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Kinetics of photocatalytic degradation of aniline in water over TiO_2 supported on porous nickel

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Abstract

The photocatalytic degradation of aniline was studied in annular photoreactor, with 2×6 W (E_{max}=365 nm) UV lamp as light source, borosilicate glass as wave filter and titanium dioxide immobilized on porous nickel as catalysts. Parameters such as the initial concentration, flow rate, initial pH, dissolved oxygen, electrolyte, hydrogen peroxide addition, temperature and external potential bias affecting the degradation rate of aniline were studied. The results showed that photocatalysis is an effective process for the degradation of aniline. The activated energy for the photocatalytic degradation of aniline is 6.13 $kJ\,mol^{-1}$. The initial quantum yield is 1.89% for aniline 1.10×10^{-4} $mol\,l^{-1}$. Total mineralization requires a much longer illumination time than the disappearance of anilines. The external potential bias can largely improve the efficiency of photocatalytic degradation of aniline. The degradation kinetic of aniline can be described by Langmuir–Hinshelwood equation. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Photocatalytic degradation; Immobilized titanium dioxide; Aniline

1. Introduction

Aniline, which is commonly produced as by-product of the petroleum, coal and chemical industries, is highly toxic. In order to avoid its presence in natural and drinking water, the study of the degradation of aromatic amines is of great interest.

The photocatalytic degradation of organic environmental pollutants in the presence of a semiconductor such as TiO_2 or ZnO, or Fe_2O_3 has become interesting enormously over the last few decades [1–3]. Partly of reason is that it may completely mineralize a variety of aliphatic and aromatic compounds under suitable conditions and it may be less expensive. However, much attention in this area has focused on the use of slurry system, thus causes a series of trouble, such as the need to separate the spent catalysts particles, and need to stir to keep the semiconductor suspended. Therefore, a technique that does not involve filtration and suspension of the photocatalysts is desirable. Recently, different suitable materials matrix have been chosen to be immobilized support, such as glass [4–8], sea sand [9,10], gel [10], ceramic membranes [11], conductive glass [12,13] and stainless steel [14].

Our group has developed a new fixation technique of TiO_2 by packing it on a porous conductive nickel substrate to degrade an organic compound that is strongly adsorbed to TiO_2 [15]. By this technique it is aimed to increase the diffusion rate of solutes and the separation of electron–hole pairs induced by illumination of UV through imposing a bias potential. Thus an expectation to improve the efficiency of degradation of organic compounds may be obtained. In this work, we report the kinetics of photocatalytic degradation of aniline over TiO_2 immobilized on a porous nickel in a both flow and stirring system. The effect of the initial concentration, flow rate, initial pH, dissolved oxygen, electrolyte, hydrogen peroxide addition, temperature and external potential on the photocatalytic reaction rate was investigated. The quantum yield of degradation reaction and the formation of nitrate and NH_4^+ ions were also determined. The degradation kinetic was considered.

2. Experimental details

TiO_2 (Shanghai, 99.9%, average particle size as measured by SEM about 0.95 μm, mainly of anatase form confirmed by X-ray diffraction, not shown here) was mixed with 3 wt.% polyvinyl alcohol (PVA) in the ratio of 3:2. Then it was

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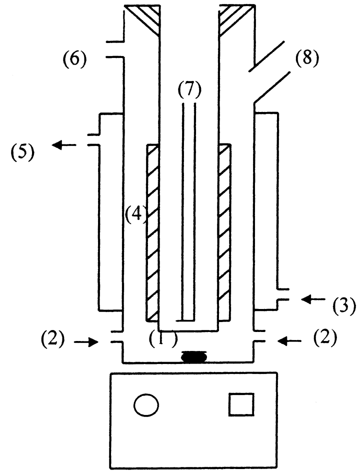


Fig. 1. Schematic diagram of apparatus: 1: magnetic stirrer; 2: purging gas; 3: cooling water inlet; 4: Ni/TiO_2; 5: cooling water outlet; 6: vent; 7: lamp; 8: sampling or reference electrode port.

