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Electrochemical process combined with UV light irradiation for synergistic degradation of ammonia in chloride-containing solutions

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ABSTRACT

An electrochemical process combined with ultraviolet light irradiation (UPE) using non-photoactive dimensionally stable anodes (DSAs) like RuO₂/Ti and IrO₂/Ti in the presence of chlorides was investigated for ammonia degradation. In this process, the *in situ* electro-generated active chlorine and *in situ* photogenerated chlorine radicals were responsible for the high efficiency of ammonia degradation. More than 97% of ammonia was converted to nitrogen and a significantly synergistic effect was confirmed. Compared with the single electrochemical (E) and photochemical (P) process, the degradation rates of ammonia and the average current efficiencies (ACEs) of the UPE process increased by 1.5 and 1.7 times using RuO₂/Ti and IrO₂/Ti electrodes, respectively. On the basis of the linear voltammograms, Electrochemical Impedance Spectra (EIS), UV-vis spectra, Electron Spin Resonance (ESR) analysis and a series of experiments designed, the synergistic mechanism was investigated. In addition, this unique process succeeded in transferring the reaction from the electrode surface to the bulk of the solution compared with the conventional photo-electrocatalytic (PEC) process. The loss of chloride decreased from 21.0% to 7.2% and the recycle of chloride was accelerated in the UPE process. Finally the effects of initial pH, current density and ammonia-nitrogen concentration were discussed. Results indicated that pH and ammonia concentration exerted little influences on the degradation rates and current density was the “rate-determining” factor.

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1. Introduction

Ammonia, as one of the major nitrogen-containing pollutants, is a source of nutrients that may accelerate the eutrophication and algal growth in natural water (Feng et al., 2003; Nemoto et al., 2006). The abatement of ammonia in wastewater discharged has become a prime issue of environmental control. High concentrations of ammonia in wastewater effluents deplete dissolved oxygen, reduce chlorine disinfection

efficiency, and exhibit acute toxicity to aquatic life. There are several methods for ammonia removal from water and wastewater, including biological process (Kalyuzhnyi et al., 2006), ammonia stripping (Bonmati and Flotats, 2003), ion exchange (Lin and Wu, 1996), breakpoint chlorination (Thomas et al., 1972), photocatalysis (Zhu et al., 2005) and electrochemical process (Chiang et al., 1995; Kim et al., 2006; Wang et al., 2006).

Electrochemical method for the advanced treatment of ammonia in the wastewater has attracted a great deal of

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attention because of its advantages such as a minimal generation of secondary waste, easy operation, remote control, etc. In general, ammonia can be transformed to other nitrogen forms electrochemically by direct anodic oxidation or indirect oxidation during the electrochemical process. In a direct anodic oxidation process, ammonia is firstly adsorbed on the anode surface and then transformed by the anodic electron transfer reaction. The overall electrochemical reaction of ammonia to nitrogen is generally considered to be a three-electron exchange reaction (Lin and Wu, 1997; Kim et al., 2006):

In an indirect oxidation process, strong oxidants are firstly produced in the bulk of solution via electrochemical reactions and then these oxidants destroy the ammonia by oxidation reactions. For example, in the chloride-containing wastewater, the electrogenerated molecular chlorine is hydrolyzed to form hypochlorous acid and hypochlorite ion:

The electrogenerated active chlorine, including hypochlorite ion and hypochlorous acid, is the main oxidant for ammonia degradation (Chiang et al., 1995; Vanlangendonck et al., 2005).

