Chemical Engineering Journal 248 (2014) 273–279

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Photo-oxidation of an endocrine disrupting chemical o-chloroaniline with the assistance of TiO_2 and iodate: Reaction parameters and kinetic models

Meijuan Chen, W. Chu *

Department of Civil and Environmental Engineering, Research Centre for Urban Environmental Technology and Management, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

HIGHLIGHTS

- The UV/TiO_2/KIO_3 system is efficient in photo-oxidation of o-ClA.
- The KIO_3 has a significant influence, which is more critical than TiO_2.
- The decay follows two stage pseudo first-order kinetics with fast k_1 and slow k_2.
- Kinetic models are successfully derived in terms of $[KIO_3]_0$, $[TiO_2]_0$ and pH levels.
- Kinetic models offer efficient approaches to predict *o*-ClA decay in this system.

ARTICLE INFO

Article history:
Received 21 November 2013
Received in revised form 6 February 2014
Accepted 11 March 2014
Available online 20 March 2014

Keywords:
Photo-oxidation
o-Chloroaniline
TiO_2
Iodate
Kinetic models

ABSTRACT

An efficient photo-oxidation system was introduced to decay a typical endocrine disrupting chemical *o*-chloroaniline (o-ClA) by using UV light with the assistant of TiO_2 and IO_3^- (UV/TiO_2/KIO_3 system). The o-ClA decay in UV/TiO_2/KIO_3 system is much superior to sole UV and UV/TiO_2. For depth evaluating the system, the effect of TiO_2 dosages, KIO_3 dosages, and initial pH levels ($[TiO_2]_0$, $[KIO_3]_0$ and pH_0) were investigated and optimized. The optimum o-ClA decay was achieved at $[KIO_3]_0$ of 66.7 mg/L and pH_0 of 7.09. The kinetics analysis showed that the o-ClA decay followed a two-stage pseudo first-order, and the decay rate constants at both stages (k_1 and k_2) are significantly influenced by $[TiO_2]_0$, $[KIO_3]_0$ and pH_0. After data analysis, both $1/k_1$ and $1/k_2$ were found linearly correlated to $[KIO_3]_0$, pH_0 and $1/[TiO_2]_0$. Mathematic models were therefore derived for predicting o-ClA decay in terms of $[TiO_2]_0$, $[KIO_3]_0$ and pH_0. Moreover, the proposed models offered efficient approaches to predict the *o*-ClA decay in UV/TiO_2/KIO_3 system under various conditions.

1. Introduction

O-chloroaniline (*o*-ClA) as one of the most important amine has been widely used in the manufacture of dye, petroleum solvents, rubber, and fungicides [1]. The widespread application of *o*-ClA has undoubtedly resulted in its ubiquity in industrial effluents, sludge and agriculture pollutants [2]. It was reported that a maximum of 0.56 mg L^{-1} of *o*-ClA was detected in the country's coastal waters of Japan in 1990 [3]. Long-term exposure of *o*-ClA may cause damage of spleen, liver, and kidney [4]. Therefore, *o*-ClA is considered by the United States Environmental Protection Agency as an indicative toxic chemical to marine organisms [5]. That is why there is a need to develop rapid and effective methods for the degradation of *o*-ClA either to less harmful compounds or to their complete mineralization.

The system of combining UV light and TiO_2 (UV/TiO_2) has received increasing attentions in organic pollutants' degradation due to its low cost, chemically stability, and low toxicity to humans and environment [6]. The UV/TiO_2 system is mainly initiated by hydroxyl radical ($^{\cdot}OH$), which is derived from photogenerated holes (h^+_{VB}) by reacting with water [7]. However, a large amount of h^+_{VB} is inactive in yielding of $^{\cdot}OH$ radicals because it recombines with photogenerated electrons (e^-) directly, which restrains the generation of $^{\cdot}OH$ radicals and thereby the degradation efficiency of organic pollutants [8].

Inorganic oxidants however have been proposed to increase quantum efficiency of UV/TiO_2 system partially by decreasing

---

* Corresponding author. Tel.: +852 2766 6075; fax: +852 2334 6389.
E-mail address: cewchu@polyu.edu.hk (W. Chu).

http://dx.doi.org/10.1016/j.cej.2014.03.038
1385-8947/

electron–hole recombination rate through scavenging conduction-band electrons at the surface of TiO_2 and partially by augmenting the UV/TiO_2 process through photochemical oxidations in the bulk solution [9]. Inorganic oxidants such as H_2O_2, IO_4^- and $S_2O_8^{2-}$ were reported to have a significant rate-enhancing effect on TiO_2 photocatalysis of organic pollutants [7,10,11]. However, the dosage of inorganic oxidants must be accurately examined before application because some of them may not have rate-increasing effect on the degradation of organic pollutants [12]; and some of them may even retard the degradation under specific conditions if the dosages are designed improperly [13]. On the other hand, the dosage of TiO_2 could not unlimitedly be increased to improve the efficiency of photodecay [14]. Researchers have reported that beyond the optimal TiO_2 dosage, the photodecay rates would be retarded due to the light scattering effect by the excess TiO_2 dispersion and the inherent rapid recombination (i.e. destruction) of electron–hole pairs [15]. Besides, the pH level has been reported to show a great influence on the decay rate and the optimal pH level was variable when process or ‘pollutants changed [16]. Although a few studies have been investigated on pollutants' degradation by the influence of inorganic oxidants dosages, TiO_2 dosages, and pH levels, the information of their contributions on reaction kinetics and predictive kinetic models remains limited.

