

The effect of solution pH and peroxide in the TiO₂-induced photocatalysis of chlorinated aniline

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Abstract

Chlorinated anilines are frequently used in the industry as starting materials for chemical synthesis. This type of compounds can end up as pollutants in wastewater. 2-Chloroaniline (2-CIA) was selected irradiating under monochromatic UV light at 300 nm. The reaction rate could be enhanced by introducing low level of H₂O₂ into the UV/TiO₂ system. Excess H₂O₂ could not increase the HO[•] generation but retarded the reaction rate. The pH effect was also investigated in UV/TiO₂ and UV/TiO₂/H₂O₂ systems. All the experimental results show that pH is a sensitive parameter to the rate of degradation. Low reaction rate at acidic pH could be accounted by the dark adsorption test which has also proven the photocatalysis of TiO₂ may contribute to a two-step process: (1) 2-CIA pre-adsorbed onto TiO₂ and (2) photoexcitation of TiO₂. At high pH, rate enhancement could be observed at UV/TiO₂ system because of the increase generation of HO[•]. However, the introduction of H₂O₂ slowdown the decay rate at such alkaline medium.

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1. Introduction

Titanium dioxide, TiO₂, being one of the popular photocatalysts, has extensively applied in the contamination treatments in either groundwater or water/wastewater engineering. Its benefits include low cost, chemically stable, and the generation of highly oxidizing electron holes [1] leading to the wide applications in degrading many organic contaminants [2]. However, the dosage of TiO₂ could not unlimitedly be increased to improve the efficiency of photodecay. Researchers have reported that beyond the optimal TiO₂ dosage, the photodecay rates would be retarded or slowdown due to the light scattering effect by the excess TiO₂ dispersion and the fast recombination process [3]. As a result, the photooxidation of TiO₂ may not be efficient when the loading of contaminant is high.

Further rate enhancement is possible via surface modification of the catalyst or by additional sensitizers. For examples, Lu et al. [4] have suggested various approaches to improve

the TiO₂ catalyzed photoreaction performance including surface modification of TiO₂ by increasing surface area of TiO₂, different UV irradiation sources selection and introducing additional external electron acceptor. Among those methods, Dillert et al. [5] have showed that the addition of hydrogen peroxide, as an additional oxidant, could assist photocatalytic degradation in TiO₂ suspensions. Wang [6] has discovered that H₂O₂ reacts to most of the organic contaminants with the hydroxyl radicals (HO[•]), which are considered to be a major oxidizing intermediate for in aqueous solutions. However, Lu et al. [7] has reported some organic contaminants such as trinitrotoluene, dichlorvos and trinitrobenzene have shown negative effects on the use hydrogen peroxide assisted photocatalytic degradation.

The probe in this study, 2-chloroaniline (2-CIA), belongs to the anilines family, which is frequently used as starting substances for chemical synthesis in polymer, rubber, pharmaceutical and dye industries [8,9]. USEPA [10] reported that it could retain in the environment as degradation products of various pesticides and it would undergo a more persistence chemical bonding with humic materials when released to soil. According to IAWR [11], it was reported that industrial processes gener-

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ated 6.1 tonnes of chloroanilines in 1985 were estimated to be released to the river Rhine. Long-term exposure of CIA may cause damage of spleen, liver and kidney [12]. Owing to its toxicity, it is included in the List II of European Union (EU) [13]. Since it is a suspected carcinogen and is highly toxic to aquatic life [14], developing strategies for pollution prevention and minimization is necessary. The possibility of 2-CIA decayed by UV has been proposed by USEPA [10] on both soil and water surfaces.

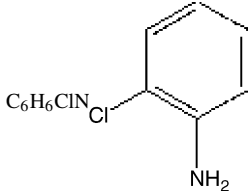
In this study, the UV-induced photodecomposition of 2-chloroaniline in H₂O₂-assisted TiO₂ suspensions was investigated. A wide range of H₂O₂ dosage in UV/TiO₂ system was studied, while the solution pH was investigated as well due to its variable nature in the industrial effluent. The pH effects in both UV/TiO₂ and UV/TiO₂/H₂O₂ were therefore discussed and the dark adsorption test was found to be useful for the understanding of the process.

