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ENHANCEMENT OF PHOTOCATALYTIC OXIDATION OF HUMIC ACID IN TiO_2 SUSPENSIONS BY INCREASING CATION STRENGTH

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ABSTRACT

This study aimed at improving the photocatalytic (PC) oxidation of humic acids in TiO_2 suspensions by adding cationic ion such as calcium or magnesium. A set of tests was first conducted in the dark to study the adsorption of HA onto TiO_2 in suspensions at different pH and calcium concentrations. The experiment demonstrated that the adsorption of HA onto the TiO_2 particles was either pH-dependent or calcium strength-dependent due to electrostatic interaction and calcium ion bridging. The photodegradation of HA in the presence of UV irradiation was investigated as a function of pH and the concentration of calcium and magnesium ions. The results showed that the adsorption behavior between HA and TiO_2 played a very important role during the PC oxidation process. The PC oxidation could be enhanced at neutral pH by increasing the cation strength. The kinetics of humic acid photocatalytic degradation in TiO_2 suspensions with different initial concentrations was also studied using the Langmuir-Hinshelwood model.

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INTRODUCTION

The presence of humic acids (HA), as part of natural organic matters (NOM), has been a problem in the water industry due to their water-soluble formation, a wide range of distribution in molecular weight and size, and their non-biodegradability. It has been confirmed that humic substances are precursors of disinfection by-products (DBPs) in chlorination processes (NCI, 1978; Li *et al*., 1996; Huck, 1999; Singer, 1999). Titanium dioxide (TiO_2)-based photocatalysis has been the focus of numerous investigations in recent years, particularly owing to its application for the complete mineralization of undesirable organic contaminants to CO_2, H_2O and inorganic constituents (Carey, 1976; Ollis *et al*., 1991; Hoffmann *et al*., 1995). Some papers reported that humic substances could be effectively degraded in TiO_2 suspensions under UV irradiation (Bekbölet and Ozkosemen, 1996; Eggins *et al*., 1997). To further improve the photooxidation of organics in aqueous TiO_2 suspension, most efforts have been addressed on the modification of TiO_2-based catalysts by doping, implanting, and depositing different dopants (Mikula *et al.*, 1992; Yang *et al.*, 1997; Linsebigler *et al.*, 1995; Vorontsov *et al.*, 1999). However, sorption of the organic substrates at the surface of TiO_2 catalysts is also an important factor that affects the photocatalytic degradation rate, since it is believed that this type of photocatalytic oxidation reaction mainly occurs at the surface of the catalysts, but not in the bulk solution. It has been reported that a strong adsorption of substances on the surface of TiO_2 catalysts at low pH could enhance the reaction rate of photocatalytic oxidation in many lab-scale experiments (Zhou and Banks, 1993; Jucker and Clark, 1994; Eggins *et al*., 1997; Chen and Jeng, 1998). However, it is not practical to pre-adjust water or wastewater pH from a neutral pH condition down to pH 2-3 and re-adjust it back after treatment. Recently, some studies have reported the influence of ionic strength in TiO_2 suspensions on photocatalytic oxidation. Dionasiou and co-workers in 2000 reported that ionic strength in TiO_2 suspensions influenced the adsorption capacity and adsorption mechanism, but did not affect the rates of the photocatalytic reactions significantly. Chen and his co-workers in 1999 reported that magnesium ions increased the photocatalytic oxidation of 2-chlorophenol in terms of dissolved organic concentration. However, it did not conspicuously increase the mineralization rate of chlorophenols. Magnesium ions enhance the oxidation rate by surface reaction, increasing photo-generated electrons and holes, and inhibiting electron/hole recombination. Actually these cationic ions also play an important role in adsorption of HA in aqueous solution. It has been reported that humic acid adsorption caused by calcium ion bridging between humic acids in solution and in deposited layer would increase with increasing pH (Nefedov *et al*., 1998; Yoon *et al.*, 1998).

This research aimed at investigating the photocatalytic oxidation of humic acids in TiO_2 suspensions at neutral pH in presence of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions.

EXPERIMENTAL DETAILS

Materials

TiO_2 powder (Degussa P25) with an average particle size of 30 nm and surface area of 50 m^2 g^{-1} was used in the experiment. Commercially available HA with ash content of about 20% was supplied by Fluka Chemical (USA). Other chemicals including $CaCl_2$ and $MgCl_2$ were obtained from BDH Laboratory Supplies (UK) as analytical grade reagents and used without further purification. Deionized distilled water was used throughout the experiment.

Preparation of HA Solution

A HA suspension was first prepared by adding the HA chemicals into the deionized water and gently heating to temperatures up to 60 ^{o}C in order to accelerate the dissolution of HA. Then the supersaturated HA suspension cooled down to room temperature gradually and was filtered through a 0.45-μm Millipore syringe filter. The HA residue on the filter was dried in an oven at 105 ^{o}C until its weight stabilized. The HA concentration in the clear solution (filtrate) was calculated as ($[HA]_{initial}$-$[HA]_{residue}$) by the gravimetric method. The HA solution was stored as a stock solution for further use.

Adsorption experiment

An adsorption study was first carried out in 250-ml beakers wrapped with aluminum foil to block any incoming light. The TiO_2 slurries were prepared by adding TiO_2 powder in 20 mg l^{-1} HA solutions and well mixed before experiment. In the adsorption experiment, two sets of tests were conducted to investigate the HA adsorption affected by different pH and calcium concentrations respectively. The first set of tests was carried out with the same initial HA concentration of 20 mg l^{-1} and TiO_2 loading of 1 g l^{-1}, but different initial pH (3.0, 5.0, 7.0 and 9.0). The second set of tests was carried out at pH 7.0, HA concentration of 20 mg l^{-1}, TiO_2 concentration of 1 g l^{-1} and calcium concentrations of 20 mg l^{-1} and 80 mg l^{-1}. Hydrochloric acid and sodium hydroxide solutions were used to adjust the pH of the HA solution.