coated on one surface of a clean $14\times15\,cm^2$ porous nickel (thickness about 0.2 cm, porosity 95%). The coated sheet (denoted hereafter as TiO_2/Ni) was dried at 60°C for 4 h and packed to thinner sheet in thickness 0.09 cm. TiO_2/Ni was rinsed with saturated Na_2CO_3 to remove grease and/or photooxidation products and washed with water to release the loosely bound particles, dried by heating at 60°C prior to usage or reused. The bare nickel with the same thickness was used as blank tests. The difference in weight between the coated and bare films gave the TiO_2 weight listed in the following experiments. Little change has been found when the reproducibility of the parallel experiments was conducted. Two types of bath photoreactor were utilized. Photoreactor 1 (P1) opened to air was similar with that in [7], i.e. P1 is an annulus reactor with a cylindrical borosilicate glass inner tube. The TiO_2/Ni film was wrapped around the borosilicate glass tube. Photoreactor 2 (P2 as shown in Fig. 1) was used to study the photoelectrochemical experiments. In this case the porous nickel ($15\times16\,cm^2$) double covered with TiO_2 was used as working photoelectrode, blank porous nickel as counter electrode and a saturated calomel electrode as reference. The light source (2×6 W UV lamp for P1, 4×6 W UV lamp for P2, E_{max}=365 nm) was fixed on the central axis of the cylinder. Potassium ferrioxalate actinometry [16] in TiO_2/Ni free solutions was used to measure the near-UV intensity entering the reactor. The photon absorption rate in the reactor P1 and P2 was 5.0×10^{-6} and 8.4×10^{-6} Einsteins min^{-1}, respectively. Solution (150 ml in P1, 30 ml in conveying tube) was placed in the annular region (width about 0.5 cm) between the borosilicate cylinder and the double-walled glass outer jacket (cooling at 25±1°C). Solutions were circulated with a peristaltic pump at a rate of 250 ml min^{-1}, pH 7.0 and kept purged with air at a rate of 16 l h^{-1} unless specified. The aniline concentration in the solution was estimated colorimetrically by the modified method [17] (coupling time was 4 h). The degradation products NO_3^- and NH_4^+ were estimated by indophenol blue [18] and phenate method [19], respectively. $HClO_4$ and/or NaOH adjusted the pH of solution before reaction. Distilled water was used throughout the work.

Aniline was the analysis reagent and used without further purification, KNO_3 was the governmental reagent and H_2O_2 was 29 wt.%. The other chemicals and solvents used were of reagent grade and used without further purification.

3. Results and discussion

3.1. Comparison of photolysis and photocatalytic degradation

As indicated in Fig. 2, a small decrease in the concentration of aniline was observed both in the presence of TiO_2 without UV light irradiation and in the absence of TiO_2 with UV light illumination. For the former it may result from its oxidation by oxygen and volatilization. For the latter it may arise from photodegradation excited by a very slight far-UV light besides the former cases, therefore its decrease was slightly higher than that of the former. In conclusion, no significant homogeneous photodegradation reaction of aniline occurred owing to most of the far-UV light getting filtered by borosilicate glass tube and aniline did not absorb the near-UV light. However, aniline can be degraded quickly over illuminated TiO_2 and the solution pH decreases as the reaction proceeds. Thus it can be inferred that the degradation of aniline resulted from photocatalytic oxidation. It has been proved [1] that photogenerated holes oxidize water or adsorbed OH^- at the surface of semiconductor to hydroxyl radicals

$$OH^- + h_{VB}{}^+ \rightarrow OH^\bullet \tag{a}$$

These highly reactive radicals can then be used to mineralize or at least partially degrade most organic pollutants.

$$OH^\bullet + \text{organic substrates} \rightarrow \text{products} \tag{b}$$

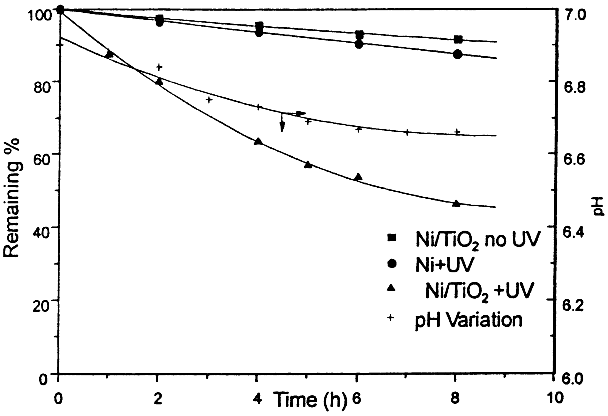


Fig. 2. Aniline photolysis and photocatalytic degradation and pH variation (Experimental conditions: c_0=84.30 ppm; TiO_2=1.94 g g^{-1} Ni).

At the same time the holes can also react with aniline directly to produce aniline cation radical.

The conjugate reaction may be

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (c)$$

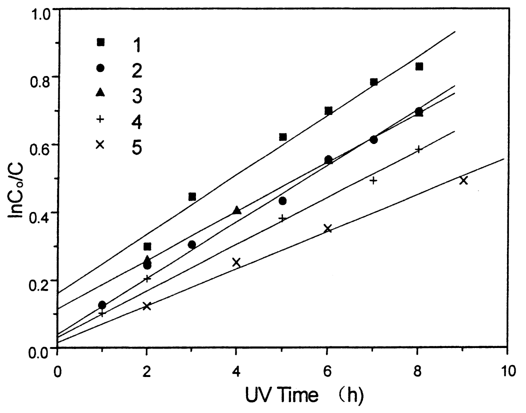
The rates of the photocatalytic degradation of aniline depend on various parameters such as initial concentration, pH, type of reactor etc. So their measurements have no absolute meaning. However, for a given set of conditions, they allow one to determine the effect of each of the experimental parameters on the photocatalytic oxidation.

