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Effect of pH and temperature on degradation of dilute dihydroxybenzene, in aqueous titanium dioxide suspension irradiated by UV light

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ABSTRACT

The degradation of p-dihydroxybenzene in a batch photocatalytic reactor, irradiated by a high intensity UV lamp, was investigated. In this experimental work, commercial anatase titanium dioxide (degussa P 25) was used as a catalyst. Various operating conditions such as initial concentration, pH of the solution, temperature, addition of H_2O_2, bubbling of oxygen, and catalyst loading were examined. A pseudo-first-order kinetics was observed with a rate constant ranging between 17.1×10^{-3} and 5.6×10^{-3} min^{-1} which was decreasing with increasing initial concentration. H_2O_2 enhanced the degradation significantly. For the experimental conditions, there was no significant effect for the added catalyst dosage. The degradation rate of p-dihydroxybenzene increased to a certain amount with increasing temperature then decreased. Further experimentation is needed to verify this observation.

1. Introduction and review of related literature

p-Dihydroxybenzene (p-DHB), known as hydroquinone, is a phenolic compound with two –OH groups. It is a toxic and strong irritant pollutant found in effluent waste streams of many processes including those concerned with dyestuff, photography, paint and varnishes industry.

Many methods are used to treat wastewater, containing phenolic pollutants. These methods include, among others, adsorption, evaporation and incineration, anaerobic digestion, chemical addition and photocatalytic treatment. Usually, multiple treatment methods are used. However, sometimes it is difficult to remove the pollutant, especially when present at low concentrations.

Biodegradation and other methods of pollutant removal are not efficient at low levels of pollutant concentrations. Therefore, photochemical oxidation processes have been employed for the treatment of such low organic concentration water.

Photocatalytic oxidation reactions of organic pollutants in aqueous solutions have been gaining more attention in the last two decades and can be considered as one of the recent advanced methods used in water detoxification. These heterogeneous reactions have the potential to mineralize organic materials and convert them into non-toxic intermediate compounds, such as water, carbon dioxide, and inorganic ions. Because of its semiconducting behavior, anatase titanium dioxide is widely used as a catalyst for this reaction with UV irradiation. Titanium dioxide is relatively inexpensive with high surface area and the photogenerated holes are highly oxidizing. In addition the photogenerated electrons are reducing enough to produce superoxide (O_2^-) from oxygen and H_2O_2 [1].

Photocatalytic degradation (oxidation) of organic substance in aqueous solutions over titanium dioxide was the subject of many studies. Chen and Ray [2] studied the photocatalytic degradation of phenol, 4-chlorophenol and 4-nitrophenol. They used a monolithic type reactor to study the kinetics of this heterogeneous process using UV light. The effects of different parameters such as catalyst dosage and layer thickness, pollutant concentration, temperature and partial pressure of oxygen were experimentally studied. They observed a first order kinetics. Low efficiency of the process was found, which may be attributed to the extreme low surface coverage. Moreover, Trillas et al. [3] found that the yield of phenol photo-oxidation depends strongly on the pH of the solution. Maximum yield was observed at pH 8 and in very alkaline media. This result was explained considering the steps taking place on the semiconductor surface where $OH^\bullet$ radicals have an important role.

Chlorophenols [4,5,6], nitrophenols [7], and alcohols [8] gained more attention than others. Mainly, these studies were concentrated on finding mechanisms and kinetics for the degradation reactions. The effect of different experimental conditions such as concentration of organic compounds, pH of the solution, oxidant concentration, UV intensity and catalyst concentration were also included.

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Oxidation of p-hydroxybenzoic acid by UV radiation and by TiO_2/UV radiation was the subject of a study by De Heredia et al. [9]. A pseudo-first-order kinetic model was reported for this reaction. Moreover, they found that the presence of TiO_2 as a catalyst increased the rate constant by (220–435%) than that obtained by UV photo-oxidation.

Rideh et al. [4] studied the degradation of 2-chlorophenol (2CP) in TiO_2 aqueous suspension. They found that the 2CP was degraded to give CO_2, H_2O and HCl in the presence of O_2. They proposed a kinetic model for the degradation of 2CP based on the Langmuir–Hinshelwood where 2CP adsorption occur in competition with that of the solvent on the same site, while oxygen adsorbed on different sites and obeys Freundlich type.

