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Solution factors affecting the photocatalytic and photoelectrocatalytic degradation of formic acid using supported TiO_2 thin films

Dong Hyun Kim, Marc A. Anderson *

Water Chemistry Program, University of Wisconsin, 660 North Park Street, Madison, WI 53706, USA

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Abstract

The solution factors, i.e. pH of the solution, initial concentration of formic acid (HCOOH), effect of silver ions (Ag(I)) in solution and the mass transfer of HCOOH, affecting the reaction efficiency of the photocatalytic (PC) and photoelectrocatalytic (PEC) degradation of HCOOH were investigated. The maximum PC and PEC (0.3 V vs. saturated calomel electrode (SCE)) degradation of HCOOH occurred at approximately pH 3.4 and no degradation reactions were detected above pH 6. The initial concentration of HCOOH did not affect the reaction rate above 3.8×10^{-4} M for the PC reaction and above 7.6×10^{-4} M for the PEC reaction (0.3 V vs. SCE). When Ag(I) was added, it was deposited on the surface of the TiO_2 film as metallic silver (Ag(0)) during both reactions. In this case, the degradation rate of HCOOH in both PC and PEC (2 V vs. SCE) reactions decreased. Finally, the mass transfer of HCOOH was shown to be necessary to sustain the PC and PEC reactions.

Keywords: Solution factor; Photocatalytic degradation; Photoelectrocatalytic degradation; Formic acid; TiO_2 thin films

1. Introduction

Many studies have investigated the effects of certain parameters on photocatalytic (PC) reaction rates, e.g. the pH of the solution [1–5], initial concentration of target chemicals [2,4,6], intensity of light [2,4,6–8], temperature of the solution [2,9,10] and presence or absence of metal ions and other inorganic anions in the solution [11–29]. The pH of the solution has a close relationship with the reaction rate because the surface charge of TiO_2 and the ionization of chemicals are dependent on this variable. The initial concentration of the target chemical is related to the reaction order. Higher intensities of UV light produce more electron–hole pairs [2,4,6–8]. However, excess light can promote a fast recombination of electron–hole pairs [4]. Therefore an optimum light intensity is required for effective performance in these systems. Higher temperatures generally give better reaction efficiencies as a result of the more frequent collision between the electrolyte and TiO_2 [2,9,10].

The destruction of harmful organic chemicals and the simultaneous recovery of hazardous or precious metals is an attractive and potentially feasible technique for water and wastewater purification. Unfortunately, a critical problem associated with the practical application of this technique to the degradation of toxic organic chemicals in water and wastewater is the presence of metal ions in the water which may be deposited on the surface of TiO_2 during PC reactions. These metals may poison the PC reactions in much the same way as traditional catalysts are poisoned. Metal deposits may occupy the active sites on the TiO_2 surface for the desired PC reactions and eventually may cause the TiO_2 to lose its PC activity. Ohtani et al. [11–14] studied the influence of Ag(I) on TiO_2 photocatalysis. They demonstrated a correlation between the PC activity and the pH of the solution, the type of reductant and the crystal structure of TiO_2. Other studies have also reported the photodeposition of Ag onto TiO_2 during PC reactions [15–17]. Furthermore, Borgarello et al. [18] have shown that other metal ions (palladium(II), rhodium(III), platinum(IV) and gold(III)) can be photochemically plated onto TiO_2. In addition, a feasible technique for recovering gold using photodeposition has been demonstrated by several researchers [19–21]. Copper (Cu(II)) was also studied in order to identify its effect in PC reactions [22–27]. Prairie et al. [28] have presented the best summary to date on the clear relationship between the reduction reactions of metal ions and the oxidation reactions of organic chemicals in TiO_2 photocatalysis.

Because PC reactions in solution can be affected by various factors, and many of these factors are interrelated, it is not

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* Corresponding author.

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easy to compare the results from different studies. In this paper, we examine some of the factors which affect both PC and photoelectrocatalytic (PEC) degradation reactions.

2. Experimental details

2.1. Chemicals

Formic acid (HCOOH, 96%, A.C.S. reagent, Aldrich), hydrochloric acid (HCl, 37%, A.C.S. reagent, Aldrich), sodium hydroxide (NaOH, pellets, better than 97%, A.C.S. reagent, Aldrich), silver nitrate ($AgNO_3$, better than 99%, A.C.S. reagent, Aldrich), titanium(IV) isopropoxide ($Ti(isoPro)_4$) ($Ti[OCH(CH_3)_2]_4$, 97%, Aldrich) and uranyl oxalate (Fluka) were used as received without further purification. The water was deionized using a Milli-Q water purification system (Millipore Corp.).

2.2. TiO_2 sol and TiO_2 thin film preparation

The TiO_2 sol was synthesized by a sol–gel method [30]. A solution with a ratio of 150 ml of H_2O to 20 ml of $Ti(isoPro)_4$ to 1 ml of HNO_3 was refluxed at 80 °C for 3 days. The TiO_2 film (500 μl of the TiO_2 sol was employed for spin coating) was prepared using a spin-coater (2000 rev min^{-1} for 30 s; Headway Research Inc.) on a tin oxide-covered glass (SnO_2, 100 Ω/□; F.J. Gray & Co.); it was dried at room temperature and fired to 600 or 400 °C as described previously [31].