On the other hand, UV disinfection and chlorination are two of the most common methods in water/wastewater applications. In many UV disinfection installations, free chlorine is present in the water as it passes through UV reactors. A major advantage of this combined process is that the UV light can inactivate protozoa that are difficult to treat by chlorination (Feng et al., 2007). From another point of view, free chlorine can also increase the UV absorbance of water thereby decreasing the UV disinfection ability (Ormeci et al., 2005). However, the free chlorine itself can be affected significantly by UV light. Some researchers (Guo, 1993; Mollna et al., 1980; Nowell and Hoigne, 1992a,b) have reported that hypochlorous acid can dissociate to hydroxyl radical ($\cdot\text{OH}$) and chlorine radical ($\cdot\text{Cl}$) upon absorption of UV photon in the 200–400 nm regions:

Compared to the UV/ H_2O_2 process, the direct photolysis of aqueous free chlorine (UV/HClO) produces $\cdot\text{OH}$ more efficiently ($1.4 > 1.0 \text{ mol E s}^{-1}$) thereby producing $\cdot\text{Cl}$ simultaneously (Michael and Karl, 2007). Thus, it is promising to treat water and wastewater with the aid of these radicals.

In this work, we developed a unique photoelectrochemical process for the treatment of ammonia wastewater containing chloride ions by combined use of electrogenerated active chlorine and photogenerated active radicals as oxidants. To the best of our knowledge, no reports regarding ammonia degradation with this method were found. Herein, common DSA electrodes, including RuO_2/Ti and IrO_2/Ti , were selected as anodes and UV irradiation was introduced into the electrochemical process to treat ammonia wastewater containing abundant chloride ions. The degradation rates of ammonia were significantly accelerated, suggesting an obvious

synergistic effect, which was further investigated in detail. Moreover, the control parameters were investigated and the results were expected to provide basic information for the application of this novel UPE process.

2. Experimental

2.1. Experimental setup

Chemical, photochemical, electrochemical and unique photo-electrochemical processes were carried out in a 600 mL, single-compartment, air-tight glass cell with a 3.5 cm-diameter quartz tube placed in the center and used as the UV bulb housing. The outside of the glass cell was covered with a circulating water system in order to keep the temperature constant at 25 °C. The experimental setup was sketched in Fig. 1. The reactor was controlled by a DC power supply source AMRFL LPS302A (Dahua instrument corporation of Beijing). The RuO_2/Ti or IrO_2/Ti mesh (100 mm × 60 mm × 2 mm, Hengli Ti Corporation of Beijing) was selected as anode with an apparent surface area of 60 cm², and Ti mesh with the same solid surface area was selected as cathode. The UV irradiation was provided by a 10 W low-pressure mercury lamp (253.7 nm) and the light intensity was 1.36 mW cm^{−2} as measured with an UV radiometer (Light and Electric instruments Factory of Beijing Normal University). The ammonia water was simulated with distilled water and $\text{NH}_4\text{Cl}/\text{NaCl}$ and the concentration of Cl^- was controlled at 5300 mg L^{−1}. In these processes, 3 mL of solution was taken regularly from the reactor cell for the analysis of NH_4^+ , NO_3^- , NO_2^- and TN. Simultaneously, the gas was drawn out and collected by a special gas bag (Sciequip Co., China) to detect nitrogen-containing gases.

Fig. 1 – Schematic diagram of lab scale batch mode UPE reactor. (1) Reactor; (2) Ti mesh cathode; (3) RuO_2/Ti or IrO_2/Ti anode; (4) low-pressure mercury lamp; (5) quartz tube; (6) magnetic stirrer; (7) DC power supply; (8) thermometer; (9) temperature control device; (10) pump; (11) gas outlet; and (12) sampling point.