2. Materials and methods

2.1. Chemical used

2-Chloroaniline (2-CIA) is used as the target pollutant and was purchased from Fluka AG (+99.5%). The physical properties of 2-CIA was listed in Table 1. The initial concentration of 2-CIA in all the experiments was fixed at 95 mmol/L. Titanium dioxide TiO₂-P25 obtained from Degussa was used in this study which contains about 80% anatase and 20% rutile with an average particle size of 30 nm and BET surface areas of 50 m²/g [16]. Hydrogen peroxide H₂O₂ (30%; AR Grade) was purchased from APS Chemicals Ltd and used as received. Acetonitrile in HPLC grade (Lab-scan) was used for the preparation of the mobile phase in the 2-CIA analysis without further purification. Solutions of 0.05 mol/L H₂SO₄ and 0.1 mol/L NaOH were used to adjust the initial pH level of mixed liquid to the predetermined levels.

Table 1
Physical properties of 2-CIA [15]

| | |
|-------------------------------|---|
| Formula |  |
| Molecular mass | 127.57 |
| Physical state | Clear amber liquid |
| Melting point (°C) | -1.94 |
| Boiling point (°C) | 208.84 |
| Density | d_4^{22} 1.2114 |
| Vapor pressure | 0.17 mmHg |
| Water solubility | Insoluble |
| Solvent solubility | Soluble in most organic solvents also in acids |
| pK _a | 2.66 |
| Maxima of absorption spectrum | 232 and 285 nm |

2.2. Experimental procedures

2.2.1. Dark adsorption test of TiO₂

The adsorption isotherm of 2-CIA was determined in the dark environment. Exact 75 mL of solution at different 2-CIA concentrations were stirred in the presence of 0.1 g/L TiO₂. Magnetic stirring was maintained for 20 h to establish the equilibrium of 2-CIA between TiO₂ particles and the aqueous phase. Each set of test was repeated by different solution pH at a temperature kept at 24 °C throughout the experiments. The remaining 2-CIA in the aqueous phase was passed through a 0.45 μm-pore filter membrane before LC quantification.

2.2.2. Photochemical reaction

The photocatalytic experiments were conducted in an RPR-200 Rayonet photochemical reactor purchased from the South New England Ultraviolet Company. Samples were irradiated by eight 300 nm phosphor-coated mercury lamps (240 W) with a total photon-intensity at 5.6×10^{-6} Einstein L⁻¹ s⁻¹ according to the manufacturer's specifications. Different TiO₂ dosages were added to a quartz cylinder containing 150 mL of 2-CIA solution. A magnetic stirrer was located at the base of reactor in order to maintain a consistent TiO₂ suspension throughout the reaction. A cooling fan was also installed at the reactor base such that the constant experimental temperature can be kept. Samples containing TiO₂ particles were collected by glass droppers at predetermined time and were filtered through the 0.45 μm membrane to ensure the TiO₂ particles did not enter the HPLC. Various initial pH levels of the solution were also studied to investigate the optimum condition on UV/TiO₂ system. For the study of H₂O₂ effect, known volume of sample was collected by pipette and transferred to the vial containing known amount of methanol to quench subsequent oxidation of H₂O₂ that remained in the samples.

2.3. Analytical methods

All the remaining 2-CIA after the reaction were analyzed by HPLC which comprises of a high pressure pump, a 20 μL-loop injector port, a Restek pinnacle octyl amine column in a dimension of 5 μm, 0.46 cm × 25 cm and UV-vis (Waters 486) detector. The selective absorbance of 2-CIA were set at 289 nm according to the strongest signal from UV-vis spectrophotometer. The mobile phase was a mixture of 60% acetonitrile and 40% distilled-deionized water and was delivered at a flow rate of 1.0 mL/min. The amount of 2-CIA in sample was quantified by comparing to its known standards correlated to the peak area.

Pseudo first-order reaction has been widely and successfully used for the description of organic decay in photoreaction [17]. The initial decay rates of the 2-CIA is therefore expressed as:

$$\frac{d[C]}{dt} = -k[C] \quad \text{or} \quad [C_t] = [C_0] \exp^{-kt} \quad (1)$$

where [C₀] is the initial concentration of 2-CIA, [C_t] the concentration at time *t*, and *k* (min⁻¹) is the pseudo-first-order decay rate constant.