2.3. Reactor system

The reactor system has been described in detail previously [31]. The system contained a borosilicate rectangular-shaped reactor (75 mm × 100 mm × 125 mm with a 2.5 mm wall; Vitro Dynamics, Inc.), a UV light (General Electric, F15T8.blb, 15 W) and a potentiostat (IBM, EC/225) for the PEC reaction (Fig. 1). The reactor, which was open to the air, contained an 800 ml sample solution. The immersed area of TiO_2 film in the solution was 35 cm^2. The distance between the TiO_2 film and the UV light was 7 cm. The counterelectrode, Pt wire, was 3 in in length and 0.4 mm in diameter. A saturated calomel electrode (SCE) was employed as reference electrode.

2.4. PC and PEC reactions

For PEC studies, the PC degradation of HCOOH was carried out in the reactor system described above with electrical potentials (vs. SCE) applied using a three-electrode system. Oxygen (O_2, Industrial Grade) was bubbled through the solution with continuous stirring. The dissolved oxygen (DO) was measured by a DO meter (Great Lakes Instruments, model 867) and found to be 36 ppm. The pH of the solution was controlled by NaOH and HCl addition. The amount of HCOOH degraded was determined by total organic carbon analysis (TOC 5000, Shimadzu).

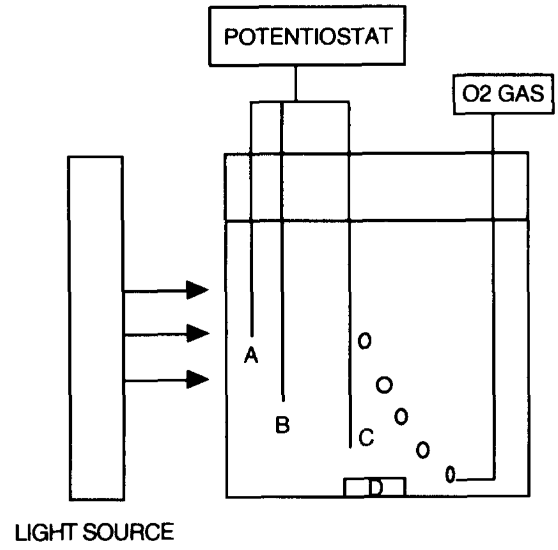

Fig. 1. Schematic diagram of the reactor system: A, counterelectrode (platinum wire); B, reference electrode (saturated calomel electrode); C, working electrode (TiO_2 electrode); D, stirring bar.

2.5. Analysis of Ag(I) and Ag

The amount of Ag(I) present in the solution was measured by an atomic absorption spectrophotometer (Perkin–Elmer 5100). The crystalline form of Ag deposited on the surface of the TiO_2 films was determined by X-ray diffraction.

2.6. Measurement of open-circuit potential

The open-circuit potential (E_{oc}) was measured by a potentiostat during UV light illumination in order to obtain the approximate position of the flat band potential for TiO_2 films under the given conditions [32].

3. Results and discussion

3.1. Blank test

3.1.1. Apparent quantum efficiency

The apparent quantum efficiency (QE) of this system is calculated as the mineralization rate of HCOOH divided by the photon flow rate impinging on the supported TiO_2 thin film following Eq. (1)

$$\mathrm{QE}=\frac{\text{(moles of HCOOH degraded per sesond)}}{\text{(moles of incident photons per second)}} \qquad (1)$$

The incident photon flow rate on the TiO_2 electrode is determined to be 3.02×10^{-7} einstein s^{-1} using a uranyl oxalate actinometer. The amount of HCOOH degraded in the PC reaction with 60 ppm (1.3×10^{-3} M) HCOOH is 2.54×10^{-8} mol s^{-1}, and 4.61×10^{-8} mol s^{-1} for the PEC

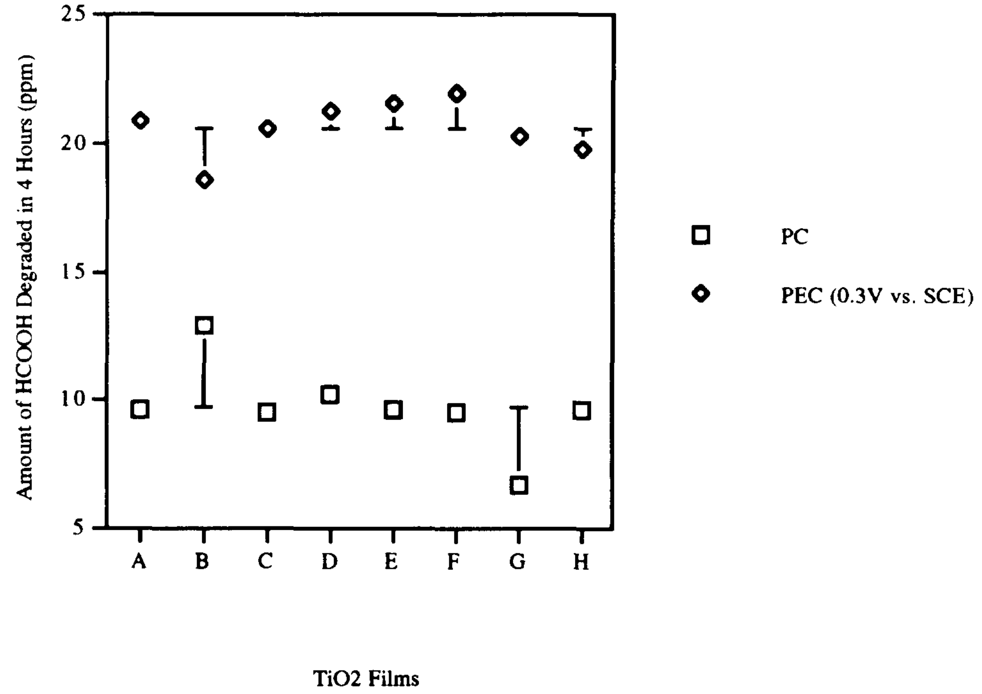

Fig. 2. Reproducibility of TiO_2 films in PC and PEC (0.3 V vs. SCE) reactions. The letters indicate TiO_2 films. The error bar for the y axis is based on the mean value of PC and PEC reactions.

