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Application of photocatalysis as a post treatment method of a heterotrophic–autotrophic denitrification reactor effluent

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ABSTRACT

The aim of this study is the application of photocatalysis as an effective post treatment scheme for the removal of the organic matter and bacteria released by an innovative biological denitrification process referred to as heterotrophic–autotrophic denitrification, which combines heterotrophic and autotrophic denitrification processes. Photocatalytic treatment was applied using TiO_2 as a photocatalyst in the loading range of 0.25–2.00 g l^{-1} for irradiation periods up to 60 min using a black light fluorescent lamp with an intensity of $I_0 = 1309$ μW cm^{-2}. The photocatalytic inactivation data were modelled to pseudo first order kinetics as well as by the areal rates to evaluate the photocatalyst loading effect. Chlorination was used as a final disinfection step to attain an overall inactivation of total coliforms as well as to the formation of very low level of trihalomethanes.

1. Introduction

Surface and subsurface water pollution by nitrate is an important environmental issue, because of both its toxicity and widespread occurrence, thus 50 mg NO_3^- l^{-1} was set as a maximum contaminant level and guide value by EEC (1998) and WHO (2003). The removal of nitrate is typically obtained using reverse osmosis, ion exchange and electrodialysis that are considered as expensive processes because of construction and management costs. The main disadvantage of these processes is the generation of nitrate concentrated waste streams (Till et al., 1998). Recently, taking into account the environmental impact concerns, application of biological processes gained an increasing interest. Biological denitrification process via both autotrophic and heterotrophic ways is basically a bacteriologically-mediated process where nitrate is converted into nitrogen gas in the absence of oxygen.

An innovative approach referred to as HAD (heterotrophic–autotrophic denitrification), combining autotrophic denitrification (AD) and heterotrophic denitrification (HD) processes was proposed by Della Rocca et al. (2006); cotton and zero-valent iron (ZVI) were used as organic carbon and hydrogen gas source, respectively. The ZVI reduces dissolved oxygen in water improving AD and HD processes, and producing cathodic hydrogen that supports AD process in the same reactor (Till et al., 1998). The cotton acts as organic carbon source for HD and provides the surface for growing of both HD and AD biofilm (Della Rocca et al., 2006). Finally, CO_2 produced during HD processes is used as inorganic carbon source by autotrophic bacteria, thus alkalinity addition is not necessary. However, the most important drawbacks of the HAD are related to nitrite accumulation, ammonium production, bacteria and organic matter (OM) releases. Nitrite formation may occur because of both denitrification process and nitrate reduction by iron as an intermediate product (Huang et al., 1998); ammonium formation may occur because of nitrate reduction by ZVI. Whilst nitrite and ammonium formation can be controlled during HAD operation (Della Rocca et al., 2006), a post treatment must be used to control bacteria and OM releases. Post-treatment processes such as membrane filtration (Buttiglieri et al., 2005), micro-filtration (Soares et al., 2000), sand filtration (Aslan and Turkman, 2005) and trickling sand filtration (Della Rocca et al., 2005) have been proposed. The concern regarding OM release is due to the formation of potentially carcinogenic disinfection byproducts, particularly trihalomethanes (THMs) which result from the reaction among natural organic matter (NOM, in particular humic and fulvic acids), bromine, and chlorine (Rook, 1974).

Photocatalysis (PC) is an emerging alternative technology for the removal of organic compounds as well as the inactivation of the bacteria (Bekbolet et al., 1996, 2005; Bekbolet, 1997; Uyguner and Bekbolet, 2007). The main mechanism of PC is the formation of highly reactive and non-selective hydroxyl radicals upon irradiation of semiconductor particles with near UV radiation

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(λ < 400 nm). The photo-generated electron-hole pairs (e^-/h^+) can migrate to the surface of semiconductor particle to form oxidizing species in the presence of oxygen. Following a sequence of consecutive redox reactions, degradation of organic compounds as well as bacteria could be attained. Due to its stability and low energy band-gap (E_{bg} = 3.2 eV), TiO_2 is accepted to be one of the most suitable semiconductor for PC.

Total inactivation of 10^3 cells ml^{-1} of *Escherichia coli* was obtained within 60 min of irradiation period using a black light fluorescent lamp in the presence of 1.0 mg ml^{-1} TiO_2 (Degussa P-25) (Bekbolet, 1997). Photocatalytic inactivation of microbial species also has been recently reviewed extensively by Bekbolet (2007). There is continuous research on the application of PC to natural waters either as pre-treatment or as a post treatment scheme for the removal of NOM as well as the bacteria.

Based on the reported findings, the performance of lab-scale continuous up-flow HAD reactor in the removal of high nitrate concentration at high flow-rates was proved to be successful provided that the destruction of OM and the bacteria in the effluent should be further investigated (Della Rocca et al, 2006). Therefore in order to fulfil this aim, the effectiveness of TiO_2 suspended photocatalytic process as post treatment to remove OM and inactivate bacteria released from the HAD reactor was studied. The disinfection efficiency of the photocatalytic reactor was investigated in terms of total coliforms (TC) because these bacteria are typically used as microbial contamination indicators in drinking water systems. The reduction in THM formation potential at 24 h ($THMFP_{24}$) by post treatment was also studied.