2.2. Analytical methods

The values of pH were adjusted with 1 M NaOH or 0.5 M H₂SO₄ using an Orion 720APLUS Benchtop meter (Thermo Orion Co., USA). Desired samples taken from the sampling point were filtered through a 0.45 µm membrane. The concentrations of NH₃-N, total nitrogen (TN), NO₃-N, NO₂-N and active chlorine were colorimetrically estimated according to the standard methods (APHA, 2005) by using an U-3010 UV-vis spectrophotometer (Hitachi Co., Japan). When total Cl was to measure, enough Na₂SO₃ was firstly added into the water samples and thereby all forms of chlorine (including active chlorine, chloramines, etc) were transferred into Cl⁻, and the concentration of Cl⁻ was determined by ion chromatograph (Metrohm 861, Switzerland). The concentration of NO_x gases were analyzed by a gas chromatography (HP5890 equipped with an electron capture detector, Agilent Co., USA) using a Porapak Q column (Wang et al., 2006). Electrochemical measurements were carried out in a conventional three-electrode cell using an EG&G model 263A potentiostat (Princeton Co., USA). A Pt wire was used as a counter electrode, whereas a saturated calomel electrode (SCE) separated by a salt bridge was used as a reference electrode (All the potentials were vs. SCE). A Bruker ESP 300E ESR spectrometer (Bruker Co., Switzerland) was applied to determine hydroxyl radicals generated in the processes. The •OH radicals were very short-lived and very reactive, so a nitron spin-trapping reagent 5,5'-dimethyl-1-pyrroline-N-oxide (DMPO), which converted the short-lived radicals into a relatively long-lived free radical products, was used to make the •OH radicals form a more stable spin adduct with the DMPO in the solution (Xiao et al., 2008).

3. Results and discussion

3.1. Electrochemical characters

It was well known that the electro-oxidation reaction may take place if the applied potential is higher than its oxidation-reduction potential (ORP) (Zhao et al., 2007). In order to evaluate the electrolytic reaction characteristics of NH₃ or NH₄⁺ at the RuO₂/Ti electrode, the voltammograms in different aqueous solutions containing SO₄²⁻ or Cl⁻ at different pH were measured and the results were shown in Fig. 2. It was known that ammonia existed in the form of NH₄⁺ under acidic conditions and in the form of NH₃ under alkaline conditions. In the case of SO₄²⁻-containing system (Fig. 2a), a rapidly rising current density was observed from ca. 0.7 V in ammonia-containing solution at pH 12, which was due to the oxidation of the adsorbed NH₃ to N₂ (Kim et al., 2006). While at pH 5.7, a rapid rise in current density did not appear until about 1.1 V, which resulted from the outbreak of oxygen. These results indicated that direct electrochemical oxidation had more significant effect on NH₃ than NH₄⁺, which might be caused by the selective adsorption of NH₃ onto the surface of electrode. In the case of Cl⁻-containing system (Fig. 2b), in the voltammogram measured at pH 12 without ammonia, a peak at ca. 0.9 V before O₂ evolution was observed, which was attributed to the chlorination current of

Fig. 2 – Electrochemical characters of ammonia in SO₄²⁻ and Cl⁻ containing systems on RuO₂/Ti electrode (scan rate = 50 mV s⁻¹).

adsorbed Cl⁻ on the surface of RuO₂/Ti electrode (Kim et al., 2005, 2006). Comparatively, a rapid increase of current density was also observed from ca. 0.7 V in the presence of ammonia at pH 12, suggesting that NH₃ preferred to being adsorbed on the surface of RuO₂/Ti electrode than Cl⁻. As a result, it could be concluded that NH₃ competed with Cl⁻ and OH⁻ for adsorption sites on the surface of electrode and NH₃ dominated in the competition (Kim et al., 2005). The voltammogram at pH 5.7 in the presence of ammonia was similar to that obtained under the same acidity in the absence of ammonia. It was also proved that NH₄⁺ could not be oxidized by direct electrochemical oxidation. Therefore, we could conclude that only molecular form of ammonia (NH₃) could be directly electro-oxidized. Thus, to avoid the direct oxidation and investigate the effect of active chlorine conveniently, the experiments were performed in acid solutions.

