

Improved nitrogen removal in dual-contaminated surface water by photocatalysis

Yongming ZHANG (✉)¹, Rong YAN¹, Zhen ZOU¹, Jiewei WANG¹, Bruce E. RITTMANN²

¹ Department of Environmental Engineering, College of Life and Environmental Science, Shanghai Normal University, Shanghai 200234, China
² Swette Center for Environmental Biotechnology, Biodesign Institute, Arizona State University, Tempe, AZ85287-5801, USA

© Higher Education Press and Springer-Verlag Berlin Heidelberg 2012

Abstract River waters in China have dual contamination by nutrients and recalcitrant organic compounds. In principle, the organic compounds could be used to drive denitrification of nitrate, thus arresting eutrophication potential, if the recalcitrant organics could be made bioavailable. This study investigated the potential to make the recalcitrant organics bioavailable through photocatalysis. Batch denitrification tests in a biofilm reactor demonstrated that dual-contaminated river water was short of available electron donor, which resulted in low total nitrogen (TN) removal by denitrification. However, the denitrification rate was increased significantly by adding glucose or by making the organic matters of the river water more bioavailable through photocatalysis. Photocatalysis for 15 min increased the Chemical Oxygen Demand (COD) of the river water from 53 to 84 mg·L⁻¹ and led to a 4-fold increase in TN removal. The increase in TN removal gave the same effect as adding 92 mg·L⁻¹ of glucose. During the photocatalysis experiments, the COD increased because photocatalysis transformed organic molecules from those that are resistant to dichromate oxidation in the COD test to those that can be oxidized by dichromate. This phenomenon was verified by testing photocatalysis of pyridine added to the river water. These findings point to the potential for N removal via denitrification after photocatalysis, and they also suggest that the rivers in China may be far more polluted than indicated by COD assays.

Keywords dual contamination, eutrophication, photocatalysis, remediation, surface water

1 Introduction

With rapid development in China, many surface waters pose a severe risk of eutrophication caused by excessive nitrogen and phosphorus levels [1–3]. At the same time, the waters are heavily contaminated with organic compounds, including persistent organic pollutants (POPs) and endocrine disrupting chemicals (EDCs) [4–6]. Thus, these surface waters present the challenge of dual contamination by nutrients and recalcitrant organic compounds. For ecological, public health, and aesthetic reasons, the quality of these surface waters needs to be remediated throughout China [7–10].

Concerning eutrophication caused by excessive nitrogen (N), different biologic means are available for eliminating the N in the form of ammonia, nitrate, and nitrite, and it is important that all forms are removed (i.e., total-N (TN) removal) [11–16] to arrest eutrophication. Ammonia N is relatively easy to be converted to nitrite or nitrate N when the dissolved oxygen (DO) concentration in the water is maintained high enough by natural or engineered aeration [17–20], but total-N removal demands that nitrate and nitrite also be removed. This can be accomplished by denitrification, as long as an electron donor is available. Based on stoichiometry [21], the donor required is at least 2.9 and 1.7 g COD per g nitrate-N and nitrite-N removed, respectively. Additional electron donor must be available to consume DO (at least 1 g COD·g⁻¹ DO).

Most surface waters have low concentrations of bioavailable electron donors, compared to total N. This situation results in the accumulation of nitrate or nitrite N, which defeats the goal of total-N removal [22,23] and does not arrest eutrophication. It is unrealistic to add an organic electron donor to a eutrophic water body in order to improve nitrogen removal.

In certain cases, dual contamination of the surface water in China could be turned into a benefit if the organic contaminants were readily biodegradable and could drive

denitrification. Some river waters in China have COD:TN ratios significantly larger than the stoichiometric requirement for denitrification. However, the organic contaminants are largely recalcitrant, which means that they persist and cause water-quality risks. Advanced oxidation processes (AOPs)—e.g., ozone, Fenton's reagent, and photocatalysis—are widely used for degradation of recalcitrant chemicals [24] and also can transform the organic pollutants into easy-to-biodegradable organic molecules [25–28].

Among the AOPs, photocatalysis is unique in that it can cause oxidation or reduction of contaminants. This unique situation occurs because the absorption of a photon with energy greater than or equal to the band gap energy excites the electron from the valence band to the conduction band, generating an electron-hole pair (e^- and h^+). The electron and hole can migrate to the catalyst surface, where they are able to react directly with contaminants adsorbed at the semi-conductor's surface or indirectly by forming hydroxyl free radicals, such as $\cdot OH$. In general, the hole oxidizes water to hydroxyl radical, leading to oxidation of organics; alternately, direct electron transfer from an adsorbed species to the positive hole may occur, resulting in more selective oxidation [29]. When the electron migrates to the surface, it may reduce an adsorbed species.

TiO_2 , the most common photocatalyst, absorbs ultraviolet (UV) light to generate the e^- and h^+ pair. Its photocatalytic activity has been recognized since the pioneering studies of water reduction through photoexcitation of TiO_2 by Fujishima and Honda [30]. While it is possible to use TiO_2 to photocatalytically oxidize organic contaminants completely to CO_2 and H_2O in a series of steps, this full oxidation is far too expensive for water remediation. Instead, TiO_2 photocatalysis will be economic if it is used only to make recalcitrant organic molecules readily biodegradable [31].