Photoreactor and photooxidation experiment

Figure 1 shows the batch photocatalytic reactor system used for the experiments. A photoreactor consists of a cylindrical borosilicate glass reactor vessel with an effective volume of 280 ml, a cooling water jacket, and a 125-W high-pressure mercury lamp (Institute of Electric Light Source, Beijing) positioned axially at the center of the reactor vessel as a light source to provide near UV radiation with a light intensity of 4.38 mW cm^{-2}. TiO_2 slurries were prepared by adding the

TiO_2 powder directly into the air-purged HA solutions followed by ultrasonic dispersion for 15 min before reaction. The reaction temperature was kept at 20 ^oC by cooling water. A special glass grit as air diffuser was fixed at the bottom of the reactor to uniformly disperse air into the solution.

The photooxidation experiment in this study included five sets of tests for different objectives. The first set of photodegradation tests with the same initial HA concentration of 20 mg l^{-1} was carried out under UV irradiation for 2.5 h at different pH (3.0, 5.0, 7.0 and 9.0) in order to determine the degree of HA degradation. The second set of tests with the same HA concentration at pH 7.0 was carried out by adding either Ca^{2+} or Mg^{2+} to determine the effect of cation strength on the photooxidation efficiency. The third set of tests was performed with different experimental conditions including UV irradiation and TiO_2 catalyst in order to determine the best experimental conditions. The fourth set of tests was carried out to determine the photodegradation rate of HA as a function of initial concentrations of HA (20, 15, 10 and 5 mg l^{-1}). The fifth set of tests was carried out with different TiO_2 loadings (1, 2 and 4 g l^{-1}) to determine the effects of TiO_2 loading and also pH change during the reaction on the photodegradation of HA.

[Fig. 1]

Analyses

Samples were collected from the TiO_2 suspension at designated time intervals during the reaction and filtered through 0.45-μm Millipore syringe filters. The filtrate was subjected to different analyses. The concentration of HA (UV_{254}) was determined by a UV-VIS spectrophotometer (Milton Roy Spectronic Genesys 2) at 254 nm. The color of the filtrate was determined by a Tintometer (Model PFX190) and expressed in Hazen units. Total organic carbon (TOC) concentration was determined by a TOC analyzer (Shimadzu TOC-5000A).

RESULTS AND DISCUSSION

The effects of different pH on the adsorption of HA

The first set of adsorption tests was carried out to study the adsorption behavior of HA on the

TiO_2 particles with the same initial HA concentration of 20 mg l^{-1} and TiO_2 concentration of 1 g l^{-1}, but at different pH (3.0, 5.0, 7.0 and 9.0). All tests were conducted in the dark for 12 h. The reaction slurry was continuously stirred at 250 rpm. The experimental results of HA adsorption at different pH are shown in Fig. 2.

[Fig. 2]

The results in Fig. 2 indicated that under the lower pH conditions, especially at pH 3.0, the TiO_2 particles demonstrated a strong ability to adsorb HA from its aqueous solution, but at pH 7.0 and pH 9.0 there was almost no adsorption of HA on TiO_2 particles. This behavior may be caused by the negative charge of both HA and TiO_2 particles at pH 7 and above. The test at pH 3 was continuously carried out for 24 h and the water samples collected at different time intervals were scanned in the full range of 200-700 nm. The results are shown in Fig. 3.

[Fig. 3]

The adsorption model of H_2O-TiO_2 in a steam atmosphere has been described by Marrison (1980) who showed that the equivalent adsorption of H^+ and OH^- on the TiO_2 takes place, while OH^- is adsorbed by the titanium cation and H^+ is adsorbed by the oxygen anion. Once the TiO_2 solid is put into aqueous solution, the adsorption of H^+ and OH^- on the TiO_2 surface is not equivalent and depends on the pH of solution:

In acidic medium, $OH^-_{ad} + H^+_{soln} = H_2O$ (1)

In alkaline medium, $H^+_{ad} + OH^-_{soln} = H_2O$ (2)

Equation 1 leads to a net positive charge on the surface of TiO_2 due to the adsorbed OH^- reacting with the H^+ in the solution; while Equation 2 leads to the net negative charge of TiO_2 due to the adsorbed H^+ reacting with the OH^- in the solution. In fact, the adsorption of H^+ and OH^- on the surface of TiO_2 depends on the point of zero charge (pzc) of TiO_2 in aqueous solution.

The pzc of P25 TiO_2 is pH 6.3 (O'Shea and Cardona, 1995). At pH < 6.3, the positively charged TiO_2-H^+ offers a suitable surface for negatively charged HA molecule adsorption, but at pH > 6.3, the surface of TiO_2 becomes negatively charged $TiO_2(OH)^-$ which provides an unfavorable condition for the HA molecule to approach. Therefore, the adsorption of HA in our experiment became very difficult at pH 7.0 and above, because the electrostatic repulsion between the HA and the surface of titanium dioxide increased.

The effects of calcium ion strength on the adsorption of HA in TiO_2 suspensions

From the experimental results of HA adsorption, it was clear that the coverage of HA on the TiO_2 catalyst surface is obviously pH-dependent. While the pH in aqueous solution was close to the pzc of TiO_2, the coverage was almost not observed. Calcium (Ca^{2+}) is one of the major hard cations in natural water and may affect the adsorption behavior of HA onto TiO_2 as well as the photocatalytic oxidation of HA. The second set of adsorption tests was performed at pH 7.0, TiO_2 = 1 g l^{-1} and C_0 (HA)= 20 mg l^{-1}, and different calcium concentrations (0, 20 and 80 mg l^{-1}) by adding $CaCl_2$. The experiments were performed for 2 h and the experimental results are illustrated in Fig. 4.

