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Journal of Photochemistry & Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



# Effect of dissolved natural organic matter on the photocatalytic micropollutant removal performance of TiO<sub>2</sub> nanotube array



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#### ARTICLE INFO

Keywords: TiO<sub>2</sub> nanotube array Natural organic matter Photocatalysis Micropollutant MCPA

#### ABSTRACT

The  $TiO_2$  nanotube array (TNA) is a promising photocatalyst for removal of micropollutants from water, but better understanding on its applicability in complex water matrices is still desired. Therefore this study investigates the effect of dissolved natural organic matter (NOMs) on 4-chloro-2-methylphenoxyacetic acid (MCPA, a typical micropollutant found in many water bodies) removal performance of TNA. The present study shows that although in bulk liquid phase NOMs would undergo photosensitization that can contribute to MCPA removal the overall effect of NOMs on MCPA removal is detrimental due to the interaction between NOMs and the TNA surface: the total removal of MCPA decreased from 94.3% to 62.0% and 61.8%, in the presence of only 5 mg/L SWR-NOM and UMR-NOM respectively. Acidic pH was found to be able to mitigate the detrimental effect of NOMs (the total removal of MCPA was only decreased from 94.5% to 83.3% and 88.8% under acidic pH, in the presence of 15 mg/L SWR-NOM and UMR-NOM respectively), and the photosensitization effect of NOMs was strengthened; while under alkaline pH conditions the detrimental effect of NOMs completely vanished (the total removal of MCPA increased from 45.7% to 55.7% and 60.5% in the presence of 15 mg/L SWR-NOM and UMR-NOM respectively). Two commonly present co-existing anions, i.e. phosphate and bicarbonate, also mitigate the detrimental effect of NOMs. With 15 mg/L SWR-NOM: the presence of 100 mg/L bicarbonate increased the total removal of MCPA from 49.1% to 65.1%; the presence of 100 mg/L phosphate increased the total removal of MCPA from 49.1% to 62.5%. With 15 mg/L SWR-NOM, the presence of 100 mg/L bicarbonate increased the total removal of MCPA from 45.2% to 56.1%; the presence of 100 mg/L phosphate increased the total removal of MCPA from 45.2% to 62.9%. The photocurrent measurement support that the presence of such anions greatly suppresses the h + scavenging effect of NOMs; while other anions, i.e. chloride, nitrate, sulfate, showed no notable effect.

## 1. Introduction

In recent decades, many micropollutants, including pharmaceuticals, antibiotics, herbicides, pesticides, personal care products, etc., have been frequently detected in different water bodies worldwide. Although the presence of those contaminants in the aquatic environment is usually at trace concentrations ranging from ng/L to  $\mu$ g/L [1–4], undesirable effects on the ecosystems are usually associated: many previous studies have pointed out that those contaminants imposes potential hazards to aquatic life at different levels, from algae to fish, even at low concentrations [5]. Vast efforts have been devoted to developing techniques for their removal, among which TiO<sub>2</sub> photocatalysis have received increasing research interests.

The principles of TiO<sub>2</sub> photocatalytic techniques have been

described in literature [6–8], which was initiated by generation of electron/hole (e<sup>-</sup>/h<sup>+</sup>) pairs via excitation by photons with energy higher than the band gap energy of TiO<sub>2</sub>. Subsequently, the photogenerated electrons and holes are able to participate in direct redox reactions with target organic contaminants. Besides, the photo-generated electrons and holes can also react with oxygen, water, or HO<sup>-</sup> to generate reactive oxidative species (ROS), *e.g* hydroxyl radicals (HO·), superoxide radical anions (O<sub>2</sub>·<sup>-</sup>), etc. Those in-situ generated ROS are able to react with many pollutants [8], and the contribution of specific ROS depends on the properties of specific pollutant. Examples of its application in micropollutants removal are abundant in literature [9–11].

However, it is also well documented that commonly present dissolved natural organic matter (NOM) in water bodies is a major limiting

https://doi.org/10.1016/j.jphotochem.2018.11.012

Received 4 July 2018; Received in revised form 2 November 2018; Accepted 7 November 2018 Available online 11 November 2018 1010-6030/ © 2018 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/BY/4.0/).