3.2. Effect of the initial concentration

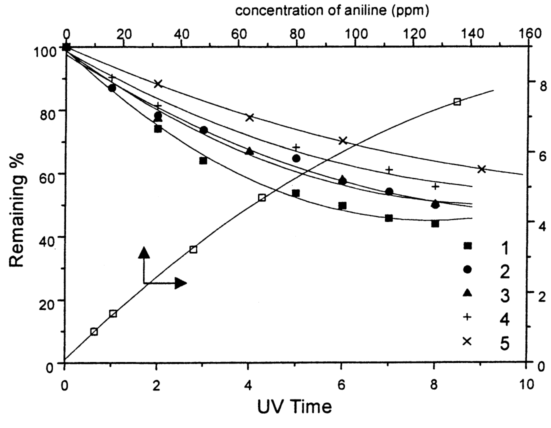
The effect of initial aniline concentration on degradation rate is shown in Fig. 3a. It is obvious that the rate increases but the apparent rate constants decrease with increasing aniline concentration. The photocatalytic degradation reaction follows a first-order expression up to an initial aniline concentration of 135.35 ppm. This is confirmed by the evidence of a straight line relationship of ln(c_0/c) versus irradiation time. The slope of the plot gives the apparent first-order rate constant k_{app} as shown in Table 1. However, the photodegradation reaction follows more like a zero-order expression when the concentration of aniline is close to 135.35 ppm. These can be explained by assuming that the photo-products were competing for the site of the surface of TiO_2 with aniline. Table 1 lists the apparent rate constants and half-lives of the photodegradation of aniline as a function of initial concentration.

Table 1
Apparent first-order rate constants k_{app}, half-life $t_{1/2}$, $t'_{1/2}$ and linear coefficient R for the degradation of aniline at different initial concentrations

Initial concentration (ppm)	k_{app} ($\times 10^2$ l h^{-1})	$t_{1/2}$ (h)	$t'_{1/2}$ (h)	R
10.2	8.760	7.91	7.84	0.9913
16.86	8.332	8.32	8.03	0.9951
44.77	7.219	9.60	8.86	0.9997
68.38	6.899	10.5	9.55	0.9949
135.35	5.480	12.65	11.53	0.9969



(a)



(b)

Fig. 3. (a) Effect of the initial concentration of aniline on the photocatalytic degradation. (b) Pseudo-first-order kinetics for anilines in photocatalytic degradation. (Experimental conditions: TiO_2, 1.94 g g^{-1} Ni; 1: 10.20 ppm; 2: 16.86 ppm; 3: 44.77 ppm; 4: 68.38 ppm; 5: 135.35 ppm).

3.3. Effect of the flow rate

In photocatalytic oxidation organic substrates follow the steps of diffusion, adsorption, and reaction. Table 2 summarizes the k_{app} values at various flow rates and the corresponding half-life $t_{1/2}$. It is found that the k_{app} were not affected by the flow rate in the range 100–250 ml min^{-1}. This can be attributed to the fact that air purge is enough to make mass transport and porous nickel support is beneficial to mass diffusion. Therefore it is not necessary to explore lesser or wider range of flow rates. (In order to fix the quantitative oxygen we did not change the volume of purge air.) Sabate et al. [7] have also not observed a significant difference in degradation rate as a function of the recirculation rate in the range between 130 and 300 ml min^{-1}.

3.4. Effect of the initial pH

Changing electrolyte pH can vary the surface charge at the TiO_2 surface and also shifts the potential of some redox reaction, thus it affects the adsorption of organic solutes, consequently, its reactivity and some reaction rate. Fig. 4 shows the dependence of degradation of aniline on the initial pH of solution. The increasing r_0 with increasing pH can be attributed to the increase in the number of OH^- ions at

Table 2
Apparent first-order rate constants k_{app}, half-life $t'_{1/2}$ and linear coefficient R of the photodegradation of aniline at different flow rates (c_0=10.80 ppm; TiO_2=2.05 g g^{-1} Ni; UV 8 h)

Flow rate (ml min^{-1})	k_{app} (l h^{-1})	$t_{1/2}$ (h)	R
Air purge only	0.1146	5.56	0.99942
100	0.13484	5.14	0.99885
170	0.13567	5.11	0.99943
250	0.13645	5.08	0.99608

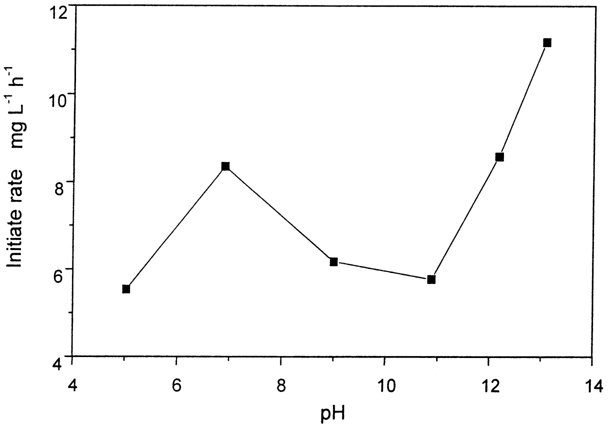


Fig. 4. Effect of the initial pH on the initial rate of aniline in photocatalytic degradation (Experimental conditions: c_0, 84.30 ppm; TiO_2=1.94 g g^{-1} Ni; UV 8 h).

