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PHOTODEGRADATION OF METHYLENE BLUE DYE IN AQUEOUS STREAM USING IMMOBILIZED TiO_2 FILM CATALYST: SYNTHESIS, CHARACTERIZATION AND ACTIVITY STUDIES

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Abstract. TiO_2 thin film photo catalyst was synthesized and immobilized on glass reactor through sol-gel method. The synthesized TiO_2 coating was transparent that enabled the penetration of ultra-violet (UV) light to the catalyst surface. A tubular photo-catalytic reactor with recirculation mode was designed, fabricated and used for activity measurements. TiO_2 film was synthesized using the formulation of 1 titanium iso-propoxide : 8 iso-propanol : 3 acetyl acetone : 1.1 H_2O : 0.05 acetic acid (in molar ratio) and gave excellent photo-catalytic activity in degradation of methylene blue dye present in aqueous solution. 50% degradation of methylene blue dye at the initial dye concentration of 40 μmol/L was observed after 5 passes of recirculation with residence time of 1.4 min. Photo catalytic degradation of methylene blue dye was insensitive to the increase of reaction temperature. The activation energy for photo degradation of methylene blue dye was 10.72 kJ/mol.

The initial methylene blue dye concentration, pH value, presence of hydrogen peroxide, air bubbling, and reaction temperature were studied as the important process variables. The synthesized TiO_2 thin photo-film was characterized using SEM, XRD and EDX analysis methods. SEM analysis showed a uniform TiO_2 coating on glass support without fractured appearance. XRD analysis revealed the appearance of anatase TiO_2 crystalline phase at calcination temperature of 500°C and rutile phase, the less active TiO_2 crystalline phase was observed above 600°C. A comparative performance between the TiO_2 thin film and a commercial sample of TiO_2 powder (99% anatase) was evaluated under the same experimental conditions. The synthetic TiO_2 film was found equally active as TiO_2 powder catalyst.

Keywords: TiO_2 film photo catalyst, methylene blue dye, photo catalytic degradation, synthesized

Abstrak. Filem fotomangkin TiO_2 telah berjaya disintesiskan dan tersekat gerak pada reaktor kaca melalui kaedah sol-gel. Lapisan TiO_2 yang berlut-sinar membenarkan penembusan cahaya ultra-ungu (UV) ke atas permukaan mangkin. Reaktor fotopemangkinan berbentuk tiub yang mempunyai mod kitar semula telah dibina. Formula sintesis TiO_2 yang baru telah dicadangkan, iaitu 1 titanium isoproposida : 8 isopropanol : 3 asetil aseton : 1.1 H_2O : 0.05 asid asetik (dalam nisbah molar) menunjukkan aktiviti proses berfotomangkin yang tinggi dalam proses penurunan bahan pencemaran metilena biru yang hadir di dalam air. Bagi reaktor fotomangkin yang berbentuk tiub, 5 pusingan kitar semula pada τ = 1.4 min di perhatikan untuk 50% degradasi metilena biru pada kepekatan awal 40 μmol/L. Proses penurunan berfotomangkin didapati tidak peka terhadap perubahan suhu tindak balas. Tenaga pengaktifan bagi metilena biru adalah 10.72 kJ/mol.

Dalam kajian ini, kepekatan awal bahan tindak balas, nilai pH, kehadiran hidrogen peroksida, udara dan suhu tindak balas merupakan pembolehubah proses yang dikaji. Pencirian ke atas lapisan TiO_2

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dijalankan dengan menggunakan analisis SEM, XRD dan EDX. Analisis SEM menunjukkan lapisan TiO_2 yang serata pada sokongan kaca tanpa kemunculan retakan. Analisis XRD mendedahkan kemunculan fasa kehabluran anatasi TiO_2 pada suhu kalsinasi 500°C dan fasa rutil, fasa kehabluran TiO_2 yang kurang aktif pada suhu melebihi 600°C. Satu kajian perbandingan keaktifan diantara lapisan filem TiO_2 disintesis dan komersial serbuk TiO_2 (99% anatasi) dinilai pada keadaan eksperimen yang sama. Filem TiO_2 didapati sama aktif seperti mangkin serbuk TiO_2.

Kata kunci: Filem fotomangkin TiO_2, metilena biru, proses penurunan berfotomangkin, sintesis

1.0 INTRODUCTION

TiO_2 heterogeneous photo-catalysis has been the subject of numerous investigations in recent years as it is an attractive technique for the complete destruction of undesirable contaminants (pollutants) in both the liquid and gaseous phases using artificial light or solar illumination [1]. Titania photo-catalysis advantages of low operation temperature, low cost, and significantly low energy consumption, have led the relevant application to the stage of commercialization [2]. The number of references and patents related to removal of toxic and hazardous compounds from water and air streams published during the last decade exceeds several thousands [3]. Whenever semiconductor materials have been tested under comparable conditions for the degradation of the same compounds, TiO_2 has generally been demonstrated to be the most active [4].

