

# Photocatalytic reduction of carbonate in aqueous solution by UV/TiO<sub>2</sub> process

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## Abstract

The temporal behavior of the photocatalytic reduction of carbonate in aqueous solution by the UV/TiO<sub>2</sub> process was studied under various conditions. The photocatalytic reduction of carbonate proceeded faster in acidic solutions than in alkaline solutions. The reaction rate increased with the UV light intensity and the amount of TiO<sub>2</sub> present in solution. However, the presence of excessive amounts of TiO<sub>2</sub> hindered the UV light penetration. The main products of the photocatalytic reduction of carbonate by the UV/TiO<sub>2</sub> reduction process were found to be methanol and methane. A Langmuir–Hinshelwood type kinetic equation was developed for modeling the photocatalytic reduction of carbonate.

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*Keywords:* Carbonate; Carbon dioxide; UV/TiO<sub>2</sub>; Photocatalytic reduction; Langmuir–Hinshelwood

## 1. Introduction

Since the beginning of the Industrial Revolution, the atmospheric concentrations of greenhouse gases, i.e. CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CO, and CFCs have been reported to increase dramatically. The concern about human-induced climate change grows out of the increasing atmospheric concentrations of these greenhouse gases. Carbon dioxide is supposed to be the most important greenhouse gas; therefore the reduction of CO<sub>2</sub> is an issue drawing the attention of many researchers. Several methods have been reported recently for the fixation, disposal, separate, recovery, reuse, and removal of CO<sub>2</sub> such as physical adsorption [1,2], chemical dissolution [3], membrane separation [4], physical and biological fixation [5], electrochemical reduction [6,7], and catalytic hydrogenation [8]. Recently, a variety of photocatalytic processes has been studied for treating gaseous streams containing CO<sub>2</sub>. Among the photocatalysts studied, titanium dioxide (TiO<sub>2</sub>) is considered to be relatively inexpensive, chemically stable and has been extensively studied for the ultraviolet (UV)-induced photocatalytic reactions. The UV-irradiated TiO<sub>2</sub> surface can generate electrons to reduce the CO<sub>2</sub> molecules present in aqueous and gaseous streams at ambient temperature and

pressure conditions. Sayama and Arakawa [9] found that the photocatalytic decomposition of water molecules proceeded over ZrO<sub>2</sub> powder under UV irradiation to generate hydrogen and oxygen. In addition to H<sub>2</sub> and O<sub>2</sub>, the evolution of CO (the photocatalytic reduction product of CO<sub>2</sub>) was evolved from NaHCO<sub>3</sub> solutions. According to their experimental results, the TiO<sub>2</sub> photocatalyst could not reduce the carbonate species in NaHCO<sub>3</sub> aqueous solutions at pH 8.3. Inoue et al. [10] reported that HCOOH, HCHO, and CH<sub>3</sub>OH were produced by the reduction of CO<sub>2</sub> by the UV/TiO<sub>2</sub> process in the presence of H<sub>2</sub>O. Anpo and Chiba [11] indicated that CH<sub>4</sub>, CH<sub>3</sub>OH, and CO were the major products from the photocatalytic reduction of CO<sub>2</sub> with highly dispersed titanium oxide anchored onto Vycor glass and suggested that both CO<sub>2</sub> and H<sub>2</sub>O molecules were adsorbed on the surface sites of titanium dioxide [12]. We investigated the photocatalytic reduction of CO<sub>2</sub> by the UV/TiO<sub>2</sub> process in aqueous solution. The effects of solution pH, TiO<sub>2</sub> dosage, UV light intensities, and initial CO<sub>2</sub> concentration on the conversion and reduction rate were studied and a Langmuir–Hinshelwood type kinetic equation has been developed for modeling the reaction.