In a recent study, Chiou et al. [10] studied the influence of operating conditions on the degradation of phenol using irradiated titanium dioxide with UV light. They conducted their experiments using a batch photo-reactor irradiated by UV–vis light. They studied the effect of catalyst dosage, initial phenol concentration, light intensity, pH, and H_2O_2 concentration, on phenol degradation. The degradation was compared using UV alone, H_2O_2/UV, TiO_2/UV and all H_2O_2/TiO_2/UV. They found that the degradation was much more effective than other systems, if using H_2O_2/TiO_2/UV. Degradation followed a first order kinetics and the addition of H_2O_2 enhanced the degradation process.

In this experimental research, a photocatalytic reaction with UV irradiation was used to study the degradation of p-dihydroxybenzene in the presence of titanium dioxide. The effect of various parameters was studied.

2. Experimental set-up and apparatus

2.1. Chemicals

All chemicals used in this study were analytical and HPLC grade. p-dihydroxybenzene was purchased from Fluka. Acetonitrile and acetic acid were HPLC/ACS reagent with minimum purity of 99.7%.

2.2. Catalyst

Titanium dioxide TiO_2, P25 (Degussa AG) was used in this study. The needed amount was supplied by Degussa Regional Office in Amman. This catalyst has an average primary particle size = 21 nm and BET surface area $\sim 50\,m^2\,g^{-1}$. It was used without any further treatment.

2.3. Apparatus

The main apparatus used in this study was a 2-L batch reactor having 14 cm ID and 19 cm height. The reactor was equipped with a tube for oxygen bubbling inside the reactor, through a flow-rate meter (rotameter) and probes to measure pH (±0.02) and temperature (±1 °C) of the solution. The reactor was placed in a water bath with a temperature controller using immersion heater with controller (Karl Kolb Type T-50). The bath was mounted on a magnetic stirrer (Biosan MSH 300). A magnetic bar, 3 cm length, was placed inside the reactor to rotate and mix the contents.

The whole set-up was placed inside a dark cabinet made of wood. The dark cabinet was manufactured locally with the interior walls painted black. This cabinet had openings to allow an oxygen tube, electrical cables and other connections into the cabinet.

2.3.1. Ultraviolet light source

A UV radiation with a wave length of 365 nm was placed on the top of the reactor using a radiation source (UVP high intensity model B-100 lamp). The lamp was cooled by a fan, placed near the set-up, to keep the temperature down and protect the lamp from overheating. At this radiation place, the average intensity of the radiation was around 700 $\mu W/cm^2$, measured at the solution surface. UV radiation source with similar wavelength was used by many researchers for the degradation of organic compounds [2,6,13].

2.4. Procedure

2.4.1. Sample preparation and collection

A 500 mL solution of the required p-DHB concentration was prepared. The amount of catalyst (± 0.01 g) and H_2O_2 were added. Oxygen at a flow-rate of 125 mL min^{-1} was bubbled through the suspension to maintain a saturated solution with oxygen. The suspension was magnetically stirred continuously. At the start of the experiment UV source, placed at a fixed distance from the suspension surface, was put on. Samples of 5 mL were withdrawn from the reactor at several time intervals. The withdrawn samples were centrifuged (using Hettich Zentrifugen-Universal 32) at 4000 rpm for 6 min. The clear solution was separated and centrifuged again for 4 min. The clear sample was then analyzed using HPLC to determine the p-DHB concentration.

2.4.2. pH control

To keep the pH of the solution constant (±0.02), HCl or NH_4OH were added.

2.4.3. Sample analysis

Chemical analysis for all samples was done using HPLC (Milton Roy) apparatus at a wavelength = 280 nm UV detector with a C-18 column. The mobile phase consisted of 50% acetonitrile including 1% acetic acid and 50% H_2O including 1% acetic acid. The flow-rate was 1 mL min^{-1}. Analysis of each sample was repeated three times and the average was used.

3. Results and discussions

Heterogeneous photocatalysis, as other heterogeneous reactions, occur in various reaction media. The steps followed by this process include; transport of reactants to the solid surface where they are adsorbed. Since the solid is present in a powder form, external resistance to this transport can be considered negligible. The photocatalytic reaction takes place on the catalyst surface, when irradiated by UV (photons). These photons have energy higher than the catalyst band gap energy. Photons are adsorbed by the catalyst surface forming free photoelectrons in the conduction band and photo holes in the valance band.

$$h\nu + S \rightarrow e^- + h^+ \tag{1}$$

$$A_{ads} + e^- \rightarrow A_{ads}{}^- \tag{2}$$

The generated electron–hole pair can also recombine. Inhibiting this recombination is essential to improve the charge transfer at the semiconductor surface. Hydroxyl ions (OH^-) are traps for the holes forming hydroxyl radical ($OH^\bullet$) which are considered strong oxidizing agents. The adsorbed oxygen molecules, on the catalyst surface, are traps for released electrons forming unstable superoxygen ions ($O_2{}^-$) [11,12].

$$h^+ + OH_{surf}{}^- \rightarrow OH^\bullet \tag{3}$$

$$e^- + O_2 \rightarrow O_2{}^- \tag{4}$$

These highly oxidizing free radicals oxidize the present organic molecules forming carbon dioxide and water.