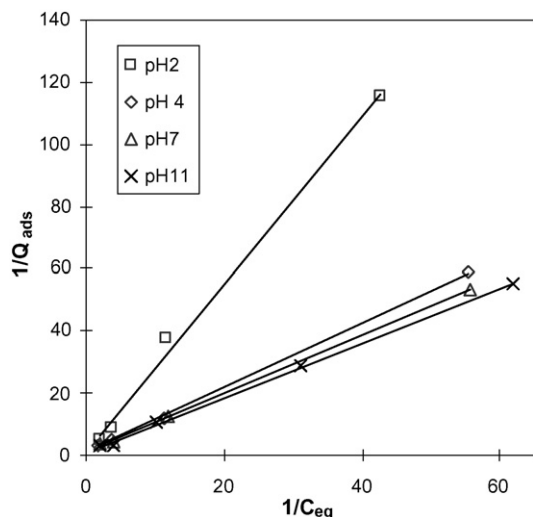


Fig. 1. Langmuir isotherm transformation ($1/Q_{\text{ads}}$ vs. $1/C_{\text{eq}}$).

3. Results and discussion

3.1. Dark adsorption of TiO_2

The adsorption behavior was characterized by the empirical Langmuir equation which has been used by various researchers for the sorption of variety of compounds. The model assumes uniform energies of adsorption onto the surface, no transmigration of adsorbate in the plane of the surface, and no interaction between the adsorption sites [18].

The Langmuir adsorption isotherm is given by Eq. (2):

$$\theta = \frac{Q_{\text{ads}}}{Q_{\text{max}}} = \frac{KC_{\text{eq}}}{1 + KC_{\text{eq}}} \quad (2)$$

where Q_{ads} (mmol/g) is the number of adsorbed molecules at the adsorption equilibrium, Q_{max} (mmol/g) the maximum adsorbable quantity, K (L/mmol) the Langmuir adsorption constant of 2-CIA on TiO_2 and C_{eq} is the concentration of 2-CIA at the adsorption equilibrium.

Eq. (2) could be further transformed into linear form as in Eq. (3) for data analysis:

$$\frac{1}{Q_{\text{ads}}} = \frac{1}{Q_{\text{max}}} + \frac{1}{Q_{\text{max}}KC_{\text{eq}}} \quad (3)$$

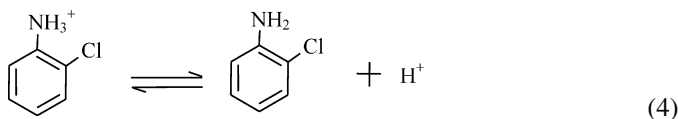
Fig. 1 shows a set of isotherm at different initial pH values. In this plot, the ordinate at the y-intercept is equal to the reciprocal of Q_{max} , whereas K can be calculated from the slope (slope = $1/Q_{\text{max}}K$). The figure presents a good correlation of the model with r^2 above 0.99 for all the tested pH. The adsorption behaviors were quite similar from neutral to basic pH levels except at extremely low pH level of 2, where a distinctive trend was observed. Judging from the calculated Q_{max} in Table 2, in general, the Q_{max} decreased from high to low pH suggesting the maximum active adsorption sites of TiO_2 are reduced as solution pH decreased. Therefore, 2-CIA molecules have lower affinity to be adsorbed by TiO_2 in strong acidic condition.

The ionization state of 2-CIA is another factor that should be involved in the discussion of adsorption characteristics. The

Table 2
Adsorption parameters of 2-CIA onto TiO_2 at different initial pH

| Initial pH | Slope | Intercept | r^2 | Q_{max} (mmol/g) | K (L/mmol) |
|------------|-------|-----------|--------|---------------------------|--------------|
| 2 | 2.690 | 1.374 | 0.9955 | 0.728 | 0.511 |
| 4 | 1.041 | 1.067 | 0.9995 | 0.937 | 1.026 |
| 7 | 0.944 | 1.168 | 0.9996 | 0.856 | 1.237 |
| 11 | 0.929 | 0.593 | 0.9989 | 1.076 | 1.566 |

properties of 2-CIA as showed in Table 1 indicated that cationic 2-CIA could dissociate one proton into its molecular form in the acidic medium as shown in Eq. (4).