the surface of TiO_2, since $OH^\bullet$ can be formed by trapping photoproduced holes. Also the dissociation of aniline probably changes its reactivity. Similarly, the decrease at the lowest pH can be explained by the lack of OH^- ions. Claire [20] found that $OH^\bullet$ was the sole oxidant under the condition of pH 11 and its role was larger in this case than in neutral and acid medium. So r_0 increases rapidly with increasing of pH when greater than 11. In general, the results indicate the efficiency of the process is not much affected over a wide range of pH, which is quite satisfactory in view of applications.

3.5. *Effect of the oxygen*

As shown in Table 3 the oxidation rate of aniline increases with increasing oxygen concentration and oxygen is crucial to photocatalytic oxidation. This can be explained by the following: As stated above, there exists a conjugate reaction in photocatalytic process. Without the electron acceptor the photocatalytic oxidation can not proceed. The rates of photocatalytic reaction are limited by the recombination of photogenerated holes and electron [1]. Adsorptive oxygen at the surface of particles is electron trapper, and it proceeds in a series of chemical processes:

$$O_2(ads) + e^- \rightarrow O_2^{\bullet -}$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$$

Table 3
Apparent first-order rate constants k_{app}, half-life $t'_{1/2}$ and linear coefficient R of the photodegradation of aniline at different oxygen concentration (c_0=10.80 ppm; TiO_2=2.05 g g^{-1} Ni; UV 8 h)

	k_{app} (10^3 l h^{-1})	$t_{1/2}$ (h)	R
Nitrogen	4.78	145.0	0.9915
Air	136.45	5.08	0.9994
Pure oxygen	200.38	3.46	0.9986

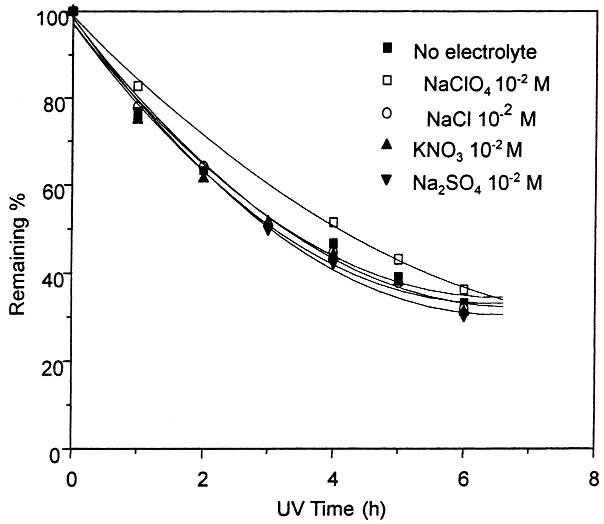


Fig. 5. Effect of the electrolyte on aniline degradation (Experimental conditions: c_0=11.5 ppm; TiO_2=2.05 g g^{-1} Ni).

$$HO_2^\bullet + O_2^{\bullet -} \rightarrow HO_2^- + O_2$$

$$HO_2^- + H^+ \rightarrow H_2O_2$$

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

It can be seen that $O_2^{\bullet -}$ may be another source of OH radial. Thus it can increase the degradation rate. In addition, oxygen acts as oxidant in the process of the hydroxylation of organic substance.

3.6. *Effect of the electrolyte*

Inorganic ions may be specific adsorption or alternative forms at the surface of TiO_2, thus they can affect the photocatalytic oxidation. Some studies [21,22] have been systematically investigated and the influence of anions such as SO_4^{2-}, NO_3^-, Cl^-, ClO_4^- and HCO_3^- on the photocatalytic activity of TiO_2 towards certain organic substrates are noted. These studies found that anions such as NO_3^- and ClO_4^- have no effect. The effect of the inorganic electrolyte on the photooxidation of aniline is shown in Fig. 5. It is found that the electrolytes employed in the experiments have no significant effect on the reaction rate. Some studies found that Cl^- is the inhibitor of photocatalytic oxidation as it competes with O_2 for electron [21,23]. However, in this study little change has been found for the degradation of aniline in the presence of NaCl.