It is known that titania surface possesses both acidic and basic sites. The acidic sites adsorb organic molecules and the basic sites

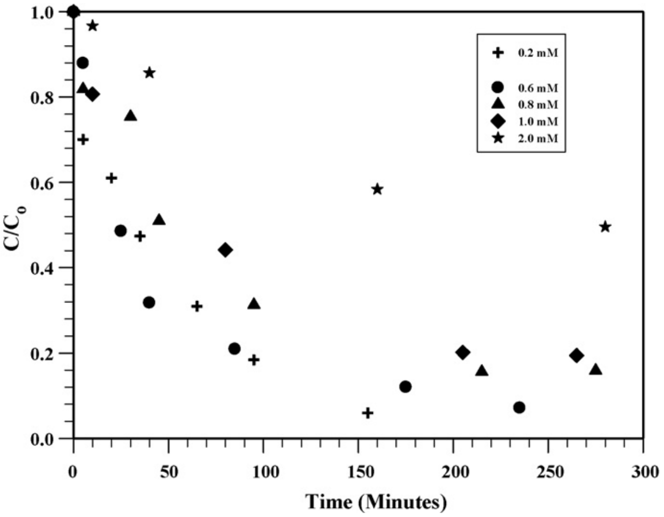

Fig. 1. Concentration ratio of p-DHB as a function of time at 18 °C with 4.00 g TiO_2 L^{-1} and 50 mM H_2O_2.

adsorb oxygen to form OH• radicals. Among other mechanism steps, the OH• radicals react with the adsorbed organic molecules on the catalyst surface. This step is considered to be the rate-determining step [12].

3.1. *Effect of initial concentration*

Fig. 1 shows the residual concentration ratios of p-dihydroxybenzene (p-DHB) as a function of time for different initial concentrations. These initial concentrations include 0.20, 0.60, 0.80, 1.00 and 2.00 mM. The initial concentration has a profound effect on the degradation rate for the same irradiation time. The percentage removal is smaller for higher initial concentration. In 200 min, the decompositions ranged from 95% for the 0.20 mM initial concentration to about 85% for the 0.80 mM initial concentration. Nevertheless, it was only around 50% removal efficiency, for the 2.00 mM initial concentration.

Heterogeneous photocatalytic reaction follows Langmuir–Hinshelwood

$$(-r_A) = \frac{k_A K_a C_A}{(1 + K_a C_A)}$$

where k_A represents the intrinsic rate constant and K_a is the adsorption equilibrium constant. In the range of the experiment, $K_a C_A \ll 1$, which simplifies this equation to be $(-r_A) = k_A K_a C_A$ which is an apparent first order reaction. This equation is represented as $(-r_A) = -dC_A/dt = k_{obs} C_A$. Upon integration, the residual concentration ratio as a function of time is

$$\ln \frac{C_{Ao}}{C_A} = k_{obs} t.$$

Plots of ln C_{Ao}/C_A versus t represent straight lines, with a slope of which, upon linear regression, is the apparent rate constant (k_{obs}). Values for k_{obs} and linear regression coefficients for different initial concentrations are listed in Table 1. From the R^2 values, which exceeded 92%, the linear relationship is obvious. Therefore, the reaction can be approximated to be pseudo-first-order. Values for k_{obs} are decreasing with initial concentration. The same observation was noted by De Heredia et al. [9] for the degradation of p-hydroxybenzoic acid and by Chiou et al. [10] for the degradation of phenol.

This decrease in k_{obs} values can be attributed to decreasing fractional site coverage of DHB with increasing initial DHB concentration. A relationship between $1/k_{obs}$ and the initial concentration of the organic compound was derived by De Heredia et al. [9] in their kinetic study for the oxidation of p-hydroxybenzoic acid as:

Table 1
Apparent first order rate constant, k_{obs} and linear regression coefficient, R^2 for different initial concentrations of p-dihydroxybenzene.

