

Photodegradation of 4-Chlorophenol using Carbon Coated TiO₂ under Solar Irradiation

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Abstract- The photocatalytic degradation of 4-Chlorophenol (4CP) using carbon C coated TiO₂ (C-TiO₂) and pristine TiO₂ under solar irradiation has been studied. The experiments were carried out in a suspension mode under custom made glass cell reactor with continuous aeration supply. Both photocatalysts worked efficiency at pH 6. It was found that 0.6 and 0.3 g were the optimum loading for C-TiO₂ and pristine TiO₂ respectively in the degradation of 20 mg L⁻¹ 4CP under solar irradiation. The optimum C-TiO₂ was found six times faster than pristine TiO₂ based on pseudo first order rate constant of 4CP photodegradation. No adsorption was observed in the photocatalysts. The intermediates observed during this photocatalytic degradation process were maleic acid, hydroquinone (HQ), benzoquinone (BQ), 4-chlorochetol (4CC) and resorcinol.

Index Terms- Carbon coated TiO₂, photocatalysis, 4-Chlorophenol, intermediates.

I. INTRODUCTION

Recently, the increased world industrialization makes the huge productions of chemical wastes, such as dyes, sulphates and a toxic compound. These chemical wastes mostly are uncontrolled and the easiest way is discarded into the rivers and definitely it will contribute to the global environmental problems. 4CP which is known as endocrine disruptor is toxic and non-biodegradable, present 4CP in wastewater as by-products of pulp and paper, dyestuff, pharmaceutical and agrochemical industries [1]. Several ways have been proposed in order to remove these compounds, such as chlorination adsorption, and incineration [2-8]. The degradation of 4CP via chlorination process facing the problem since it generates carcinogenic by-products [3-4]. Another process of degradation is adsorption process using granular activated carbon as adsorption media. However, this process needs further treatment in order to reuse the activated carbon [5-6]. Incineration process of organic wastes was not always effective. Moreover, it can generate large quantities of toxic compound emissions into the atmosphere [7-8]. Indeed, such treatment process should be completely degrading all the pollutants without produced any hazardous residues [9].

Photocatalysis has been reported as an effective since it can degrade a wide range of pollutants both from water and air [9-15]. TiO₂ has emerged as the most viable semiconductor

photocatalyst as it is stable in aqueous medium and is tolerant to both acidic and alkaline media [10]. Various modification of TiO₂ photocatalytic properties have been widely investigated since TiO₂ is only active under UV light region which was only consist 5% from the energy of the sun [11]. The modification of TiO₂ with nonmetal like C, N, S, F and P is considered as one of the most promising methods to efficiently develop TiO₂-based photocatalysts sensitive in visible light irradiation for decomposition of various environmental pollutants [11-15]. Among of these nonmetal modified TiO₂, C coated TiO₂ is one of the methods that being extensively studied [11,13,16-18].

Several investigations of the photocatalytic decomposition of 4CP using metal oxide semiconductors either in suspensions or in an immobilized form [19-5] have been studied. Wongwisate et al. [19] was reported the photodegradation 4CP and its mechanism using Au-Ag supported on sol-gel TiO₂ under UV light (200-280 nm). Another study by Qin et al. [20] was observed the degradation of 4CP using bifunctionalized dye-sensitized TiO₂ film under 300 W Xenon lamp (500 nm) used as the visible light source. Yang et al. [21] observed the effects of hydroxyl radicals and oxygen species on the 4CP degradation by photoelectrocatalytic reactions with TiO₂-film electrodes under 100W high-pressure mercury lamp. The degradation of 4CP under solar irradiation using nitrogen doped TiO₂ have been studied by Sun et al. [22], it was observed that 82% of 4CP being degraded at 6 h of irradiation and Guillard et al. [23] was studied the effect of different commercially available of TiO₂ toward degradation of 4CP and its intermediates under solar light.

For the best of our knowledge, many studies were conducted using TiO₂ for the degradation of 4CP involving various methods which are expensive, used toxic chemicals and UV light that has harmful effects. However, only few a works have studied for the degradation of 4CP under solar irradiation with no such publication in the presence of C coated TiO₂ as photocatalyst.