It can be noticed that the cationic species is dominant when pH is below 2. Under these circumstances, the physicochemical properties of 2-CIA has significantly altered. The measurement of UV absorbance at 300 nm (the working wavelength) under different solution pHs (see Fig. 2) reveals that the domination of cationic species significantly reduced the absorbance of 2-CIA at low pH conditions which justifies our assumption. In addition, Wang [6] has reported that the point of zero surface charge of P25 TiO_2 is at pH level of 6.25. When the solution pH is below 6.25, the surface of TiO_2 particles is positively charged; on the other hand, when the pH is above 6.25, the TiO_2 surface carries negative charge.

By combining the TiO_2 surface charge and 2-CIA cationic properties in the acidic medium. The repulsive force between the two positively charged species (TiO_2 and 2-CIA) is the main reason to cause the low adsorption at low pH levels.

3.2. Effect of H_2O_2 in UV/ TiO_2 system

The effect of hydrogen peroxide assisted photocatalytic degradation of 2-CIA in 1.33 g/L TiO_2 suspension was inves-

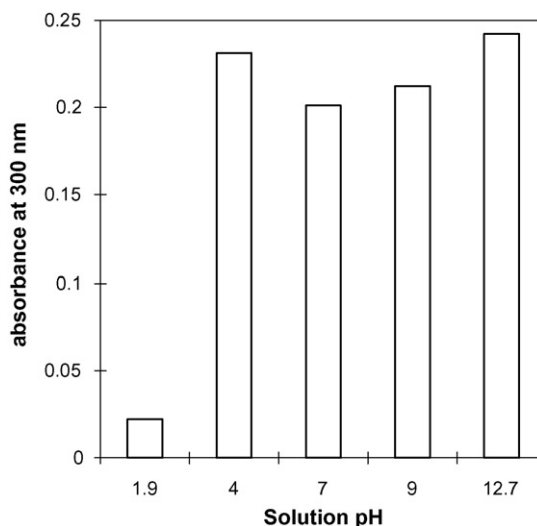


Fig. 2. The absorbance of 2-CIA at different pH ($[\text{2-CIA}] = 94.85 \text{ mmol/L}$; absorbance was measured at 300 nm).

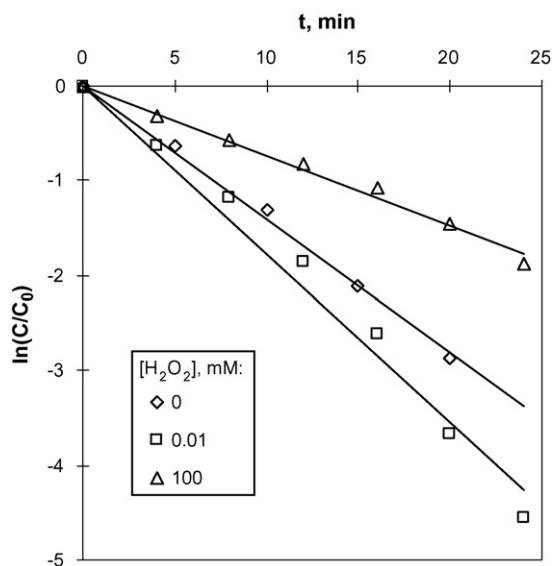


Fig. 3. First-order decay curve at different $[H_2O_2]$ in UV/TiO₂ system ($[TiO_2] = 1.33$ g/L; $[2-CIA]_0 = 94.85$ mmol/L; pH₀ were kept at 3.5 for all the experiment runs).

tigated in the wavelength of 300 nm. Fig. 3 compares the photodecay of 2-CIA at different H₂O₂ dosage, where the decay follows pseudo first-order kinetics. Comparing to the original UV/TiO₂ process, rate improvement was observed by simply adding 0.01 mmol/L H₂O₂ to the reaction, while about 26% rate retardation was observed when the addition of H₂O₂ was overdosed at 100 mmol/L.

Although the use of pseudo first-order kinetics can successfully describe the process without obvious error, it should be noted that the photodegradation rate was slightly increased as more 2-CIA was degraded in the solution, as revealed in the mild downward trend of curves in Fig. 3. The faster decay rate is possibly contributed by the relatively low 2-CIA concentration remaining in the reactor. It is reported that the amount of organic compounds is usually inversely related to the photodegradation rate [19]. The remaining portion of 2-CIA would undergo a faster degradation along with the reaction time. When using a high concentration of 2-CIA to undergo the process, the active sites on the TiO₂ particles were saturated by the excess of 2-CIA molecules therefore the interactions of UV photons with these active sites was inhibited. In addition, the intermediates must not so competitive to the activate reagent in the solution such as UV, H₂O₂, hydroxyl radical (generated from either UV/H₂O₂ or UV/TiO₂) and TiO₂ surface site.