C_o	R^2	$k_{obs} \times 10^3$, min^{-1}
0.20	0.991	17.1
0.40	0.985	11.9
0.60	0.921	10.4
0.80	0.980	9.1
1.00	0.892	5.6

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{C_{HBO}}{k_2}$$

where k_1 and k_2 are constants and C_{HBo} is the initial concentration of the organic compound. This relationship shows that k_{obs} decreases with increasing initial concentration of the organic compound.

When the data reported in Table 1 is plotted as $1/k_{obs}$ versus initial concentration of DHB, a linear relationship is obtained. The adsorption equilibrium constant, K_a for p-DHB, was calculated from the slope and the intercept of the line and found to be 5.2. This linear behavior is consistent with De Heredia et al. [9] observation.

3.2. *Effect of oxygen bubbling*

Fig. 2 shows the effect of oxygen bubbling, on the degradation of DHB as compared to the degradation if no oxygen was bubbled. It is clear from the figure that the effect of bubbling is insignificant. This could be due to unchanging oxygen content in the solution.

The original DHB solution was prepared in the normal environment, which assumes saturated solution with oxygen. Knowing that the oxygen consumption during the experiment is very low and the solution surface is in contact with atmospheric oxygen, assumes constant oxygen content in the suspension, even without bubbling. Therefore, bubbling more oxygen, into the suspension, will not affect its content.

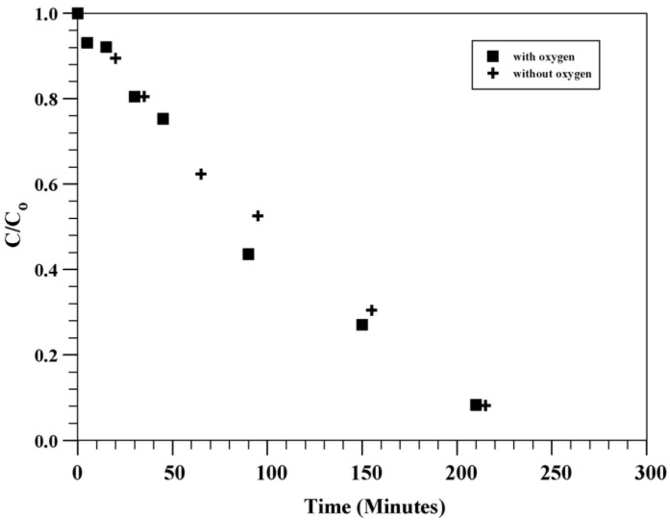

Fig. 2. Effect of oxygen bubbling (125 mL min^{-1}) on the degradation of 0.40 mM p-DHB at 18 °C with 4.00 g TiO_2 L^{-1} and 50 mM of H_2O_2.

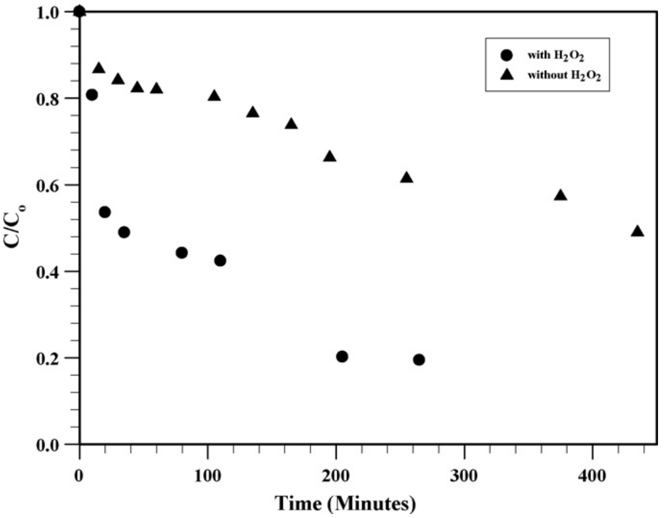

Fig. 3. Effect of adding 50 mM of H_2O_2 on the degradation of 1.00 mM p-DHB at T = 18 °C and 4.00 g TiO_2 L^{-1}.