In our recent publication [24], a thin layer C coated TiO₂ with 0.25% C content had been successfully prepared. This C coated TiO₂ had improved the photocatalytic activity for the degradation of RR4, MB and phenol under 45 W fluorescent lamp and solar irradiation respectively. The improved of its photoactivity is due to the lowering of electron-hole recombination process as consequence of coated C on surface of TiO₂. Nevertheless, the literature data concerning application of C coated TiO₂ for degradation of pollutants under solar irradiation is limited. There are still some important issues

concerning C coated TiO₂ photocatalysts, which require further studies. The objective of this research is to study the photodegradation of 4CP under direct solar irradiation using C coated TiO₂ as photocatalyst. The study will be focused on effects of catalyst loading, aeration, pH, weather conditions and mineralization study with identification of intermediates, subsequently to propose the possible degradation pathways.

II. METHOD

Material

TiO₂ with 99% anatase (Sigma - Aldrich) was used as the starting material in the preparation of C coated TiO₂. Epoxidized natural rubber (ENR-50, Kumpulan Guthrie Sdn. Bhd.) dissolved in toluene to make an 11.4 % solution (w/v) was used as the C precursor. Acetone solvent (R&M chemicals) was used for dilution of sample mixtures for the homogenization process via ultra-sonication. 4CP with 99% pure was obtained from Aldrich, was employed as model pollutant. Hydroquinone (HQ, 99%) and benzoquinone (BQ, 99 %) from Acros, 4-Chlorocatechol (4CC, 98%) from Fluka and resorcinol (99%) from BDH were used to identify the intermediate products. Reagent grade hydrochloric acid and sodium hydrochloride were used to adjust the pH of the reacting mixture. Table 1 summarized chemical structure, molecular weight and λ max for 4CP, HQ, BQ, 4CC and resorcinol respectively. Ultra pure water (18.2 MΩ cm⁻¹) was used to prepare all solutions in this work.

Preparation of C coated TiO₂ samples

C coated TiO₂ was prepared using the method describes by Nawi et al. [24]. 1.0 g (± 0.03) of ENR solution mixed with 12 g (± 0.03) of TiO₂ into 60 mL of acetone. The mixture was than sonicated for 8 hours using 50Hz Crest Ultrasonicator to allow for homogeneous distribution of the carbon precursor on the TiO₂ sample. After drying off the solvent in an oven at 100 °C, the TiO₂ mixed ENR sample was calcined under 560°C temperature under N₂ flow for 5 hours. The product was cleaned by sonicating the sample in distilled water and centrifuged to isolate the contamination. After drying process, pure C coated TiO₂ sample was than produced with light brown in color.

Adsorption study

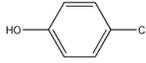
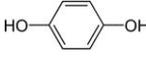
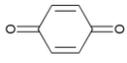
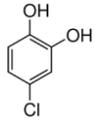
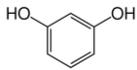
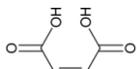
For adsorption study, experiment was conducted in the dark. 0.3 g (± 0.03) of photocatalyst sample was added into 60 ml of 20 mg L⁻¹ 4CP to form suspensions. This suspensions were then poured into glass cell with dimension 60 x 10 x 250 mm (L x B x H) mm and aerated in the dark. The treated 4CP with TiO₂ in suspension mode was taken at every 15 minutes interval up to 1 hour, than filtered with 0.45µm syringe filter to separate the treated 4CP and TiO₂. The percentage of the degradation of 4CP was determined by Shimadzu HPLC, Model LC-10AT chromatograph equipped with a LC-18 Supelcosil reversed phase column (Supelco) with (60:40) methanol-water as mobile phase and UV wavelength detector set at 220 nm.

Photocatalytic study

0.3 g (± 0.03) of photocatalyst sample was added into 60 ml of 20 mg L⁻¹ 4-CP solution to form suspensions. The suspensions were then poured into a glass cell and irradiated

under solar. The entire solar experiments were conducted under time of irradiation between 11 am to 3 pm in the month of March to September.