## 2. Experimental

The TiO<sub>2</sub> particles used in this study, Degussa P-25, was approximately spherical, nonporous, greater than 99.5% in

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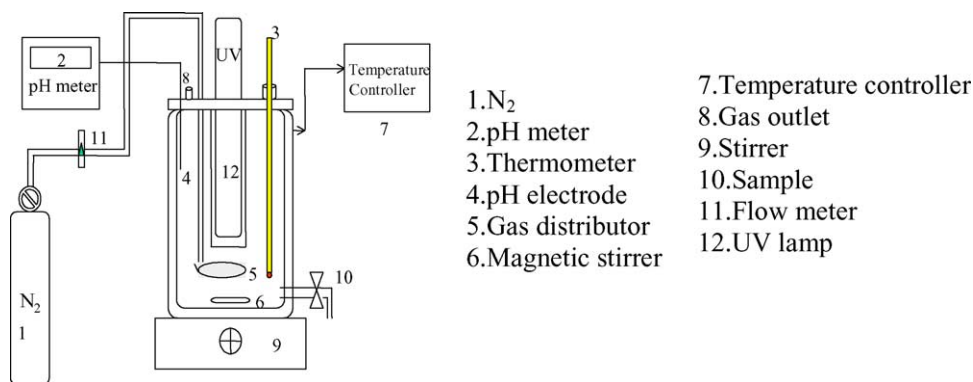


Fig. 1. Schematic diagram of the experimental setup.

purity, its composition was determined by a Philips MP 710 XRD; it consisted of 80% of anatase and 20% of rutile, as previously reported [13]. The specific BET surface area of the  $\text{TiO}_2$  particles was found to be  $50.7 \text{ m}^2/\text{g}$  with a Micromeritics ASAP 2000 analyzer. The average particle size of the  $\text{TiO}_2$  particles in aqueous solutions was proved to be 30 nm by our previous study [14]. Sodium bicarbonate ( $\text{NaHCO}_3$ ) was used as-purchased from Merck to prepare the carbonate solution. The photocatalytic reduction was carried out using a double wall cylindrical reactor made of Pyrex glass as shown in Fig. 1. The reactor was water-jacketed to maintain the solution temperature at  $25 \pm 0.2^\circ\text{C}$  for all experiments. The photoreactor consisted of a 25 cm diameter quartz tube to house a GTE F15T8/BLB lamp with approximately 15 W maximum output at about 365 nm. The light intensity of the UV lamp was adjusted by a variable voltage transformer and monitored by a Spectroliner model DRC-100X digital radiometer combined with DIX-365 radiation sensors. The solution pH values were maintained constant at desired levels with NaOH and HCl solutions by manual adjustment and were monitored continuously.

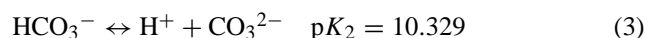
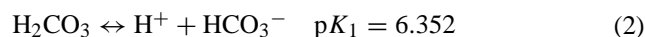
The  $\text{TiO}_2$  catalyst was dispersed in the reactor containing carbonate solution, and nitrogen gas was then bubbled through the solution for 30 min to remove dissolved oxygen before UV irradiation started. The dissolved oxygen in solution was determined to be less than 0.5 mg/l by an Orion model 820 DO analyzer. Batch adsorption experiments were performed for all equilibrium studies. The solution was agitated with a magnetic stirrer at 300 rpm. The carbonate solution was mixed with predetermined amount of  $\text{TiO}_2$  particles in an isothermal shaker bath. The pre-warmed UV lamp was then turned on after the temperature and pH level of the solution in the completely-mixed reactor became steady. Usually, the reaction was conducted for about 300 min. At desired reaction times, samples were withdrawn and the catalyst was removed by centrifugation before the solution was analyzed by a China Chromatography 9800F GC/FID gas chromatograph and a HP-G1800A GCD/MS equipped with a HP-5 capillary column (30 m length, 0.25 mm inner diameter,  $2.5 \mu\text{m}$  film thickness) and an electron ionization detector (ECD) to determine the reaction products. The amount

of total organic and inorganic carbon in reaction solution was analyzed by an O.I.C. model 700 TOC (total organic carbon) analyzer.