Building on a series of successful experiments with coupled photocatalytic + biologic treatment for recalcitrant and inhibitory wastewaters [31–33], we treated dual-contaminated river water by combining photocatalysis and biodegradation in order to accelerate the rate of COD removal by making the organic matter more biodegradable [34]. We used potassium dichromate as the strong oxidant, in the presence of silver sulfate catalyst and heating, to oxidize organic pollutants in our COD assays [35,36]. However, some organic compounds, particularly N-containing heterocycles, are not well oxidized in the dichromate assay [35–38]. This opens up the possibility that some of the organic material in the river water is not oxidized by potassium dichromate until it was transformed by photocatalysis.

Here, we investigated the potential for using TiO_2 photocatalysis to treat dual-contaminated waters for simultaneous COD and total-N removal by denitrification. We evaluated actual dual-contaminated river water after TiO_2 photocatalysis and with added glucose to evaluate

key principles of the concept. We also investigated the possibility that the dichromate-based COD test was not measuring all of the organic material in the water. Specifically, we investigated if the COD test gave systematically low values when the river water contained certain organic materials that are not oxidized by dichromate: for example, heterocyclic compounds containing nitrogen, like pyridine.

2 Materials and methods

2.1 Preparation of the TiO_2 film by sol-gel

Chemicals: Titanium (IV) *n*-butoxide (C.P.) and ethanol (A.R.) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd.; nitric acid (A.R.) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd.

Preparation of the sol: 5 mL of titanium (IV) *n*-butoxide was added to 20 mL of ethanol, and then the mixture was stirred for 1 h at $60\text{ r}\cdot\text{min}^{-1}$, followed by adjusting the pH to 3 by adding nitric acid.

Coating the TiO_2 film [39]: A clear glass piece ($4.5\text{ cm} \times 6\text{ cm}$) was immersed into the sol under ultrasound (59 kHz frequency) for 15 to 20 s and then lifted vertically from the sol at speed of $30\text{ cm}\cdot\text{min}^{-1}$ to generate the semi-finished material. The mat glass coated with the TiO_2 sol was calcined at 480°C after drying. The two-step coating processes were repeated 6 times to get a sufficiently thick TiO_2 film. X-ray analysis [32] indicated that the coated TiO_2 was anatase.

2.2 Denitrifying biofilm reactor

We made the denitrifying biofilm reactor, shown schematically in Fig. 1, of polymethyl methacrylate with a 150-mL working volume. A honeycomb ceramic (supplied by Pingxiang Sanyuan Ceramic Plant, Pingxiang, China) installed in the center of the reactor was the biofilm carrier, and a small magnetic stirring bar below the carrier mixed the liquid contents. This reactor was operated in the batch mode.

2.3 Cultivation of denitrifying biofilm

Anaerobic sludge: We obtained sludge from the anaerobic part of anoxic/oxic (A/O) process at the Longhua municipal wastewater treatment plant in Shanghai. To select for denitrifying bacteria, we placed the sludge in a sealed flask, added medium, and incubated the mixture at $35^\circ\text{C} \pm 1^\circ\text{C}$ [40], in the dark, and isolated from the air. The selection process lasted for 30 days, with medium replaced every 3 days. The medium contained $500\text{ mg}\cdot\text{L}^{-1}$ glucose and $450\text{ mg}\cdot\text{L}^{-1}$ potassium nitrate dissolved in river water (described below). The sludge's color changed from tan to dark brown during the selection process.

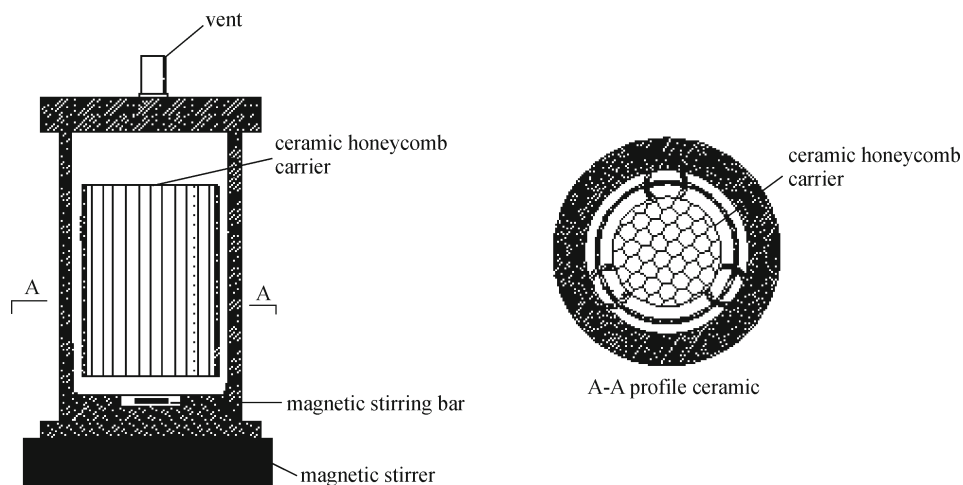


Fig. 1 Denitrifying biofilm reactor with a 150-mL working volume

Denitrifying biofilm: We immersed the ceramic honeycomb carrier into the denitrifying sludge for 48 h before moving the carrier (with microorganisms) into the reactor (Fig. 1). Denitrifying biofilm accumulated further as we replaced the river water every day for two weeks, during which time we observed the build up of a layer of dark brown biofilm on the surface of the carrier.