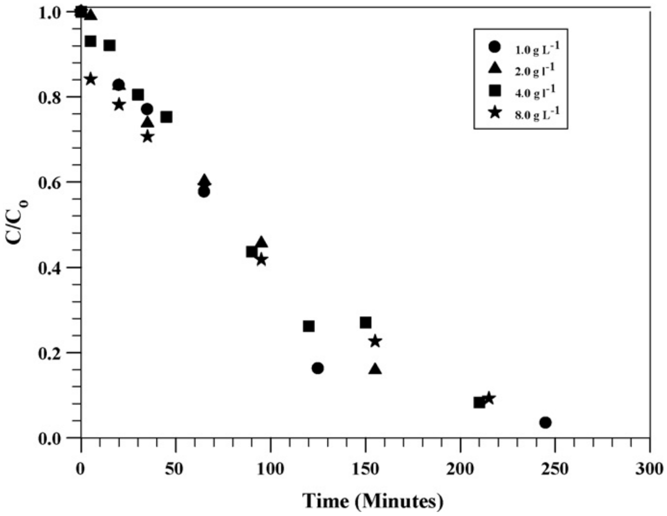

Fig. 4. Effect of catalyst loading on the degradation of 0.40 mM p-DHB at 18 °C and 50 mM H_2O_2.

3.3. *Effect of H_2O_2*

Fig. 3 shows the effect of adding 50 mM H_2O_2 on the degradation of p-DHB. Adding H_2O_2 to the reaction vessel containing 1.00 mM p-DHB has a significant effect on the degradation rate. As shown in the figure, after 200 min reaction time, the removal efficiency has increased to about 80% when H_2O_2 was added, while it did not exceed 37% if the reaction proceeds without H_2O_2. This increase is expected, because of the high oxidizing capacity of hydroxyl radicals, which are produced from H_2O_2 by the following degradation mechanism [13]:

$$H_2O_2 \rightarrow 2OH^\bullet$$

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

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

A preliminary test showed that the effect of H_2O_2 alone is insignificant on the degradation of DHB.

3.4. *Effect of catalyst loading*

Fig. 4 shows the effect of catalyst content on the degradation rate of p-DHB. It is obvious that there is no significant difference noticed on the degradation rate for catalyst loadings between 1.00 and 8.00 g L^{-1}.

It is known that many factors affect the degradation rate; radiation (photon) intensity and catalyst loading are two of them. Radiation intensity, in this case, is constant producing a constant effect on the degradation rate. It seems that the catalyst loading is high enough to keep the catalyst effect of no significant on the degradation rate, for the studied loading range. Other determining factors control the rate, but not the catalyst content. Therefore, increasing the catalyst content produced no effect on degradation, as shown in Fig. 4.

3.5. *Effect of pH*

pH of the solutions as a function of time is recorded for different initial concentrations of p-DHB in Fig. 5. Decreases in the pH values are observed for all initial concentrations. This decrease is probably due to the production of intermediate acids. It was also observed that a sharp drop in the pH of the solution occurred when the catalyst amount was added. This decrease was, for example, from 5.37 to 4.04 for 0.40 mM initial concentration. Another drop in pH (from 4.04 to 3.86) occurred when H_2O_2 was added. These sharp drops could be due to acidic property of these added materials.

Fig. 6 shows the degradation of p-DHB with irradiation time for different pH values. There is no significant difference in removal efficiency when the pH was 3.0 and 6.8, but there is a sharp increase as the pH increased to 10.0. For example, the removal efficiency was around 70% in the acidic pH region, but this efficiency increased to more than 97% as the pH value increased to 10.0. An increase amount of OH^- at high pH values could enhance the production of hydroxyl radicals, as indicated above [13,14].

3.6. *Effect of temperature*

Fig. 7 shows the effect of temperature on the degradation rate of 0.40 mM DHB concentration. The figure shows the concentration residual ratio as a function of time for different temperatures. The removal efficiency increased from 70% for temperature 18 °C to 93%

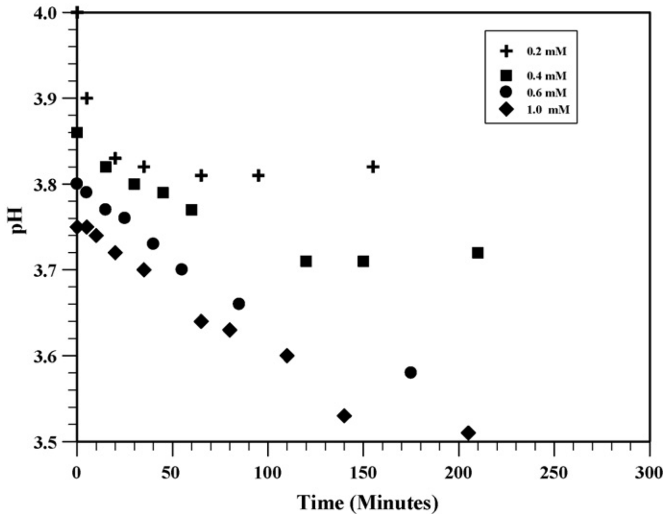

Fig. 5. pH values for p-DHB solutions, with different initial concentrations, as a function of time at 18 °C with 4.00 g TiO_2 and 50 mM H_2O_2.