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Journal of Photochemistry & Photobiology A: Chemistry 371 (2019) 216-222

## 2. Experimental methods

## 2.1. Materials

Titanium foil ( $\geq$ 99.5%, 0.3 mm thick) was purchased from the Titaniumshop (The Netherlands). Ammonium sulphate ( $\geq$ 99.0%), ammonium fluoride ( $\geq$ 98.0%), tert-Butanol ( $\geq$ 99.0%), formic acid  $(\geq 96\%)$  were obtained from Sigma-Aldrich (Germany). MCPA  $(\geq 98.0\%)$  was purchased from Dr Ehrenstorfer GmbH (Germany). All chemicals were used without further purification. Stock solution of MCPA was prepared at concentration of 200 mg/L. Sodium bicarbonate  $(\geq 99.9\%)$ , hydrochloric acid (1 mol/L), sodium sulphate ( $\geq 99.0\%$ ). sodium chloride (100%), sodium nitrate ( $\geq$ 99.0%), tri-sodium phosphate dodecahydrate (≥98.0%) and sodium hydroxide aqueous solution (1 mol/L) were purchased from VWR (Belgium) and was used as received. Aquatic NOM Suwannee River NOM (SWR-NOM) (2R101 N) and Upper Mississippi River NOM (UMR-NOM) (1R110 N) were obtained from International Humic Substances Society (IHSS) and received as dry solid extracts. Stock solutions of the NOMs were prepared at concentration of 100 mg/L. Ultrapure water from a Milli-Q Advantage A10 system (Merck Millipore, Darmstadt, Germany) was used for preparation of stock solutions and reaction solutions.

# 2.2. Fabrication and characterization of the $TiO_2$ nanotube array

The TNA employed in this study was prepared with the electrochemical anodization method we previously reported [12]. The titanium foil was first degreased by successively ultra-sonication for 15 min in 2-propranol, acetone and Milli-Q water, and then dried in N2 atmosphere, as pretreatment. The electrochemical anodization was performed in a two-electrode chemical cell connected to an EST150 DC power supply (Delta Elektronika, The Netherlands). The titanium foil with a size of  $3 \text{ cm} \times 4.5 \text{ cm}$  was used as anode, and another titanium foil with a size of  $4.5 \text{ cm} \times 5 \text{ cm}$  was used as cathode. The interval between the electrodes was 2 cm. The titanium foil was anodized in 100 mL aqueous electrolyte  $(0.15 \text{ mol/L NH}_4\text{F} + 1 \text{ mol/L (NH}_4)_2\text{SO}_4)$ [33] under 20 V for 2 h. Then the obtained foil was first rinsed and then further sonication washed with Milli-Q water to remove residue electrolyte and impurities on the surface. Subsequently, the treated Ti foil was annealed at 600 °C for 0.5 h in a furnace (Nabertherm, Germany) in air atmosphere and was cooled gradually back to ambient temperature after annealing. The surface morphologies of the TNAs electrode were characterized by scanning electron microscopy (SEM) and the chemical composition of the prepared TNAs was measured by EDX. The SEM/ EDX analyses were performed using a JEOL JSM 6480 scanning electron microscope (JEOL Europe B.V., Nieuw-Vennep, The Netherlands) equipped with a EDX system. Raman spectra of the prepared TNA were recorded using a Horiba LabRAM spectrometer equipped with a mpc3000 laser (532.2 nm), an 800 mm focal length achromatic flat field monochromator (grating of 600 grooves/mm) and a Synapse multichannel air cooled (-70°C) CDD detector. The crystallographic phases of the prepared TNA were further confirmed by X-ray diffraction (XRD) and collected on a Bruker D8 advanced diffractometer.

## 2.3. Photocatalytic MCPA degradation experiments

The photocatalytic experiments were conducted in a crystallizing dish with a 450 mW UV-LED light source module placed on the top. The UV-LED light source module consisted of a UV-LED (NCSU033B, NICHIA, Japan) and has peak emission wavelength of 365 nm, and an aluminium plate served as heat dispenser. A schematic of the set-up is shown in Fig. 1.