3.2. Comparative study on degradation of ammonia in several processes

Fig. 3a showed the NH₃-N degradation curves in the P, E and UPE processes with both RuO₂/Ti and IrO₂/Ti electrodes at pH

5.7. Single P process in the presence of RuO₂/Ti or IrO₂/Ti electrodes contributed no effect on the degradation of NH₄⁺. While in single E process, the electrogenerated Cl₂ was hydrolyzed to form hypochlorous acid and hypochlorite ion, which could decompose the ammonia because of their high oxidative potentials. It was observed that the ammonia concentrations decreased linearly with the reaction time and the degradation rates were kept constant in the processes, which could be described as pseudo zero-order kinetics (Li and Liu, 2009; Sun and Chou, 2000; Vanlangendonck et al., 2005):

$$-\frac{d[\text{NH}_3\text{-N}]}{dt} = k \quad (5)$$

where $d[\text{NH}_3\text{-N}]/dt$ is the ammonia degradation rate ($\text{mg L}^{-1} \text{min}^{-1}$) and k is a constant ($\text{mg L}^{-1} \text{min}^{-1}$). The calculated pseudo zero-order constants of k values were 5.39 and $4.84 \text{ mg L}^{-1} \text{min}^{-1}$ with RuO₂/Ti and IrO₂/Ti as anodes, respectively. Meanwhile, the ACE was calculated from the total nitrogen moles generated from the decomposition of ammonia divided by the total supplied current in view of the three-electron reaction for the ammonia decomposition to nitrogen (Cossu et al., 2005). The calculated ACE for half

ammonia degradation was presented in Fig. 3b. It was seen that only 31.3% and 28.2% of ACE was obtained in the single E process, respectively. While a 10 W low-pressure mercury lamp was introduced into the E process, the UPE process showed apparently higher degradation rates and ACE than single E or single P process. The pseudo zero-order constant k and ACE increased 1.5 times reaching $8.03 \text{ mg L}^{-1} \text{min}^{-1}$ and 46.9%, respectively, on RuO₂/Ti electrode in the UPE process. And an increase of 1.7 times was also acquired on IrO₂/Ti electrode with the pseudo zero-order constant and ACE reaching $8.24 \text{ mg L}^{-1} \text{min}^{-1}$ and 48.0% separately. Thus, an obviously synergistic effect was confirmed by combining P and E processes with both RuO₂/Ti and IrO₂/Ti electrodes as anodes, although the ACE was still a little low, which might be limited by the design of reactor such as the electrode gap (quartz tube placed between the two electrodes) and mass transfer (controlled by the magnetic stirrer).

3.3. Conversion of ammonia in the processes

Several researchers (Kim et al., 2005, 2006; Lin and Wu, 1997) had reported that ammonia-nitrogen mainly transferred to N₂ and partially converted into various nitrogen compounds (NO₃⁻ and NO₂⁻) in the electrochemical process. Ammonia and in situ active chlorine reacted to form products collectively known as chloramines, which consisted of three species: monochloramine (NH₂Cl), dichloramine (NHCl₂) and trichloramine (NCl₃). Finally, most chloramines were converted to non-toxic nitrogen gas. The reaction mechanism between ammonia and active chlorine was like the breakpoint chlorination (Chiang et al., 1995; Lee et al., 2002; White, 1992) which could be represented by:

To sum up, the overall reaction occurring between the HClO and NH₄⁺ could be expressed as follows (Kim et al., 2006; Lin and Wu, 1997):

Similar results were obtained as shown in Fig. 4. In the E process with the current density of 40 mA cm^{-2} at pH 5.7, about 89.7% reduction of TN in the solution was achieved after 120 min reaction. In our experiments, the decrease of TN was due to the generation of nitrogen-containing gases. The possible gaseous products were N₂ and NO_x (NO and N₂O) or NCl₃. In the process, the gases were firstly collected and then analyzed to detect no gaseous NCl₃ and negligible NO_x less

Fig. 3 – (a) Variation of NH₃-N versus time and (b) average current efficiencies in different processes with RuO₂/Ti and IrO₂ electrodes (NH₃-N 700 mg L⁻¹, pH 5.7, current density 40 mA cm^{-2} and Cl⁻ concentration 5300 mg L⁻¹).

than 0.5 ppm. The results demonstrated that N element removed from water was mainly transformed into N_2 gas. Thus, the production of N_2 could be calculated as equal to the loss of TN according to the N conservation law. Simultaneously, intermediate nitrate and nitrite ions were formed in the water. After 120 min of E process, about $15.8 \text{ mg L}^{-1} \text{ NO}_3^-$ -N, formed by the oxidation of ammonia or the decay of chloramines (Li and Liu, 2009; Michael and Karl, 2007), and a low level of $0.5 \text{ mg L}^{-1} \text{ NO}_2^-$ -N, probably due to the reduction of NO_3^- (Wang et al., 2006), remained in the solution.