3.7. *Synergetic effect of hydrogen peroxide addition and irradiation*

The effect of H_2O_2 addition on the photocatalytic oxidation of aniline was shown in Fig. 6. It can be seen that H_2O_2 could rapidly increase the rate of aniline degradation, even in the presence of nitrogen purge. H_2O_2, an oxygenant,

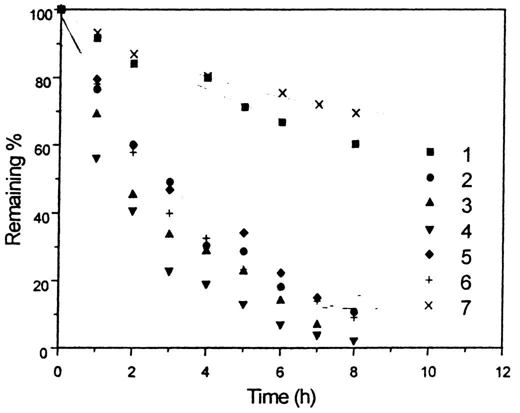


Fig. 6. Effect of hydrogen peroxide on the photocatalytic degradation of aniline (Experimental conditions: c_0=82.94 ppm; TiO_2=1.65 g g^{-1} Ni; H_2O_2 (ml h^{-1}): 1: 0; 2: 0.1; 3: 0.4; 4: 0.7; 5: 0.4, no UV; 6: 0.4, N_2 purge; 7: 0, N_2 purge).

is often used as a hydroxyl radical generating agent in advanced oxidation processes. Brillas et al. [19] found that it can effectively degrade aniline. In the presence of UV illumination it can be through the following reaction to produce more hydroxyl radicals:

$$H_2O_2 \xrightarrow{h\nu} 2OH^\bullet,$$

therefore it can increase the oxidation rate of aniline. There existed a synergetic effect in the presence of TiO_2-UV and H_2O_2 (see curves 1, 3, 5 and 6 in Fig. 6). Similar results were observed in the photocatalytic system of substrates such as chloroethylenes [24] and phenol [25]. The H_2O_2 presumably increases the oxidation rate in these cases via its role as a better electron scavenger than dissolved oxygen. On the other hand, a report [26] described that in the presence of an excess of H_2O_2 the photocatalytic activity may be adversely affected via short-circulating of the semiconductor microelectrode. That is, the excess H_2O_2 begins to consume $OH^\bullet$ via the following reaction:

$$H_2O_2 + OH^\bullet \rightarrow H_2O + HO_2$$

$$HO_2 + OH^\bullet \rightarrow H_2O + O_2$$

But this phenomena in the range 0.1–0.7 ml h^{-1} of H_2O_2 was not observed in the experiments. It may be attributed to its less or batch addition.

3.8. Effect of the temperature

In general, the activated energy of photocatalytic reaction is slightly affected by the temperature, but consecutive redox reaction may be largely influenced by temperature which affects both collision frequency of molecules and adsorption equilibria. So the overall effect on the photocatalytic performance will depend on the relative importance of these phenomena. Fig. 7 shows the Arrhenius plot of k_{app} versus T^{-1}. The result obeyed the Arrhenius law. The activated energy of aniline degradation is 6.13 kJ mol^{-1}. This is less than the value of 10 kJ mol^{-1} obtained for phenol [27], 11 kJ mol^{-1} for salicylic acid [5] and 13 kJ mol^{-1} for oxalic acid [28].

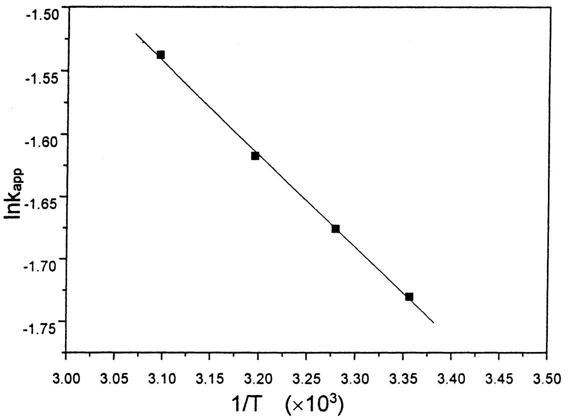


Fig. 7. Effect of the temperature on photocatalytic degradation of aniline (Experimental conditions: c_0=11.60 ppm; TiO_2=2.05 g g^{-1} Ni; UV 8 h).

3.9. Formation of nitrate ions and ammonia ions

In order to determine whether the aniline was completely mineralized, photocatalytic degradation in P2 reactor was conducted. The $NH_4{}^+$, CODcr and $NO_3{}^-$ were measured and the results were shown in Fig. 8. It shows that the aniline completely disappeared when illuminated for 18 h and 12 m, while only 23.77 and 15.96% of $NH_4{}^+$ and $NO_3{}^-$ was formed, respectively. The formation of $NH_4{}^+$ ions is rather quick in initial stage and then close to a plateau at 10 h and 33 m, while the formation of $NO_3{}^-$ almost linearly increases with increasing illumination time. These indicated that the remaining nitrogen exists in others compounds and the oxidation of nitrogen to $NO_3{}^-$ may occur via the intermediate formation of NH_3. Similar results were found in the photocatalytic degradation of other compounds containing nitrogen atoms [18,22,29]. Fig. 8 also shows that the degradation of CODcr is a more slow process, which indicates that the oxidation of aniline to carbon dioxide is slow. In order to confirm this, an experiment was conducted using a concentration of aniline 47.40 ppm for illuminating for 28 h (oxygen purge; carbon dioxide in the effluent passes through a trap filled with a solution of $Ba(OH)_2$ as measurement of the CO_2 produced by reaction), only about 19.8% of the expected CO_2 is obtained. This means total mineralization requires a much longer illumination time than the disappearance of aniline in this kind of experiments. This may be attributed to the poor power of light source.