(2 V vs. SCE) reaction. (These data were collected from a previous study [33].) According to Eq. (1), the QE of the PC reaction is 0.084 mol einstein^{-1} and that of the PEC reaction is 0.153 mol einstein^{-1}. The improved QE in the PEC reaction is probably due to the reduced electron–hole pair recombination rate induced by the applied potentials [31].

3.1.2. Reproducibility of TiO_2 films

In order to measure the reproducibility of the TiO_2 films, the PC and PEC (0.3 V vs. SCE) reactions were performed in two different ways; one experiment was conducted with TiO_2 films made from the same TiO_2 sol, and the other was performed with a single TiO_2 film. In these experiments, all of the experimental conditions were fixed as previously

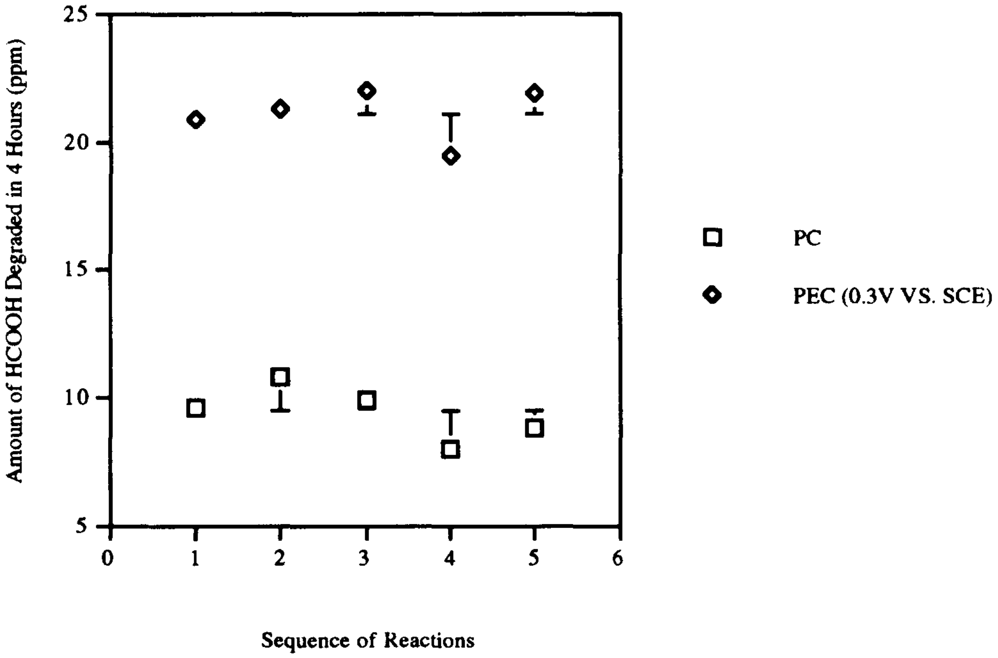

Fig. 3. Reproducibility of a TiO_2 film in PC and PEC (0.3 V vs. SCE) reactions. The numbers on the x axis indicate the sequence of reactions. The error bar for the y axis is based on the mean value of PC and PEC reactions.

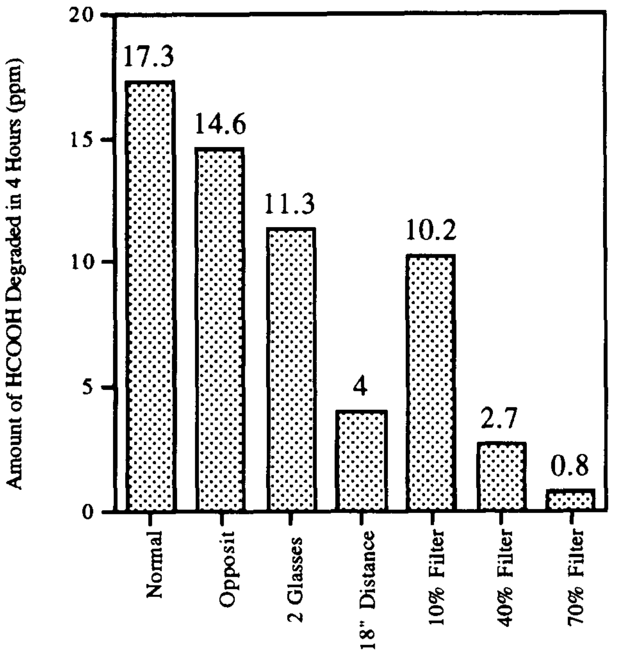

Fig. 4. The effect of filters, blocking glass and distance between the light and the TiO_2 film on the PC reactions: normal, usual experiment; opposite, TiO_2 film installed in the reactor in the reverse direction compared with the normal case; 18" distance, distance between light and TiO_2 film (in normal case it is 7 cm); 10%, 40% and 70% indicate the amount of light cut out by the filters at 365 nm.