Table 1: Summary of the organic pollutants

Chemical structure	Chem. formula	Molecular weight (g mol ⁻¹)
 4-Chlorophenol	C ₆ H ₅ ClO	128.6
 Hydroquinone	C ₆ H ₆ O ₂	110.1
 Benzoquinone	C ₆ H ₄ O ₂	108
 4-Chlorocatechol	C ₆ H ₅ ClO ₂	144.6
 Resorcinol	C ₆ H ₆ O ₂	110.1
 Maleic acid	C ₄ H ₄ O ₄	116

The UV detector Radiometer (Solar light co. PMA 2100) connected with a UV-A, UV-B detector (260 - 400 nm) and PAR Quantum Light Sensor detector (401-700 nm) was used to determine the UV and visible light irradiance of solar respectively. An aquarium pump model NS 7200 was used as the aeration source. A direct reading air flowmeter (Gilmont) was used to determine the aeration rate supply to the reactor. Samples were taken at a specific time interval until almost complete degradation was attained. The percentage of the degradation of 4CP was determined by using HPLC. The concentration of the pollutant was plotted against the contact time of irradiation in order to determine the degradation rate of the pollutant. The dependencies of the rate of the degradation on its concentration as irradiation proceeds have been described well by the Langmuir-Hinshelwood model [25] (equation 1). Where r is rate constant, C is the substrate concentration (mg L⁻¹) at a given time (t, second); K is Langmuir- Hishelwood adsorption

equilibrium constant (ppm^{-1}) and k' is the surface reaction rate constant ($\text{mg L}^{-1} \text{min}^{-1}$). For highly diluted solution ($M < 10^{-3}$, $C < 108 \text{ mg L}^{-1}$), the term KC is negligible with respect to time t , the above equation becomes simplified as an apparent or pseudo first-order equation as shown below:

$$r = \frac{dc}{dt} = \frac{k' KC}{1 + KC}$$

$$r = k' KC = kC$$

$$\ln \frac{C_0}{C} = kt$$

This experiment were also applied for the effect of catalyst loading, aeration rate, pH and whether condition.

COD analysis

The photocatalytic mineralization of the dye was monitored by using chemical oxygen demand (COD) using standard method ASTM D1252. Low COD values of the related solution indicated that mineralization process has taken place since it reflects the low content of the organic in the solution due to their conversion into CO_2 and H_2O by the photocatalytic process. 20 mg L^{-1} of 4CP was irradiated for 2 hours. Air was supplied from the bottom of the reactor. At every 20 min interval 6 mL aliquot was drawn out from the reactor and filtered with a $0.45 \text{ }\mu\text{m}$ polyethylene terephthalate (PET) syringe filter to remove the catalyst particle before being analyzed. 3.0 mL of COD reagent was pipetted into three clean COD vials. 0.1 g mercury sulphate was added into each vial to remove chloride interferences. 2.0 mL of the sample was pipetted into each reagent. The vials were shaken to mix the sample with the reagent. The samples were refluxed using COD reactor at 140°C for two hours. 2 mL of deionised water was pipetted in the reagent and refluxed under the same condition as the other samples serve as a blank. After 2 hours, the samples were cooled down to room temperature before their absorbancies measured using the HACH DR2000 spectrophotometer at 620 nm.

Intermediates Study

The intermediates were determined using HPLC model. All substances were detected by UV detector at 220 nm. The peaks of 4CP and intermediates appeared from the chromatogram were identified by their respective retention times. The percentage of peak are relative to the total peak area was calculated and plotted as function of degradation time. The individual compounds were identified using 2 ways, either by comparing their retention times and retention times with those obtained for pure standard as shown in Table 2, or by spiking of pure standards into the degraded sample and photocatalytic degradation of some intermediates.

III. RESULTS AND DISCUSSION

Effect of the catalyst loading

Fig. 1a shows the pseudo first order rate constant for C-TiO₂ and pristine TiO₂ at different amount of catalysts loading. It was observed that the degradation of 4CP was always batter for C-TiO₂ as compare with pristine. The optimum amount of loading for pristine TiO₂ was found at 0.6 g with the rate constant was *c.a.* 0.098 min^{-1} while optimum loading for C-TiO₂ was observed at 0.3 g, it was observed that C-TiO₂ loading requires a half as compared with pristine TiO₂ to reach optimum efficiency. This could be due to the grey color of C-TiO₂ as early discuss in our previous study [24] may produced a dark condition of suspension media that scattering the light to penetrate deeply inside the mixture of 4CP and C-TiO₂. The same explanation was also observed by increased the C-TiO₂ loading beyond the optimum (0.3g) where it reduced the photodegradation of 4CP. The pseudo first order rate constant for optimum loading of C-TiO₂ was *c.a.* 0.422 min^{-1} which takes only 10 minutes to complete 4CP removal and it's more than 4 times faster than the optimum loading of pristine TiO₂ as can be seen in Fig. 1b

