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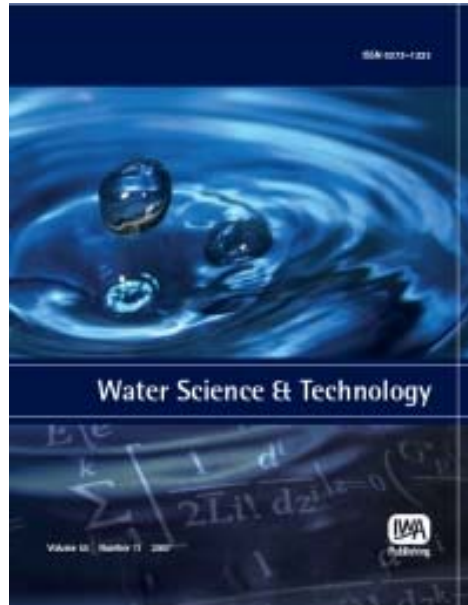
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## Aniline chlorination by *in situ* formed Ag–Cl complexes under simulated solar light irradiation

Xuefeng Hu, Xiaowen Wang, Liulu Dong, Fei Chang and Yongming Luo

### ABSTRACT

Ag speciation in a chloride medium was dependent upon the Cl/Ag ratio after releasing into surface water. In this study, the photoreaction of *in situ* formed Ag–Cl species and their effects on aniline photochlorination were systematically investigated. Our results suggested that formation of chloroaniline was strongly relevant to the Cl/Ag ratio and could be interpreted using the thermodynamically expected speciation of Ag in the presence of  $\text{Cl}^-$ . AgCl was the main species responsible for the photochlorination of aniline. Both photoinduced hole and  $\bullet\text{OH}$  drove the oxidation of  $\text{Cl}^-$  to radical  $\bullet\text{Cl}$ , which promoted the chlorination of aniline.  $\text{Ag}^0$  formation was observed from the surface plasmon resonance absorption during AgCl photoreaction. This study revealed that  $\text{Ag}^+$  released into  $\text{Cl}^-$ -containing water may result in the formation of chlorinated intermediates of organic compounds under solar light irradiation.

**Key words** | aniline, Ag–Cl complexes, Cl/Ag ratio, photochlorination

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### INTRODUCTION

It is attractive to explore the photochemical formation of aromatic chloroderivatives in a real environment because of their increased toxicity (Calza *et al.* 2008; Ofner *et al.* 2012). Lederer proposed that photoexcitation of transition metal chlorides  $\text{M–Cl}$  ( $\text{FeCl}_3$ ,  $\text{CuCl}_2$ ,  $\text{Na}[\text{AuCl}_4]$  and  $\text{H}_2[\text{PtCl}_6]$ ) followed by electron transfer from the ligand to the metal was associated with the formation of  $\text{Cl}\bullet$  radicals (Lederer *et al.* 1992). Generally, the  $\text{Cl}_2^{\bullet-}$  radicals are formed through the reaction of  $\text{Cl}\bullet$  with  $\text{Cl}^-$  present in aqueous solutions (Liu *et al.* 2009).  $\text{Cl}_2^{\bullet-}$  radicals are reactive species which are able to react with numerous organics to produce chlorinated derivatives. The reaction of  $\text{Cl}_2^{\bullet-}$  radicals with aromatic compounds may involve connection of Cl atoms to the ring. Chlorination of aniline, phenol, and bisphenol A in a homogeneous aqueous solution occurs in the presence of  $\text{FeCl}_3$  (Vione *et al.* 2005; Liu *et al.* 2009; Wu & Hu 2012). These reactions are usually performed in acidic conditions ( $\text{pH} \leq 3$ ). However, research on the photochlorination of

aromatic compounds in the pH range of natural waters (6–8.5) is more significant.

Silver species ( $\text{Ag(I)}$  and silver nanoparticles) are often introduced into the aquatic environment from industrial effluents relating to mining and photographic development and ultimately from municipal water treatment plants. A global demand of 27,333 metric tonnes in 2010 was reported by the Silver Institute (Silver Institute 2011), and more than 13,420 metric tonnes of silver were emitted annually to the environment (Eckelman & Graedel 2007). Total silver concentration in wastewater influent ranges from 1.78 to 105  $\mu\text{g/L}$ , and measurable background concentrations in the aqueous environment were between 0.03 and 1,000  $\text{ng/L}$  (Yang *et al.* 2012). Silver chloride species are predicted to form when  $\text{Ag}^+$  ions exist in the environment, particularly in oxidative environments where the amount of sulfide is low. In this case Ag speciation depends on Cl/Ag ratios (Reinfelder & Chang 1999). AgCl, as a known photosensitive material, was also adopted as photocatalyst

for organic pollutants' photodegradation (Wang *et al.* 2008). However, little is known about the photochlorination of aromatic compounds in the presence of heterogeneous photosensitive substance AgCl at neutral pH.