Despite the effectiveness of the heterogeneous photo-catalysis process, the operating cost for the total mineralization of hazardous organic effluents remains high. The reasons are due to the two serious drawbacks found in the conventional TiO_2 slurries system which limit its practical applications [5]. First, the settling velocity of powder TiO_2 (average diameter of 0.2 μm) is very slow, requiring a long retention time in the clarifier. Second, as the dosage of TiO_2 is increased in order to increase the photo-catalytic rate, the high turbidity created by the high TiO_2 concentration can actually decrease the depth of UV penetration. This “shadowing effect” can drastically lower the rate of photo-catalytic reaction on a unit TiO_2 weight basis. Therefore, attention has recently turned to the immobilization of TiO_2 on solid carrier to eliminate the need for a follow-up clarifier and separation of TiO2 particles. [6].

In the present research work, the objective is to develop an effective TiO_2 film immobilization method using the simplest, yet promising sol-gel method and to immobilize it on a tubular glass reactor. The performance of the immobilized photo-catalytic reactor was tested for degradation of methylene blue dye present in aqueous stream. The performance of the synthetic TiO_2 film catalyst was compared with a commercial TiO_2 sample powder catalyst.

2.0 EXPERIMENTAL

2.1 Synthesis of TiO_2 Film Catalyst

340 ml of synthesized TiO_2 mixture via sol-gel route was prepared using 0.34 mol of titanium isopropoxide (Fluka, 98%) and 2.72 mol isopropanol (Acros, 99%), mixed under constant speed at room temperature. This mixture was stirred for 2 hours to undergo a hydrolysis process for the formation of a homogeneous solution. 0.374 mol distilled water, and 0.017 mol acetic acid (Fluka, 99%) were mixed and added drop wise to the above hydrolyzed mixture under constant stirring. Once the mixture became cloudy, 1.02 acetyl acetone (Fisher, 99%) was added to the mixture and left for continuous stirring for 30 minutes. The synthesis mixture was sealed and left for aging for at least 1 day before it could be used. Dip-coating method was used to immobilize the synthesized TiO_2 mixture on the cleaned glass tube which was used as the catalyst support material. 1.5 mm/s of withdrawal speed was used to obtain a uniform thin film coating on the glass tube. The TiO_2 coated glass tube was air-dried for a few minutes before putting into an oven at 120°C for 30 minutes, then followed by calcination at 300 to 700°C at 2°C/min for at least 1 hour. The process from dipping to heat treatment was repeated in order to obtain a thicker uniform photo-catalyst film. 7 coating cycles which are equivalent to 0.295 mg/cm^2 of TiO_2 per coated film surface area was used in the present study.

2.2 TiO_2 Film Characterization

The structure and morphology of the synthetic TiO_2 thin film was studied using Scanning Electron Microscope (SEM), Model Leica Cambridge S-360. The SEM unit was operated at 15 kV of accelerating voltage. Energy dispersive X-ray spectroscopy (EDX) analysis was used to characterize the elemental composition of the TiO_2 films. The crystallinity of the photo catalyst was determined from X-ray diffraction (XRD) using X-ray diffract meter, (Siemens D-500) which was carried out with Cu Kα radiation operated at 40 kV and 40 mA.

2.3 Experimental Set-Up

The tubular photo-catalytic reactor can be operated in two modes: (1) single-pass mode (2) recirculation mode. The flow system consisted of a feed pump connected to a solution tank, and a TiO_2 coated glass reactor for the photo catalytic reaction to take place and recycled back to the feed tank. The experimental rig consisted of a stainless steel tank with height = 30 cm, diameter = 10 cm together with a heating element and controller to study the effect of temperature in the process, a pump (Master flex, model 07591-00) to pump the reactants from the tank to the reactor, flow meter (Cole-Parmer, model 32464-12) to control the feed flow rate, multi-channels digital temperature scanner (Cole-Parmer, model 89500-10) connected to thermocouple-type K (Cole-Parmer, model

88500-10) used to display the temperature reading at respective location, two UV lamps (Fisher, model UVL-28) to illuminate the TiO_2 photo catalyst film, two thermocouples placed at inlet and outlet of the reactor to monitor the temperature differences during the process, stirrer (Janke & Kunkel, model RW 20 DZM) to ensure complete mixing in the tank, and an air pump (Sinku Kiko, model DA-30S) to supply air (oxygen) which worked as an electron scavenger to prevent the recombination of electron-hole pairs. A schematic diagram of the photo-catalytic tubular reactor is shown in Figure 1. The tubular glass reactor was made of Pyrex glass tube (O.D. = 3.5 cm, I.D. = 3.3 cm and L = 35 cm) with TiO_2 film catalyst coated on the inner wall of the reactor. All experiments were run at initial methylene blue (MB) concentration, $C_{MBo,} = 40\ \mu mol/L$, reaction temperature, T = 30°C, treated volume, V = 1L, and TiO_2 catalyst amount, W = 0.1g, unless stated otherwise.