[Fig. 4]

The results shown in Fig. 4 demonstrated that the adsorption of HA onto the surface of TiO_2 at pH 7.0 was significantly enhanced due to the presence of calcium ion. In the absence of calcium ion, the adsorption of HA onto TiO_2 was insignificant. This phenomenon may result because of several reasons: (1) TiO_2 powder and HA gains its negative charge with increasing pH and loses this with increasing calcium ion concentration. The repulsion between humic acids and TiO_2 powder was expected to decrease with increasing calcium ion concentration; (2) There was a function of calcium ion bridging between the HA in solution and the HA adsorbed on the surface of TiO_2 (Yoon *et al.* 1998); (3) The charge neutralization may be another reason to improve HA adsorption in the neutral pH condition. The experiment demonstrated that increase of calcium concentration accelerated the rate of HA adsorption on the TiO_2 surface.

The effects of pH on the photodegradation of HA

In the photodegradation study, the first set of tests was performed to investigate the photodegradation of HA as a function of pH. Four tests were conducted with the same initial HA concentration of 20 mg l^{-1}, TiO_2 concentration of 1g l^{-1} and light intensity of 4.38 mW cm^{-2}, but at different initial pH (3.0, 5.0, 7.0 and 9.0). Each of the tests was performed for 2.5 h. The experimental results presented in Fig. 5 revealed that the decreasing rate of HA concentration increased with decreasing pH. At pH 3.0 there was a sharp reduction of HA concentration during the first half hour of photoreaction. This may indicate that the adsorption played a significant role on the photocatalytic degradation, since the photoreaction mainly occurred on the surface of catalyst, but not in the bulk solution.

[Fig. 5]

Some TiO_2 particle samples were also collected at different time intervals through the reaction at pH 7. They were first filtered by 0.45-μm Millipore filter paper and then examined by visual observation. While the raw TiO_2 powder was pure white in color, the TiO_2 sample collected from photoreaction slurry at 5 min was brown similar to that of adsorbed in the dark test, which demonstrated that the accumulation of HA on the TiO_2 surface indeed took place. The TiO_2 sample collected at 10 min was light brown, the TiO_2 sample at 30 min was almost yellow and the TiO_2 sample at 1 h was white again. These results may indicate that the accumulation of HA on the TiO_2 surface occurred during the early stage of the reaction because the adsorption rate was faster than the photoreaction rate, then disappearing gradually during the later stage of the reaction because the adsorption rate was behind the photoreaction rate.

Photooxidation of HA in the presence of calcium or magnesium ion

Although HA molecules could not be effectively adsorbed onto the TiO_2 particle at pH 7.0, the existence of calcium ion in the solution demonstrated the significant improvement of HA adsorption onto TiO_2. Considering groundwater frequently has a hardness (mainly calcium and magnesium) above 300 mg l^{-1} as $CaCO_3$ (Lisley *et al.,* 1992), calcium and magnesium were added in the second set of tests to explore their effects on the photooxidation of HA. The reaction suspensions with TiO_2 loading of 1 g l^{-1} was prepared by dispersing TiO_2 powder into the 20 mg l^{-1} HA aqueous solution containing either 80 mg l^{-1} Ca^{2+} or 80 mg l^{-1} Mg^{2+} by adding either $CaCl_2$ or $MgCl_2$ respectively. The suspension was irradiated for 2.5 h. The experimental results are shown in Fig. 6. For comparison, the photodegradation of HA in the absence of Ca^{2+} or Mg^{2+} was also carried out and the results are also shown in Fig. 6. It can be seen that the presence of either calcium or magnesium enhanced the rate of HA removal significantly. While the reaction without addition of calcium or magnesium took more than 2.5 h to remove more than 90% of HA from solution, the reaction with addition of calcium or magnesium took only less than 1 h for achieving the same removal efficiency.

[Fig. 6]

To study the mineralization of HA in the reaction, TOC was also monitored against reaction time and compared with the variation of HA concentration as shown in Fig. 7. In the absence of cationic ion, both HA and TOC concentrations were reduced slowly during the reaction. After 2.5 h of reaction time, the HA removal efficiency was 94%, while the TOC removal efficiency was 78%. This indicates that the reaction only achieved incomplete mineralization of HA, and that a longer irradiation time was needed for complete mineralization. In the presence of calcium, both HA and TOC concentrations were reduced much faster, especially during the first half-hour. The TOC removal was almost as fast as HA removal, which indicates that degradation and mineralization of HA occurred simultaneously. After 2.5 h of UV irradiation, both HA and TOC concentrations were reduced by 95% which means that almost complete mineralization was achieved under the experimental conditions. In the presence of magnesium, the TOC removal was not as fast as the HA degradation during the first 1.5 h, but it was very close to the HA removal at the end of test. These experimental results further demonstrated that the existence of divalent cationic ions in aqueous solution could enhance the adsorption rate of HA on the TiO_2 surface and therefore improve the photoreduction rate.

[Fig. 7]

Comparison of PC Oxidation under different conditions

In order to clarify the role of catalyst and UV light as well as their combined efforts on the HA degradation, the third set of photooxidation tests was performed with the same initial HA concentration (20 mg l^{-1}) and the same initial pH 7.0, but different combination of UV and TiO_2. The experimental results are shown in Fig. 8. Two control tests were conducted in the absence of either UV radiation or TiO_2 catalyst. In the presence of TiO_2 only (reaction in the dark), no degradation of HA occurred, since TiO_2 alone could not oxidize HA. In the presence of UV only (photolysis) without addition of TiO_2, it was found that HA was removed by 68% while TOC was removed by 38%. In the presence of both UV irradiation and TiO_2 (photocatalytic oxidation), the experimental results demonstrated that the photocatalytic oxidation process achieved the highest HA degradation with 90% removal of HA in 2.5 h.