2. Experimental

2.1. Water source

Considering the typical characteristics of groundwater located in the province of Salerno (southern Italy), described by parameters as turbidity (0.4 NTU), nitrate (1.63 mg l^{-1}), alkalinity (42 mg $CaCO_3$ l^{-1}), OM (total organic carbon, TOC = 0.3 mg l^{-1}, and UV absorbance at 254 nm, UV_{254} = 0.8 m^{-1}), to attain uniformity throughout the experiments, a synthetic water sample was prepared using tap water spiked with potassium nitrate, KNO_3 (100 mg l^{-1} as NO_3^-) and potassium phosphate, K_2HPO_4 (3 mg l^{-1} as P) from Carlo Erba (Italy) to be used as water source for HAD reactor. The effluent of the HAD reactor (HAD_{out}) was used for the photocatalytic oxidation experiments.

2.2. Chemicals and reagents

Unprocessed cotton and steel wool were used as the solid support material. TiO_2 (Degussa P-25) supplied from Degussa (Germany) with BET surface area of 50 m^2 g^{-1} and an average particle size of 30 nm was used as a photocatalyst for photocatalytic oxidation experiments. Humic acid (HA) was purchased from Sigma Aldrich. Deionized water by MilliQ membrane system (Millipore) was used as necessary.

2.3. Heterotrophic–autotrophic denitrification (HAD) reactor

HAD reactor was composed of a reactor made of PVC (90 cm height and 8 cm internal diameter) with a support layer of PVC net at the bottom (Della Rocca et al., 2006). The reactor was equipped with three intermediate sampling taps (ST) at 22.5 cm (ST1), 45.0 cm (ST2) and 67.5 cm (ST3) from the bottom of the reactor. It worked in continuous up-flow mode by means of a peristaltic pump. The reactor was packed with 300 g of steel wool as ZVI source (12 cm layer at the bottom) and 380 g of raw cotton pre-mixed with around 10 g of inoculated cotton taken from an active HAD reactor as carbon source and biofilm growth support (78 cm upper layer). Denitrifying bacteria inoculum was prepared using 5 g of subsurface soil (0.3 m of depth) taken from a pristine and humic-acid-rich area; a detailed description is reported elsewhere (Della Rocca et al., 2005). The reactor was fed by the synthetic water and the column studies were carried out at room temperature (23 ± 5 °C).

2.4. Photocatalytic oxidation reactor

Batch photocatalytic oxidation experiments were performed using a 100 ml cylindrical Pyrex reaction vessel (7.5 cm diameter, 3.5 cm height) as the photoreactor. Water sample (50 ml) was taken from the effluent of the HAD reactor. The photoreactor was confined in a box with internal walls covered with Al thin layer to assure reflecting surface and to maximize the light intensity in the reaction medium. A 125 W black light fluorescent lamp emitting radiation between 300 and 420 nm with a maximum at 350 nm was used as the light source (Bekbolet et al., 1996; Bekbolet, 1997). The light intensity in the reaction medium was measured as I_0 = 1309 μW cm^{-2} by Avantes spectrometer, model AvaSpec 2048. The photoreactor was illuminated from the top and slowly mixed by a magnetic stirrer to attain a homogeneous suspension. Prior to analytical measurements and after photocatalytic oxidation experiments, the samples were filtered through 0.45 μm borosilicate filters (Millipore) to remove TiO_2 particles. The efficiency of photocatalytic process was investigated for photocatalyst loadings in the range of 0.25–2.00 g TiO_2 l^{-1}, and for reaction periods of 5–60 min irradiation time (PC5-PC60).

2.5. Analytical measurements

The concentrations of nitrogen containing inorganic species as ammonium, nitrate, nitrite were monitored in the inlet (HAD_{in}) and outlet (HAD_{out}) of the HAD reactor according to the respective procedures as given in the Standard Methods (APHA, 1998). Dissolved organic carbon, DOC (mg C l^{-1}) was measured with TOC Shimadzu analyser, Model 5000A, after filtering the outlet samples using 0.45 μm borosilicate filters. UV absorbance at 254 nm (UV_{254}, m^{-1}) as well as the UV–vis spectra (200–600 nm) were measured using Perkin Elmer Lambda 12 UV–vis spectrophotometer equipped with 1 cm quartz cell. In order to evaluate the formation of chlorination byproducts, particularly THMs, water samples from the effluent of the HAD reactor were chlorinated before and after photocatalytic treatment. A 7 ± 2% NaOCl solution was used to prepare a 1.0 g l^{-1} (as active chlorine) stock solution. The samples were chlorinated in order to obtain 0.2 mg l^{-1} of chlorine residual after 24 h contact time. According to chlorine demand of water samples, around 2.0 mg Cl_2 l^{-1} were added. 20 ml of chlorinated water samples were collected in 40 ml vials to be analysed for THMs. THMs were measured using a Varian GC (model STAR 3440 CX) equipped with a DB5 chromatographic column (60 m length, 0.53 mm inner diameter) by static head space technique (the samples were heated at 70 °C for 15 min) (Ottaviani and Bonadonna, 2007).

2.6. Bacterial counts

For the enumeration of the TC bacteria, membrane filter method (acetate cellulose type filter with 0.45 μm) was used according to Standard Methods (APHA, 1998). Bacterial count was performed using m-Endo medium (Oxoid) for detection of TC, and agar R2A for heterotrophic plate count (HPC). The plates were incubated at 37 °C for 24 h for m-Endo and for 36 h for R2A. The results are expressed in terms of colony forming units ml^{-1} (expressed as CFU