Therefore, in this study, the objective is to investigate the reaction kinetics of the photo-oxidation system in the presence of TiO_2 and IO_3^- with the irradiation of 300 nm UV light. The *o*-ClA was chosen as target compound. The degradation of *o*-ClA was carried out on the variation of dosages of TiO_2 and KIO_3, and pH levels. Reaction kinetics and rate constants were analyzed and determined for each specified condition. Furthermore, mathematic models were derived for the prediction of *o*-ClA degradation in terms of the dosages of KIO_3 and TiO_2, as well as initial pH levels.

2. Methodologies

2.1. Materials

All chemicals were of analytic reagent grade and used as received without further purification. Titanium dioxide (TiO_2) nanoparticles of Degussa P25 (80% anatase and 20% rutile in weight) was purchased from Degussa Company (Germany) with a surface area of 50 m^2/g and primary particle size of 30 nm. The probe *o*-ClA (C_6H_6ClN) was purchased from Fluka (USA). The inorganic oxidant of potassium iodate (KIO_3) was obtained from International Laboratory USA. Other chemicals such as sulfate acid (H_2SO_4) and sodium hydroxide (NaOH) for pH adjustment were obtained from Sigma-Aldrich Inc. USA. All solvents were of HPLC grade. A resistivity of 18.2 MΩ of distilled-deionized water was used for preparing mobile phase and stock solution, generated by a Bamstead NANOpure water treatment system (Thermo Fisher Scientific Inc., USA).

2.2. Experiments

The *o*-ClA decay was conducted in a Rayonet RPR-200 photochemical reactor manufactured by the Southern New England Ultraviolet Company. Eight phosphor-coated low-pressure mercury lamps with irradiation wavelength of 300 nm were installed in the photochemical reactor and showed a total photon intensity of 6.64×10^{-3} Einstein L^{-1} min^{-1}. A predetermined amount of TiO_2 was dispensed into 150 mL of *o*-ClA solution in a 300 mL quartz cylinder. To ensure a thorough mixing, mechanical stirring was supplied continuously before and during the reaction. The pH level of the solution was adjusted by either 0.1 M H_2SO_4 or 0.1 M NaOH. The degradation was started by exposing the well dispersed suspension (containing *o*-ClA, TiO_2 and KIO_3) to the pre-heated light source. Samples were withdrawn at a predetermined reaction interval and were filtered through a 0.45 μm membrane to keep the TiO_2 free from the solution before quantification. All experiments were carried out at room temperature (23 ± 2 °C) in duplicate. The standard deviation values of [o-ClA] were all below 10%.

2.3. Analytical protocols

The remaining *o*-ClA was analyzed by High Performance Liquid Chromatography (HPLC). The HPLC system was comprised of a 515 HPLC pump, a 20-μL-loop injector port, an Econosphere C18 (5 μm, 0.46 × 25 cm) column, and a UV detector. The absorption wavelength was set at the maximum adsorption of *o*-ClA as 285 nm. A mixture of 60% acetonitrile and 40% water was used as the mobile phase running at a flow rate of 1 mL/min. Adequate degassing of the mobile phase prior to injection was performed to inhibit the generation of gas bubbles during the analysis.

3. Results and discussion

3.1. The decay of o-ClA in the UV/TiO_2/KIO_3 system

The degradations of *o*-ClA in three systems, i.e. sole UV photodecay, UV/TiO_2 and UV/TiO_2/KIO_3 were compared in Fig. 1. In general, the decay of o-ClA in all three systems followed pseudo first-order kinetics. The decay rate (*k*) was determined to be 0.011, 0.0312, and 0.3076 min^{-1} for the system of sole UV, UV/TiO_2, and UV/TiO_2/KIO_3, respectively. As compared to sole UV, the UV/TiO_2 system improved the o-ClA decay due to the TiO_2 gives birth to an efficient $^{\cdot}OH$ radicals under the irradiation of UV lights. Moreover, the decay rate was further improved in the UV/TiO_2/KIO_3 system. This improving effect can be rationalized by the reason that the IO_3^- can defer the recombination of e^- and h_{VB}^+ through the capture of e^- ejected from TiO_2 surface as shown in Eq. (1) [17].

$$IO_3^- + 3H_2O + 6e^- \rightarrow I^- + 6OH^- \qquad (1)$$

After dosing KIO_3, the number of available h_{VB}^+ is increased and their longer lifetime would be beneficial to the degradation of the o-ClA. In addition, other than $^{\cdot}OH$ radicals, additional reactive radical intermediates (e.g., $IO_3^{\cdot}$) that generated during the application of IO_3^- [17,18] could offer extra pathways to enhance the degradation of *o*-ClA.

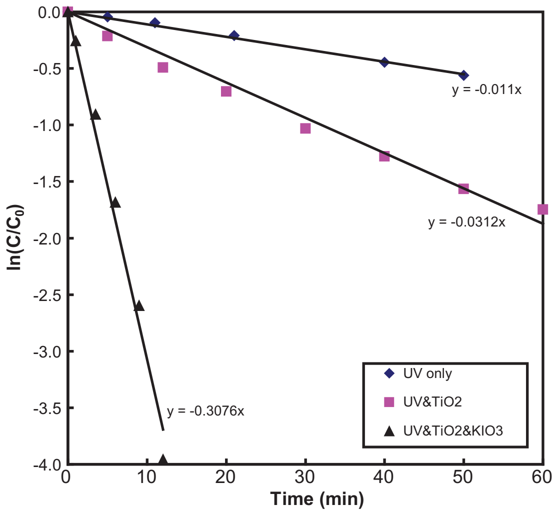

Fig. 1. Degradation of *o*-ClA in different systems. (Notes: $[o\text{-ClA}]_0$ = 40.0 mg/L, $[TiO_2]_0$ = 100.0 mg/L, $[KIO_3]_0$ = 66.7 mg/L, and pH = 7.09).