In this paper, aniline was chosen as a model organic pollutant. Catechol, hydroquinone and chlorinated anilines were possible intermediates during its photodegradation, as reported before (Wu & Hu 2012). The primary objective was to derive insight into the possible natural photochlorination of aniline in  $\text{Cl}^-$ -containing water in the presence of  $\text{Ag}^+$ , and more specifically, to explore the influence of pH,  $\text{Ag}^+$  and  $\text{Cl}^-$  ratio on the generation of  $\text{Cl}_2^-$  and then on the formation of aniline chlorides. The interest in the chlorinated anilines' intermediates was due to their recognized toxicity and low natural biodegradability in the environment. The chlorinated intermediates may be formed in aquatic environments, which may cause secondary pollution and thus require urgent attention.

## EXPERIMENTAL

### Chemicals

Aniline was purchased from Kermel (Tianjin, China).  $\text{AgNO}_3$  and NaCl were purchased from Sinopharm (Tianjin, China). 4-Chloroaniline (4CA) and 2-CA were purchased from Aladdin (Shanghai, China). Catechol and hydroquinone were of analytical purity and were purchased from Fuchen (Tianjin, China). Aqueous solutions were prepared by deionized water purified with a Milli-Q water system (Millipore, Bedford, MA, USA) with desired concentrations.

### Irradiation apparatus and procedure

Experimentally designed concentrations of aniline,  $\text{AgNO}_3$  and NaCl solutions were prepared in a 30 mL quartz bottle, and continuously stirred with a Teflon-coated stir bar for half an hour in the dark. After equilibration, the solution was irradiated by a 300 W Xe lamp (Beijing Changtuo Lighting Corporation, China) equipped with a 290 nm cut-off heat-resistant filter. The light intensity was  $39 \text{ mW/cm}^2$  as measured by a radiometer (CEL-NP2000, Beijing Aulight Co., Ltd), and the ambient temperature was  $25^\circ\text{C}$ . At a given time, the reaction suspension samples were collected, centrifuged, and then filtered (PES needle type filter, Shanghai Anpel Scientific Instrument Co. Ltd, Shanghai, China) to remove the insoluble particles before analysis.

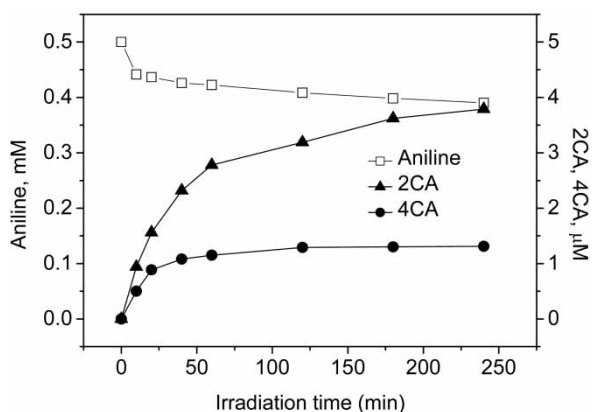
## Analysis

The solutions were analyzed by HPLC (Waters, Milford, MA, USA), consisting of a Waters 2695 Separations Module, a Waters 2998 photodiode array detector and a Waters SunFire C18 column ( $4.6 \times 250 \text{ mm}$ ,  $5.0 \mu\text{m}$ ). Methanol and water (40/60, v/v) were used as a mobile phase at a flow rate of  $1 \text{ mL/min}$ . The injection volume was  $20 \mu\text{L}$ . Aniline, 4CA, 2CA, catechol, and hydroquinone were compared with standard reagents. Electron spin resonance (ESR) signals of hydroxyl radicals spin trapped by 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were detected at ambient temperature on a Bruker (ESP 300E) spectrometer (Bruker, Rheinstetten, Germany) under 355 nm laser irradiation.