2.4 River water

We collected river water from the Caohejing River in Shanghai. Table 1 lists its average, minimum, and maximum values for key water-quality parameters monitored from June to December 2009. While the river-water quality varied substantially, its average quality was inferior to Class V (classification of poorest quality) of the Chinese national surface water environmental quality standards [41]. Furthermore, the average COD : TN ratio of 6.2 g COD · g⁻¹ TN is much larger than the stoichiometric ratio needed for denitrification. In some experiments, we added glucose to increase the concentration of readily available organic electron donor. In other cases, we added pyridine into tap water as a readily photocatalyzed organic to investigate the principle that the measured COD would increase with photocatalysis.

2.5 Analytical methods

We determined the COD concentration using potassium dichromate oxidation according to standard procedures [35,36] that involve providing a stoichiometric excess of potassium dichromate, strong acid and heating conditions, silver sulfate as a catalyst, and mercury sulfate to avoid the interference of chloride ion. The non-reacted potassium dichromate was titrated with ferrous ammonium sulfate, and the COD concentration was calculated from the consumption of ferrous ammonium sulfate.

DO was measured by using portable dissolved oxygen instrument (model: YSI550A, Instrument Co., Ltd. Jinquan, USA), pH was measured by portable pH meter (LP-3000, Shanghai Aiwang Industrial Co., Ltd., China), ammonia nitrogen was determined by using salicylic acid – hypochlorite spectrophotometric [36], and total nitrogen was determined by using persulfate – UV spectrophotometry [36], which gave the sum of ammonium, organic, nitrate, and nitrite nitrogen.

We measured pyridine with a high performance liquid chromatograph (HPLC, model: Agilent 1100, Agilent Instruments, ASU) equipped with a diode array detector (DAD) with wavelength of 250 nm and ZORBAX SB-C18 column (5 μm × 4.6 mm × 250 mm). The mobile phase

Table 1 Water-quality parameters of the Caohejing River, June – December 2009. **Boldface** values indicate violations of the Class V standard [41]

index	NH ₄ ⁺ - N/(mg · L ⁻¹)	DO/(mg · L ⁻¹)	COD/(mg · L ⁻¹)	TN/(mg · L ⁻¹)	COD/TN	pH
class V standard	2.0	2.0	40	2.0	none	6–9
average value	5.6	0.9	40.3	6.5	6.2	7.2
minimum value	3.2	0.2	10.5	4.4	19	6.5
maximum value	9.5	2.3	115	10.7	1.5	7.8

was a methanol:water solution (60:40, v/v), and the flow rate was $1 \text{ mL} \cdot \text{min}^{-1}$.

2.6 Treatment experiments

2.6.1 Glucose as supplemental electron donor for denitrification

We added 25 to $200 \text{ mg} \cdot \text{L}^{-1}$ of glucose into the actual river water as a supplemental electron donor to test for accelerated denitrification in the biofilm reactor.

2.6.2 Effect of DO on the ratio of ΔCOD and ΔTN

Here, ΔCOD and ΔTN mean the difference between influent COD (or TN) and effluent COD (or TN). Synthetic water was prepared with $135 \text{ mg} \cdot \text{L}^{-1}$ of glucose and $15 \text{ mg} \cdot \text{L}^{-1}$ of KNO_3 dissolved in tap water, and DO was adjusted by sparging nitrogen for different times. The water was used for denitrification to investigate effect of DO on ratio of ΔCOD and ΔTN .

2.6.3 Photocatalysis

For photocatalysis experiments, we placed the glass plate coated with TiO_2 on the bottom of a culture dish (50-mL working volume), poured 50 mL of river water into the dish, and mixed the contents with a magnetic stirrer. Then, we illuminated the dish with UV light (32 W at 254 nm) located 20 mm above the dish. The distance between the UV light and the water surface was approximately 40 mm, and the water depth was 5–10 mm. We took water samples from the dish periodically to determinate their COD and TN concentrations.

In some experiments, we used a $50\text{-mg} \cdot \text{L}^{-1}$ pyridine solution in tap water and followed the same photocatalysis protocol as that of the river water.

2.6.4 Denitrification

We tested two kinds of river water — without photocatalysis (the control) and after photocatalysis — for denitrification in the biofilm reactor. We added river water to the biofilm reactor, which was well mixed. We took samples of treated water and analyzed them for COD and TN. During the tests, the reactors were not isolated from the atmosphere, which means that DO was present. The initial concentration ranged from 0.5 to $2.0 \text{ mg} \cdot \text{L}^{-1}$, but we were unable to monitor DO throughout the tests. Thus, oxygen respiration was occurring in parallel to denitrification. Before the beginning of each denitrification test, we deoxygenated the water by means of N_2 sparging; the DO concentration was less than $0.5 \text{ mg} \cdot \text{L}^{-1}$ at that time.