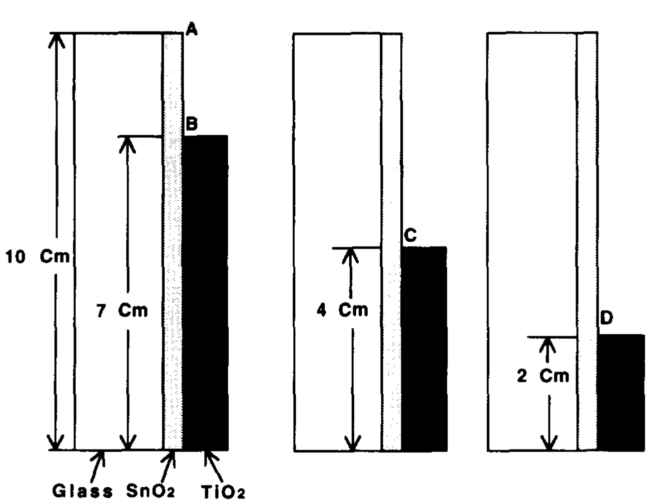

Fig. 5. Ohmic contact point and other points on PEC (2 V vs. SCE) films: A, ohmic contact point; B, 3 cm away from A; C, 6 cm away from A; D, 8 cm away from A.

described in Section 2. As shown in Fig. 2, the mean value (standard deviation) of the amount of HCOOH degraded in a 4 h period using several TiO_2 films is 9.7 (1.56) ppm for the PC reactions and 20.6 (0.90) ppm for the PEC reactions. The different PC reaction rates of films B and G compared with the others may be due to surface defects of the TiO_2 films, which may be attributed to foreign particles falling onto the TiO_2 sol during the coating process. The PEC reactions are more reproducible because negative effects, such as recombination, caused by the defects in these films can be overcome. In PC and PEC reactions performed with the same TiO_2 film, the mean value (standard deviation) of the amount of HCOOH degraded in a 4 h period is 9.42 (1.07) ppm for the PC reactions and 21.1 (1.01) ppm for the PEC reactions (Fig. 3). On the basis of these data, we assume that the reproducibility of the TiO_2 films is in the range 10%–20% and the PC and PEC reactions can be clearly distinguished by the data.

3.1.3. *Intensity of UV light*

In Fig. 4, the effect of the light intensity is examined. The clearest result comes from the experiment using optical filters to block out 10%, 40% and 70% of the light at 365 nm. The PC reaction rates decrease as the filter cuts out more UV light. Furthermore, the blocking of UV light by the Pyrex glass supporting the film ("opposite" and "2 glasses") and an increase in the distance between the UV light and the film to 18 in (normally 7 cm) lead to a decrease in the rate of the PC reactions. From these results, we can see that the light intensity affects the PC reaction. We are probably light limited in our system, and as such do not have sufficient light intensity to obtain an optimum efficiency for the PC reactions.

3.1.4. *Conductivity of SnO_2 glass*

The SnO_2-coated glass has a resistivity of 100 Ω/□ according to the information provided by F.J. Gray & Co. When a potential is applied to the SnO_2 glass in the PEC reactions, we may expect a potential drop between the ohmic contact point (A) and the other points B (3 cm from A), C (6 cm from A) and D (8 cm from A) (Fig. 5). The areas of the TiO_2 films coated onto the SnO_2 substrates are 35 cm^2 (3 cm from A), 20 cm^2 (6 cm from A) and 10 cm^2 (8 cm from A). As shown in Fig. 6, the efficiency of the PC reactions increases as the area of TiO_2 increases. In addition, the efficiency of the PEC reactions (0.3 V vs. SCE) increases as the area of TiO_2 increases and the increase in the degradation efficiency is nearly proportional to the increase in area of

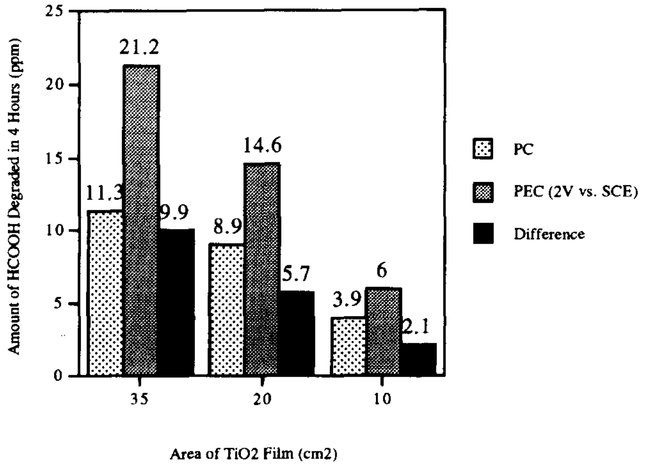

Fig. 6. The effect of the area of the TiO_2 film. Difference indicates the difference between PC and PEC (2 V vs. SCE) reaction efficiencies.

TiO_2. This result implies that the applied potential has the same (or at least sufficient) effect from the top to the bottom of the substrate to obtain an optimum bias, even though the potential may be expected to decrease substantially near the bottom of the SnO_2-coated glass.