## RESULTS AND DISCUSSION

### Aniline photochlorination upon irradiation of $\text{Ag(I)}/\text{Cl}^-$

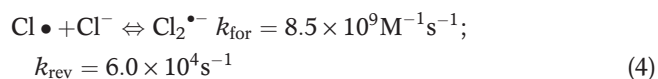
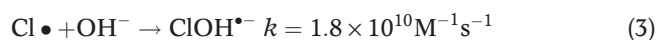
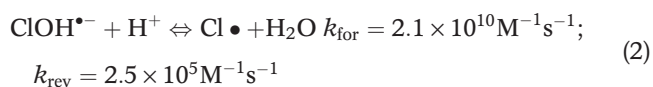
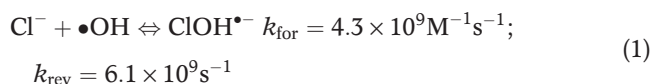
Irradiation of aniline aqueous solutions in the presence of various Ag–Cl complexes, insoluble AgCl and other soluble  $\text{AgCl}_x^{(x-1)-}$  ( $x = 2, 3, 4$ ) species formed *in situ* produces 2-CA and 4-CA as chloroderivatives at pH 7.0. Figure 1 shows that the concentration of both 2CA and 4CA increased quickly, reaching 2.78 and  $1.15 \mu\text{mol/L}$  after the first hour of irradiation, respectively. The fraction of transformed aniline accounted for by CA is about 5% at this time. At the same time, the formed CAs underwent photodegradation. When the formation rate of CAs equals its degradation rate, the concentration of CAs will not change. The curves of both 2CA and 4CA concentrations as a function of time reached a plateau after a 1 h reaction, indicating that the degradation rate of CAs is equal to its formation rate.



**Figure 1** | Aniline (0.5 mmol/L) photodegradation, 2CA and 4CA formation in the presence of 0.5 mmol/L  $\text{Ag(I)}$  and 2 mmol/L NaCl at pH 7.0 under simulated solar irradiation.

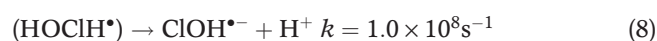
From the simulation of the Ag speciation with Visual MINTEQ, the prevailing Ag species under the conditions adopted in Figure 1 are  $\text{Ag}^+$  (22.7%),  $\text{AgCl}$  (68.0%), and  $\text{AgCl}_2^-$  (9.3%). Formation of  $\text{Cl}\cdot$  by photoexciting M–Cl complexes ( $\text{Fe–Cl}$ ,  $\text{Cu–Cl}$ ) usually originated from their charged complex ( $\text{FeCl}_2^+$ ,  $\text{CuCl}_3^-$ ) but not the neutral complex (Mereshchenko *et al.* 2014; Wu & Hu 2012). However,  $\text{AgCl}$  will produce an electron and a hole after absorbing a photon. The hole transferred to the  $\text{AgCl}$  surface and caused the oxidation of  $\text{Cl}^-$  to  $\text{Cl}\cdot$  (Yang *et al.* 2015). An alternative pathway that can be postulated for the generation of  $\text{Cl}\cdot$  from hydroxyl radicals ( $\cdot\text{OH}$ ) was shown as Equations (1) and (2) (Grebel *et al.* 2010). To confirm the formation of  $\cdot\text{OH}$ , the ESR spin-trap technique was employed. Under 355 nm laser irradiation, the *in situ* formed Ag–Cl complexes give the characteristic four peaks of  $\text{DMPO}\cdot\text{OH}$  with an intensity ratio 1:2:2:1 (Figure S1, available online at <http://www.iwaponline.com/wst/071/149.pdf>). Catechol and hydroquinone were identified as the transformation intermediates of aniline by comparing with authentic samples. The results indicated that  $\cdot\text{OH}$  radicals were indeed generated and contributed to the formation of catechol and hydroquinone when aniline conducted photoreaction in the presence of Ag–Cl complexes under solar light irradiation. Formation of  $\cdot\text{OH}$  could originate from two pathways. One way is the photogenerated electron formed by photoirradiating  $\text{AgCl}$  transferred to  $\text{O}_2$  with the production of  $\text{O}_2^{\cdot-}$  and its further disproportionation products  $\cdot\text{OH}$ . The other way is the oxidation of  $\text{OH}^-$  by  $\text{Cl}\cdot$ , as depicted in Equations (3) and (1) (the reverse reaction).