[Fig. 8]

The effect of initial HA concentration on the photodegradation of HA

This set of photooxidation tests was performed to determine the kinetic constant of the first order reaction for the HA photodegradation with different initial HA concentration. Four tests with the same initial pH 7.0, TiO_2 concentration of 1 g l^{-1} and light intensity of 4.38 mW cm^{-2}, but different initial HA concentrations (5, 10, 15 and 20 mg l^{-1}) were conducted in the presence of UV irradiation. The tests lasted for 2.5 h and samples for analysis were collected at different time intervals during the reaction. The experimental results are shown in Fig. 9.

[Fig. 9]

Several studies (Pruden and Ollis, 1983; Ollis *et al*., 1984; Matthews, 1988) indicated that the rate of photocatalytic degradation of various organic contaminants over illuminated TiO_2 could be explained with the Langmuir-Hinshelwood (L-H) kinetic expression. When the initial concentration of organic contaminants was low, the L-H rate form reduced to an apparent first-order kinetics form. If we assume that the photocatalytic degradation reaction of HA simply follows the first-order kinetics under $C_o \leqslant 20$ mg l^{-1}, the apparent first-order rate constant k in the tests can be calculated from the straight line of $\ln(C/C_o)$ versus illumination time. These results are listed in Table 1. The experimental results show that the degradation rate increased with increasing HA concentration, but the apparent kinetic constant k decreased with increasing HA concentration.

[Table 1]

The effect of TiO_2 loading on the photodegradation and photodecolorization of HA

To investigate the effect of TiO_2 dosage on the degradation and decolorization of HA in aqueous solution, another set of photooxidation tests was performed under the same initial HA concentration (20 mg l^{-1}), initial pH (7.0) and light intensity of 4.38 mW cm^{-2}, but different TiO_2 dosages (1, 2 and 4 g l^{-1}). These test were carried out for 2.5 h. Samples were collected during the reaction and analyzed for UV_{254}, color and pH. The experimental results shown in Fig. 10 demonstrated that the removal rate of HA was increased with increasing TiO_2 concentration in the range of 1- 4 g l^{-1}.

[Fig. 10]

The results for color reduction and pH change during the reaction are listed in Table 2. These data indicate that the decolorization followed the same trend as that of degradation, but increased faster than degradation with increasing TiO_2 concentration. A decrease of pH in the reaction solution observed suggests that the intermediates of HA degradation could be some organic acids.

[Table 2]

CONCLUSIONS

The photocatalytic oxidation of HA in TiO_2 suspensions has been studied under different experimental conditions in a batch photoreactor. The results demonstrated that the degradation of HA could be significantly enhanced either at low pH (below 4) or by adding calcium and magnesium ions. The increase of cation strength in aqueous solution could provide a favorable condition for adsorption of HA on the TiO_2 surface and therefore enhance the photooxidation rate.

These results provide an alternative for improving the photooxidation rate in TiO_2-based photooxidation processes without adjusting pH. The degradation rate of HA was also a function of its initial concentration and TiO_2 dosage. It was found that the photocatalytic oxidation could be an effective process for the mineralization of HA in water.

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REFERENCES

Bekbölet, M., Ozkosemen, G., 1996. A preliminary investigation on the photocatalytic degradation of a model HA. Wat. Sci. Technol. 33(6), 189-194.

Carey, J.H., 1976. Photodechlorination of PCBs in the Presence of Titanium Dioxide in Aqueous Suspensions. Bull. Environ. Contam. Toxiol. 16, 663-677.

Chen, J.N., Chan, Y.C., Lu, M.C., 1999. Photocatalytic oxidation of chlorophenols in the presence of manganese ions. Wat. Sci. Technol. 39(10-11), 225-230.

Chen, P.H., Jeng, C.H., 1998. Kinetics of photocatalytic oxidation of trace organic compounds over titanium dioxide. Environ. Int. 24(8), 871-879.

Dionasiou, D.D., Suidan, M.T., Bekou, E., Baudin, I, Laine, J.M., 2000. Effect of ionic strength and hydrogen peroxide on the photocatalytic degradation of 4-chlorobenzoic acid in water. App. Catal. B 26(3), 153-171.

Eggins, B.R., Palmer, F l., Byrne, J.A., 1997. Photocatalytic treatment of humic substances in drinking water. Wat. Res. 31(5), 1223-1226.

Hoffmann, M.R., Martin, S.T., Choi, W.Y., Bahnemann, D.W., 1995. Environmental applications of semiconductor photocatalysis. Chem. Rev. 95, 69-96.

Huck, P.M., 1999. Development of a framework for quantifying the removal of humic substances by biological filtration. Wat. Sci. Technol. 40(9), 149-156.

Jucker, C., Clark, M.M., 1994. Adsorption of aquatic humic substances on hydrophobic ultrafiltration membranes. J. Membrane. Sci. 97, 37-52.

Li, J.W., Yu, Z.B., Gao, M., 1996. Effect of ultraviolet irradiation on the characteristics and trihalomethanes formation potential of HA. Wat. Res. 30(2), 347-350.

Linsebigler, A., Lu, G., Yates, J.T., 1995. Photocatalysis on the TiO_2 surfaces: principles, mechanisms, and selected results. Chem. Rev. 95, 735-758.

Marrison, S.R., 1980. Electrochemistry at Semiconductor and Oxidation Metal Electrodes. Kluwer Academic/Plenum Publishers.