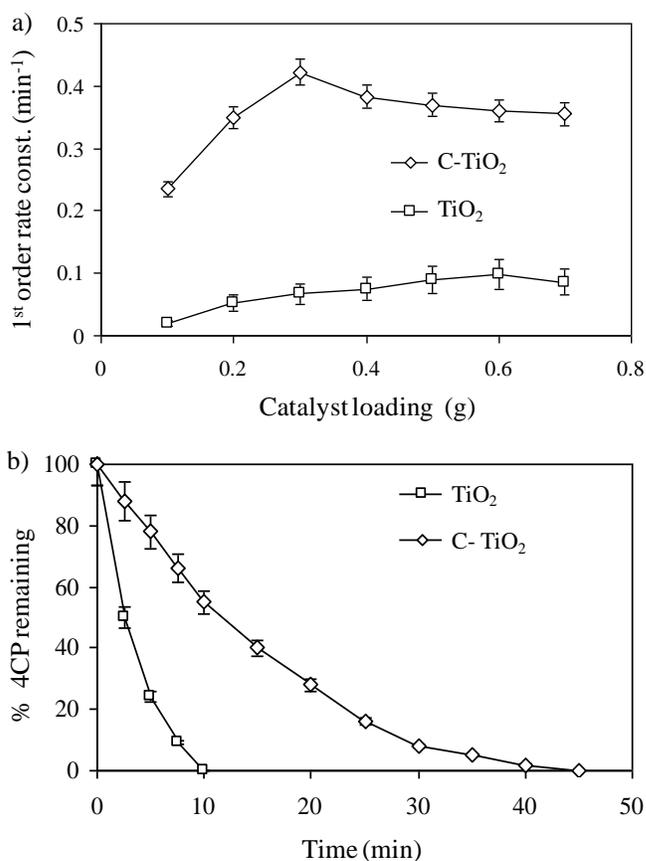


Figure 1: Photodegradation of 4CP; a) effect of catalyst loading vs degradation rate, b) graph % remaining on the optimum loading for pristine TiO₂ and C-TiO₂ at 0.6 and 0.3 g respectively

Effect of the aeration

The presence of dissolved oxygen plays a significant role in the photocatalytic degradation of 4CP. Oxygen molecule can act as an electron scavenger to trap and separate electron out from the positive holes that help to reduce the chance of electron-hole pair recombination. In order to determine the effect of dissolved oxygen on the 4CP degradation, one of studied without aeration while others were carried out at different aeration rate by bubbling air into the solution. As seen from Fig. 2 (a) and (b) the degradation rates of 4CP in the presence of dissolved oxygen was much higher than those of the systems run in the absence of dissolved oxygen for both catalysts. As the rate of aeration increased, the degradation rate increased until it reached an optimum value. However, increasing too much aeration would slow down the rate of degradation due to scattering of light by air bubbles.

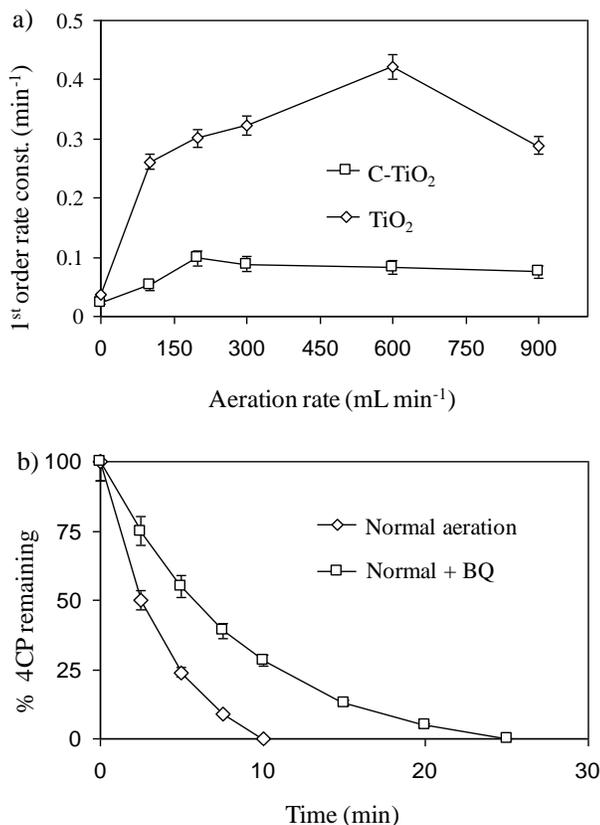


Figure 2: Graphs of; a) effect of aeration rate in the 4CP photodegradation and b) a control study of 4CP photodegradation under normal and BQ additive for C-TiO₂.