### 3. Results and discussion

The  $\text{TiO}_2$  particles dispersed in aqueous solution were reported to behave like a diprotic acid after the hydration of the surface functional groups [13]. The surface charge of  $\text{TiO}_2$  particles is a function of the crystal types (anatase or rutile) and the matrix of solution. The pH of zero point of charge ( $\text{pH}_{\text{ZPC}}$ ) for Degussa P-25 was found to be  $7.52 \pm 0.05$  in this research, in contrast to the reported  $\text{pH}_{\text{ZPC}}$  of 6.0–6.4 for some other anatase types of  $\text{TiO}_2$  [15].

A series of experiments were carried out to study the equilibrium adsorption behavior of carbonate on the Degussa P-25  $\text{TiO}_2$  particles in different solution pH range. The amount of carbonate adsorbed by  $\text{TiO}_2$  particles is scarce, indicating that the photocatalytic reduction rate of carbonate by  $\text{TiO}_2$  is controlled by the adsorption rate. Experimental results also imply that the adsorption of carbonate varied markedly with solution pH; more carbonate was adsorbed by  $\text{TiO}_2$  particles in acidic and neutral solutions. In alkaline solutions (pH greater than 8), the adsorption of carbonate was significantly reduced. The dependence of carbon adsorption on the solution pH may be explained by the fact that the concentration distribution of various carbonate species, including  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , in aqueous solution varies noticeably with solution pH, which can be expressed by the following reactions [16]:



$\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$  are the dominant species in acidic solutions, while  $\text{CO}_3^{2-}$  species predominates in solutions with pH greater than 6. Since the  $\text{pH}_{\text{ZPC}}$  of the Degussa P-25  $\text{TiO}_2$  used in this experiment was  $7.52 \pm 0.05$ , the

surface of TiO<sub>2</sub> particles carries more positive charges in acidic solutions. For solution pH less than 6, the positively charged surface of TiO<sub>2</sub> has higher affinity for the negatively charged H<sub>2</sub>CO<sub>3</sub> and HCO<sub>3</sub><sup>-</sup> species. The surface charge of TiO<sub>2</sub> gradually became negative for solutions with pH greater than 6; therefore, the adsorption of CO<sub>3</sub><sup>2-</sup> species on the surface of TiO<sub>2</sub> may be reduced.

Kinetic experiments were conducted under various conditions to study the temporal adsorption behavior of carbonate on TiO<sub>2</sub> particles in aqueous solution. The results indicate that the adsorption equilibrium was approached at about 30 min of contact time. The stirring speed in the reactor was kept high enough so that the boundary layer resistance was considered to be negligible. The adsorption kinetics of carbonate can be described by a Langmuir–Hinshelwood type rate equation:

$$r = -\frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (4)$$

where  $C$  is the carbonate concentration in the solution at time  $t$ ;  $k$  and  $K$  are the rate constant and the equilibrium constant for adsorption, respectively. Because the initial carbonate concentrations employed in this study were relatively low, the rate equation is simplified to be a pseudo-first order rate equation with respect to the carbonate concentration:

$$-\frac{dC}{dt} = kKC = k_{\text{ads}}C \quad (5)$$

Integrating Eq. (5) gives

$$\ln \frac{C_0}{C} = k_{\text{ads}}t \quad (6)$$

where  $C_0$  is the initial carbonate concentration (mg/l) in solution,  $C$  is the carbonate concentration (mg/l) in solution at time  $t$ ,  $k_{\text{ads}}$  is the apparent pseudo-first order adsorption rate constant (min<sup>-1</sup>), and  $t$  is the contact time (min).