Because the rate improvement and retardation were both observed in the UV/TiO₂/H₂O₂ process, a more comprehensive investigation by varying the H₂O₂ dosages was shown in Fig. 4. The optimum concentration of H₂O₂ was found to be 0.01 mmol/L in the UV/TiO₂/H₂O₂ process with a decay rate of 0.178 min⁻¹. Further addition of H₂O₂ from 10 to 100 mmol/L will lower the system efficiency in degradation of 2-CIA these elevated H₂O₂ concentrations, the photodecay efficiencies were worse than the original photocatalysis process of UV/TiO₂.

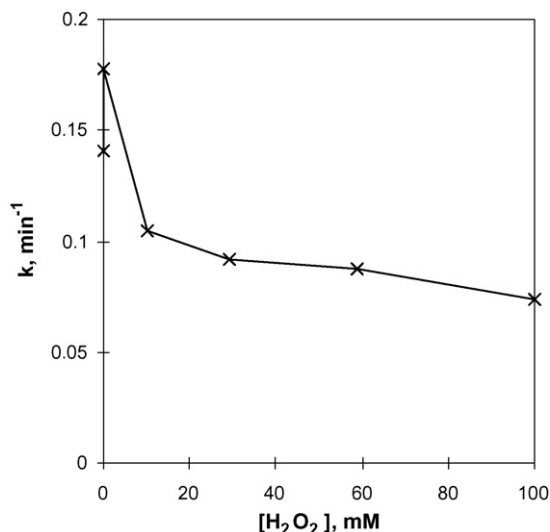


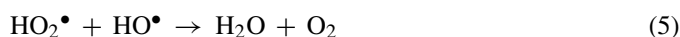
Fig. 4. Variation of reaction rate in the range of $[H_2O_2]$ dose from 0 to 100 mmol/L ($[TiO_2] = 1.33$ g/L; $[2-CIA]_0 = 94.85$ mmol/L).

3.2.1. Low H₂O₂ dosage

When TiO₂ under the excitation of 300 nm UV light, photoinduced electrons (e⁻) and positive holes (h⁺) are generated. The photoinduced electrons (e⁻) and positive holes (h⁺) can further produce reactive radicals. The photooxidation of OH⁻ by highly oxidizing positive hole generates free hydroxyl radical (HO•), which is the dominant oxidizing species contributing to the mineralization process due to TiO₂ photocatalyst [20]. When small amount of H₂O₂ is introduced into the UV/TiO₂ system, rate enhancement is likely due to the increased generation of hydroxyl radicals by UV/H₂O₂. Also, H₂O₂, being a stronger electron acceptor than oxygen, reacts with the electrons which are emitted from valence band of the photocatalyst to generate HO• and OH⁻ (instead of generating a weaker •O₂⁻ radical). If these reactive species, such as oxygen and H₂O₂, are not present nearby the surface of the TiO₂, the electron hole pair will recombine and the energy absorbed will be dissipated as heat. Therefore, at low dosage of H₂O₂, the H₂O₂ is capable of suppressing the electron hole pair from recombination—an undesirable process in the photocatalytic process [21,22].

3.2.2. Excess H₂O₂ dosage

However, when H₂O₂ dosage is overdosed (higher than 0.01 mmol/L in this study), the photodecay rate retarded due to the presence of excess H₂O₂. The excess H₂O₂ molecules scavenge the valuable HO• that are generated by either the direct photolysis of H₂O₂ or the photooxidation of OH⁻ by h⁺ and generate a much weaker peroxy radical, HO₂•. As shown in Eq. (5), the peroxy radical can further react with the remaining strong HO• to form ineffective oxygen and water. In addition, the photocatalytic oxidation could be inhibited when the excess H₂O₂ reacts with oxidative h⁺ on catalyst surface (Eq. (6)), where the overall oxidation capabilities of the system are significantly reduced by generating oxygen [17].