3 Results and discussion

3.1 Effect of glucose on TN removal

To demonstrate that denitrification and total-N removal in the river water were limited by having a readily bioavailable electron donor, we added glucose to river water that had concentrations of $30 \text{ mg} \cdot \text{L}^{-1}$ COD and $5 \text{ mg} \cdot \text{L}^{-1}$ TN. Figure 2 shows that the TN removal (ΔTN) increased linearly with increasing glucose-COD added, thus proving that the actual river water lacked readily available organic electron donors. Although the COD in the river water was about $30 \text{ mg} \cdot \text{L}^{-1}$, TN removal was only about $0.3 \text{ mg N} \cdot \text{L}^{-1}$ without supplemental donor. In contrast, adding $210 \text{ mg COD} \cdot \text{L}^{-1}$ of glucose to the river water increased removal to almost $4 \text{ mg N} \cdot \text{L}^{-1}$; during this process, COD removal (ΔCOD) was about $192 \text{ mg} \cdot \text{L}^{-1}$. The ratio of ΔCOD added per ΔTN removed was about $48 \text{ g COD} \cdot \text{g}^{-1} \text{ N}$, which is much larger than the stoichiometric ratio $2.9 \text{ g COD} \cdot \text{g}^{-1} \text{ N}$. The extra consumed glucose (COD) was related to the presence of DO, and Fig. 3 shows the relationship between DO and ratios of ΔCOD and ΔTN . Figure 3 demonstrates that glucose was consumed in oxygen respiration, as well as denitrification, since the biofilm reactor was not isolated from the air.

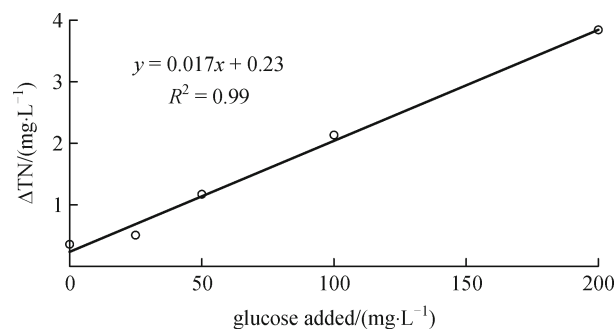


Fig. 2 Relationship between glucose-COD added and TN removal

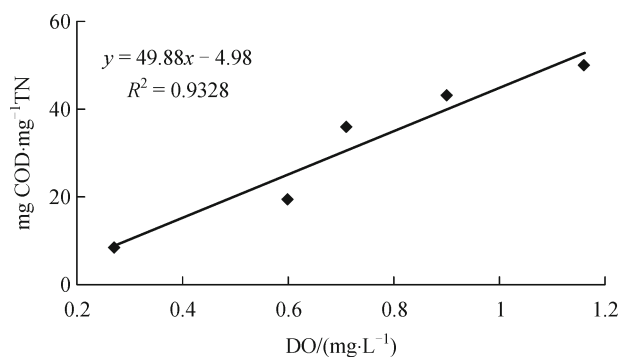


Fig. 3 Ratio of ΔCOD and ΔTN increased with increasing DO

3.2 COD during photocatalysis

Twenty independent experiments showed that the COD concentration in the actual river water changed during photocatalysis experiments, but the TN did not change. Table 2 summarizes the time of photocatalysis, the starting COD, the peak COD during the test, and the ratio of the peak COD to the starting COD for all 20 experiments. Figure 4 presents the changes of COD during three representative experiments. One clear trend is that the starting COD values differed significantly among the experiments. This reflects the high degree of variability in river-water quality during the time of our experiments (Table 1). A second trend is that the COD concentrations increased near the beginning of each photocatalysis experiment. This trend could have occurred for two reasons. The first reason is that the free-radical reactions involved in photocatalysis reduced organic components, with H₂O being the ultimate electron donor. The second and more likely reason is that some original organic components could not be oxidized by potassium dichromate until they were transformed by photocatalysis. We evaluated the latter explanation directly with pyridine.

We explored the phenomenon of the COD increase during photocatalysis by conducting an experiment with pyridine, a heterocycle known to be resistant to oxidation

in the COD test [35,36,38]. The results in Fig. 5 show that the COD in the pyridine solution increased during photocatalysis as pyridine was removed. If pyridine were oxidized fully to carbon dioxide and water with release of ammonium, $C_5H_5N + 5.25O_2 = 5CO_2 + 0.5H_2O + NH_4$, then 50 mg·L⁻¹ of pyridine would contribute 106 mg·L⁻¹ of COD and 8.9 mg·L⁻¹ of NH₄⁺-N. The starting COD values were almost zero, which supports that the dichromate method for COD was not able to oxidize pyridine. However, the COD concentration increased up to 80 mg·L⁻¹ (75% of 106 mg·L⁻¹) by 30 min, which supports that the dichromate method was able to assay for COD only after the molecular structure of pyridine was transformed in the photocatalysis process. The increase in COD up to 75%, instead of 100%, probably was caused by partial oxidation of the pyridine during photocatalysis, since the original molecule was completely removed by 40 min. The ammonium concentration increased by 5.1 mg N·L⁻¹ during loss of 50 mg·L⁻¹ of pyridine.