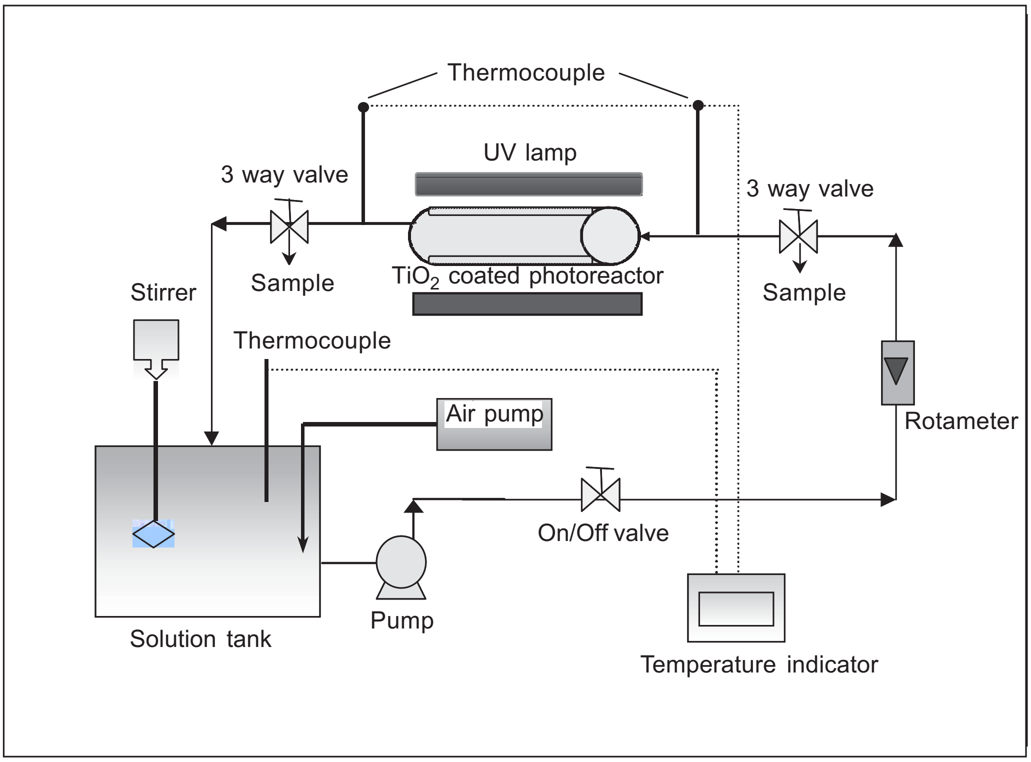


Figure 1 Schematic diagram of the photo catalytic reactor

2.4 Analysis

The photo catalytic degradation of methylene blue of both initial and irradiated samples was determined by mean of UV-vis spectrophotometer analysis (Shimadzu UV-1601) through indication of color disappearance. A calibration curve of methylene blue solution obtained at 660 nm wave length at different concentrations was prepared in order to correlate the concentration of methylene blue at different reaction time by converting the absorbance of the sample to methylene blue concentration.

3.0 RESULTS AND DISCUSSION

3.1 TiO_2 Film Characterization

3.1.1 Scanning Electron Microscopy (SEM)

Figure 2 shows the SEM micrograph of the TiO_2 film coated on glass tube surface under 15600X magnification. The micrograph shows a plain and smooth surface of TiO_2 film with minor crack lines on the glass surface. This indicates that the synthetic TiO_2 thin film using sol-gel route was successfully coated on the glass tube without any fractured film fall from the support material.

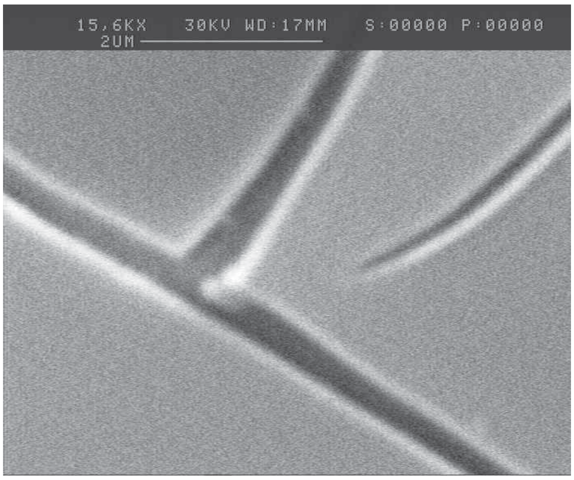


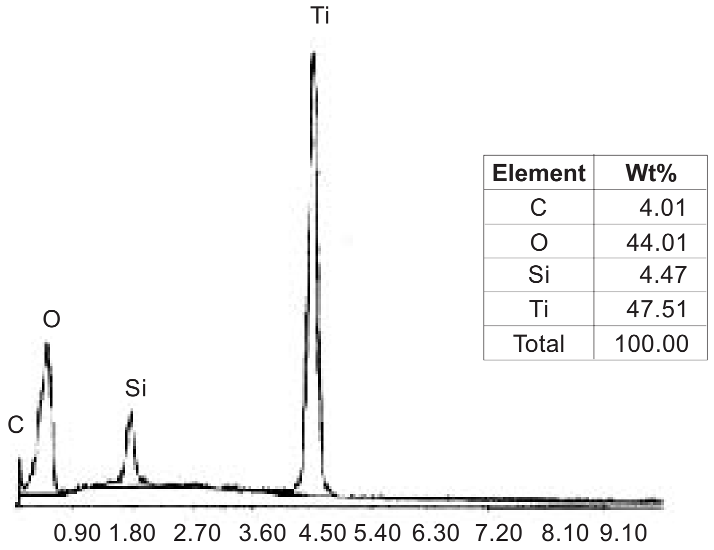
Figure 2 SEM micrograph of the TiO_2 thin film coated on glass tube

