

Increase the Degradation Efficiency of Organic Pollutants with a Radical Scavenger (Cl⁻) in a Novel Photoelectrocatalytic Reactor

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Abstract: Photoelectrocatalytic degradation performance of quinoline in saline water was investigated using a new-designed continuous flow three-dimensional electrode-packed bed photocatalytic reactor. It is interesting to find that chloride ion has an obvious enhancement effect rather than a scavenging effect on the photoelectrocatalytic degradation of quinoline, and create a kinetic synergetic effect in the photoelectrocatalytic reactor.

Keywords: Photoelectrocatalytic reactor, photocatalytic, radical scavenger, chloride ion, quioline.

Chloride ion, a very common inorganic ion that frequently present in the nature water or anthropogenic wastewaters, has been found an efficient scavenger for heterogenous photocatalytic process by competing substrate for surface active sites and then forming weaker $\cdot\text{Cl}$ radical¹⁻⁴. NaCl was often used as supporting electrolyte for the photoelectrocatalytic degradation of organic contaminants⁵⁻⁶. Thus, with respect to photoelectrochemical process, chloride ion not only may be a scavenger of $\cdot\text{OH}$ radicals in the photocatalytic process, but also a supporting electrolyte in the electrochemical process. A few researches have been studied to investigate the effects of chloride ions on the photoelectrocatalytic degradation of organic contaminants in water⁵⁻⁷. Candal *et al.*⁶ found that when potentials were applied across the titania coatings the photoelectrocatalytic activities were not inhibited significantly in the presence of sodium chloride. But, we found the external electric field can depress the deactivation of TiO₂ photocatalyst in the presence of higher concentration of chloride ion⁷. Unfortunately, all researchers did not find any photocatalytic enhancement effect at all tested concentration of chloride ion.

Up to date, there is a controversial topic relating to the effect of chloride ion on photoelectrocatalytic process. Thus, it is of interest to know how chloride ion influences the photoelectrocatalytic degradation of organic pollutants in water. The aim of present study is to investigate the photoelectrocatalytic degradation of quinoline in saline water using a novel three dimension electrode - packed bed photocatalytic reactor.

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Experimental

Quinoline (98%) used as analytic grade was purchased from Sigma. The reaction setup includes a 250 mL flow-through photoelectrocatalytic reactor connected to a 500 mL reservoir. Photoelectrocatalytic reactor is a continuous flow three-dimensional electrode-packed bed photocatalytic reactor, which was improved on the three-dimensional electrode-slurry photocatalytic reactor⁸⁻⁹ and the slurry photoelectrocatalytic reactor¹⁰. NaCl was used as supporting electrolyte in the photoelectrocatalytic process, and the prepared material of quartz sand coated by Degussa P25 TiO₂ was used as the filler both for the three-dimensional electrode and for the packed bed photocatalyst in this photoelectrocatalytic reactor. The quantity of TiO₂ coating on quartz sand was about 0.0182 g/g.

A 500 mL solution of quinoline was pumped through the photoelectrochemical reactor by a peristaltic pump at the flow of 190 mL min⁻¹, and the residual solution is well stirred by a magnetic stirrer. The general treating conditions were as follows: 30 V direct current cell voltage, 0.05 Mpa airflow, 0.25 mmol/L quinoline, natural pH value and 0.5 mol/L NaCl solution. Analysis was achieved by a Hewlett Packard 1100 system equipped with an UV/Vis detector and a reverse phase C₁₈ column (Dieckman, 250×4.6 mm i.d.). The column was eluted with a mixture of water-methanol 40:60 v/v with a flow rate of 1.0 mL min⁻¹. 5 μL filtered sample was injected into HPLC system and the detection was performed by UV absorption at 225 nm.

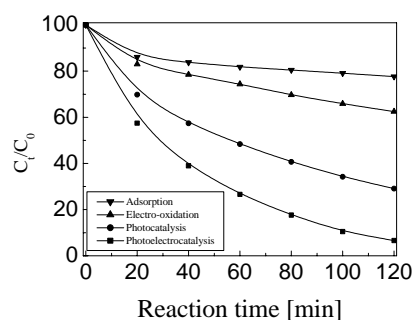
Results and Discussion

The change trends of quinoline degradation at various processes were presented in **Figure 1**. It is obviously to see that the quinoline can be removed from the solution in all four processes. However, only a 22% of quinoline was removed by adsorption of packed material at 120 min, while in the single process of photocatalytic and electrochemical oxidation, 71% and 38% of quinoline were removed, respectively. But these degradation efficiencies were all apparently lower than that of photoelectrocatalytic process (93%). When the adsorption effect was taken out from above three processes, 15%, 49% and 71% of quinoline were degraded in the electrochemical oxidation, photocatalytic and photoelectrocatalytic process, respectively. It is easy to find that the net efficiency of photoelectrocatalytic process was not only greater than the net efficiencies of photocatalytic or electrochemical process alone, but also greater than the sum of both processes. This enhancement effect of quinoline degradation may be an evidence of photoelectrocatalytic synergetic effect.