The slope of the regressed line for a plot of  $\ln(C_0/C)$  versus  $t$  corresponds to the adsorption rate constant ( $k_{\text{ads}}$ ). The effects of various operating variables on the  $K_{\text{ads}}$  values are summarized in Table 1. It indicates that carbonate is adsorbed by TiO<sub>2</sub> particles in acidic solutions (solution pH less than 6.0) at fairly constant rate and much faster than in alkaline solutions. The adsorption rate of carbonate progressively decreases with an increase in the initial carbonate concentration, indicating that the assumption of a pseudo-first order rate equation for this adsorption system does not apply to the solutions containing higher concentration of carbonate. The apparent reaction order with respect to the carbonate concentration lies between 0 and 1, depending on the carbonate concentration. The variation of TiO<sub>2</sub> dosage has a slight impact on the adsorption rate of carbonate.

The temporal variation of reaction products for carbonate reduction by the UV/TiO<sub>2</sub> process in aqueous solution at pH 3 is shown in Fig. 2. More than 30% of carbonate was reduced to form organic compounds (indicated as total organic carbon, TOC) and methane for a reaction time of 300 min.

Table 1

The pseudo-first order rate constant for the adsorption of carbonate by TiO<sub>2</sub> in aqueous solution

Concentration of carbonate (mg/l)	Dosage of TiO <sub>2</sub> (g/l)	pH	Pseudo-first order adsorption rate constant (min <sup>-1</sup> )
60	0.2	3.0	0.00898
120		3.0	0.00783
180		3.0	0.00640
240		3.0	0.00600
300		3.0	0.00533
300	0.2	3.0	0.00533
		4.0	0.00476
		5.5	0.00456
		6.0	0.00447
		8.0	0.00038
		11.0	0.00015
60	0.2	3.0	0.00898
		0.5	0.00901
		1.0	0.00935
		2.0	0.01096

About 70% of the reduction products (based on carbon balance) are organic compounds while methane accounts for the rest. Among the organic compounds, methanol was identified as the primary product (more than 60% of TOC), even though little amounts of other organic compounds were also identified. The effect of the TiO<sub>2</sub> dosage on the formation of methanol by the photocatalytic reduction of carbonate at pH 3 is shown in Fig. 3. The formation of methanol increased with increasing TiO<sub>2</sub> dosage less than 1.0 g/l, in a similar way to the results observed by Bhoopendra et al. [17].

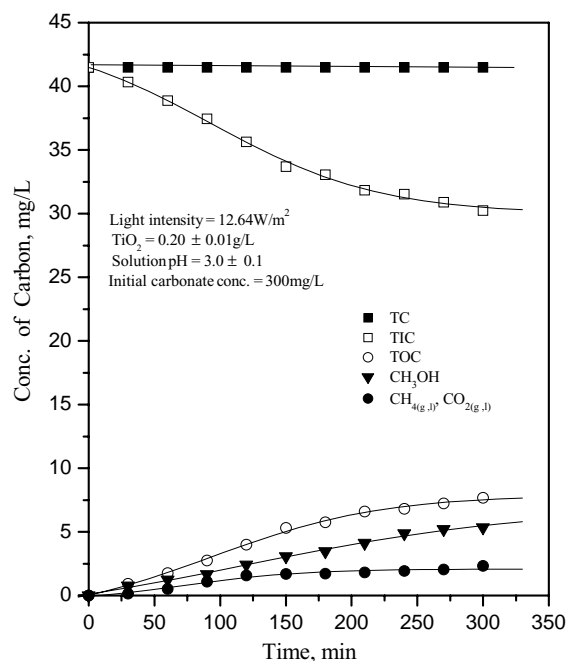


Fig. 2. The temporal distribution of carbon species for the photocatalytic reduction of carbonate in aqueous solution.