Matthews, R.W., 1988. Kinetics of photocatalytic oxidation of organic solutes over titanium dioxide. J. Catal. 111, 264-272.

Mikula, M., Blecha, J., Ceppan, M., 1992. Photoelectrochemiecal properties of anodic TiO_2 layers prepared by various current densities. Electrochem. Soc. 139, 3470-3474.

National Cancer Institute (NCI), 1978. Carcinogenesis bioassay of chloropirin, RS No. 65. Washington, D.C.

Nefedov, V.I., Teterin, M., Yu, A., Lebedev, A.M., 1998. Electron spectroscopy for chemical analysis investigation of the interaction of uranyl and calcium ions with Has. Inorg. Chim Acta. 273, 234-237.

Ollis, D.F., Pelizzetti, E., Serpone, N., 1991. Destruction of Water Contaminants. Environ. Sci. Technol. 25, 1523-1529.

Ollis, D.F., Hsiao, C.Y., Budiman, L., Lee, C l., 1984. Heterogeneous photoassisted catalysis: conversion of perchloroethylene. dichloroethane, chloroacetic acids, and chlorobenzenes. J. Catal. 88, 89-96.

O'Shea, K.E. and Cardona, C., 1995. The reactivity of phenol in irradiated aqueous suspensions of TiO_2 mechanistic changes as a function of solution pH. J. Photoch. Photobio. A 91, 67-72.

Pruden, A l., Ollis, D.F., 1983. Photoassisted heterogeneous catalysis: The degradation of trichloroethylene in water. J. Catal. 82, 404-417.

Singer, P. C., 1999. Humic substances as precursors for potentially harmful disinfection by-products. Wat. Sci. Technol. 40(9), 25-30.

Vorontsov, A.V., Savinov, E.N., Jin, Z.S., 1999. Influence of the form of photodeposited platinum on titania upon its photocatalytic activity in CO and acetone oxidation. J. Photoch. Photobio. A 125, 113-117.

Yang, J.C., Kim, Y.C., Shul, Y G., Shin, C.H., Lee, T.K., 1997. Characterization of photoreduced

Pt/TiO_2 and decomposition of dichloroacetic acid over photoreduced Pt/TiO_2 catalysts. Appl. Surf. Sci. 121/122, 525-529.

Yoon, S.H., Lee, C.H., Kim, K.J., Fane, A G., 1998. Effect of calcium ion on the fouling of nanofilter by HA in drinking water production. Wat. Res. 32(7), 2180-2186.

Zhou, J l., Banks, C. J., 1993. Mechanism of HA colour removal from natural waters by fungal biamass biosorption. Chemosphere 27, 607-620

Table 1. First-order reaction rate constant *k* and correlation coefficient R for the photodegradation of HA with different initial concentrations

HA_0 (mg l^{-1})	*k* (min^{-1})	R
20	0.0186	0.9727
15	0.0220	0.9915
10	0.0272	0.9920
5	0.0311	0.9971

Table 2. Photodecolorization of HA and pH variation with different TiO_2 dosage

Conditions: $HA_0 = 20$ mg l^{-1}; initial pH 7.0; light intensity = 4.38 mW cm^{-2}

Time, h	$TiO_2 = 1$ g l^{-1}		$TiO_2 = 2$ g l^{-1}		$TiO_2 = 4$ g l^{-1}	
	Color Removal %	pH	Color Removal %	pH	Color Removal %	pH
0.0	0.0	7.05	0.0	6.98	0.0	7.08
0.5	34	5.36	45	5.31	67	6.16
1.0	64	4.98	84	5.18	94	5.62
1.5	87	4.70	98	5.59	99	5.76
2.0	95	4.89	100	5.86	100	6.21
2.5	97	5.55	100	5.92	100	6.29

List of figure captions

Fig. 1. Schematic of the photocatalytic reactor

Fig. 2. The effect of pH on the adsorption of HA onto TiO_2

Conditions: HA_0 = 20 mg l^{-1}, TiO_2 = 1 g l^{-1}

Fig. 3. UV absorbance of HA (C_o=20 mg l^{-1}) vs. wavelength in the adsorption tests

Spectra 1, 2, 3, 4, 5 and 6: Adsorption time at 0, 0.25, 0.75, 1.0, 12.0 and 24.0 h.
Conditions: TiO_2 = 1 g l^{-1}; pH 3.0

Fig. 4. The effect of Ca^{2+} on the adsorption of HA onto TiO_2
Conditions: pH 7.0; TiO_2 = 1 g l^{-1}; HA_0 = 20 mg l^{-1}

Fig. 5. The effect of pH on the photodegradation of HA

Conditions: HA_0=20 mg l^{-1}; TiO_2 =1 g l^{-1}; light intensity = 4.38 mW cm^{-2}

Fig. 6. Photodegradation of HA vs. irradiation time in the presence of Ca^{2+} or Mg^{2+}

Conditions: HA_0 = 20 mg l^{-1}; TiO_2 = 1 g l^{-1}; pH 7.0; light intensity = 4.38 mW cm^{-2}

Fig. 7. Removals of HA and TOC vs. irradiation time during the PC oxidation process

Conditions: HA_0 = 20 mg l^{-1}; TiO_2 = 1 g l^{-1}; pH 7.0; light intensity = 4.38 mW cm^{-2}