3.1.2 Energy Dispersive X-ray Spectroscopy (EDX)

EDX pattern of the synthetic TiO_2 film coated on the glass tube is shown in Figure 3. The elemental composition of the TiO_2 film was found as 47% Ti, 47% Si, and 4% O where the presence of TiO_2 on the film was confirmed.

3.1.3 X-ray Diffraction (XRD)

Figure 4 shows the XRD pattern of the TiO_2 films calcined at different temperatures. Anatase peak, the most active crystalline form of TiO_2 was observed at calcination temperature of 500°C. Below this temperature, only amorphous structure was observed.



Element	Wt%
C	4.01
O	44.01
Si	4.47
Ti	47.51
Total	100.00

Figure 3 EDX spectrum of TiO2 thin film coated on glass tube

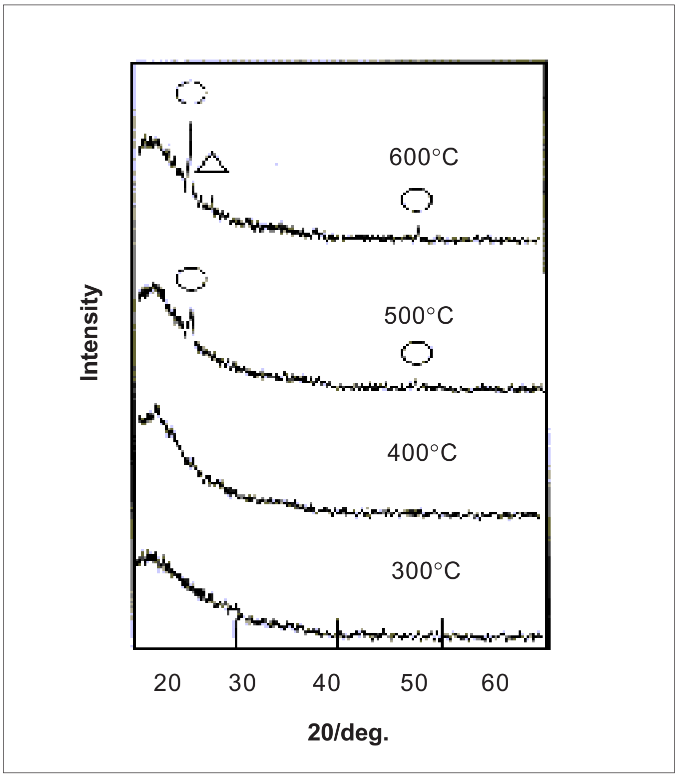


Figure 4 XRD pattern of the TiO_2 film calcined at different temperature
O : Anatase Δ : Rutile

At temperature above 600°C, anatase converted to the comparatively photo-inactive rutile phase. The excellent photo-catalytic activity of anatase phase of TiO_2 had been reported by many researchers for the decomposition of organic pollutants [7,8]. Thus, 500°C temperature was chosen to prepare the active anatase phase of TiO_2 photo-catalyst film.

3.2 Activity Studies of Synthetic TiO_2 Thin Film Photo-catalyst

The photo-catalytic activity of the synthetic TiO_2 film was studied by comparing the activity of commercial sample of TiO_2 powder under the same experimental conditions. Figure 5 shows that the synthetic TiO_2 film gave 50% of MB degradation after 5 passes of recirculation at the residence time, $\tau = 1.4$ min, whereby the commercial TiO_2 powder gave 58% of MB degradation after 5 passes. This result is quite encouraging since the difference in catalytic degradation activity between immobilized catalyst and powder catalyst was only 8% (5 passes at $\tau = 1.4$ min).