The photocatalytic MCPA degradation experiments were carried out with a reaction solution volume of 60 mL, with the presence of TNA (size of  $3 \text{ cm} \times 3 \text{ cm}$ ), at ambient temperature. The distance between the UV-LED and the surface of TNAs was 2 cm, and the radiant power of

moval performance of TiO<sub>2</sub> photocatalytic techniques. Such inhibitory effect of NOMs can be attributed to three main facts. Firstly, the NOMs present in water matrices act as the "inner UV filter". NOMs have strong absorption in UV and near UV range, so the presence of NOMs in water would decrease the availability of UV light for TiO<sub>2</sub> to produce ROS, thus decreasing the ROS and h<sup>+</sup> production. This "inner UV filter" effect is dependent on the wavelength of photons, in general stronger "inner UV filter" effect is expected in shorter wavelength UV range [12]. Secondly, NOM can also act as scavenger of  $\cdot$ OH and h<sup>+</sup> [13], which are known as the primary oxidants in TiO<sub>2</sub> photocatalytic systems [12,14]. Thirdly, NOMs can inhibit the target pollutant degradation via competitive adsorption on the  $TiO_2$  surface [15]. The inhibitory effect of NOM on TiO<sub>2</sub> based photocatalytic micropollutants removal processes has been documented in previous studies on TiO<sub>2</sub> slurry systems. For instance, Brame et al. conducted a mechanistic study on the inhibitory effect of NOMs on TiO<sub>2</sub> slurry system, and a mechanistic model was developed which suggesting the competitive adsorption by NOMs and ROS scavenging were the most influential inhibitory mechanisms [16]. A recent work presented by Peng et al. suggested that the reactivity of TiO<sub>2</sub> nanoparticles could change significantly after long exposure to natural water, because: (1) a NOM layer can be formed on and cap the TiO<sub>2</sub> particles surface via adsorption; (2) the adsorbed NOM layer can act as ROS scavenger and subsequently reduce the concentration of ROS in the bulk liquid phase [17]. For TiO<sub>2</sub> slurry systems where TiO<sub>2</sub> nanoparticles are employed, the presence of NOMs can also interfere with the system performance by changing the stability of the TiO<sub>2</sub> nanoparticles [18]. Focus was given to TiO<sub>2</sub> slurry systems, where TiO<sub>2</sub> nanoparticles are used, in previous studies on the effect of NOM [19], but regarding real life applications immobilization of TiO<sub>2</sub> should be considered to achieve better retention and reuse of the catalyst. The electrochemical anodic produced TiO<sub>2</sub> nanotube array (TNA) is a promising option because of its multiple merits: (1) large surface area; (2) high stability; (3) oriented electron transport which can reduce  $e^{-}/h^{+}$  pairs recombination; (4) relatively easy to make and (5) tunable morphologies. Examples of using of TNAs for organic pollutants elimination are available in literature [12,20–23]. The change in TiO<sub>2</sub> morphology may have an impact on the effect of NOM, but very little is known about the effect of NOM on TNA based photocatalytic system.

factor that imposes significant inhibitory effect on micropollutants re-

In practice, the presence of NOM in water bodies is associated with the presence of inorganics. For example, phosphate, sulfate, bicarbonate, chloride, etc., are the most commonly present inorganic anion species in a broad range of water matrices. The photocatalytic removal of micropollutants by  $TiO_2$  photocatalytic processes can also be affected by those co-existing inorganic anions by competitive adsorption and interaction with ROS [24–26]. In this context, the presence of co-existing inorganic anions may impose impact on the effect of NOMs on a photocatalytic system. In a recent study by Long et al., the change in the detrimental effect of humic acids on photocatalytic performance of  $TiO_2$ particles by the presence of phosphate was reported [27]. However, the combined effects of NOMs and other commonly present inorganic anions have not been well documented in literature.

Given this context, the present work aims to study the effect of NOM on the photocatalytic micropollutant removal performance of TNA. The model micropollutant compound employed in this study is 4-chloro-2-methylphenoxyacetic acid (MCPA), which is a frequently encountered pollutant in different water bodies including ground water and tap water sources at  $\mu$ g/L level [28,29] and in many aqueous wastes including wastewaters from herbicide manufacturing industry at higher concentrations (1–1000 mg/L) [30], and its toxicity and endocrine disrupting effects on living species has been abundantly evidenced in literature [31,32]. The effect of NOM on MCPA removal during photocatalytic degradation by TNA is investigated. The effect of pH and the effects of co-existing common inorganic anions are documented.



Fig. 1. Schematic representation of the experimental set-up.