Fig. 8. Reduction of HA under different experimental conditions

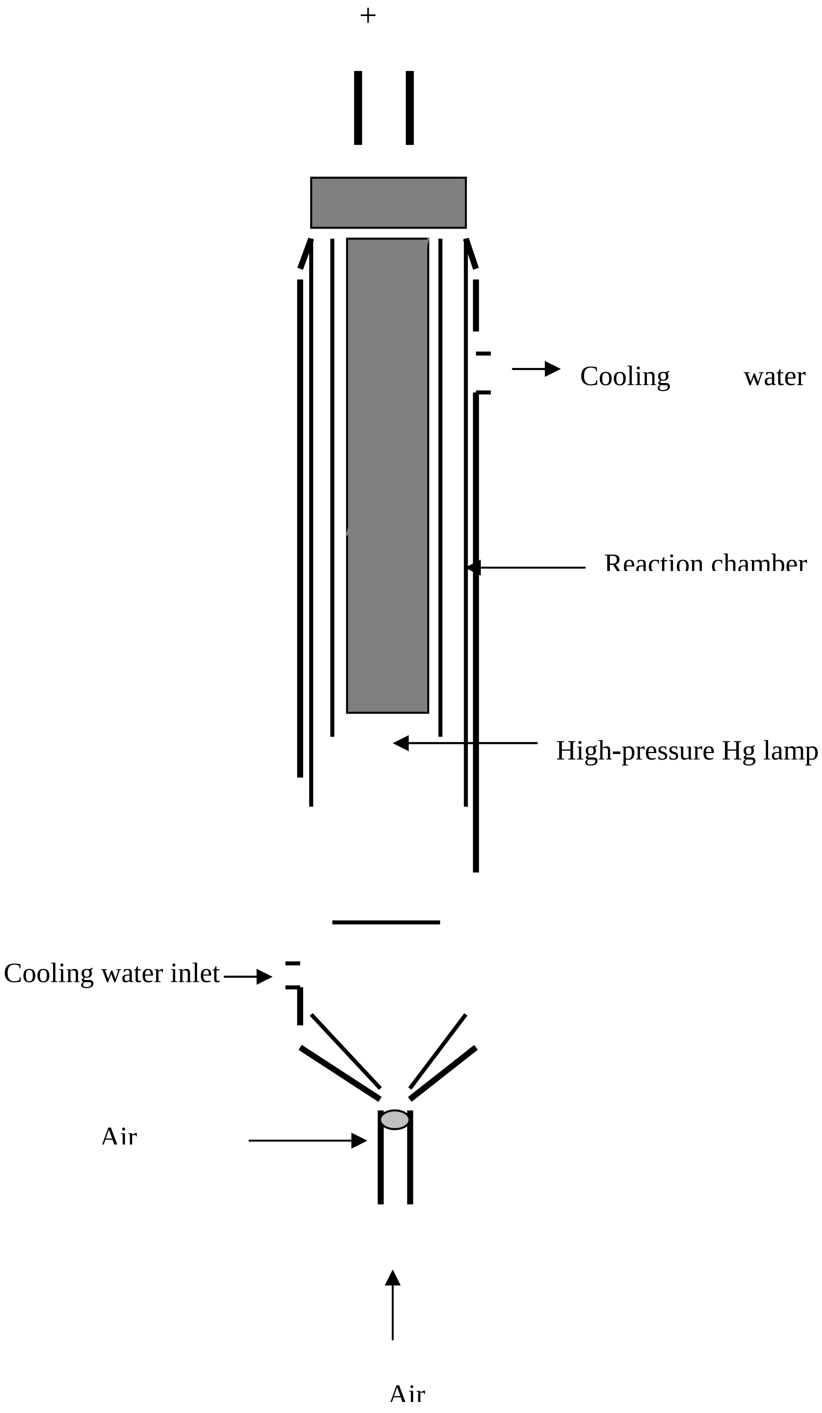
HA_0 = 20 mg l^{-1}; pH 7.0; TiO_2 = 1 g l^{-1}; light intensity = 4.38 mW cm^{-2}

Fig. 9. Photodegradation of HA with different initial concentrations of HA

Conditions: pH 7; TiO_2 = 1 g l^{-1}; light intensity = 4.38 mW cm^{-2}

Fig. 10. The effect of TiO_2 concentration on the photodegradation of HA

Conditions: HA_0 = 20 mg l^{-1}; Initial pH 7.0; light intensity = 4.38 mW cm^{-2}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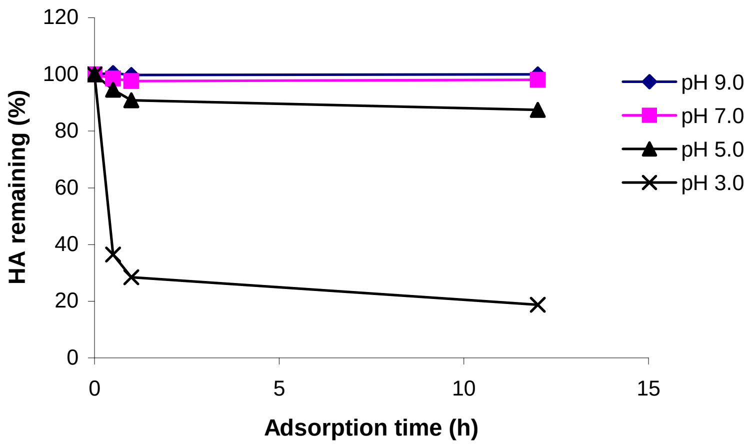
Reaction chamber
High-pressure Hg lamp
Cooling water inlet
Air
Air