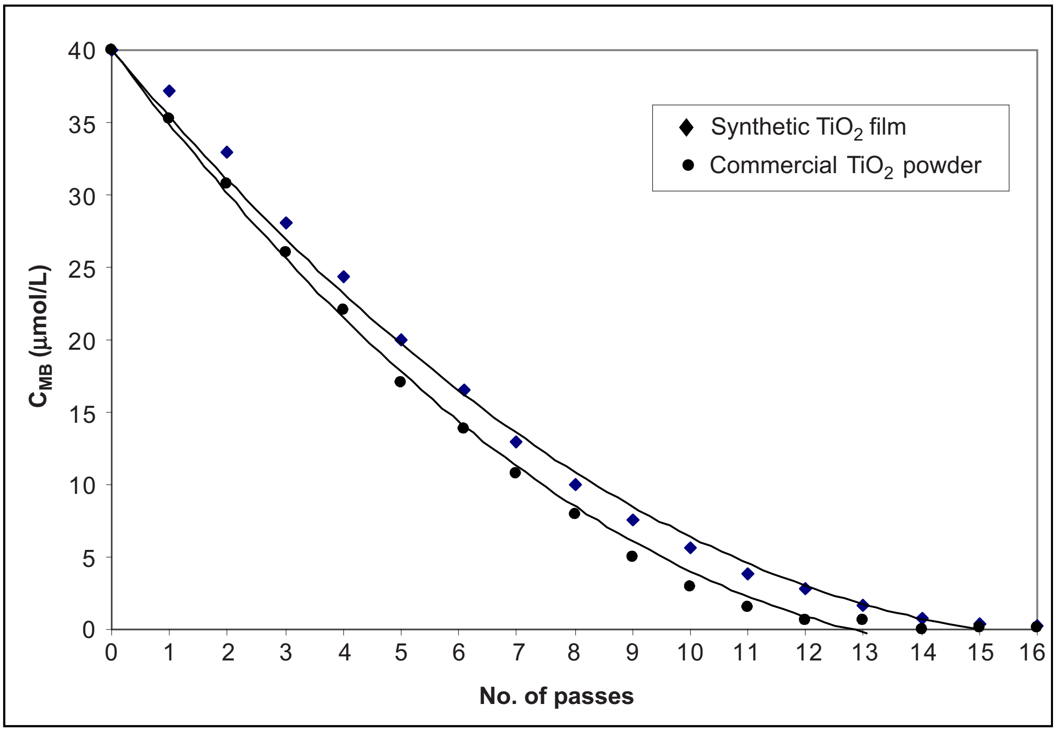


Figure 5 Comparison between synthetic TiO_2 film and commercial TiO_2 powder

3.2.1 Effect of Initial MB Concentration

Figure 6 shows the photo-catalytic degradation of methylene blue against residence time. It is clear from the figure that the rate of photo-catalytic degradation of MB was higher at lower initial MB concentration, whereas at higher initial MB concentration, C_{MBo} = 160 µmol/L, the photo-degradation of MB was almost constant. However, better results could be obtained using recirculation mode in the tubular photo-catalytic reactor. The large amount of adsorbed dye inhibited the reaction of dye molecules with photo-generated holes or hydroxyl radicals because there was no direct contact of photo-catalyst with the dye molecules. Increasing concentration of dye also caused the dye molecules to adsorb light and the photons never reached the photo-catalyst surface [9]. Thus, typical applications of photo-catalytic degradation of MB was found excellent at low concentration, i.e. $C_{MBo} < 40$ µmol/L [10].

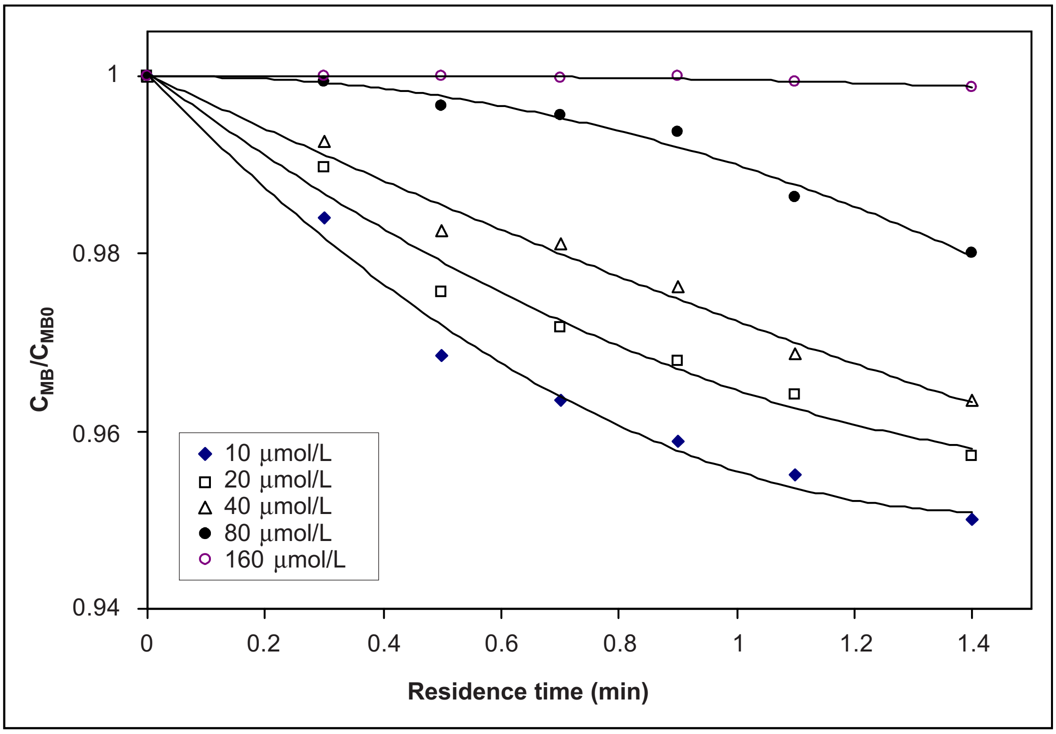


Figure 6 Photo catalytic degradation of MB at different initial dye concentration