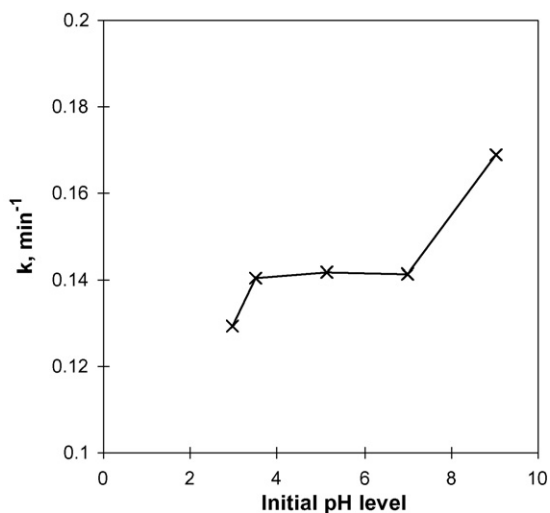


Fig. 5. Comparison of first-ordered kinetic at different initial pH levels ($[\text{TiO}_2] = 1.33 \text{ g/L}$; $[\text{2-CIA}]_0 = 94.85 \text{ mol/L}$; sampling time = 25 min).



3.3. Solution pH

3.3.1. UV + TiO₂

The effect of initial pH level to the photocatalytic degrade of 2-CIA in the UV/TiO₂ process was investigated by the adjustment the solution with NaOH and H₂SO₄. The results were shown in Fig. 5, where the photocatalytic degradations rates were found to be dependent on the initial pH. At relatively higher and lower pH levels of 9.02 and 2.98, the degradation rate of 2-CIA was highest and lowest at 0.169 and 0.128 min⁻¹, respectively. The difference of the two extreme rate constants was about 31%. In alkaline medium, high level of hydroxide ions (OH⁻) induced the generation of hydroxyl free radicals (HO[•]), which came from the photooxidation of OH⁻ by holes forming on the TiO₂ surface. Since hydroxyl free radical is the dominant oxidizing species in the photocatalytic process, the photodecay of 2-CIA is therefore accelerated at higher solution pH. This observation has been justified by Ollis [22] and Wong and Chu [17].

The charge effect of 2-CIA and TiO₂ can partly cause the lower degradation rate at lower solution pH. As discussed previously, the TiO₂ particle surface was positively charged at acidic solution (below 6.25). The collision of the charged 2-CIA cation and TiO₂ will be significantly reduced when the solution pH approaches to 2.66 or lower. The electrostatic repulsion occurring between the TiO₂ surface and 2-CIA cation tends to inhibit the coupling effect and therefore reduce the reaction rate in the acidic condition.

The anion Cl⁻ was identified as one of the end products during the photodecay process of 2-CIA [8]. When the pH level of the aqueous media was lower than 6.25, the generated Cl⁻ may decrease the photodecay rate of the TiO₂. It is because the accumulation of anions nearby the positively charged TiO₂ particles may hinder the access of other target compounds to the surface. Therefore, the adsorption of chloride on the positive-

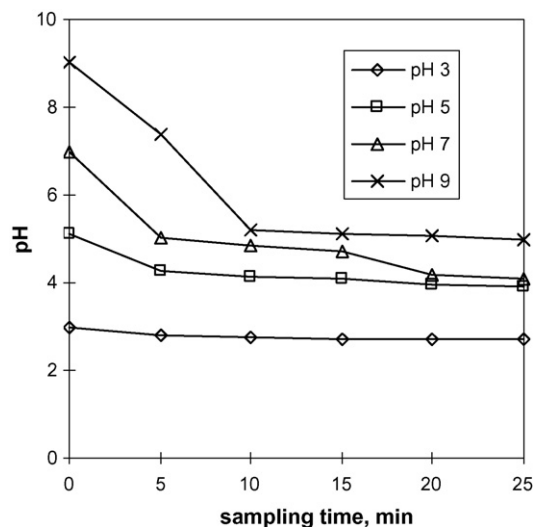


Fig. 6. Variation of pH throughout the photodecay of 2-CIA in TiO₂.

charged TiO₂ surface could be another reason resulting the lower decay rate.