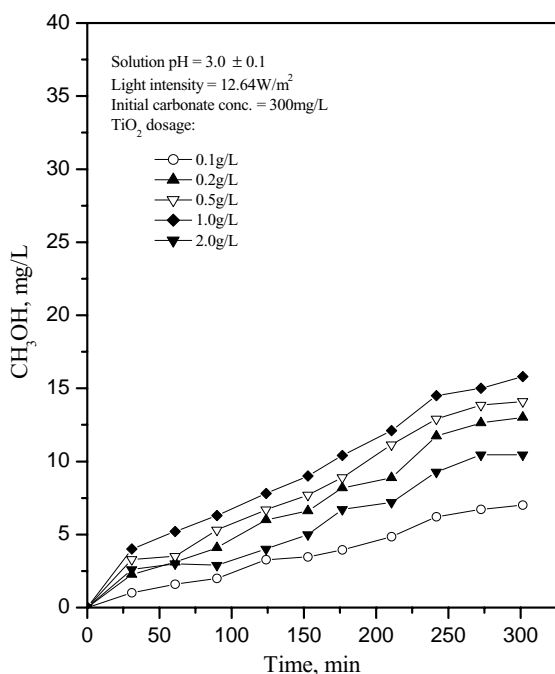


Fig. 3. The effect of  $\text{TiO}_2$  dosage on the formation of methanol for the photocatalytic reduction of carbonate in aqueous solution.

However, the reaction rate was reduced for solutions containing higher amounts of  $\text{TiO}_2$  possibly because of the shielding effect on UV light penetration in the aqueous solution caused by the presence of excessive amounts of  $\text{TiO}_2$ .

The formation of  $\text{CH}_3\text{OH}$  by the photocatalytic reduction of carbonate at pH 3 with UV light intensity ranging between 9.69 and 12.64  $\text{W/m}^2$  is shown in Fig. 4. The photocatalytic

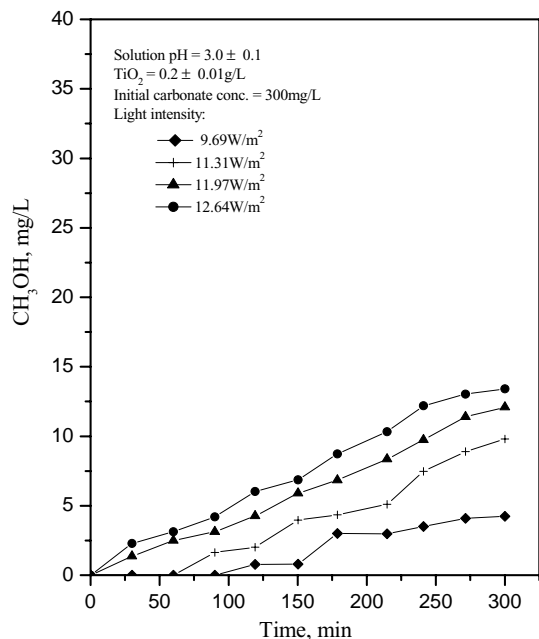


Fig. 4. The effect of UV light intensity on the formation of methanol for the photocatalytic reduction of carbonate in aqueous solution.

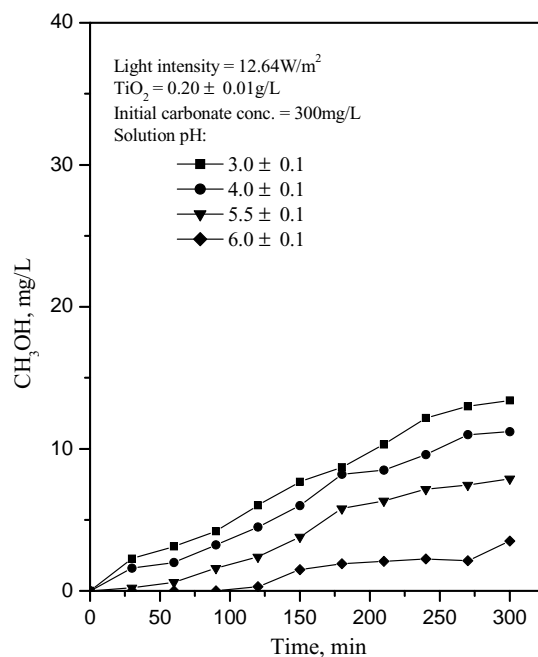


Fig. 5. The effect of solution pH on the formation of methanol for the photocatalytic reduction of carbonate in aqueous solution.