All photocatalytic evaluations were carried out under continuous aeration. The presence of dissolved oxygen plays a significant role in the photocatalytic degradation of 4CP. Dissolved oxygen is usually employed as an electron acceptor [26]. The presence of an electron acceptor improved the

photocatalytic process by increased the separation of the photogenerated electrons and holes. During the photocatalysis process in aerated condition, the oxygen molecule is adsorbed onto the catalyst surface. The adsorbed oxygen molecules will be reduced to O₂⁻ by electron that is promoted into the conduction band, leading to the formation of perhydroxyl radicals. In addition, perhydroxyl radical will produce hydrogen peroxide which can produce super hydroxyl radicals. The role of oxygen as an electron acceptor is summarized by the following equations [27]:

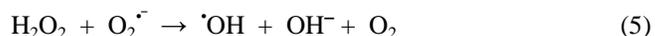


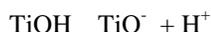
Figure 2a shows the effect of aeration flow rates towards photodegradation rate of 4CP under C-TiO₂ as a photocatalyst. The optimum aeration rate for C-TiO₂ was found at 600 mL min⁻¹, the rate was almost 11 times faster than the system running without aeration with the rate was *ca.* 0.037 min⁻¹. Therefore all photocatalytic and adsorption experiments in this work were carried out under this optimum aeration rate.

Photocatalytic degradation of 4CP dye using C-TiO₂ in the presence of 1,4-benzoquinone (BQ) under aerated condition was also carried out in order to provide evidence for the role of O₂ in the photocatalytic process since BQ is known as superoxide scavenger. It was found that the degradation of 4CP presence of BQ reduced significantly as compared to the experiment ran under aeration without BQ as can be seen in Fig. 2b. This clearly indicates that BQ has significantly reduced the efficiency of the photocatalytic degradation of 4CP even though the solution was optimally aerated. Apparently superoxide produced via equation 1 was consumed by BQ thus making reactions 2-6 ceased to exist.

Effect of pH solution

The pH of the solution has strong effect on the photodegradation process for both TiO₂ and C-TiO₂ as shown in Fig. 3. Degradation rate of 4CP has not been found to be significant at low pH values but increased rapidly with increase of the pH, attaining a maximum degradation at pH 6. Further increase in pH has showed decreased in the photodegradation efficiency. The surface charge development of TiO₂ is affected by the pH. Upon hydration, surface hydroxyl group (TiOH) are formed in TiO₂. These surface hydroxyl groups can undergo photon dissociation reaction, thereby bringing out surface charge which is pH dependent:





Where, TiOH^+ , TiOH and TiO^- are positive, neutral and negative surface hydroxyl groups respectively. A low pH is associated with a positively charge surface which cannot provide hydroxyl groups which are needed for hydroxyl radical formation. Consequently, the rate of 4CP degradation may decrease. On the other hand, higher pH value can provide higher concentration of hydroxyl ion (OH^-) to react with the hole to form hydroxyl radicals (OH^\cdot), thereby enhancing the photodegradation of 4CP [28].

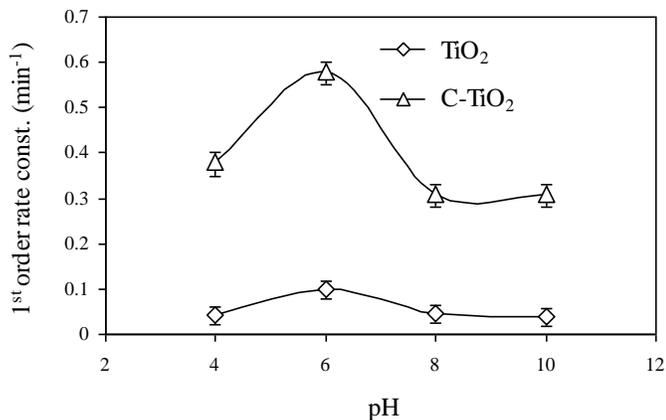


Figure 3: Effect of different pH suspension towards degradation of 4CP.