The solution pH during the reaction was monitored and recorded in Fig. 6. Generally, a drop of pH was observed for all the pre-selected pH level. The drop of pH is likely due to the generation of low molecular-weight organic acids in the oxidation process such as formic acid as the end-products during 2-CIA degradation [23].

3.3.2. UV + TiO₂ + H₂O₂

The pH effect in UV/TiO₂/H₂O₂ system was also studied. The dosage of TiO₂ and H₂O₂ were fixed at 1.33 g/L and 0.01 mmol/L, respectively. In UV/TiO₂ process, photodecay rate generally increased from low to high pH. It was interesting to note that this pattern has been changed after incorporating H₂O₂ to the UV/TiO₂. From Fig. 7, the highest decay rate was observed at pH 3.76, while increase of pH further lower the

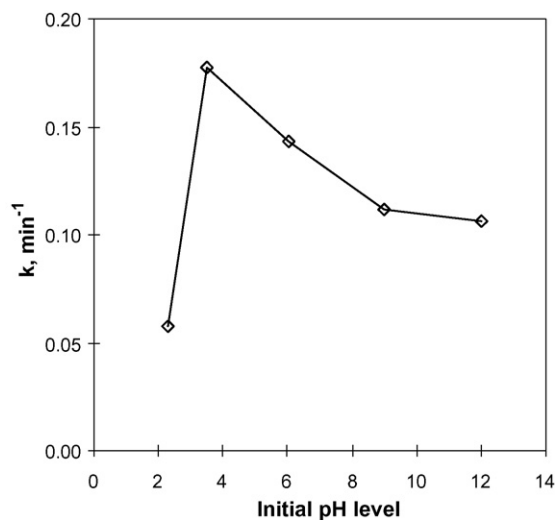


Fig. 7. Comparison of first-ordered kinetics on the UV/TiO₂/H₂O₂ system ($[\text{TiO}_2] = 1.33 \text{ g/L}$; $[\text{2-CIA}]_0 = 94.85 \text{ mmol/L}$; $[\text{H}_2\text{O}_2] = 0.01 \text{ mmol/L}$; sampling time = 20 min).

degradation rates. The lowest photodecay rate in UV/TiO₂/H₂O₂ process was found again at extremely low pH level around 2 due to the same reasons as discussed beforehand. The reason for lower performance of the UV/TiO₂/H₂O₂ at higher pH levels is likely because the special property of H₂O₂. In alkaline medium, the H₂O₂ becomes highly unstable and self-decomposition of H₂O₂ occurs, which is strongly dependent on pH [24]. The self-decomposition will rapidly break down the H₂O₂ molecules into water and oxygen (see Eq. (7)) and makes the molecule losses its characteristics as oxidant and most importantly the source of hydroxyl radicals.



The reaction rate of 2-ClA in UV/TiO₂/H₂O₂ process was therefore reduced significantly at higher pH levels.

4. Conclusion

The photodecay of 2-ClA is a feasible clean-up method by the use of TiO₂ and H₂O₂. Care should be taken when it is put into practice as the working system depends very much on the dosage of oxidant and the solution pH. Little amount of H₂O₂ (mmol/L) is good enough to speed up the reaction rate while over-dosage would lead to the formation of less reactive hyperoxyl radical and retarded the degradation. Also, the charge distribution of TiO₂ and 2-ClA governs the degradability in various solution pH. UV/TiO₂ system is poorly functioned at low pH environment, it is mainly due to the strong repulsive force between the charged TiO₂ surface and the 2-ClA cation as justified in the dark absorption test. However, slower decay of 2-ClA was discovered at high pH in the UV/TiO₂/H₂O₂ system. It is because H₂O₂ could undergo self-decomposition and reduce the generation of HO• at this pH range. Therefore, the alkali working environment should be avoided when H₂O₂ is used.