reaction rate was promoted almost linearly with the UV light intensity. An increase of light intensity may increase the number of photons striking on the surface of  $\text{TiO}_2$  particles to form more electrons and holes, therefore, increasing the reduction rate of carbonate [17]. The formation of methanol by the photocatalytic reduction of carbonate with UV light intensity 12.64  $\text{W/m}^2$  at pH ranging between 3.0 and 6.0 is shown in Fig. 5. In acidic solutions, more hydrogen ions ( $\text{H}^+$ ) are adsorbed on the surface of  $\text{TiO}_2$  particles to form the  $\text{TiOH}_2^+$  species. Consequently, the predominant  $\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$  species in aqueous solution are preferably adsorbed on the  $\text{TiOH}_2^+$  to promote the reduction of carbonate. With the application of UV irradiation, electrons and electric holes are generated on the surface of  $\text{TiO}_2$ . Water molecules are accordingly oxidized by electric holes to form hydrogen ions and oxygen molecules, while carbonate species are reduced to form methanol and other organic intermediates by electrons. The effect of initial concentration on the formation of methanol at pH 3.0 is shown in Fig. 6. It was found that an increase of the initial carbonate concentration could increase the formation of methanol. Based on the experimental results obtained in this study and research reports from the literature [18], the reaction mechanism for the photocatalytic reduction of carbonate in aqueous solution is suggested as shown in Fig. 7.

The photocatalytic reduction rate of carbonate by the UV/ $\text{TiO}_2$  process can be described by a modified Langmuir–Hinshelwood type kinetic equation. It is assumed that the reaction rate has a linear relation to light intensity for experiments conducted at constant pH value and  $\text{TiO}_2$  dosage.

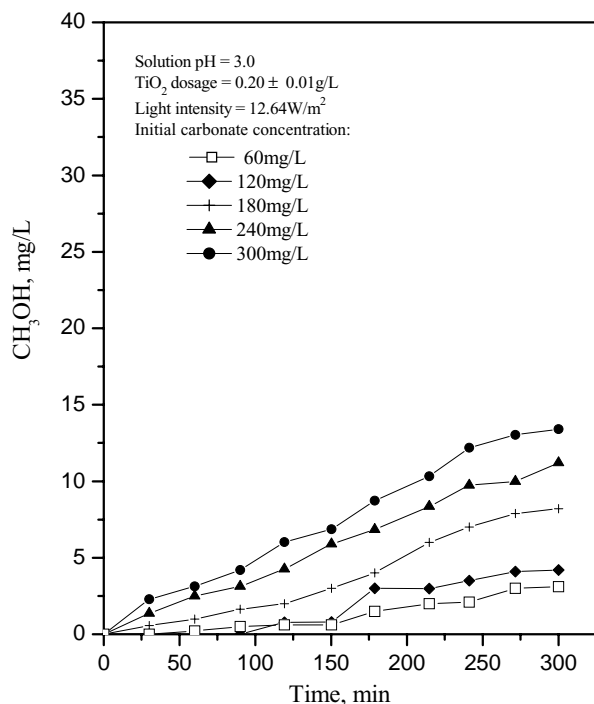


Fig. 6. The effect of initial carbonate concentration on the formation of methanol for the photocatalytic reduction of carbonate in aqueous solution.

$$-r_A = -\left. \frac{dC}{dt} \right|_{t=T} = kI \frac{KC_A}{1 + KC_A} \quad (7)$$