3.1.5. Specific adsorption of Ag(I)

There is no measurable change in the concentration of Ag(I) ($C_o = 10^{-3}$ M in HCOOH) due to specific adsorption on the surface of the reactor, the TiO_2 film or the pure SnO_2-coated glass during a 4 h period. This does not imply that Ag(I) is not adsorbed by these surfaces, but rather that there is insufficient surface area to produce any analytically detectable change in the concentration of Ag(I) in the solution over this time period.

3.1.6. Homogeneous reactions of Ag(I)

Ag(I) and HCOOH do not absorb light in the spectral range 320–400 nm and no significant change in concentration of Ag(I) or HCOOH occurs in the reactor described above during UV illumination for 3 h in the absence of a TiO_2 film. Therefore we conclude that the disappearance of Ag(I) and HCOOH in our studies is due to PC or PEC reactions.

3.1.7. Effect of SnO_2 on Ag deposition

In a blank experiment involving a glass covered with SnO_2, no PC degradation of HCOOH is observed, and no Ag deposits are formed during a 4 h time period. However, Ag deposits are observed on a TiO_2 film during PC reactions. This result indicates that the photodeposition of Ag occurs on TiO_2, but not on SnO_2, or there is an insufficient surface area of SnO_2 to cause any detectable reaction over this time period.

3.1.8. Electrochemical oxidation of HCOOH in PEC reactions

In a pure HCOOH solution containing no Ag(I) species, the amount of HCOOH oxidized electrochemically is negligible (1.5 ppm in 4 h) even with an applied potential of 2 V (vs. SCE). However, the electrochemical oxidation of HCOOH is enhanced in an HCOOH solution containing 10.1 ppm of Ag(I). This result may be attributed to the lowered resistance of the solution due to the added ions Ag(I) and NO_3^-, or to the conversion of Ag(I) to Ag(0).

3.2. pH of solution

As shown in Fig. 7, the PC and PEC (0.3 V vs. SCE) reactions of HCOOH over a 4 h time period are affected by changes in the pH of the solution. The maximum degradation efficiency in both PC and PEC (0.3 V vs. SCE) reactions is obtained at approximately pH 3.4. Above or below this pH value, PC and PEC degradation declines. No degradation of HCOOH is detected above pH 6. The PC degradation of HCOOH at pH 7.5 and the better PC reaction rate at pH 4.6 may be due to experimental error.

The effect of pH on the PC and PEC reactions of HCOOH may be mainly explained by the surface charge of TiO_2 (isoelectric point, IEP) and its relation to the acid dissociation constant ($pK_a = 3.75$ at 25 °C) of HCOOH. The adsorption of the formate ion ($HCOO^-$) onto TiO_2 is probably the first step in the process of PC degradation. At pH_{IEP}, the surface charge of TiO_2 is neutral. Positive charges predominate above pH_{IEP} and negative charges below pH_{IEP} as shown in Fig. 8. The percentage ratio between anatase and rutile of TiO_2 supported on SnO_2-coated glass fired at 600 °C is 80 : 20 [33], and the IEPs of TiO_2 in previous studies have indicated

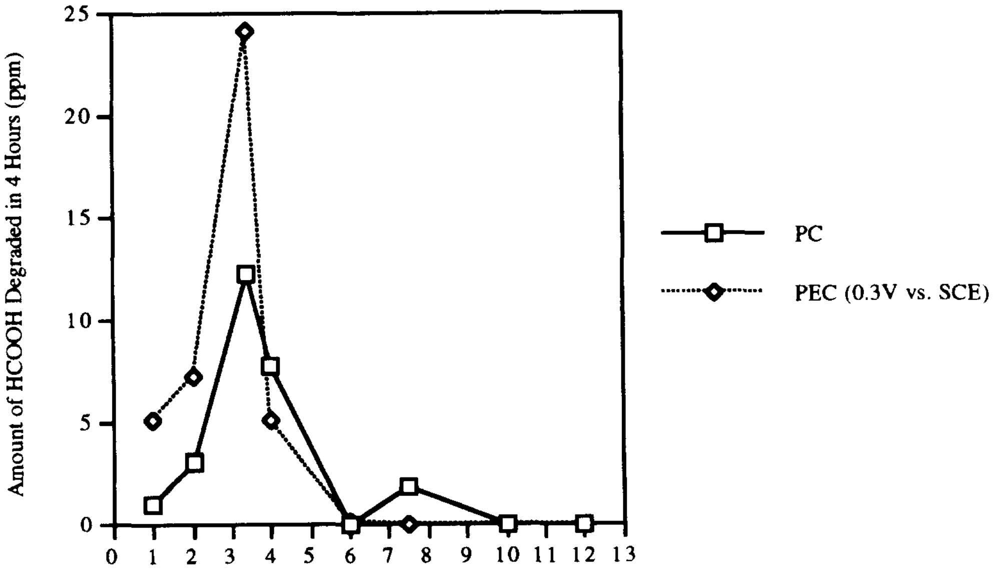

Fig. 7. Effect of the pH of the solution in PC and PEC (0.3 V vs. SCE) reactions.