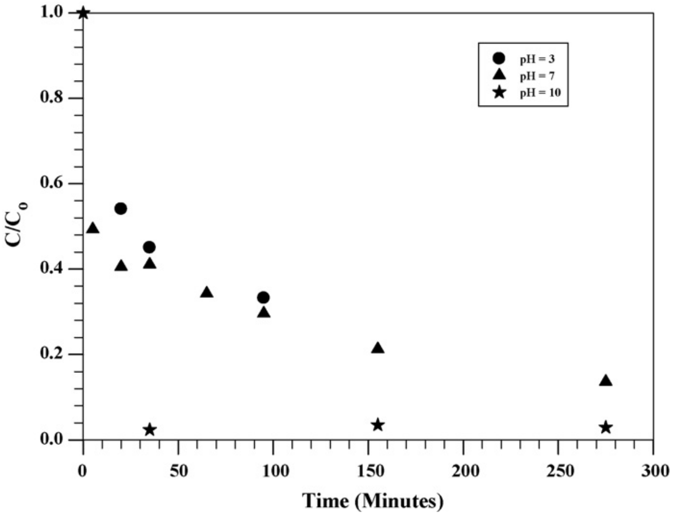

Fig. 6. Effect of pH on the degradation rate of 0.40 mM p-DHB at 18 °C, with 4.00 g TiO_2 L^{-1} and 50 mM H_2O_2.

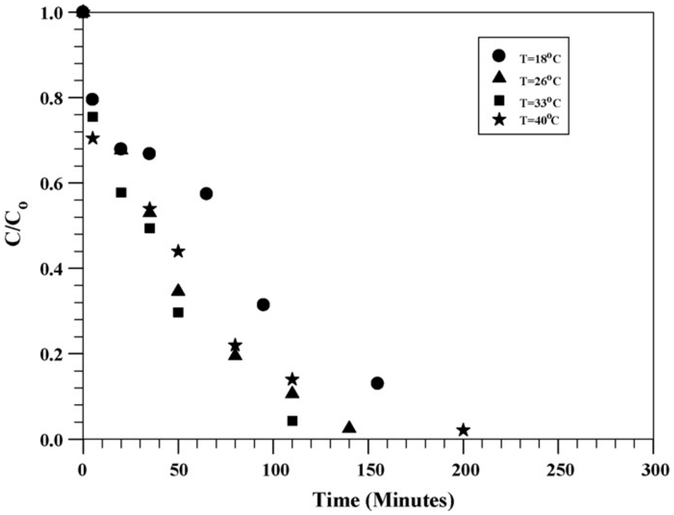

Fig. 7. Effect of temperature on the concentration residue of 0.40 mM p-DHB concentration with 4.00 g TiO_2 L^{-1} and 50 mM H_2O_2.

for temperature 33 °C, and then decreased to 83% when the temperature increased to 40 °C. This trend in degradation rate could be due to the effect of temperature on the previously derived rate constant ($k_{obs} = k_A K_a$). Both k_A and K_a affect the degradation rate in a competitive manner. k_A, the intrinsic rate constant, increases with increasing temperature, while K_a, the adsorption equilibrium constant, decreases with temperature. It seems that k_A dominates the degradation rate at 18, 26 and 33 °C, while K_a is more dominant at 40 °C.

4. Conclusions

The photocatalytic degradation of p-dihydroxybenzene using anatase TiO_2 has been studied. The experimental results fit a pseudo-first-order kinetics with a decreasing rate constant as the initial concentration of p-DHB increases. This means that the more diluted initial solution, the higher is degradation rate of p-DHB. This trend could be attributed to decreasing fractional site coverage by DHB molecules. Oxygen bubbling and catalyst loading, in the range of the experiment, have no significant change on the degradation. This could be due to the unchanging oxygen content in the solution and to very high catalyst doses, respectively. The effect of pH and H_2O_2 has been also studied. Degradation rate in the basic media is much higher than that in the acidic media. The addition of H_2O_2 enhanced the degradation rate, because it produced hydroxyl radicals in the presence of TiO_2 under UV radiation. Temperature increased the rate at 18 and 33 °C but it decreased at 40 °C.

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