3.10. Quantum yield

The quantum yield, which is of great value in photocatalytic process, can be defined as the ratio of the number of molecules of aniline reacting to the number of photons supplied. Since the quantum yield depends on the experimental

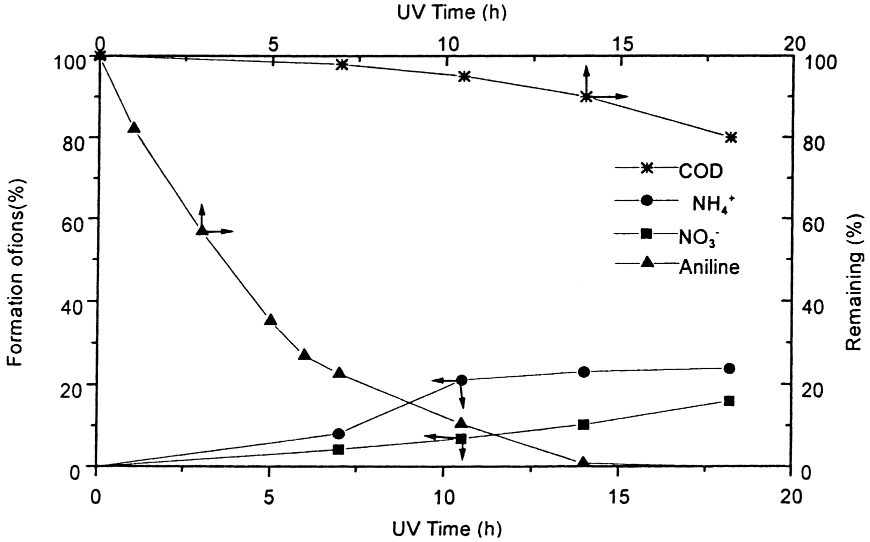


Fig. 8. Ions formation, CODcr and aniline degradation (Experimental conditions: c_0, 17.60 ppm; TiO_2=2.02 g g^{-1} Ni; oxygen purge).

parameters and here we have assumed that all the incident light was absorbed by titanium dioxide. So it gets the minimum apparent quantum. Under the experimental conditions (in P1 reactor; c_0, 1.10×10^{-4} M; other conditions see Fig. 3), the initial rate of aniline was found to be 1.59×10^{-7} M min^{-1}. Therefore the initial quantum yield for the degradation of aniline is 1.89%.

3.11. Effect of the external potential bias

As indicated above, the quantum yield was low due to the significant recombination of electron–hole pairs. Therefore, improvement in the efficiency of photon utilization is important in photocatalytic reaction. Vinodgopal et al. [12] first reported that the recombination between the photogenerated charge carriers can be suppressed by applying an external anodic bias, by which it can accelerate the photocatalytic reaction for 4-chlorophenol. Dong Hyun Kim and A. Anderson [13] also found that formic acid showed efficient degradation over a wide range of conditions when used with the bias. (The TiO_2 films have been immobilized on conductive SnO_2 by thermally fusing TiO_2 particles in their systems.) The effect of the potential bias on the photocatalytic degradation of aniline is shown in Fig. 9. As stated above, there was negligible or no degradation in photocatalytic system in the presence of nitrogen purge. In the presence of UV and external potential, the k_{app} is larger than the case of only external potential. This means that the anodic bias can be efficiently improve photocatalytic reaction. The only reason is that bias potential applied to the photocatalyst film had separated the photogenerated carriers thereby improving the quantum yield. This approach has the advantage of not only the ease of treating the photocatalyst after use but also is capable of applying a bias potential to the interface between conductive substrate and semiconductor to separate the photo-generated carriers. By this, a detailed study of the photoelectrochemical behavior of organic substrates is under way in our laboratory.