Effect of weather conditions

Fig. 4 shows the effect different weather conditions (cloudy and sunny day) on the photodegradation rate of 4CP for pristine and C-TiO₂ as photocatalyst. The average of UV and VIS light intensity for these conditions are listed in Table 2. The UV light intensities of cloudy and sunny day were 19 and 23 W m⁻² while for VIS light intensity were 200 and 300 W m⁻². The photocatalytic activity for both pristine and C-TiO₂ on a sunny day were higher as compared to its photocatalysts under cloudy day. As can be observed in Fig. 4, the degradation rate for C-TiO₂ is faster by 5 times on sunny day compared with C-TiO₂ on cloudy day, this is due to the low intensity of UV and VIS light irradiations under cloudy day which influenced the process of photo-induced of electron-hole during photocatalysis process.

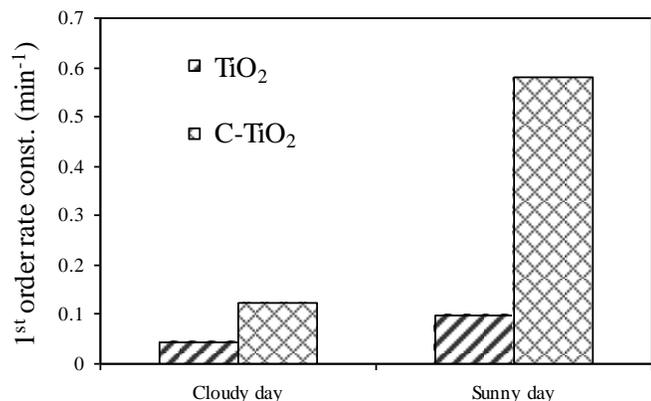


Figure: Photodegradation rate of 4CP at different weather condition.

It also happened for pristine TiO₂ where the degradation rate of 4CP was faster by 3 times when the photodegradation was applied under sunny day. The same observation was also reported by Dong et al [29] for the photodegradation of azo dyes under different condition.

Table 2: Light intensity at different weather condition.

Conditions	UV light Intensity (W m ²)	Visible light Intensity (W m ²)
Cloudy day	19	200
Sunny day	23	300

Chemical Oxygen Demand (COD)

The decreasing trend in the test of COD against irradiation time in the degradation of 4CP using pristine and C-TiO₂ are depicted in Fig. 5. The COD removal efficiency of unmodified anatase TiO₂ is lower than that of C-TiO₂ under identical experimental conditions. The optimum COD degradation of 4CP was achieved at 2.5 mg L⁻¹ for 60 minutes of irradiation under C-TiO₂, while optimum COD under pristine TiO₂ was achieved at 3 mg L⁻¹ for 100 minutes. No further degradation was observed beyond of that the irradiation time. The experimental results revealed that the dopant in TiO₂ plays significant role in the enhancement of photocatalytic activity, but it is not enough to achieve a complete mineralization of 4CP.

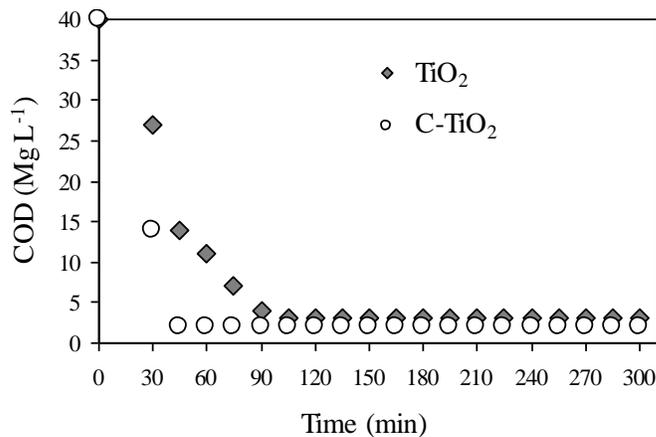


Figure 5: Mineralization study determined by COD values for photodegradation of 4CP.

Intermediates study

Fig. 6 shows the HPLC chromatogram for the 4CP intermediates during photocatalysis degradation process which maleic acid, hydroquinone (HQ), benzoquinone (BQ), resorcinol and 4-chlorocatechol (4CC) has been detected with the main of intermediates compound are maleic acid and 4CC which also

reported other researcher [30]. The photodegradation of 4CP and its intermediates under solar irradiation of optimum condition C-TiO₂ is shown in Fig. 7. It was observed that 4CC and resorcinol were completely degraded after 15 and 20 minutes irradiation respectively. BQ was appeared at first 5 minutes of solar irradiation and completely degraded after extended for 15 minutes.