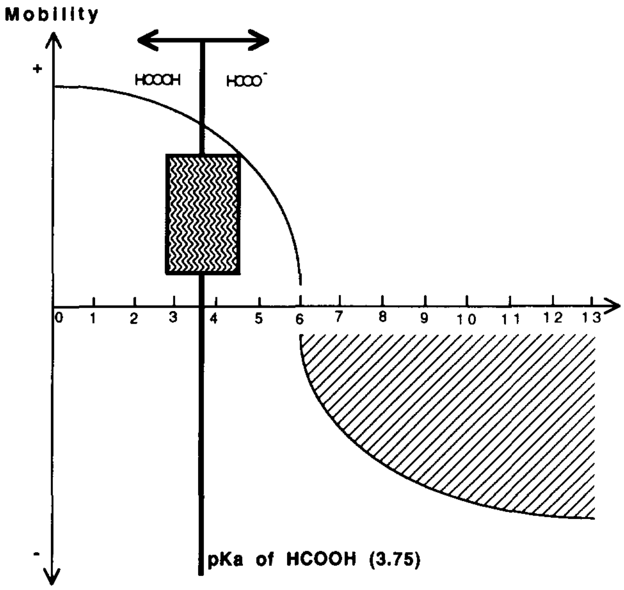

Fig. 8. Surface charge of TiO_2 (anatase) according to the pH of the solution. The dotted area indicates the positively charged surface of TiO_2. The hatched area indicates the negatively charged surface of TiO_2. The box containing wavy lines indicates the assumed range of pH for the optimum PC and PEC reactions.

$pH_{IEP} \approx 4$ for rutile and $pH_{IEP} \approx 6$ for anatase [30]. Therefore the IEP of supported TiO_2 is probably between pH 4 and 6. Consequently, the pH range 3.75–6 may be the optimum condition for the adsorption of $HCOO^-$ onto TiO_2. Therefore the best PC and PEC degradation efficiencies may be expected within this pH range. Below pH 3, the predominant species is HCOOH rather than $HCOO^-$. This may be the reason for the decreased PC and PEC performance even though the surface of TiO_2 is positively charged. Meanwhile, above pH 6, the surface of TiO_2 is negatively charged. Therefore the adsorption of $HCOO^-$ onto TiO_2 may be difficult, and may explain the lack of PC and PEC reactions even though $HCOO^-$ is the predominant species. On the basis of these results, the electrostatic attraction between the surface of supported TiO_2 and target chemicals should be established for non-specific adsorbates in order to favor PC reactions. In some cases, this may diminish the activity of supported TiO_2 in PC reactions for chemicals with pK values above pH 6.

It should be cautioned that, in this experiment, the ionic strength was not controlled, but was altered by HCl or NaOH addition. In this case, the thickness of the double layer near the surface of the TiO_2 thin film was varied and may have affected the adsorption of $HCOO^-$ onto the surface of TiO_2. Further research to determine the effect of the ionic strength on the PC and PEC reactions will be conducted in the near future.

3.3. Initial concentration of HCOOH

Fig. 9 illustrates the effect of the initial concentration of HCOOH on the PC and PEC (0.3 V vs. SCE) reactions. For these studies, the TiO_2 film employed was fired at 400 °C.

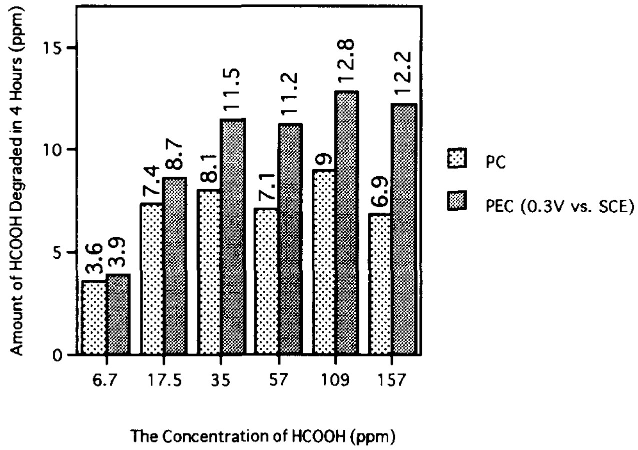

Fig. 9. Effect of the initial concentration of HCOOH on PC and PEC (0.3 V vs. SCE) reactions.

Above 17.5 ppm (3.8×10^{-4} M) of HCOOH, there is no effect of the initial concentration on the 4 h performance of the PC reactions. This implies that the surface of TiO_2 may be saturated with HCOOH above 17.5 ppm. PEC reactions are unaffected by initial concentrations above 35 ppm (7.6×10^{-4} M). The different initial concentrations for PC and PEC reactions above which no effect is observed may be due to the more positively charged surface of TiO_2 in PEC studies as positive bias potentials were applied to the TiO_2 electrode.

3.4. Ag(I) ions in HCOOH solution

3.4.1. Shift of open-circuit potential (E_{oc}) of TiO_2 films

At the beginning of our experiment, the E_{oc} value of the TiO_2 film in a solution of HCOOH during UV illumination is approximately −0.45 V (vs. SCE). However, when Ag(I) is added, this shifts to +0.29 V (vs. SCE). When the TiO_2 film is covered with Ag deposits, the E_{oc} value is +0.32 V (vs. SCE). In another experiment, we completely covered the TiO_2 film with Ag deposits and installed this film into our reactor with HCOOH solution. During UV illumination, the starting E_{oc} value in this case was −0.03 V (vs. SCE). These results indicate that Ag(I) in solution and Ag deposits on the TiO_2 film cause a shift in the E_{oc} value of the TiO_2 film towards more positive potentials (vs. SCE).