Integrating Eq. (7) gives

$$\int_{C_0}^{C_A} \left( \frac{1}{C} + K \right) dC = -\int_0^T kIK dt \quad (8)$$

$$\ln \frac{C_A}{C_0} + K(C_A - C_0) = -kIKT \quad (9)$$

In Fig. 8,  $\ln(C_0/C_A)/(C_0 - C_A)$  is plotted against  $I/(C_0 - C_A)$  to calculate  $k$  and  $K$  (adsorption constant). Based on the experimental results, the rate equation for the photocatalytic reduction of carbonate by UV/TiO<sub>2</sub> process could be

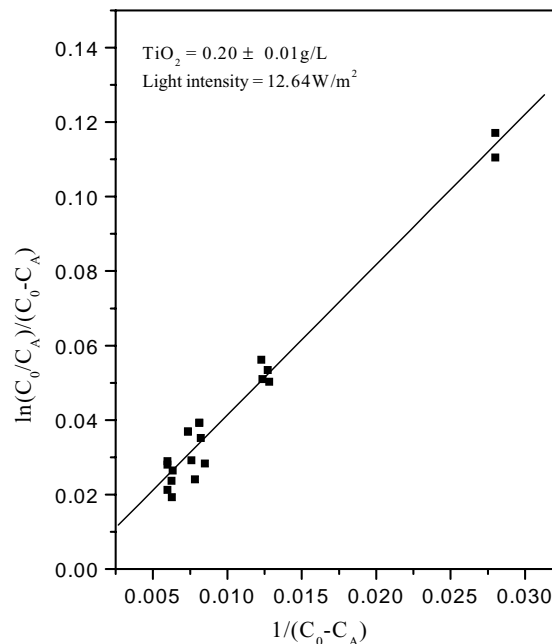


Fig. 8. Determination of the adsorption equilibrium constant for the photocatalytic reduction of carbonate in aqueous solution.

expressed as:

$$-r_A = -\frac{dC}{dt} = \frac{1.03 \times 10^{-3} I C_A}{1 + 9.8 \times 10^{-4} C_A} \quad (10)$$

#### 4. Conclusion

The photocatalytic reduction of carbonate in aqueous solution by the UV/TiO<sub>2</sub> process is feasible, however, the rate of reduction should be improved significantly. The photocatalytic reduction of carbonate is more effective in acidic solutions. The carbonate reduction rate was linearly increased with light intensity and TiO<sub>2</sub> dosage. However, the presence of excessive amounts of TiO<sub>2</sub> may hinder the penetration of UV light. The products for of the photocatalytic reduction of carbonate by the UV/TiO<sub>2</sub> reduction process were mainly methanol and methane. The temporal behavior for the photocatalytic reduction of carbonate by the UV/TiO<sub>2</sub> process in aqueous solution can be modeled by a Langmuir–Hinshelwood type kinetic equation. Even though the preliminary results indicate that the photocatalytic reduction rate of carbonate by the UV/TiO<sub>2</sub> process is adsorption-controlled, detailed reaction mechanism should be studied in order to develop more selective and effective photocatalysts and photoreactors for the formation of valuable chemicals.

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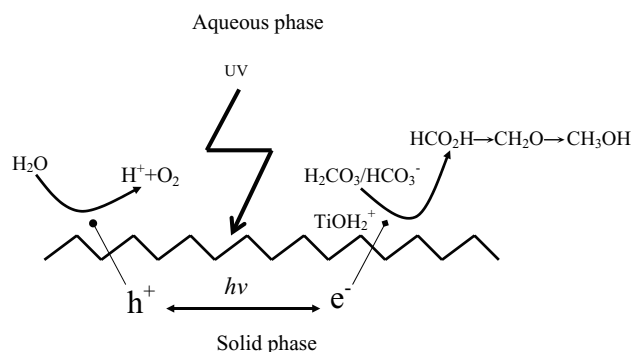


Fig. 7. Simplified reaction scheme for the reduction of carbonate in aqueous solution by UV/TiO<sub>2</sub> process.

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