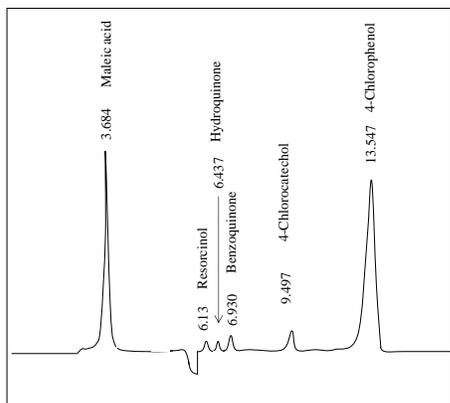


Figure 6: HPLC chromatogram for 4CP and intermediates at 5 minute solar irradiation treatment.

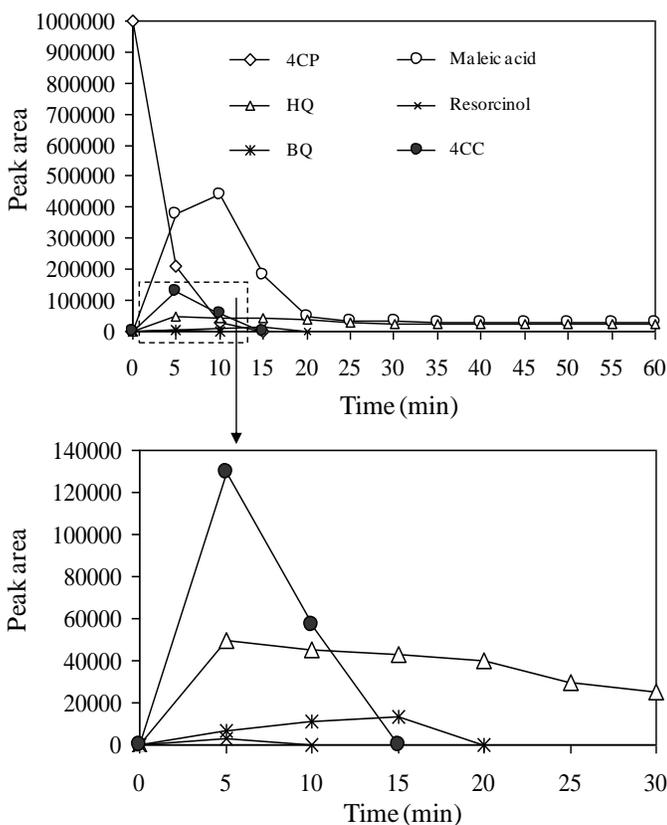


Figure 7: Graph detection of 4CP and intermediates during photocatalysis process.

However, maleic acid and HQ were not completely degraded with reached to the maximum degradation limits and remained

stable after 10 minutes of irradiation. This is due to the fact that maleic acid in acidic medium can exist in equilibrium with 4CC. Thus, the released electron can neutralized the holes formed on TiO₂. While, BQ is known as electron acceptor which can reduced the photocatalytic efficiency. This uncompleted degradation intermediates are the reason for previous COD analysis reading was remained incomplete after prolongs the irradiation.

IV. CONCLUSION

The photocatalytic degradation of 4CP in aqueous TiO₂ suspension by solar energy has been examined using two different catalysts, unmodified anatase TiO₂ and carbon coated TiO₂. In particular, the influence of the catalyst loading has been studied and the optimum catalyst loading for both catalysts were found to be 10 and 3.0 g L⁻¹ respectively. The photo catalytic activity in the degradation of 4CP was found to be more efficient for the carbon doped TiO₂ than the unmodified anatase TiO₂ at pH6. The reaction rate constant was found to be six times higher for the carbon doped TiO₂ than unmodified anatase TiO₂. The mineralization of 4CP was studied by monitoring of COD removal and chlorine ion formation during its photocatalytic degradation process. The presence of dissolved oxygen plays a significant role in the photocatalytic degradation of 4CP. The degradation rate on a sunny day was about five times more than on cloudy day for both catalysts. The main intermediated formed during the photocatalytic degradation of 4CP were found to be maleic acid, hydroquinone, hydroquinone, benzoquinone, resorcinol and 4CC. The pH and catalyst loading have an effect on the concentration and degradation of intermediates.

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