3.4.2. PC and PEC reactions

In the PC reaction, gray and white colored Ag deposits begin to occur as soon as the UV light is turned on. X-Ray diffraction measurements indicate that the deposit on TiO_2 is pure metallic silver. Ag is deposited over the entire area of the TiO_2 electrode immersed in solution. This result implies that excited electrons in the conduction band of UV-illuminated TiO_2 can be consumed by reduction reactions using Ag(I) as an electron acceptor instead of oxygen. (These processes may also occur in parallel.) In the blank experiment involving a glass coated with pure SnO_2, no PC degradation of HCOOH is observed and no Ag deposits are formed. This

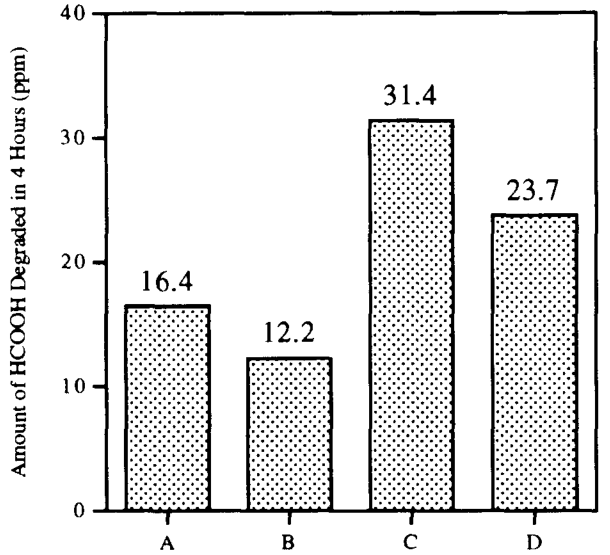

Fig. 10. Effect of Ag(I) on the extent of degradation of HCOOH via PC and PEC (2 V vs. SCE) reactions during a 4 h period: A, PC reaction in HCOOH; B, PC reaction in HCOOH containing Ag(I); C, PEC reaction in HCOOH; D, PEC reaction in HCOOH containing Ag(I).

result implies that the photodeposition of silver occurs only on TiO_2 and not on SnO_2.

For the corresponding PEC reaction (2 V vs. SCE), when the illumination source is turned on, Ag precipitation only occurs on the counterelectrode Pt wire. After a few minutes of reaction, Ag starts to deposit on the TiO_2 anode. Application of the applied potential reduces the amount of Ag deposited on the TiO_2 electrode relative to the amount deposited in the PC reaction. This result is probably due to the forced reduction of Ag(I) on the Pt wire, although Ag deposits on the photoanode cannot be avoided completely.

The amount of HCOOH degraded in PC and PEC (2 V vs. SCE) reactions decreases in systems in which $AgNO_3$ is present (10^{-3} M) (see Fig. 10). The decrease in the extent of degradation in both reactions may be attributed to a combination of the blocking of UV illumination by deposits of Ag and obstruction of the reaction sites on the surface of TiO_2.

3.4.3. Effect of silver deposits in PC reactions

Over the course of a PC experiment lasting 10 h, Ag(I) in solution is totally converted into an Ag deposit within 6 h (Fig. 11). However, in spite of the accumulation of Ag deposits and in the absence of Ag(I) in solution, the PC reaction continues for an additional 4 h. This result implies that contact still exists between the solution and the TiO_2 electrode and that O_2 acts as an electron acceptor after the solution has been depleted of Ag(I) (see Fig. 11).

In order to determine the effect of Ag deposits on the TiO_2 electrode, a film covered with Ag deposits, created during a PC reaction (see bar B in Fig. 12), was employed as a photocatalyst for the degradation of HCOOH in the absence of an applied potential (see bar C in Fig. 12). In this case, the activity is decreased compared with its previous performance.

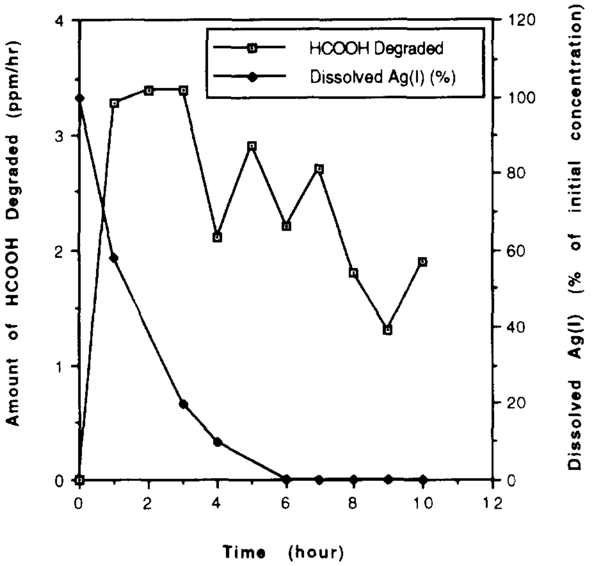

Fig. 11. Effect of the presence of Ag(I) on the extent of PC degradation of HCOOH and the amount of Ag(I) reduced during 10 h.