In this work, photocatalytic degradation of quinoline fits well with pseudo-first order equation. Moreover, the pseudo-first order kinetics was also confirmed in the photoelectrocatalytic process by the linear transforms $\ln(C_0/C_t) = k(t)$ of the data in **Figure 1**. The apparent rate constant for the processes of photoelectrocatalysis and photocatalysis were 0.0225 and 0.0110 min⁻¹, respectively. The rate constant of photoelectrocatalysis is 2.0 folds of that in the photocatalytic process. That is, an apparent synergetic effect in the degradation of quinoline was created in the photoelectrocatalytic reactor in which combined the photocatalytic with the

three-dimensional electrode technology. This synergetic effect may be attributed to three factors. Firstly, external electric field and expanded specific area of three-dimensional electrode both can capture photogenerated electrons, reducing the recombination of these electrons and holes; Secondly, the external electric field can also result in the direct or indirect electrochemical oxidation of quinoline besides photoelectrocatalytic synergetic effect.⁸⁻⁹ Thirdly, increasing electrolyte concentration can also increase the degradation efficiency of quinoline by direct and/or indirect electrochemical oxidation under high cell voltage. This hypothesis can be convinced subsequently in the paper.

Figure 1 Comparison of quinoline degradation efficiency



From above mentioned, though chloride ion has been found an efficient scavenger for heterogenous photocatalytic process¹⁻⁴, NaCl was often used as supporting electrolyte for the photoelectrocatalytic degradation of organic contaminants⁵⁻⁶. In order to elucidate how a radical scavenger - chloride ion and its concentrations affected on the photoelectrocatalytic degradation of quinoline, we used NaCl as an electrolyte in the new-designed photoelectrocatalytic reactor, and the results were presented in **Figure 2**. From the profiles, we can easily see that with the increase of the concentration of chloride ions the rate constant increases gently at low concentration, and then increases rapidly at the concentration above 0.2 mol/L. The rate constant is only 0.0089 min⁻¹ without any Cl⁻ ion adding, while the apparent rate constant increases by 3.7 folds and up to 0.0327 min⁻¹ when the Cl⁻ ion concentration was 1.0 mol/L. It is of interest to find that chloride ion has an obvious enhancement effect rather than a scavenging effect on the degradation of quinoline in this photoelectrocatalytic reactor. The enhancement can be interpreted by the fact that at the lower Cl⁻ ion concentration, the Cl⁻ ion took part in a competition for oxidizing radicals or the active sites of the catalyst, resulting in a scavenging effect on the photoelectrocatalytic degradation of quinoline to some extent. However, with the increase of Cl⁻ ion concentration the adsorption of Cl⁻ ion reaches equilibrium, the surplus free Cl⁻ ion as an electrolyte can enhance charge-transfer in the photoelectrocatalytic reactor, leading to the increase in capture effect of photogenerated electron by external electric field. Moreover, increasing the NaCl concentration can lead to a strong increase of degradation efficiency of quinoline by direct and/or indirect electrochemical oxidation under high cell voltage. In order to confirm this viewpoint, the same experiments with another stronger electrolyte, NaClO₄, instead of NaCl, were

also carried out, and the comparison results were shown in **Table 1**. It is found that in the presence of the same conductivity as 500 mmol L⁻¹ NaCl, NaClO₄ also had an apparent increase in degradation efficiency of quinoline, but the apparent rate constant (0.0154 min⁻¹) was much less than that of NaCl (0.0224 min⁻¹). The difference in the two rate constants may be due to the oxidation effect of Cl₂ and other active species, forming by direct or indirect electrochemical reaction from Cl⁻ ion in the reactor.

Figure 2 Effect of Cl⁻ ion concentration on the rate constant

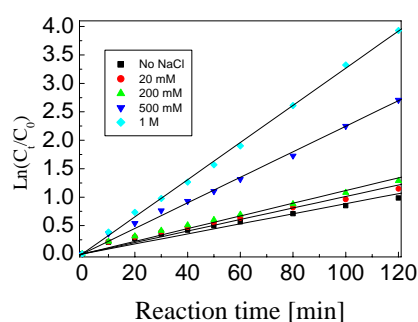


Table 1 Photoelectrocatalytic kinetic rate constants without or with electrolytes

Item	No electrolytes	NaCl	NaClO ₄
Kinetic constant (min ⁻¹)	0.0089	0.0224	0.0154
Regression coefficient	0.992	0.999	0.991

Acknowledgments

This work was financial support from Guangdong Province Science Innovation Foundation (99B06901G), and the Opening Project of State Key Lab of Organic Geochemistry (OGL-200210).

References

1. M. Abdullah, G. K. Low, R. W. Matthews, *J. Phys. Chem.*, **1990**, *94*, 6820.
2. R. A. Burns, J. C. Crittenden, D. W. Hand, S. R. Salman, *J. Environ. Eng.*, **1999**, *125*, 77.
3. A. Piscopo, D. Robert, J. V. Weber, *Appl. Catal. B: Environ.*, **2001**, *35*, 117.
4. M. Sokmen, A. Ozkan, *J. Photochem. Photobiol. A: Chem.*, **2002**, *147*, 77.
5. D. H. Kim, M. A. Anderson, *Environ. Sci. Technol.*, **1994**, *28*, 479.
6. R. J. Candal, W. A. Zeltner, M. A. Anderson, *Environ. Sci. Technol.*, **2000**, *34*, 3443.
7. Y. Xiong, T. C. An, C. H. Zha, X. H. Zhu, *J. Appl. Geochem.*, **2003**, in press.
8. T. C. An, X. H. Zhu, Y. Xiong, *J. Environ. Sci. Health*, **2001**, *36A*, 2069.
9. T. C. An, X. H. Zhu, Y. Xiong, *Chemosphere*, **2002**, *46*, 897.
10. T. C. An, Y. Xiong, G. Y. Li, X. H. Zhu, *J. Photochem. Photobiol. A: Chem.*, **2002**, *152*, 155.

Received 7 April, 2003