Fig. 2. Surface morphology (a) and the Raman spectrum (b) of the  $\rm TiO_2$  nanotube array.

the UV-LED at this distance was  $18.6 \text{ mW/cm}^2$  measured by a THOR-LABS S150C radiant power meter (THORLABS, USA). Vigorous mixing was applied as soon as the reaction solution was added into the reactor. Before switching on the UV-LED, the reaction system was kept in dark for 1 h to establish equilibrium of any possible adsorption of MCPA on the TNA surface. Then the photocatalytic experiments started, for the duration of 120 min. At designated time intervals 1 mL samples were taken, and stored in dark at 4 °C till LC–MS/MS analysis. All experiments were carried out in duplicate. Except for experiments conducted in designated acidic or alkaline conditions, all other experiments were conducted with natural initial pH (circum-neutral: 6–7) and without pH adjustment. For experiments conducted in designated acidic or alkaline



Fig. 3. Effect of NOMs on the photocatalytic MCPA removal performance of TNA. Conditions: natural pH (~7), [MCPA]<sub>0</sub>  $\approx$  1 mg/L, 120 min treatment.



**Fig. 4.** Photosensitization effect of NOMs on MCPA removal. Conditions: natural pH (~7),  $[MCPA]_0 \approx 1 \text{ mg/L}$ , 120 min treatment, no TNA.

conditions, hydrochloric acid or sodium hydroxide aqueous solution were applied to adjust the pH. The experiments were carried out in ambient temperature ( $\sim\!25~^\circ\!C$ ) without temperature control.

#### 2.4. MCPA concentration measurement procedures

For MCPA concentration measurement, an Agilent LC–MS/MS system consisting of Agilent infinity 1260 LC-system (degasser, binary pump, auto sampler with cooled tray and column oven) and Agilent 6420 triple Quadrupole Mass Spectrometer with Electrospray ion source was used. Detailed information of the analytical method used can be found in literature [34].

# 3. Results and discussion

## 3.1. Characterization of the $TiO_2$ nanotube array

Fig. 2a shows the SEM top view image of the TNA, demonstrating the self-organised tubular structure layer, which has average pore size of around 80 nm. The Raman spectrum of the TNA surface shown in Fig. 2b and the XRD patterns shown in Fig. 2c demonstrate that the TNA layer has a crystallographic phase consisting of both anatase and rutile. Good photocatalytic performance of TiO<sub>2</sub> containing both anatase and rutile has been documented in literature [12,35].

#### 3.2. Effect of NOM on photocatalytic MCPA removal performance of TNA

Experiments were carried out in the presence of two different types NOMs originating from two large rivers at varied concentrations ranging from 5 mg/L to 15 mg/L, to examine the effect of NOMs on photocatalytic MCPA removal performance of TNA.



Fig. 5. Effects of NOMs on the photocatalytic MCPA removal performance of TNA, under different pH conditions.



Fig. 6. Photosensitization effect of NOMs on MCPA removal at different pH conditions. Conditions:  $[MCPA]_0 \approx 1 \text{ mg/L}, 120 \text{ min treatment, no TNA}.$ 



Fig. 7. Effects of NOMs on the photocatalytic MCPA removal performance of TNA, with the presence of phosphate anions. Conditions: natural pH ( $\sim$ 7), [MCPA]<sub>0</sub>  $\approx$  1 mg/L, 120 min treatment.



Fig. 8. Effects of NOMs on the photocatalytic MCPA removal performance of TNA, with the presence of bicarbonate anions. Conditions: natural pH ( $\sim$ 7), [MCPA]<sub>0</sub>  $\approx$  1 mg/L, 120 min treatment.

The results (see Fig. 3) show that the presences of both NOMs impose significant detrimental effect on the removal of MCPA over TNA. The TNA based photocatalytic process enabled rather rapid MCPA

degradation with a total removal of 94.3% after 120 min treatment in absence of NOMs. The presence of 5 mg/L NOM resulted in a drastic decrease in MCPA removal: the total removal of MCPA decreased to



Fig. 9. Time dependent photocurrent generation by TNA. Conditions: 0.1 M NaClO<sub>4</sub> electrolyte, [NOM] = 15 mg/L, [Anion] = 100 mg/L.