Comparatively, more than 97% of TN was removed from the solution and converted into N_2 within 90 min in the UPE process. However, about 2 mg L^{-1} more nitrate formed during the UPE process, which might be caused by the accelerated decay of NH_2Cl under adequate UV irradiation (Michael and Karl, 2007). In the end, 13.96 mg L^{-1} of TN remained, which was almost equal to the sum of $13.51 \text{ mg L}^{-1} \text{ NO}_3^-$ -N and $0.37 \text{ mg L}^{-1} \text{ NO}_2^-$ -N, indicating no chloramines in the solution. Therefore, the UPE process in the presence of chlorides showed a higher capacity and selectivity in ammonia transformation into nitrogen gas.

3.4. Effect of speciation in UPE on ammonia degradation

To investigate the synergistic effect in the UPE system, all the possibilities for the effect when UV light was introduced into the E process were, respectively, investigated, including the responses of the electrode, reactants and intermediate active species to the UV light irradiation. Photocurrent and EIS measurements are the most common methods to characterize the photocatalytic activities of semiconductor electrodes (Liu et al., 2000; Qu and Zhao, 2008; Zhao and Zhu, 2006). Thus, the cyclic voltammetry curves and the EIS

Nynquist spectra were, respectively, measured in the 0.1 M Na_2SO_4 solution under darkness and photoirradiation conditions as shown in Fig. S1 (Supplementary data). It was obviously seen that almost no photocurrent and variation of EIS Nynquist plots were observed from darkness to photoirradiation, suggesting that the RuO_2/Ti electrode was of no photoactivity. So the conventional photoelectrocatalytic mechanism, bias potential promoted the separation between holes and electrons, was not suitable for the UPE process. Meanwhile, the absorption spectra of ammonia and active chlorine were measured, respectively, as shown in Fig. S2 (Supplementary data), which indicated that only active chlorine succeeded in absorbing the energy of UV light of 254 nm used in the UPE process (Calvert and Pitts, 1966; Michael and Karl, 2007). Simultaneously, when the UV irradiation was introduced into the chemical chlorination with enough free chlorine, the degradation efficiency of ammonia increased from 82.9% to 92.3% in Fig. S3 (Supplementary data). In addition, when UV irradiation was introduced into E process, the degradation rates of ammonia increased little at pH 12 as shown in Fig. S4 (Supplementary data), which might be caused by the dominant absorption of NH_3 on the electrode surface thereby inhibiting the generation of active chlorine. Therefore, it could be concluded that the reaction between active chlorine and UV must play a dominant role in the UPE process.

Fig. 4 – Conversion of NH_3 -N in the E and UPE processes (NH_3 -N 700 mg L^{-1} , pH 5.7, current density 40 mA cm^{-2} and Cl^- concentration 5300 mg L^{-1}).

Fig. 5 – (a) ESR spectra of 20 mg L^{-1} electrogenerated HClO in the dark and under UV irradiation; (b) variation of ammonia in E, UPE (10 mM CO_3^{2-} , NH_3 -N 700 mg L^{-1} , pH 5.7, current density 40 mA cm^{-2} and Cl^- concentration 5300 mg L^{-1}) and $\text{UV}/\text{H}_2\text{O}_2$ processes ($10 \text{ mM H}_2\text{O}_2$, $7 \text{ mg L}^{-1} \text{ NH}_3$ -N).