3.2.2 Effect of pH

Figure 7 shows the effect of pH value in photo-catalytic degradation of MB. The pH range studied was from acidic to basic solution (pH 3 to pH 12). At τ = 1.4 min, 5.05% photo-degradation of MB was observed at pH 12, 4.32% at pH 9, 3.91% at pH 6.8, and 3.20% at pH 3 respectively. The pH influenced the adsorption property of organic compounds and their dissociating state in solution [11]. The surface charge properties of TiO_2 were also changed with the changes in pH value due to amphoteric behavior of semi-conducting TiO_2 [12]. The point of zero charge (pzc) for titanium dioxide is at pH 6.5. The TiO_2 surface is positively charged in acidic solution and negatively charged in basic solution.

$$\text{(Acidic solution) pH} < \text{pzc: Ti-OH} + H^+ \rightarrow TiOH^{2+}$$
$$\text{(Basic solution) pH} > \text{pzc: Ti-OH} + OH \rightarrow TiO + H_2O$$

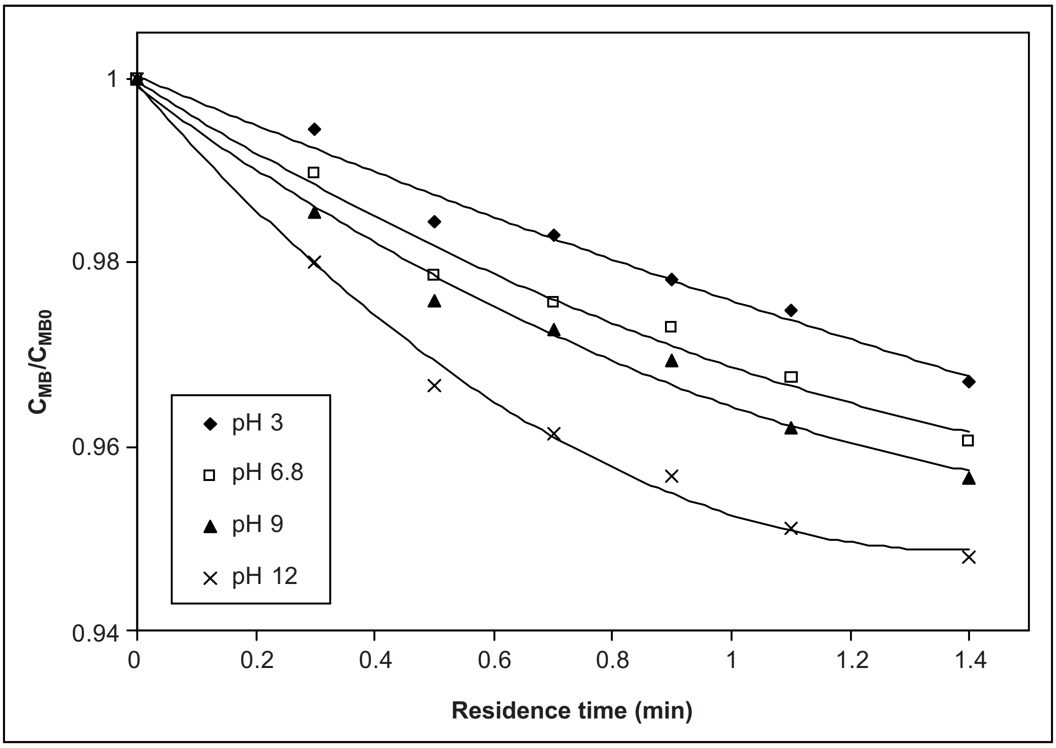


Figure 7 Photo catalytic degradation of MB at various pH values

Since methylene blue is a cationic dye (Figure 8), it is conceivable that at higher pH value, its adsorption is favored on a negatively charged surface.

Figure 8 Molecular structure of methylene blue

3.2.3 *Effect of Hydrogen Peroxide*

The effect of hydrogen peroxide (H_2O_2) was studied from 50 μmol/L to 200 μmol/L. Figure 9 shows the photo catalytic degradation of MB at different concentration of H_2O_2. At residence time of 1.4 min, 6.5% photo catalytic degradation of MB was observed in the presence of 200 μmol/L H_2O_2, 5.2% in 100 μmol/L H_2O_2, 4.4% in 50 μmol/L H_2O_2, and 3.9% in the absence of H_2O_2 (i.e. using TiO_2 thin film only). These observations were due to the electron acceptor behavior of H_2O_2, which reacted with conduction band electrons to generate hydroxyl radicals, required for photo catalytic degradation of organic pollutants [13]:

$$H_2O_2 + e^-_{CB} \rightarrow OH\bullet + OH^-$$

$$H_2O_2 + O_2^-\bullet \rightarrow OH\bullet + OH^- + O_2$$

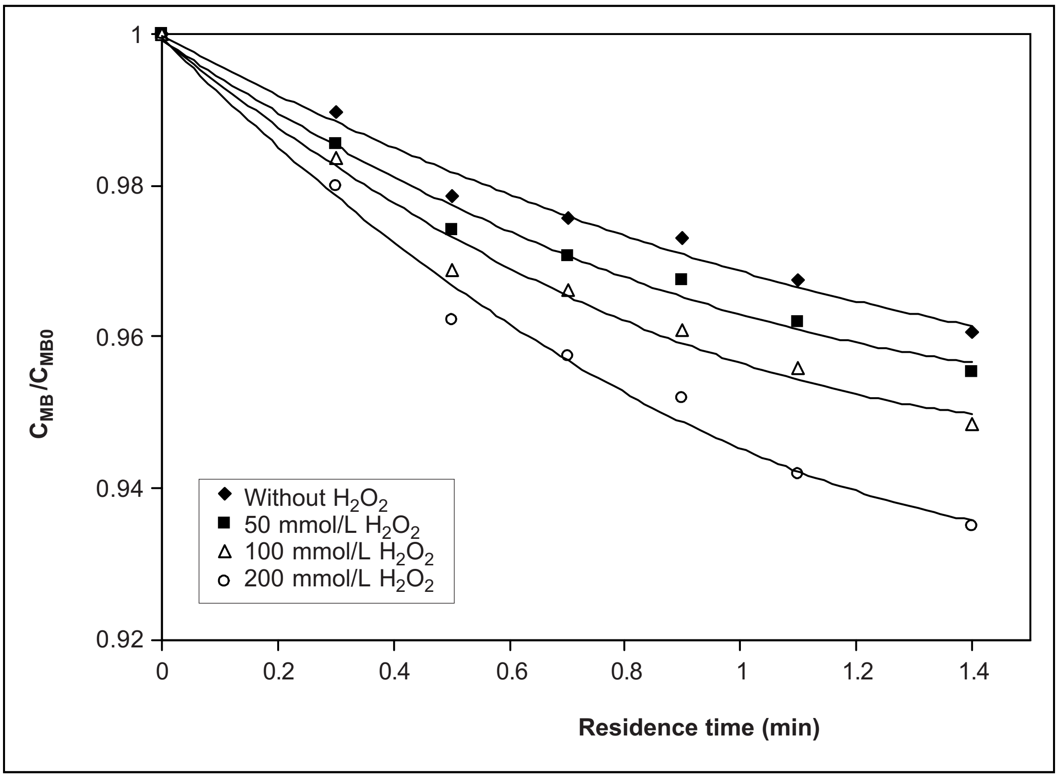


Figure 9 Photo catalytic degradation of MB at various H_2O_2 concentrations

3.2.4 *Effect of Air Bubbling*

The effect of air bubbling was studied in the range of 1 cm^3/s to 2.5 cm^3/s. Figure 10 shows the photo catalytic degradation of MB at different air bubbling flow rates. At τ

= 1.4 min, 4.5% of MB degradation was achieved in the presence of 2.5 cm^3/s air bubbling, 4.2% at 1 cm^3/s of air bubbling, and 3.9% in the absence of air bubbling. The presence of air in the current photo reactor worked as the electron scavenger to prevent the recombination of electron-holes pairs [14]. It was found that the photo catalytic activity was completely suppressed in the absence of oxygen [15].

