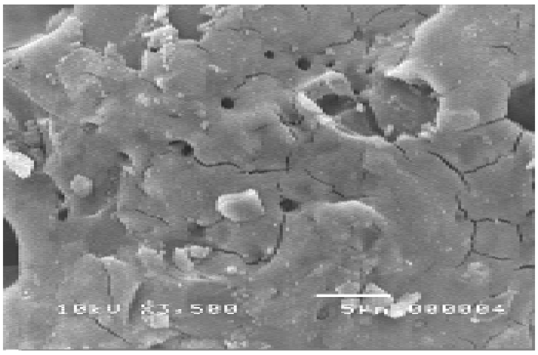


Fig. 14: SEM image of immobilized catalyst after 6- hour irradiation

Effect of Catalyst Loading

For suspended catalyst (see Fig. 12), the color removal increases when the catalyst loading was increased from 1g to 2g however, the color removal decreases when catalyst loading was further increased to 3g catalyst per liter of dye solution. This result implied that as the catalyst loading is increased, the number of active sites on catalyst surface increases resulting in an increase of $OH^{\bullet}$ radicals that can take part in the degradation of dye molecules. However, as the catalyst loading reaches an optimum level, the catalyst started to reduce the penetration of light in the solution thereby lowering dye degradation. This result is in contrast when using immobilized catalyst at similar conditions. Shielding effect due to increased catalyst loading did not occur in immobilized catalyst. Suspended AC/nanoTiO_2 is superior over immobilized AC/nanoTiO_2 at catalyst loading of 2g L^{-1} which suggests that there is an optimum AC and TiO_2 loading in AC/nanoTiO_2 that provides synergistic effect for adsorption and photocatalytic reaction.

Results on Stability Test of Immobilized Catalyst

Elemental composition of fresh and used catalyst (Fig 13) revealed the stability of TiO_2 in the surface of AC. Also, white spots on the surface of AC (Fig 14) are still evident showing that TiO_2 was not detached from the substrate due to stirring. Moreover, only 5.5% weight removal of the catalyst from the glass plate was observed after 6-hour irradiation.

CONCLUSION

Result showing 1:10 favorable over 2:10 and 3:10 AC/nanoTiO_2 in both suspended and immobilized catalysts indicates that high TiO_2 component for photocatalytic reaction is favored over adsorption. The BET surface area of 1:10 AC/nanoTiO_2 in its powder form is higher compared to 1:10 AC/nanoTiO_2 immobilized in glass plates. The efficiency of color removal for Turquoise blue dye using AC/nanoTiO_2 is favored at acidic initial dye solution pH. Suspended catalyst exhibited higher initial rate of color removal compared to immobilized catalyst. Turquoise blue dye is totally removed in 215 minute- irradiation using suspended 1:10 AC/NanoTiO_2 while only 25% color removal was observed in 360 minute – irradiation using immobilized 1:10 AC/NanoTiO_2. The performance of immobilized catalyst can still be improved by increasing the catalyst loading since it is not affected by shielding effect. Enhanced photocatalytic activity of AC/nanoTiO_2 for Turquoise blue removal is found at AC loading 1:10 AC/NanoTiO_2, initial dye solution pH 3, initial dye concentration of 20ppm and catalyst loading of 2g L^{-1} and 3g L^{-1} of dye solution for suspended and immobilized catalyst respectively. Moreover, the stability of AC/nanoTiO_2 attached in glass plates using PEG was established. There are no new absorption bands observed for Turquoise blue dye solution when irradiation time is increased. With these results, AC/nanoTiO_2 immobilized in glass plates using PEG for dye degradation has seen potential for large - scale application.

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