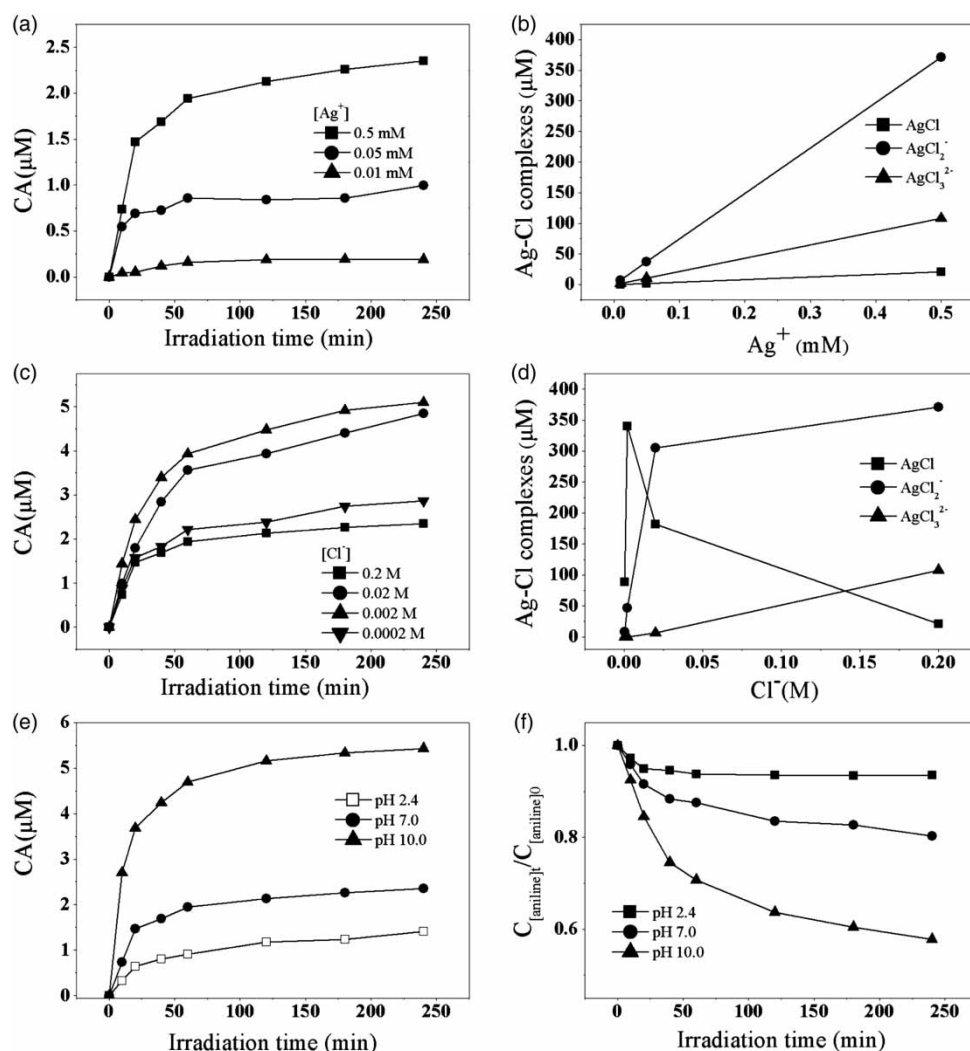
Generally,  $\text{Cl}_2^{\cdot-}$  is formed through the equilibrium reaction (Equation (4)) and becomes the dominant species in a  $\text{Cl}^-$ -containing aqueous solution (Vione *et al.* 2005; Liu *et al.* 2009; Grebel *et al.* 2010). Aniline can be oxidized by  $\text{Cl}_2^{\cdot-}$  into anilino radical cations, which further react with  $\text{Cl}_2^{\cdot-}$  to generate CAs, as we reported before (Equations (5) and (6)) (Wu & Hu 2012).