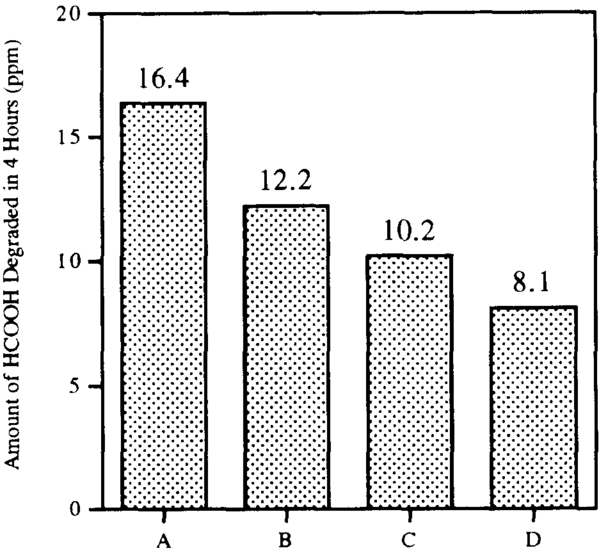

Fig. 12. Effect of Ag deposits on TiO_2 film in consecutive PC reactions during a 4 h period: A, PC reaction in HCOOH; B, PC reaction in HCOOH containing Ag(I); C, PC reaction in HCOOH using the TiO_2 film employed in B; D, PC reaction in HCOOH containing Ag(I) using the TiO_2 film employed in C.

Following these experiments, the film was again employed for the PC degradation of HCOOH in the presence of Ag(I) (see bar D in Fig. 12). In this experiment, the Ag deposits on the TiO_2 electrode increase in thickness and the efficiency of the degradation reaction is decreased compared with the original reaction efficiency of pure TiO_2. However, the amount of Ag(I) reduced during the reaction (see bar D in Fig. 12) is decreased compared with the result observed with the pure TiO_2 film (see bar B in Fig. 12). We expect that, eventually, all of the active sites on the TiO_2 electrode will be covered by silver deposits if the reaction continues indefinitely.

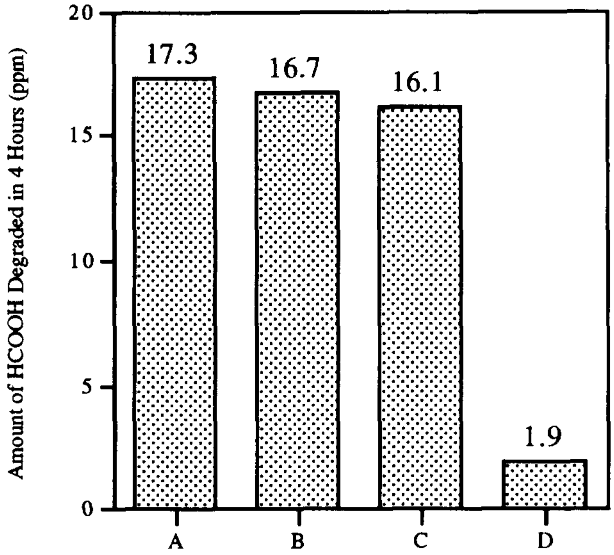

Fig. 13. Effect of mass transfer of HCOOH due to stirring and bubbling of O_2: A, PC reaction with stirring and bubbling; B, PC reaction with O_2 bubbling; C, PC reaction with stirring; D, PC reaction without stirring and O_2 bubbling.

3.5. Mass transfer of HCOOH

When O_2 is bubbled into a solution with stirring, the DO content reaches 36 ppm. Without the addition of pure O_2 but with stirring, the system can sustain 10 ppm of DO in solution because the reactor system is open to the air. However, without O_2 bubbling and stirring, DO in the solution falls to below approximately 0.7 ppm. In Fig. 13, a very low PC reaction rate is obtained when no O_2 is introduced and the system is not stirred. This low reaction rate may be due to insufficient O_2 in the solution (which acts as an oxidant) and difficulties in the mass transfer of HCOOH to the reaction surface. However, when only O_2 or only stirring is employed, the same, or a slightly decreased, reaction rate is obtained compared with the reaction with oxygen bubbling and stirring. This implies that, by stirring the solution, sufficient O_2 can be supplied from the air to the solution in this open system and O_2 bubbling can facilitate the mass transfer of HCOOH. Unfortunately, we could not control the O_2 flow rate and stirring rate. Because of this, the optimum flow rate of O_2 and the optimum stirring rate were not identified. However, the rate of oxygen supply and stirring were held constant in our experiments.

4. Conclusions

The pH of the solution is an important parameter for PC reactions using TiO_2 because of the correlation between the surface charge of TiO_2 and the ionization of target chemicals. The concentration of the target chemical affects the PC and PEC reaction rates. Ag(I), which is deposited on the surface of TiO_2 during PC reactions, eventually acts as an inhibitor of these reactions. Even with the applied potentials in PEC (2 V vs. SCE) reactions, Ag cannot be prevented completely from depositing onto TiO_2, although the amount of Ag deposits on TiO_2 is decreased compared with that in PC reactions. By stirring the solution open to air, enough O_2 is provided for PC reactions. Stirring is necessary for the mass transfer of HCOOH.

In this study, the influence of several factors was evaluated. We may divide these factors into three categories: light, solution and catalyst. Light must be utilized in the most efficient manner, i.e. the reactor design must be optimized. The catalyst has been optimized previously to perform with maximum efficiency [33]; however, a more efficient catalyst may be required. Currently, we may apply this technique in certain applications, such as wastewater containing few electrolytes except for a low concentration of the target organic chemicals.

Acknowledgements

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