The results in Fig. 5 support that the increases in COD in Fig. 4 and Table 2 were at least partly explained by the limitations of the COD test for organic compounds recalcitrant to dichromate oxidation. While not all the COD in the river water was made up of dichromate-resistant molecules like pyridine, the results in Fig. 4 and Table 2 imply that the true COD of the river water was higher than given in Table 1.

Table 2 Effect of UV illumination on COD and ratio of the peak COD to the starting COD

experiment number	illumination time corresponding to peak COD/min	starting COD/(mg·L ⁻¹)	peak COD/(mg·L ⁻¹)	ratio of peak COD to starting COD
1	20	61	166	2.7
2	90	95	169	1.8
3	60	20	32	1.6
4	50	48	135	2.8
5	50	43	78	1.8
6	50	52	80	1.5
7	50	74	114	1.5
8	20	61	137	2.7
9	300	95	141	1.4
10	60	92	121	1.3
11	90	78	166	1.8
12	10	53	115	2.4
13	50	81	125	1.5
14	150	81	156	1.9
15	120	42	127	3.0
16	120	42	63	1.5
17	60	52	176	3.4
18	120	52	136	2.6
19	120	51	61	1.2
20	120	48	51	1.1

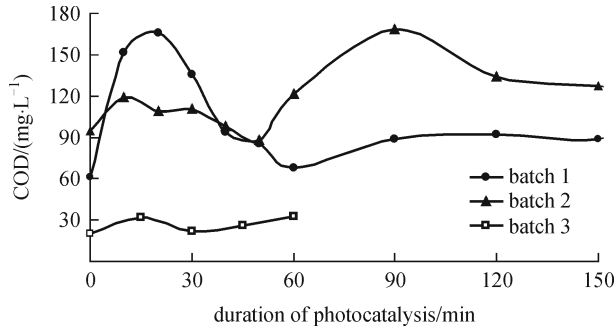


Fig. 4 COD concentrations in river water increased during photocatalysis for three representative experiments. Values of the starting and peak COD concentrations for all experiments are given in Table 2

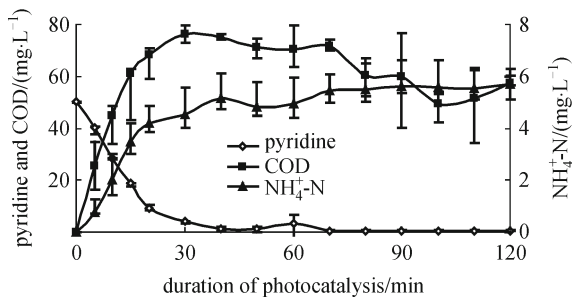
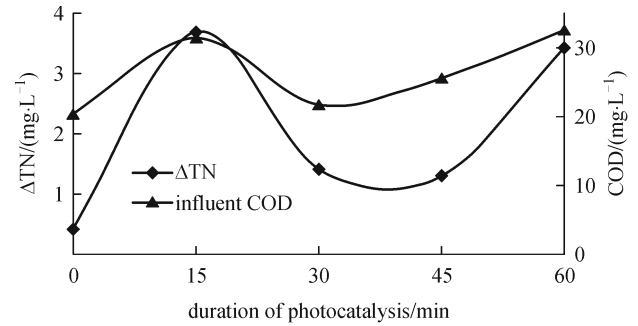


Fig. 5 COD, ammonium, and TN concentrations during photocatalysis of pyridine

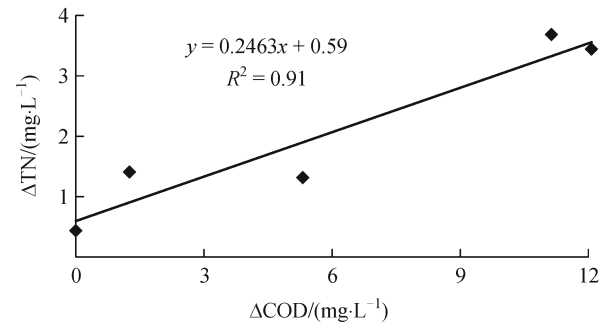
3.3 Effects of prior photocatalysis on TN removal in denitrification

Samples of the actual river water taken during batch 3 in Fig. 4 were subjected to denitrification for 24 h. Figure 6 presents the TN removals over 24 h and the COD concentrations in the water samples used for the denitrification experiments. The trends in the two curves in Fig. 6(a) indicate that Δ TN generally followed the initial COD concentration, and Fig. 6(b) quantifies that Δ TN increased linearly with Δ COD during the denitrification test. TN removal by denitrification was only about $0.5 \text{ mg N} \cdot \text{L}^{-1}$ with the control river water, but it increased up to $3.5 \text{ mg N} \cdot \text{L}^{-1}$ when photocatalysis increased the COD of the river water by about $12 \text{ mg} \cdot \text{L}^{-1}$. The greatest TN removal and increased COD concentration occurred with 15 min of photocatalysis (Fig. 6(a)), and we chose this photocatalysis time for more comprehensive testing.