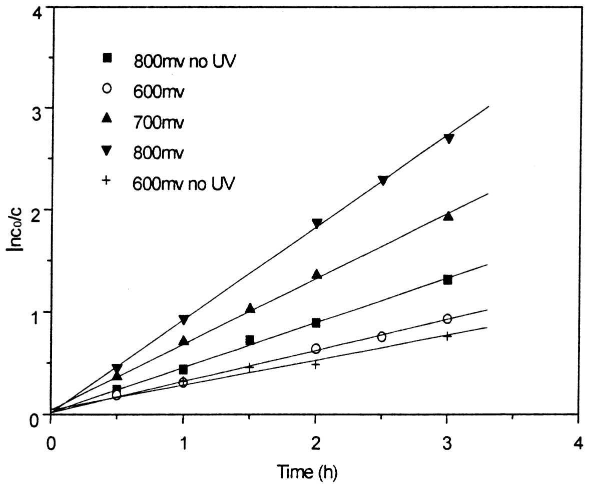


Fig. 9. Effect of applied potential (vs. SCE) on the photocatalytic degradation of aniline (Experimental conditions: c_0=9.3 ppm; TiO_2=4.0 g g^{-1} Ni; N_2 purge; solution 180 ml in P2 reactor).

3.12. Kinetic analysis

Many studies [1,4–6,15,16] have applied the Langmuir–Hinshelwood (L–H) expression to the analysis of heterogeneous photocatalytic reaction. Here we suppose that the photocatalytic oxidation of aniline can be fitted to L–H model. For the conditions in our experiments, it is given by

$$r = -\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{k_r k_a c}{1 + k_a c + k_w c_w + \sum_{i=1}^{n} k_i c_i} \tag{1}$$

where r (ppm h^{-1}) is the reaction rate for the oxidation of aniline, c (ppm) is the concentration of aniline, k_r (ppm h^{-1}) is the specific reaction rate constant for the oxidation of aniline, k_a (ppm^{-1}) is the equilibrium adsorption constant of aniline, c_w (ppm) is the concentration of solvent, k_w (ppm^{-1}) is the equilibrium adsorption constant of solvent, c_i (ppm) is the concentration of products, k_i (ppm^{-1})is the equilibrium adsorption constant of products and t (h) is the reaction time.

By integrating Eq. (1), we get

$$t = \left[\frac{1 + k_w c_w + \sum_{i=1}^{n} k_i c_i}{k_r k_a}\right] \ln\left(\frac{c_0}{c}\right) + \frac{c_0 - c}{k_r} \tag{2}$$

If there is no competition in adsorption between reactant and reaction products, $\sum_{i=1}^{n} k_i c_i = 0$, then Eqs. (1) and (2) become Eqs. (3) and (4), respectively,

$$\frac{1}{r} = \frac{1}{k_r} + \frac{(1 + k_w c_w)/k_r k_a}{c} \tag{3}$$

$$\ln\left(\frac{c_0}{c}\right) + \left[\frac{k_a}{1 + k_w c_w}\right](c_0 - c) = \left[\frac{k_r k_a}{1 + k_w c_w}\right] t \tag{4}$$

especially, when there exists no competition adsorption between reactant and solvent, i.e. $k_w c_w = 0$, we get

$$\frac{1}{r} = \frac{1}{k_r} + \frac{1}{k_r k_a c} \tag{5}$$

$$\ln\left(\frac{c_0}{c}\right) + k_a (c_0 - c) = k_r k_a t \tag{6}$$

By substituting $c = c_0$ into Eqs. (3) and (5), it can be obtained that

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{(1 + k_w c_w)/k_r k_a}{c_0} \tag{7}$$

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r k_a c_0} \tag{8}$$

For a general system it has the following relationship: $c_w > c$, where c_w is a constant, when it was plotted using $1/r_0$ versus $1/c_0$ from Eqs. (7) and (8), a straight line can be obtained.

If c_0 is small, by Eqs. (4) and (6), we get Eqs. (9)and (10), respectively.

$$\ln\left(\frac{c_0}{c}\right) = \left[\frac{k_r k_a}{1 + k_w c_w}\right] t = Kt \tag{9}$$

$$\ln\left(\frac{c_0}{c}\right) = k_r k_a t = K' t \tag{10}$$

It is obvious that a straight line can be obtained when it were plotted by $\ln(c_0/c)$ versus t from Eqs. (9) and (10).

In addition, by substituting $c = c_0/2$ into Eq. (2), we get,

$$t_{1/2} = \frac{0.5 c_0}{k_r} + \left(\frac{1}{k_r k_a} + \frac{k_w c_w}{k_r k_a}\right) \ln 2 \tag{11}$$

When there exists no competition adsorption between reactant and solvent, i.e. $k_w c_w = 0$, we get,

$$t_{1/2} = \frac{0.5 c_0}{k_r} + \frac{\ln 2}{k_r k_a} \tag{12}$$

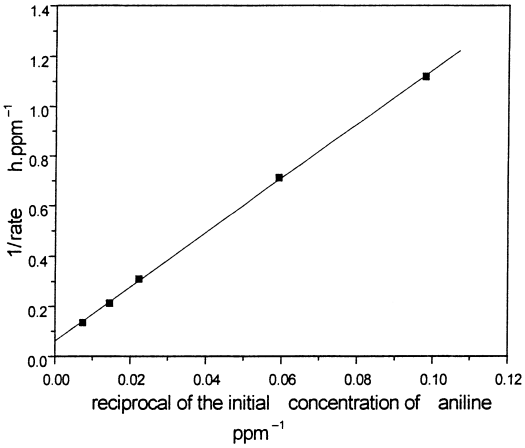


Fig. 10. Linearized reciprocal kinetic plot for the photocatalytic degradation of aniline (Experimental conditions: see Fig. 3).