Fig. 1.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80
60
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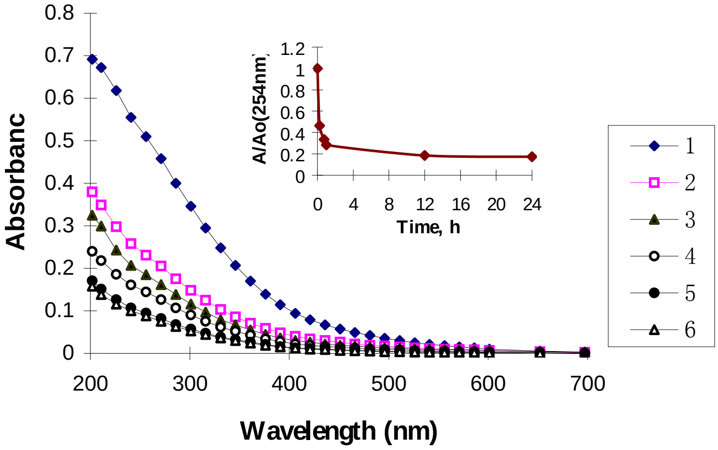
pH 5.0
pH 3.0

Fig. 2.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700
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Time, h
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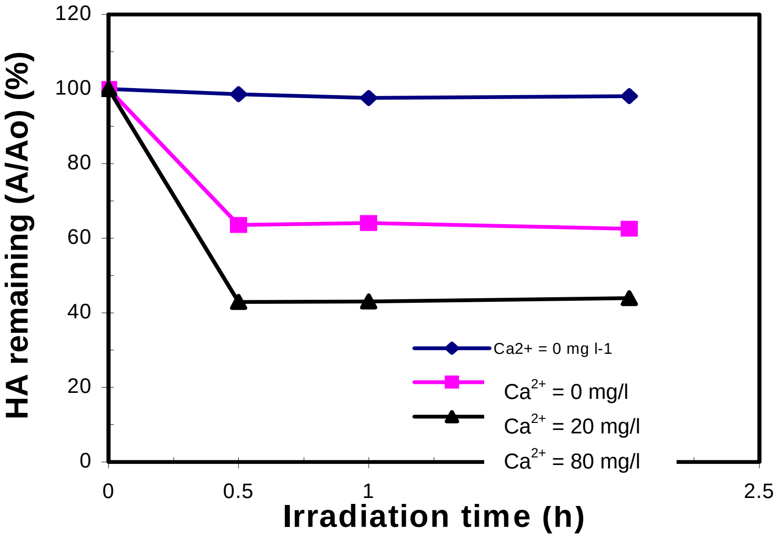
Fig. 3.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0
0
0.5
1
2.5
HA remaining (A/Ao) (%)
Irradiation time (h)
Ca2+ = 0 mg l-1
Ca2+ = 0 mg/l
Ca2+ = 20 mg/l
Ca2+ = 80 mg/l

Fig. 4.

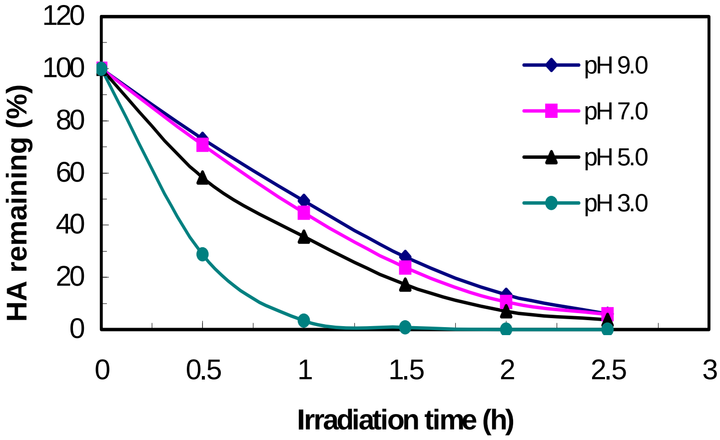

120
100
80
60
40
20
0
HA remaining (%)
0
0.5
1
1.5
2
2.5
3
Irradiation time (h)
pH 9.0
pH 7.0
pH 5.0
pH 3.0

Fig. 5.

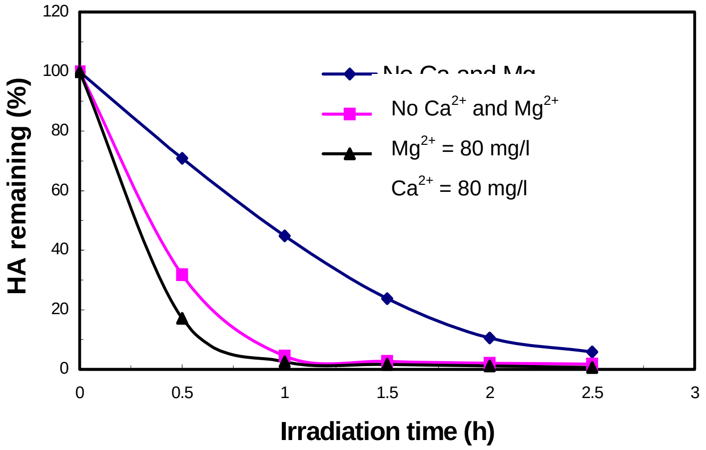

120
100
80
60
40
20
0
HA remaining (%)
0
0.5
1
1.5
2
2.5
3
Irradiation time (h)
No Ca and Mg
No Ca^{2+} and Mg^{2+}
Mg^{2+} = 80 mg/l
Ca^{2+} = 80 mg/l

Fig. 6.