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References

- [1] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. C: Photochem. Rev.* 1 (2000) 1–21.
- [2] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, *Prog. Solid State Chem.* 32 (2004) 33–177.
- [3] Y.B. Wang, C.S. Hong, Effect of hydrogen peroxide, periodate and persulfate on photocatalysis of 2-chlorobiphenyl in aqueous TiO₂ suspensions, *Water Res.* 33 (1999) 2031–2036.
- [4] M.C. Lu, J.N. Chen, K.T. Chang, Effect of adsorbents coated with titanium dioxide on the photocatalytic degradation of propoxur, *Chemosphere* 38 (3) (1999) 617–627.
- [5] R. Dillert, I. Fornefett, U. Siebers, D.J. Bahnemann, Photocatalytic degradation of trinitrotoluene and trinitrobenzene: influence of hydrogen peroxide, *J. Photochem. Photobiol. A: Chem.* 94 (1996) 231.
- [6] C.C. Wang, The Photodegradation of 2-Chlorophenol in Aqueous TiO₂ Suspensions: The Effect of Hydrogen Peroxide Addition. M.Sc. Thesis, Michigan State University, Michigan, 1994, pp. 4–9.
- [7] M.C. Lu, G.D. Roam, J.N. Chen, C.P. Huang, Factors affecting the photocatalytic degradation of dichlorovos over titanium dioxide supported on glass, *J. Photochem. Photobiol. A: Chem.* 76 (1993) 103–110.
- [8] J.F. Jen, C.T. Chang, C. Yang, On-line microdialysis-high-performance liquid chromatographic determination of aniline and 2-chloroiline in polymer industrial wastewater, *J. Chromatogr. A* 930 (2001) 119–125.
- [9] R.D. Voyksner, R. Straub, J.T. Keever, H.S. Freeman, W.N. Hsu, Determination of aromatic amines originating from azo dyes by chemical reduction combined with liquid chromatography/mass spectrometry, *Environ. Sci. Technol.* 27 (1993) 1665.
- [10] USEPA, Health and Environmental Effects Document for Chloroanilines ECAO-CIN-G003 (Final Draft), 1987, pp. 7, 12, 13, and 15.
- [11] IAWR, Rheinbericht 1996–1998. Julich, Internationale Arbeitsgemeinschaft der Wasserwerke im Rheineinzugsgebiet, 1998.
- [12] R. Kuhn, M. Pattard, K.D. Pernak, A. Winter, Results of the harmful effects of selected water pollutants (anilines, phenols, aliphatic compounds) to *Daphnia magna*, *Water Res.* 23 (1989) 495–499.
- [13] 76/464/EEC, Council directive of May 4, 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the community. Official Journal no. L129, 18/05/1976 (1976) p. 23.
- [14] S. Laha, R.G. Luthy, Oxidation of aniline and other primary aromatic amines by manganese dioxide, *Environ. Sci. Technol.* 24 (1990) 363–373.
- [15] The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals, 10th ed., Merck & Co. Inc, 1983, p. 2088.
- [16] D. Beydoun, H. Tse, R. Amal, G. Low, S. McEvoy, Effect of copper (II) on the photocatalytic degradation of sucrose, *J. Mol. Catal. A: Chem.* 177 (2002) 265–272.
- [17] C.C. Wong, W. Chu, The direct photolysis and photocatalytic degradation of alachlor at different TiO₂ and UV sources, *Chemosphere* 50 (2003) 981–987.
- [18] I. Bouzaida, C. Ferronato, J.M. Chovelon, M.E. Rammah, J.M. Herrmann, Heterogeneous photocatalytic degradation of the anthraquinonic dye, acid blue 25 (AB25): a kinetic approach, *J. Photochem. Photobiol. A: Chem.* 168 (2004) 23–30.
- [19] S. Irmak, E. Kusvuran, O. Erbatur, Degradation of 4-Chloro-2-methylphenol in aqueous solution by UV irradiation in the presence of titanium dioxide, *Appl. Catal. B: Environ.* 54 (2004) 85–91.
- [20] W.Z. Tang, UV/titanium dioxide, in: *Physicochemical Treatment of Hazardous Wastes*, Lewis Publishers, 2004, p. 322, Chapter 9.
- [21] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic water contaminants: mechanism involving hydroxyl radical attack, *J. Catal.* 122 (1990) 192–478.
- [22] D.F. Ollis, Contaminant degradation in water, *Environ. Sci. Technol.* 19 (1985) 480–484.
- [23] M. Styliadi, D.I. Kondarides, X.E. Verykios, Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous TiO₂ suspensions, *Appl. Catal. B: Environ.* 40 (2003) 271–286.
- [24] C.Y. Chan, S. Tao, R. Dawson, P.K. Wong, Treatment of atrazine by integrating photocatalytic and biological processes, *Environ. Pollut.* 131 (2004) 45–54.