Though it is usually reported that hypochlorous acid can dissociate to $\cdot\text{OH}$ and $\cdot\text{Cl}$ radicals under UV irradiation, $\cdot\text{Cl}$ radical is difficult to be measured directly. However, the unstable and very short-lived $\cdot\text{OH}$ radical in the solution could be identified. Assuming that $\cdot\text{OH}$ radical is one photolytic product of HClO , it can be ascertained that $\cdot\text{Cl}$ radical must be the other product. To find out whether such radicals could be generated in the UPE process, electrogenerated active chlorine containing DMPO was taken out with a capillary and measured by ESR in the dark or under UV irradiation. The results were presented in Fig. 5a. No DMPO- OH signal occurred in the dark and typical spectra of the DMPO- OH adduct ESR with peaks of 1:2:2:1 were observed in the presence of UV irradiation. This indicated that $\cdot\text{OH}$ radical could be in situ generated by the photolysis of the in situ electrogenerated active chlorine. Besides, in the high concentration of active chlorine/UV system, some yellow-green gas with irritating odor, which could be an indicator of the generation of Cl_2 , was generated probably due to the combination of two $\cdot\text{Cl}$ radicals. Thus, it could be concluded that active chlorine would indeed dissociate to $\cdot\text{OH}$ and $\cdot\text{Cl}$ radicals under UV irradiation and the photogenerated radicals should be responsible for the accelerating effect on ammonia degradation in the UPE process.

To investigate the role of $\cdot\text{OH}$ radical in the decomposition of NH_4^+ , two groups of experiments were carried on. Firstly, 10 mM carbonates (an $\cdot\text{OH}$ radical scavenger) was added in the E and UPE processes, respectively, as shown in Fig. 5b. Compared to those in Fig. 3a, the degradation rates in the presence or absence of CO_3^{2-} were almost the same. Thus, CO_3^{2-} did not influence the degradation of ammonia in both E and UPE processes. Secondly, 10 mM H_2O_2 was used to degrade $7 \text{ mg L}^{-1} \text{ NH}_4^+$ under UV irradiation. As is known, UV/ H_2O_2 is an effective way to produce $\cdot\text{OH}$ radicals. Almost no NH_4^+ decreased in the UV/ H_2O_2 process (Fig. 5b). Therefore, it was confirmed together that $\cdot\text{OH}$ radical generated in the UPE process exerted little effect on NH_4^+ degradation. Consequently, it was $\cdot\text{Cl}$ radical that worked in the UPE process.

3.5. Recycle of chloride

As to the breakpoint chlorination, the active chlorine added would like to react with ammonia rapidly and be reduced to Cl^- . Comparatively, Cl^- was circular following the first route in E process and both routes of Eq. (17) in the UPE process.

The concentrations of active chlorine in the E and UPE processes were measured in the presence or absence of ammonia as shown in Fig. 6a. It was proved again that active chlorine was the major oxidant for the ammonia degradation

Fig. 6 – (a) Production of active chlorine with and without ammonia, and (b) variation of total Cl concentrations in the E and UPE processes.

due to the significant reduction of active chlorine in the presence of ammonia. In addition, the concentrations of active chlorine were a little lower in the UPE process, which indicated indirectly that active chlorine might be dissociated to $\cdot\text{Cl}$ radicals under UV irradiation. Furthermore, the total concentrations of Cl were recorded in Fig. 6b. The total concentrations of Cl decreased probably because of Cl_2 escaping into the air. And the loss ratio of total Cl decreased

from 21.0% to 7.2% in the UPE process when ammonia was depleted, which implied that the recycle of chloride was accelerated and the elapse of Cl_2 decreased greatly in the UPE process.

Fig. 7 – (a) Effect of initial pH on ammonia degradation and (b) variation of pH in the UPE process with the initial pH of (1) 3.0, (2) 5.3, (3) 8.0, (4) 9.0, (5) 10.0, and (6) 12.0. ($\text{NH}_3\text{-N}$ 700 mg L⁻¹, current density 40 mA cm⁻² and Cl^- concentration 5300 mg L⁻¹).