### Effect of $\text{Ag}^+$ concentration

The effect of  $\text{Ag}^+$  concentration on aniline chlorination was investigated to further illustrate the role of Ag–Cl complexes. It is reasonable that the plateau concentration of chloroanilines (2CA + 4CA) increases as the  $\text{Ag}^+$  concentration increases, as shown in Figure 2(a). The plateau concentration of CAs also increases ca. five times (from 0.16  $\mu\text{mol/L}$  to 0.86  $\mu\text{mol/L}$ ) after 1 h photoreaction when the  $\text{Ag}^+$  concentration increases from 0.01 to 0.05 mmol/L, correspondingly. However, when  $\text{Ag}^+$  concentration further increased from 0.05 to 0.5 mmol/L, there was only a ca. 2.2 times increase of CAs' plateau concentration (Figure 2(a)). Photoexcitation of Ag–Cl complexes produced  $\text{Cl}_2^{\cdot-}$  and  $\cdot\text{OH}$ , which are responsible for the CAs' formation and degradation, respectively. Figure 2(b) shows that the concentration of all Ag–Cl complexes increased proportionately to the increase of  $\text{Ag}^+$  concentration in the presence of 0.2 mol/L  $\text{Cl}^-$ . At low  $\text{Ag}^+$  concentration, Ag–Cl complexes fully absorb irradiated light and the formed chlorine radicals react with aniline effectively, then the formation of CAs increased linearly. However, the competition for light absorption of various Ag–Cl complexes at higher concentration will reduce the fraction of excited Ag–Cl complex, and then slow down the photochlorination reaction of aniline. The rate constant of reaction of  $\text{Cl}_2^{\cdot-}$  with aniline is  $1.2 \times 10^7 \text{M}^{-1}\text{s}^{-1}$ , and the rate constant of reaction between  $\text{Cl}_2^{\cdot-}$  and  $\text{H}_2\text{O}$  is  $1,300 \text{s}^{-1}$  (Equation (7)) (Hasegawa & Neta 1978). The large rate constants associated with Equation (7) indicate that, unless  $\text{Cl}_2^{\cdot-}$  reacts with aniline rapidly, its decay by reaction with  $\text{H}_2\text{O}$  will be significant, which will result in the formation of  $\cdot\text{OH}$  via Equation (8) and the reverse reaction of Equation (1). Although  $\text{Cl}_2^{\cdot-}$  and  $\cdot\text{OH}$  concentration simultaneously increased, the rate constant of  $\cdot\text{OH}$  and aniline ( $4.99 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$ ) is remarkably higher than that of  $\text{Cl}_2^{\cdot-}$  and aniline ( $1.2 \times 10^7 \text{M}^{-1}\text{s}^{-1}$ ) (Bakken & Jurs 1999). For all the above reasons, the plateau concentration of CA is not proportional to the increase of Ag–Cl complexes at higher  $\text{Ag}^+$  concentration.





**Figure 2** | Time course of CA formation (a) and Ag-Cl complexes' concentrations (b) at different  $\text{Ag}^+$  concentrations, reaction conditions: 0.2 mol/L  $\text{Cl}^-$ , 0.5 mmol/L aniline, pH 7.0; time course of CA formation (c) and Ag-Cl complexes' concentrations (d) at different  $\text{Cl}^-$  concentrations, reaction conditions: 0.5 mmol/L  $\text{Ag}^+$  and aniline, pH 7.0; CAs formation (e) and time course of aniline photodegradation (f) at different pHs, reaction conditions: 0.5 mmol/L  $\text{Ag}^+$  and aniline, 0.2 mol/L  $\text{Cl}^-$ . The concentrations of Ag-Cl complexes in (b) and (d) were simulated with Visual MINTEQ.

### Effect of $\text{Cl}^-$ concentration

The effect of  $\text{Cl}^-$  concentration on aniline chlorination was investigated to assess the relative contribution of the photolysis of various Ag species. It is plausible that the aniline chlorination increases as the Ag-Cl complexes increase; however, aniline chlorination did not increase with increasing  $\text{Cl}^-$  concentration in a single direction. Figure 2(c) shows the formation of CA at the initial  $\text{Cl}^-$  concentration of 0.0002, 0.002, 0.02 and 0.2 mol/L. It is interesting to note that when  $\text{Cl}^-$  concentration increased from 0.0002 to 0.002 mol/L, aniline chlorination was evidently enhanced. Further increase of  $\text{Cl}^-$  concentration resulted in an obvious decrease of the CA concentration.