We performed seven similar 24-h denitrification experiments after 15 min of photocatalysis. Figure 7 presents the COD before and after photocatalysis and TN removals by denitrification. The average COD increased by $31 \text{ mg} \cdot \text{L}^{-1}$ after the river water was treated with 15 min of photocatalysis, and this correlated to an average $2 \text{ mg} \cdot \text{L}^{-1}$ increase in TN removal in subsequent denitrification.



(a)



(b)

Fig. 6 TN removal during denitrification for river water subjected to different photocatalysis time: (a) relationship between the initial COD concentration after photocatalysis and TN removal during denitrification; (b) correlation between increasing of the initial COD during photocatalysis and TN removal during denitrification

The average TN removal of the river water using photocatalysis was about 4 times the removal without photocatalysis. According to the results in Fig. 2, the TN removal with photocatalysis was equivalent to adding $92 \text{ mg COD} \cdot \text{L}^{-1}$ of glucose to the actual river water.

3.4 Relationship between COD and TN removals in denitrification

Figure 8 summarizes the changes in COD and TN concentrations during denitrification tests for all of the waters tested. Losses of TN and COD followed similar patterns. TN removal was the highest with addition of $200 \text{ mg} \cdot \text{L}^{-1}$ glucose (G data), but the TN removal after photocatalysis of the river water (P data) was higher than for the untreated river water (A data). The improved TN removal after photocatalysis supports that part of the recalcitrant organic material in the river water was converted into readily available COD that fueled denitrification. During the denitrification process, organic carbon (represented as COD) supplies electrons to reduce nitrate or nitrite into nitrogen gas, and this supplies energy for the growth and maintenance of the denitrifying bacteria. Photocatalysis increased the biodegradable COD in the river water, since it altered the chemical

form to be more susceptible to measurement by the COD assay (Fig. 4), and it also made the COD more biodegradable for driving denitrification (Figs. 7 and 8).

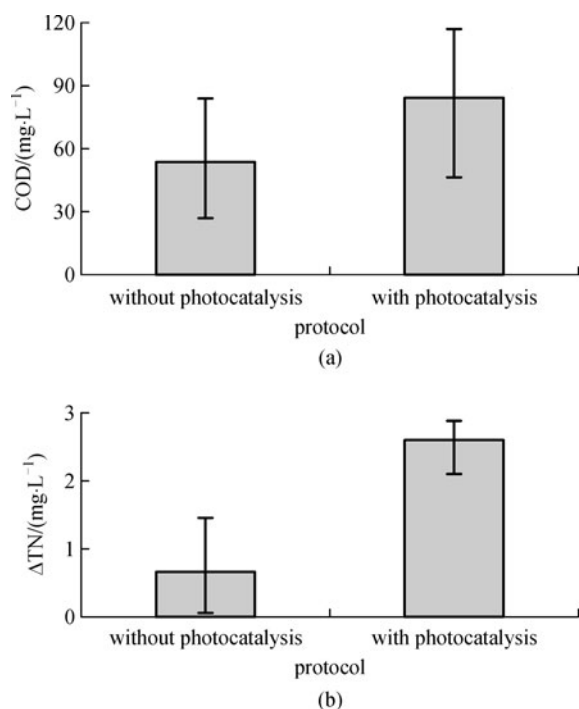


Fig. 7 Comparison of river water without and with photocatalysis: (a) COD before and after photocatalysis; (b) TN removal without and without photocatalysis

4 Conclusions

Dual-contaminated river water was short of available electron donor, which resulted in low TN removal by denitrification in a biofilm reactor. The denitrification rate could be increased significantly by adding glucose or by making the organic material of the river water more bioavailable through photocatalysis. TN removal increased 4-fold with photocatalysis for 15 min, and this gave the same effect as adding 92 mg·L⁻¹ of glucose. Clearly, photocatalysis of the river water would be helpful to drive denitrification as a means to remove TN.

During the photocatalysis experiments, the COD increased. While it is possible that some of the organic matter was reduced during photocatalysis, the more likely phenomenon is that photocatalysis transformed organic molecules from those that are resistant to dichromate oxidation in the COD test to those that can be oxidized by dichromate. This phenomenon is well known for certain N-containing heterocycles and was verified by testing pyridine added to the river water. These results imply that the true COD concentration in the river water contaminated by recalcitrant organic compounds was