3.6. Effects of control parameters in the UPE process

3.6.1. Effect of initial pH

To investigate the effect of initial pH on the degradation rates, solutions were adjusted from pH 3.0 to 12.0. The results were shown in Fig. 7a. Expectedly, single P process in the presence of RuO_2/Ti contributed no effect on ammonia degradation in the whole pH range. In the E process, the degradation rates were kept constant between pH 3 and 9 and increased a lot at pH above 10, which might be caused by the combined effect of indirect oxidation, direct oxidation and air (in situ electro-generated air, including O_2 , Cl_2 , H_2 , etc) stripping (Kim et al., 2006). While in the UPE process, the rate constants changed little in the whole pH range, and thus the initial pH influenced slightly on the ammonia degradation, which widened the application of the UPE process. Stimulatingly, pH dropped at first due to the abundant formation of H^+ through Eq. (13) and then increased due to the formation of OH^- by the pure electrolysis of Cl^- after the complete degradation of ammonia (shown in Fig. 7b). As a result, the turning point could be

Fig. 8 – Effect of current density on ammonia degradation in the UPE process; inset, ACE at different current densities ($\text{NH}_3\text{-N}$ 700 mg L⁻¹, pH 5.7 and Cl^- concentration 5300 mg L⁻¹).

regarded as an indicator when the ammonia was depleted in the UPE process.

3.6.2. Effect of current density

Generally speaking, increasing current density was always an easy means of speeding up the electrochemical oxidation. Fig. 8 presented the degradation rates of ammonia versus the current density in the UPE process. It could be observed that the ammonia oxidation rate was linearly fitted with current density at controlled conditions and the linear correlation coefficient was about 0.98. As a result, the degradation rates could improve linearly the increase of current density and thus current density was a determining step for the ammonia degradation. Simultaneously, the increase in current density occurred without any loss of ACE (Fig. 8 inset) and the ACE was kept constant at about $48 \pm 3\%$.

Fig. 9 – Effect of ammonia-nitrogen concentration on ammonia degradation in the UPE process: (1) 350, (2) 1050, (3) 1400 and (4) 2100 mg L⁻¹; (pH 5.7, current density 40 mA cm⁻² and Cl^- concentration 5300 mg L⁻¹).

3.6.3. Effect of ammonia concentration

The dependence of ammonia degradation kinetics on different initial concentrations of ammonia was examined with the constant current density of 40 mA cm^{-2} at pH 5.7. As shown in Fig. 9, it was interesting to observe that the degradation rates were almost constant in the ammonia concentration range of $350\text{--}2100 \text{ mg L}^{-1}$. The k values were 7.84, 7.67, 7.76 and $7.76 \text{ mg L}^{-1} \text{ min}^{-1}$, respectively. Although the *in situ* generated active species were equal at controlled conditions, they preferred to react with ammonia with the increase of ammonia concentration rather than elapse into the air. The results showed that the utilization efficiency of active chlorine species was proportional to the initial concentration of ammonia, which might result in the constant rates.

4. Conclusions

The experimental results demonstrated that the UPE process provided a synergistic effect on the degradation of ammonia. The degradation rates increased separately by 1.5 and 1.7 times using RuO_2/Ti and IrO_2/Ti electrodes. It also showed a high selectivity of the products that about 98% of $\text{NH}_3\text{-N}$ was converted into the N_2 gas remaining little NO_3^- and NO_2^- in the solution. Among the several influencing parameters, controlling the current density was the limiting factor and the degradation rates of ammonia increased linearly with the current density. In the UPE process, the cycle of Cl^- was accelerated. Cl^- in the solution was firstly electrochemically oxidized to Cl_2 ; the *in situ* electrogenerated Cl_2 was hydrolyzed to generate active chlorine; and then active chlorine dissociate to $\cdot\text{OH}$ and $\cdot\text{Cl}$ radicals under UV irradiation in the UPE process. Thus, these *in situ* electrogenerated active chlorine and the *in situ* photogenerated chlorine radicals were responsible for the synergistic effect on ammonia degradation.

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Supplementary information

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