Straight lines can also be obtained when it were plotted by $t_{1/2}$ versus c_0 both from Eqs. (11) and (12).

As indicated in Fig. 3b the straight line relationship of $\ln(c_0/c)$ versus irradiation time were observed. The plot of the reciprocal initial rate r^{-1} as a function of the reciprocal initial concentration c_0 yields a straight line (see Fig. 10). The linear transform of this expression yields $k_r = 16.95$ ppm h^{-1} and $k_a = 5.43 \times 10^{-3}$ ppm^{-1} ($r = 0.99984$). By substituting into Eq. (12), the estimated half-lives $t'_{1/2} = 0.029495 c_0 + 7.5348$ are obtained and listed in Table 1. Fig. 11 shows the dependence of $t_{1/2}$ and $t'_{1/2}$ on the initial concentration of anilines and their relationships are also a straight line. So the photocatalytic oxidation of aniline fits well to the L–H model.

It can also be seen that $t_{1/2}$ and $t'_{1/2}$ are almost identical at low initial aniline concentration. However, the gap between $t_{1/2}$ and $t'_{1/2}$ becomes larger with increasing initial concentrations. It was explained by assuming that the reaction by

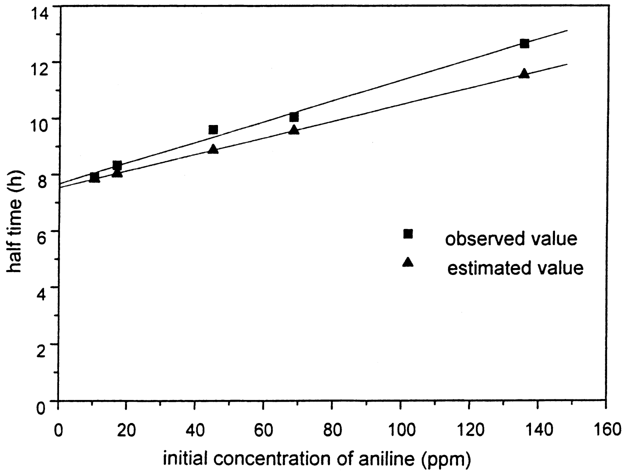


Fig. 11. Relationship between observed and estimated half-time with the initial concentration of aniline in the photocatalytic degradation (Experimental conditions: see Fig. 3).

products compete with aniline so as to delay the half-life of these reactions. Thus the effect of by-products on the reaction rate should be considered.

3.13. *Some questions about the TiO_2/Ni*

It was not observed that powder TiO_2 escapes from the substrate during the process of photocatalytic degradation. Ni^{2+} concentration in solution measured by atomic absorption was less than $1\,mg\,l^{-1}$ when pH was higher than 7.0 and less than $70\,mg\,l^{-1}$ at pH 1.8 due to the dissolving of porous nickel for 7 days. This is because of the inhibition of TiO_2 on bare nickel. Contrast tests were conducted (not shown here) in the range pH 2.0–12.5, Ni^{2+} 0–100 $mg\,l^{-1}$ in slurry system. Negligible differences in the absence and presence of Ni^{2+} were observed. This shows that there was no catalysis of Ni^{2+} in solution for photocatalytic reaction. The physical chemistry properties of the Ni/TiO_2 were stable. Little change was observed even after using for 80 h.

Unfortunately, the binder, PVA is also a sacrificial electron donor, so it can react with a positive hole, which was confirmed by several researchers [30,31]. Thus it reduces the hydroxyl radical number for its competition reaction to hole with water or OH^-. Therefore, it is not a stable and good binder. We have used polytetrafluoroethylene (PTFE) as a binder but the results were not satisfactory for its poor performance of binding. It seems that to probe a suitable binder is necessary and this is under way in our laboratory.

4. Conclusions

It is not only a simple technique but also an effective approach of catalysis immobilization to support TiO_2 on porous nickel for photodegradation aniline. By this process aniline can be destroyed to mineral products though complete mineralization needs a quite longer irradiation time. The initial quantum yield is small. However, external potential bias can sharply improve the efficiency of photocatalytic reaction. This provides a desirable approach to degrade organic substrates.

The results indicated that the degradation rate of aniline was not obviously affected by the flow rate and electrolyte in the experiments, however, largely affected by the aniline concentration, oxygen concentration and hydrogen peroxide addition. The activation energy for the photocatalytic degradation of anilines is $6.13\,kJ\,mol^{-1}$ and L–H equation can be used to describe the photodegradation reaction.

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