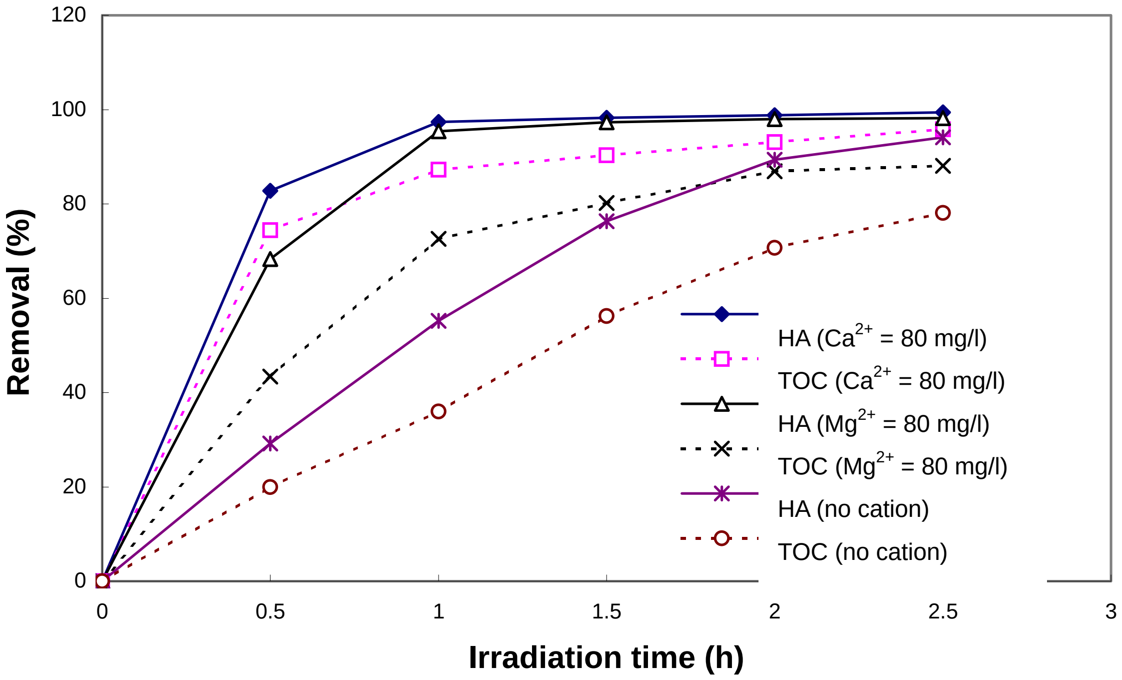

120
100
80
60
40
20
0
Removal (%)
0
0.5
1
1.5
2
2.5
3
Irradiation time (h)
HA (Ca^{2+} = 80 mg/l)
TOC (Ca^{2+} = 80 mg/l)
HA (Mg^{2+} = 80 mg/l)
TOC (Mg^{2+} = 80 mg/l)
HA (no cation)
TOC (no cation)

Fig. 7.

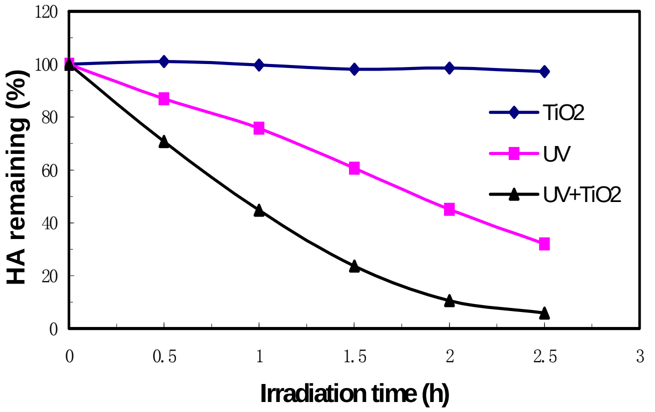
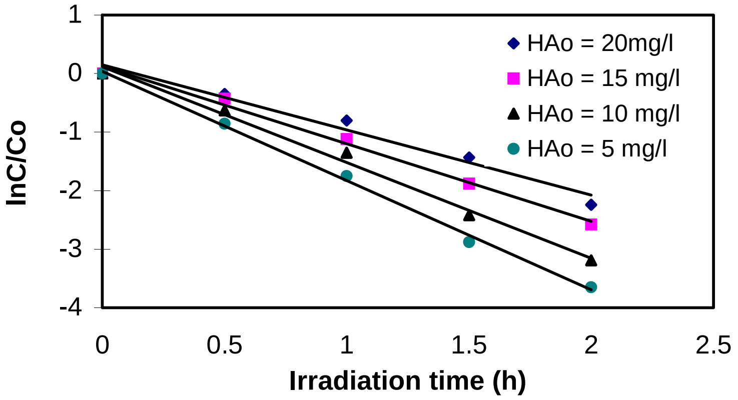

120
100
80
60
40
20
0
HA remaining (%)
0
0.5
1
1.5
2
2.5
3
Irradiation time (h)
TiO2
UV
UV+TiO2

Fig. 8



1
0
-1
-2
-3
-4
lnC/Co
0
0.5
1
1.5
2
2.5
Irradiation time (h)
◆ HAo = 20mg/l
■ HAo = 15 mg/l
▲ HAo = 10 mg/l
● HAo = 5 mg/l

Fig. 9

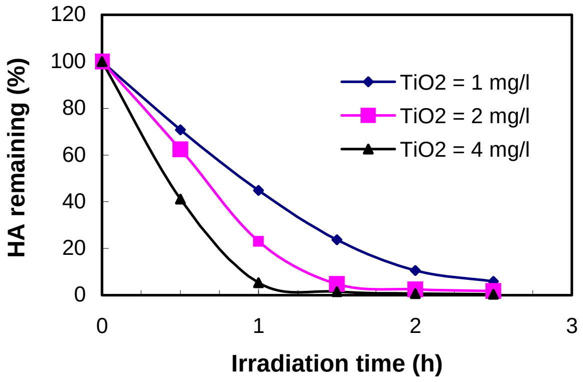

120
100
80
60
40
20
0
HA remaining (%)
0
1
2
3
Irradiation time (h)
TiO2 = 1 mg/l
TiO2 = 2 mg/l
TiO2 = 4 mg/l

Fig. 10

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