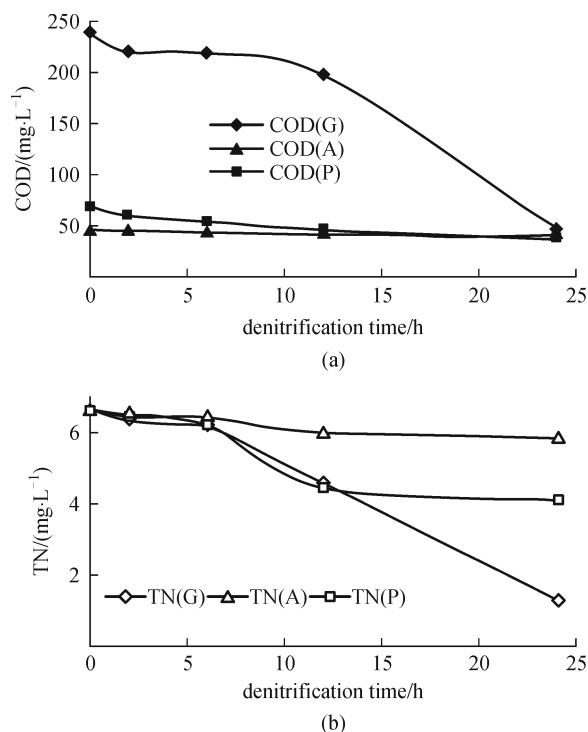


Fig. 8 COD (a) and TN (b) concentrations during 24-h denitrification experiments using the actual river water without photocatalysis (A), with photocatalysis (P), and with added glucose (G)

more than that measured by standard COD test method. While our findings point to the potential for N removal via denitrification after photocatalysis, they also suggest that the rivers in China may be far more polluted than indicated by COD assays.

Acknowledgements The authors acknowledge the financial support by the National Natural Science Foundation of China (Grant Nos. 50978164 and 50678102), the Major Science and Technology Program for Water Pollution Control and Treatment (No. 2009ZX07313-003), the Innovation Fund for Key Projects of Shanghai Municipal Education Commission (No. 10ZZ82), the Special Foundation of Chinese Colleges and Universities Doctoral Discipline (Nos. 20113127110002 and 20070270003), the Shanghai Leading Academic Discipline Project (No. S30406), and the United States National Science Foundation (No. 0651794).

References

1. Pei H P, Wang Y. Eutrophication research of West Lake, Hangzhou, China: modeling under uncertainty. *Water Research*, 2003, 37(2): 416–428
2. Hu X L. Summing up the research on eutrophication mechanisms of lakes and reservoirs. *Water Resources Protection*, 2009, 25(4): 44–47 (in Chinese)
3. Zhou J B, Zhang Z Y. Production Origin and Control Countermeasures of Water Eutrophication in China. *Journal of Anhui Agriculture Science*, 2009, 37(21): 10126–10128 (in Chinese)