It is understandable that at low concentration of  $\text{Cl}^-$ , the formation of Ag-Cl complexes is responsible for the enhancement of  $\text{Cl}_2^-$ , which is beneficial for the formation of CA. However, Ag-Cl complexes' speciation is a function of  $\text{Cl}^-$  concentration, as shown in Figure 2(d). At low  $\text{Cl}^-$  concentration, the dominant Ag-Cl complex is the uncharged neutral chloride complex,  $\text{AgCl}$ . At higher  $\text{Cl}^-$  concentrations, higher-order chlorocomplexes of Ag ( $\text{AgCl}_2^-$ ,  $\text{AgCl}_3^{2-}$ ) become dominant.  $\text{AgCl}$  shows the highest concentration at 0.002 mol/L  $\text{Cl}^-$ , while  $\text{AgCl}_2^-$  and  $\text{AgCl}_3^{2-}$  concentration increased with  $\text{Cl}^-$  at the determined concentrations. The results indicate that CA formation is dominated by the uncharged neutral complex  $\text{AgCl}$  while higher-order chlorocomplexes



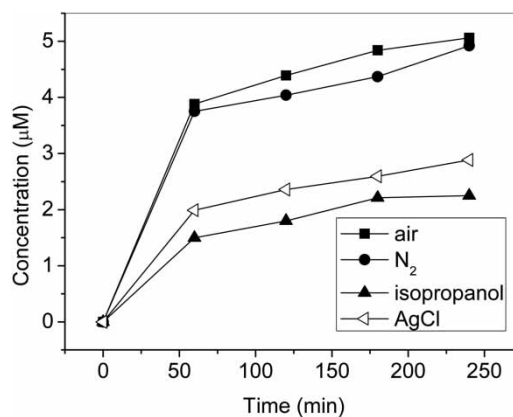
( $\text{AgCl}_2^-$ ,  $\text{AgCl}_3^{2-}$ ) do not play a significant role in aniline chlorination.

### Effect of pH

The formation of CAs occurs in a wide pH range and increases with increasing pH value (Figure 2(e) and 2(f)). Aniline is oxidized by  $\text{Cl}_2^-$  into anilino radical cations in acidic conditions (pH 2.4), which further reacts with  $\text{Cl}_2^-$  to generate CAs (Wu & Hu 2012). The intermediate anilino radical cations tend to eliminate protons from amino substituents to form the more stable aniline radicals at high pH values, which will facilitate the formation of CAs. Corresponding to the  $\text{pK}_a$  7.05 of anilino radical cation, the formation of CAs increased slightly when pH increased from 2.4 to 7.0, but a considerable increase of CAs formation was observed when pH increased from 7 to 10. The rate constants for reaction of  $\text{Cl}_2^-$  with various organic compounds were low at low pH values and vice versa (Hasegawa & Neta 1978). The reaction of  $\cdot\text{OH}$  with aniline is also easier under alkaline rather than acidic conditions (Jiang et al. 2002). As shown in Equations ((1)–(4)),  $\cdot\text{OH}$  and  $\text{Cl}\cdot$  inter-convert via  $\text{ClOH}^-$  intermediates during photoreaction, and high pH value facilitates the conversion from  $\text{Cl}\cdot$  to  $\cdot\text{OH}$ . The enhanced CAs' formation at high pH values indicated that  $\text{Cl}\cdot$  originated mainly from the hole oxidation of  $\text{Cl}^-$  and  $\text{Cl}_2^-$  reacted with aniline with a high reaction rate in basic conditions.

### Generation of chlorine radicals

As mentioned above, two possible pathways for the formation of chlorine radicals from AgCl were discussed. In order to deeply understand the reaction mechanism, we investigated effects of oxygen,  $\cdot\text{OH}$ , and free  $\text{Cl}^-$  on the chlorination of aniline (Figure 3). The addition of isopropanol as  $\cdot\text{OH}$  scavenger causes an evident but not complete inhibition of CA formation, revealing that both  $\cdot\text{OH}$  and hole oxidation of  $\text{Cl}^-$  are important source of chlorine radicals. However, the formation of chlorinated products under aerated and  $\text{N}_2$  atmospheres does not show a significant discrepancy during photoreaction, indicating that  $\cdot\text{OH}$  produced from  $\text{O}_2$  plays a negligible role in the generation of  $\text{Cl}\cdot$ . The addition of isopropanol inhibits the conversion from  $\cdot\text{OH}$  to  $\text{Cl}\cdot$ , then decreases the formation of CAs. To study the role of free  $\text{Cl}^-$ , photoreaction over prepared AgCl particles in the absence of free  $\text{Cl}^-$  was performed. The formed CAs were reduced significantly compared with those in the presence of free  $\text{Cl}^-$  even when the addition



**Figure 3** | Time course of chloroaniline (2CA + 4CA) formation under controlled conditions. Reaction conditions: solid symbols: 0.5 mmol/L  $\text{Ag}^+$  and aniline, 0.02 mol/L  $\text{Cl}^-$ , 1 mmol/L isopropanol, pH 7.0; open symbols: 72 mg/L AgCl, 0.5 mmol/L aniline, pH 7.0.

amount of AgCl particles was higher than the overall Ag-Cl complex in the presence of free  $\text{Cl}^-$ . The oxidation of free  $\text{Cl}^-$  by  $\cdot\text{OH}$  and hole should play an important role in the formation of chlorine radicals.