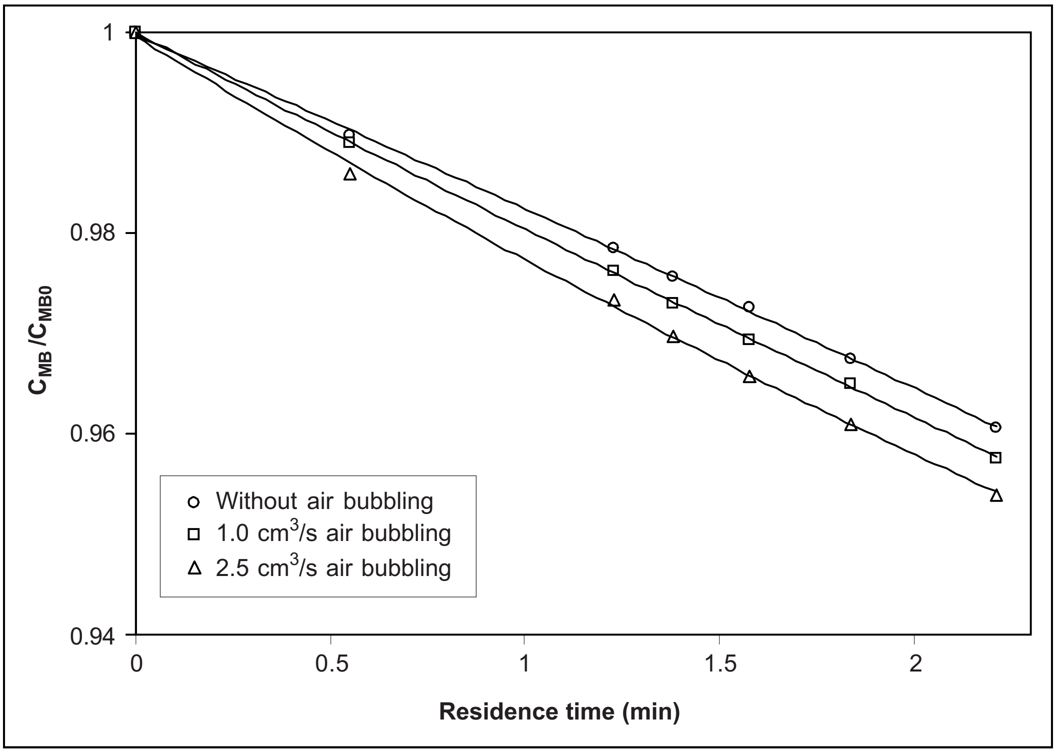


Figure 10 Photo catalytic degradation of MB at different air bubbling rate

3.2.5 Effect of Reaction Temperature

Figure 11 shows the effect of reaction temperature in photo catalytic degradation of MB. The process temperature was varied from 30 to 50°C. Photo catalytic degradation of MB was found to be less temperature dependent as the rate of reaction did not vary with temperature. The activation energy for photo degradation of MB was found as 10.72 kJ/mol. The activation energy of photo catalysis reaction is reported as 5 to 20 kJ/mol in the literature [14]. These values are quite close to that for a hydroxyl radical reaction, suggesting that the photo degradation of most organic pollutants may be governed by hydroxyl radical reaction. As a consequence, the optimum operating temperature is usually around 40°C.

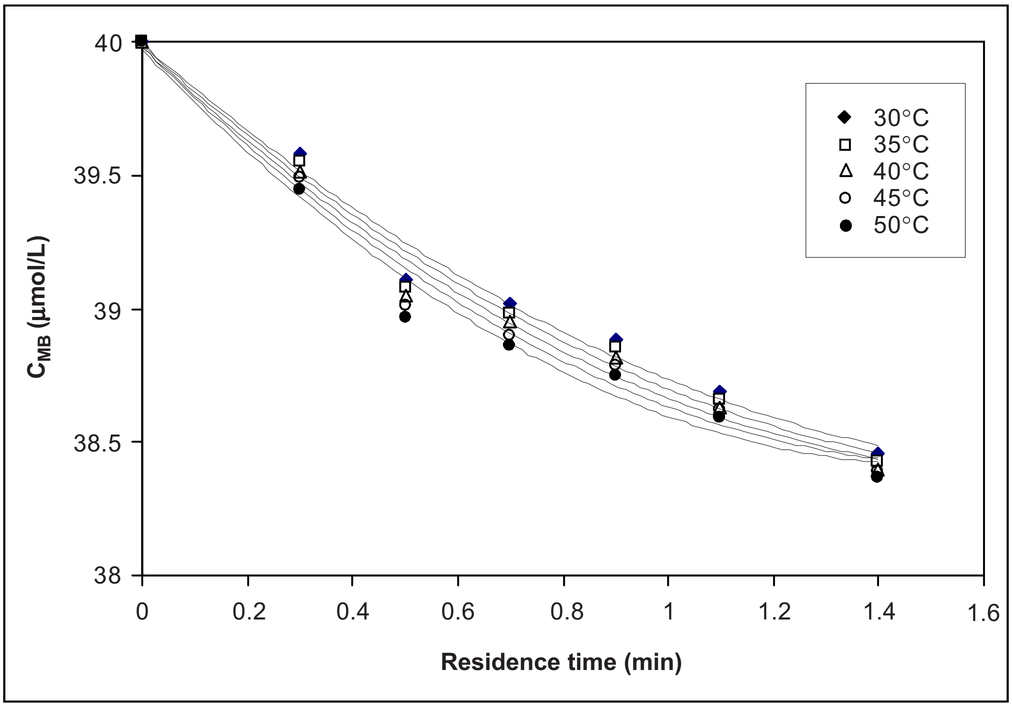


Figure 11 Concentration of methylene blue as a function of residence time at different reaction temperatures

5.0 CONCLUSIONS

The present study focused on the synthesis of TiO_2 thin film photo catalyst using sol-gel technique for the degradation of organic pollutants. The immobilization of TiO2 photo catalyst on Pyrex glass tube was successfully developed using Dip-coating process. The synthetic TiO_2 coating was adhered strongly on the glass tube support at withdrawal speed of 1.5 mm/s.

Scanning electron microscope (SEM) results showed uniform TiO_2 thin film attached on the glass tube surface without any fractured appearance. X-ray diffraction analysis showed the presence of anatase crystalline phase of TiO_2 at the calcination temperature of 500°C and this phase was responsible for photo catalytic activity.

The performance of the sol-gel derived TiO_2 film was compared with commercial TiO_2 photo catalyst powder and was found equally effective in treating methylene blue present in aqueous streams. 50% of MB degradation was observed using film catalyst as compared to 58% degradation over powder catalyst under similar conditions. The activation energy value of 10.72 kJ/mol reflected the low range of reaction temperature (30°C – 50°C) for photo catalysis process.

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