4. Hu G J, Sun C, Li J, Zhao Y G, Wang H, Li Y Q. POPs accumulated in fish and benthos bodies taken from Yangtze River in Jiangsu area. *Ecotoxicology* (London, England), 2009, 18(6): 647–651
5. Shi W, Wang X Y, Hu W, Sun H, Shen O X, Liu H L, Wang X R, Giesy J P, Cheng S P, Yu H X. Endocrine-disrupting equivalents in industrial effluents discharged into Yangtze River. *Ecotoxicology* (London, England), 2009, 18(6): 685–692
6. Blocksom K A, Walters D M, Jicha T M, Lazorchak J M, Angradi T R, Bolgrien D W. Persistent organic pollutants in fish tissue in the mid-continental great rivers of the United States. *The Science of the total environment*, 2010, 408(5): 1180–1189
7. Qu J H. Dual-contaminated water control. *Impact of Science on Society*, 2000, 20(1): 35–39 (in Chinese)
8. Zhu Y M, Li J S, Yang A L, Wang N. Study on non-point source pollution of surface drinking water. *Source of Cities. Urban Environment and Ecology*, 2000, 13(4): 1–4 (in Chinese)
9. Wang S. Shanghai landscape water research and analysis. *China Water Resources*, 2004, 55(11): 40–42 (in Chinese)
10. Wittmer I K, Bader H P, Scheidegger R, Singer H, Lück A, Hanke I, Carlsson C, Stamm C. Significance of urban and agricultural land use for biocide and pesticide dynamics in surface waters. *Water Research*, 2010, 44(9): 2850–2862
11. Mulder A, Graaf A A, Robertson I A, Kuenen J G. Anaerobic ammonium oxidation discovered in a denitrifying fluidized bed reactor. *FEMS Microbiology Ecology*, 1995, 16(3): 177–184
12. dos Santos V A P M, Bruijnse M, Tramper J, Wijffels R H. The magic-bead concept: an integrated approach to nitrogen removal with co-immobilized micro-organisms. *Applied Microbiology and Biotechnology*, 1996, 45(4): 447–453
13. Kuai L, Verstraete W. Ammonium removal by the oxygen-limited autotrophic nitrification-denitrification system. *Applied and Environmental Microbiology*, 1998, 64(11): 4500–4506
14. Third K A, Sliekers A O, Kuenen J G, Jetten M S M. The CANON system (completely autotrophic nitrogen-removal over nitrite) under ammonium limitation: interaction and competition between three groups of bacteria. *Systematic and Applied Microbiology*, 2001, 24(4): 588–596
15. Rittmann B E. Biofilms in the Water Industry. In: Ghannoum M A, O'Toole G A, eds. *Microbial Biofilms*. Washington DC: ASM Press, 2004, 359–378
16. Sengupta S, Ergas S J, Lopez-Luna E, Sahu A K, Palaniswamy K. Autotrophic biological denitrification for complete removal of nitrogen from septic system wastewater. *Water, Air, and Soil Pollution*, 2006, 6(1–2): 111–126
17. Zhang D M, Yang H F. Progress in microbial nitrogen removal. *Microbiology Bulletin*, 1998, 25(6): 348–350 (in Chinese)
18. Zhao D, Ren N Q, Ma F, Shen Y L, Li Y. Microbiology and research progress in biological nitrogen removal. *Journal of Harbin University of C.E.& Architecture*, 2002, 35(5): 60–65 (in Chinese)
19. Kong Q X, Li J W. Review of research in aerobic denitrification by microorganisms. *Journal of Environmental Health*, 2004, 21(3): 189–191 (in Chinese)
20. Yan Z Y, Liao Y Z, Li X D, Liu X F, Yuan Y X, Song L. Progress in Research of Biological Removal of Nitrogen. *Chinese Journal of Applied and Environmental Biology*, 2006, 12(2): 292–296 (in Chinese)
21. Rittmann B E, McCarty P L. *Environmental Biotechnology: Principles and Application*. Columbus: McGraw Hill publishing Company, 2001
22. Henze M, Gujer W, Mino T, Matsuo T, Wentzel M C, Marais G. Wastewater and biomass characterization for the activated sludge model No. 2: biological phosphorus removal. *Water Science and Technology*, 1995, 31(2): 13–23
23. Carucci A, Kuhni M B, Brun R, Carucci G, Koch G, Majone M, Siegrist H. Microbial competition for the organic substrates and its impact on EBPR systems under conditions of changing carbon feed. *Water Science and Technology*, 1999, 39(1): 75–85
24. Scott J P, Ollis D F. Integration of chemical and biological oxidation processes for water treatment: review and recommendations. *Environment and Progress*, 1995, 14(2): 88–103
25. Agrios A G, Gray K A, Weitz E K. Narrow-band irradiation of a homologous series of chlorophenols on TiO₂: charge-transfer complex formation and reactivity. *Langmuir*, 2004, 20(14): 5911–5917
26. Enriquez R, Beaugiraud B, Pichat P. Mechanistic implications of the effect of TiO₂ accessibility in TiO₂-SiO₂ coatings upon chlorinated organics photocatalytic removal in water. *Water Sci Technol*, 2004, 49(4): 147–152
27. Han W Y, Zhu W P, Zhang P Y, Zhang Y, Li L S. Photocatalytic degradation of phenols in aqueous solution under irradiation of 254 and 185 nm UV light. *Catalysis Today*, 2004, 90(3–4): 319–324
28. Sakthivel S, Neppolian B, Palanichamy M, Arabindoo B, Murugesan V. Photocatalytic degradation of leather dye over ZnO catalyst supported on alumina and glass surfaces. *Water Sci Technol*, 2001, 44(5): 211–218
29. Stafford U, Gray K A, Kamat P V. Radiolytic and TiO₂-assisted photocatalytic degradation of 4-chlorophenol – comparative-study. *Journal of Physical Chemistry*, 1994, 98(25): 6343–6351
30. Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 1972, 238(5358): 37–38
31. Marsolek M D, Torres C I, Hausner M, Rittmann B E. Intimate coupling of photocatalysis and biodegradation in a photocatalytic circulating-bed biofilm reactor. *Biotechnology and Bioengineering*, 2008, 101(1): 83–92
32. Zhang Y, Wang L, Rittmann B E. Integrated photocatalytic-biological reactor for accelerated phenol mineralization. *Applied Microbiology and Biotechnology*, 2010, 86(6): 1977–1985
33. Zhang Y, Liu H, Shi W, Pu X, Zhang H S, Rittmann B E. Photobiodegradation of phenol with ultraviolet irradiation of new ceramic biofilm carriers. *Biodegradation*, 2010, 21(6): 881–887
34. Zou Z, Zhang Y. Change law of urban river water with complex-pollution under photocatalytic oxidation. *Journal of Shanghai Normal University (Natural Sciences)*, 2009, 38(2): 197–202
35. American Public Health Association (APHA). *Standard Methods for the Examination of Water and Wastewater*. 22nd ed. Washington DC: American Water Works Association and Water Pollution Control Federation, 2001
36. Wei F. *Monitoring and Analytic Methods of Water and Wastewater*. 4th ed. Beijing: Environmental Science Press of China, 2002 (in Chinese)
37. Moore W A, Kroner R C, Ruchhoft C C. Dichromate reflux method for determination of oxygen demand. *Analytical Chemistry*, 1949,

- 21(8): 953–957
38. Chudoba J, Dalešický J. Chemical oxygen demand of some nitrogenous heterocyclic compounds. *Water Research*, 1973, 7(5): 663–668
39. Mallak M, Bockmeyer M, Löbmann P. Liquid phase deposition of TiO₂ on glass: Systematic comparison to films prepared by sol–gel processing. *Thin Solid Films*, 2007, 515(20–21): 8072–8077
40. Zhang Z. *Drainage Engineering (the second volume)*. 4th ed. Beijing: China Architecture and Building Press, 1999 (in Chinese)
41. Environmental Protection Administration of China (EPAC). *Surface Water Quality Standards (GB 3838–2002)*. Beijing: The People’s Republic of China National Standard, 2002 (in Chinese)