### Photoreaction of AgCl

Under solar light irradiation, an electron and a hole will be produced after AgCl absorbs a photon (Equation (9)). Subsequently, the hole transfers to the surface of AgCl and causes the oxidation of  $\text{Cl}^-$  to  $\text{Cl}\cdot$  (Equation (10)), while the electrons will be trapped by adsorbed oxygen to form  $\text{O}_2^-$  or combine with silver ions to form  $\text{Ag}^0$  atoms (Equations (11) and (12)). Silver nanograins will be formed on the surface of AgCl along with photoreaction, which will show surface plasmon resonance absorption. The absorption spectra changes of photoreaction solution are shown in Figure S2 (available online at <http://www.iwaponline.com/wst/071/149.pdf>). The surface of AgCl particles is most likely terminated by  $\text{Cl}^-$  ions, and is therefore negatively charged. Consequently, Ag nanograins deposited on the surface of AgCl particles should polarize its electron distribution such that the regions of its negative and positive charges are far from and close to the Ag/AgCl interface, respectively (Wang et al. 2008). The polarization field around the AgCl core can also force excited surface electrons in Ag nanograins further away from the Ag/AgCl interface under illumination. The migration of photo-excited electrons away from the AgCl core prevents further photoreduction of AgCl to Ag. The other reason may be that Ag nanoparticles are sensitive to oxygen; under oxygenated conditions  $\text{Ag}^0$  was oxidized and encapsulated by a

secondary phase in aqueous solution containing chloride that was attributed to the formation of AgCl at the surface of the Ag nanoparticles (Chambers *et al.* 2014).



Based upon the above discussion, we proposed a AgCl photoreaction and aniline photochlorination pathway under simulated solar light as shown in Figure 4.

## CONCLUSION

Our work demonstrated that photolysis of AgCl occurred under simulated solar light irradiation, resulting in the formation of reduced  $\text{Ag}^0$  and oxidized chlorine radicals. Chlorine radicals drove the aniline chlorination to form 2-CA and 4-CA.  $\text{Ag}^0$  may be oxidized to  $\text{Ag}^+$  and complexed with chlorine ions again if chlorine ions exist in aqueous solutions. The present fundamental information is helpful for understanding the possibility of photochlorination of organic compounds in water containing both Ag and chloride. Although chlorinated organic compounds generated in this process are of trace levels, they show significant effects on the environment due to their persistence and high toxicity. The photoreactions of Ag in  $\text{Cl}^-$ -containing water and their

effects on organic pollutants have significant implications for the fate of Ag and organic pollutants in the environment.

Our present work demonstrated the occurrence of aniline chlorination in the presence of AgCl under simulated sunlight irradiation, which may attract attention from both industrial and research communities over chlorinated derivatives formed in  $\text{Cl}^-$ -containing media when Ag-based photocatalysts are used.

## ACKNOWLEDGEMENTS

The generous supports by the National Natural Science Foundation of China (nos 41076040 and 41230858) are acknowledged.

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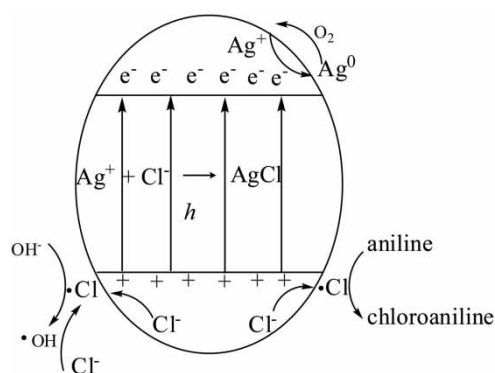


Figure 4 | AgCl photoreaction and aniline photochlorination pathway under simulated solar light.



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First received 9 November 2014; accepted in revised form 18 March 2015. Available online 30 March 2015