Table 1 Surface processes related photocurrent decay rate constants under different conditions.

| Conditions   | $k_{s} (s^{-1})$                             |
|--|--|
| SWR-NOM only<br>UMR-NOM only<br>Phosphate + SWR-NOM<br>Phosphate + UMR-NOM<br>Bicarbonate + SWR-NOM<br>Bicarbonate + UMR-NOM | 0.99<br>1.00<br>0.70<br>0.31<br>0.65<br>0.26 |
|  |  |

only 62.0% and 61.8%, in the presence of SWR-NOM and UMR-NOM respectively. Increasing NOM concentrations led to a further decrease in MCPA removal. With elevated concentration of SWR-NOM to 10 mg/ L and 15 mg/L, the total removal of MCPA decreased to 58.5% and 49.1%. For UMR-NOM, when its concentration increased to 10 mg/L and 15 mg/L, the total removal of MCPA reduced to 52.0% and 45.2%. It is also found that the two tested NOMs exert the same inhibitory effect on MCPA removal performance of the TNA, and no significant difference between the two NOMs can be found.

It should be noticed that, upon absorbing UV photons, NOMs can also initiate photosensitized degradation of organic pollutants [36,37]. Experiments were conducted to examine this photosensitization effect of NOMs, and the results (Fig. 4) show that the presence of SWR-NOM and UMR-NOM can indeed contribute to MCPA removal in the bulk liquid phase. However, the negative effect of both NOMs outweighs the photosensitization effect; making the presence of NOMs exhibits detrimental effect on MCPA removal in the TNA based photocatalytic system.

# 3.3. The pH influences the effect of NOMs

100

80

60

40

20

0

O

Total removal (%)

Previous studies have pointed out that the pH conditions impose impact on the adsorption of NOMs on TiO<sub>2</sub> surfaces [15,38].

Considering the adsorption of NOMs on the catalysts surface is a crucial factor contributing to its inhibitory effect, it is of importance to elucidate the effect of pH on the detrimental effect of NOM on the micropollutants removal performance of TNA. Therefore, experiments were conducted to examine the effects of NOMs at varied concentrations under different pH conditions on MCPA removal over TNA.

The results (Fig. 5) suggest that the change in pH conditions would change the effect of NOMs significantly. At neutral pH, the presence of even low level of NOMs led to drastic decrease in MCPA removal. Although the alkaline pH itself induced a decrease in the removal target pollutant (as documented in our previous study [12]), the inhibitory effects of NOMs were not observed under alkaline conditions. On the contrary, a slight increase in the MCPA removal with increasing NOM concentration was observed. This finding can be attributed to two facts: (1) the alkaline conditions mitigate the competitive adsorption by NOMs [15,38]; and (2) the NOMs still impose photosensitization effect which can contribute to MCPA removal in the liquid phase (Fig. 6). More interestingly, although many previous studies have documented that the acidic pH would benefit the adsorption of NOMs [15,38], only minor inhibitory effects were observed in the presence of NOMs at high concentration level (15 mg/L) under acidic conditions. This can be attributed to strengthened adsorption of MCPA [39] on TNA surface and therefore strengthened oxidation by valence band holes and surface adsorbed hydroxyl radicals, as well as largely strengthened photosensitization effect of NOMs (Fig. 6).

## 3.4. Role of co-existing inorganic anion species

To study the impact of co-existing inorganic anions on NOM's inhibitory effect, experiments were performed to examine the photocatalytic MCPA removal performance at various NOMs concentrations with the presence of some most common inorganic anion species, i.e. phosphate, bicarbonate, sulfate, nitrate, chloride.

The results (see Fig. 7 and Fig. 8) suggest that both phosphate and



Fig. 10. Effects of NOMs on the photocatalytic MCPA removal performance of TNA, with the presence of sulfate anions. Conditions: natural pH (~7), [MCPA]<sub>0</sub> ≈ 1 mg/L, 120 min treatment.



Fig. 11. Effects of NOMs on the photocatalytic MCPA removal performance of TNA, with the presence of nitrate anions. Conditions: natural pH (~7),  $[MCPA]_0 \approx 1 \text{ mg/L}$ , 120 min treatment.



Fig. 12. Effects of NOMs on the photocatalytic MCPA removal performance of TNA, with the presence of chloride anions. Conditions: natural pH ( $\sim$ 7), [MCPA]<sub>0</sub> = 1 mg/L, 120 min treatment.

bicarbonate can mitigate the inhibitory effect of NOMs. Without the presence of inorganic anions, the MCPA removal lowered from 94.3% to 45.2% and 49.1%, with the presence of 15 mg/L UMR-NOM and SWR-NOM respectively. In the presence of 50 mg/L phosphate anions, even at highest NOMs concentration (15 mg/L), the inhibitory effects of NOMs were significantly reduced: 73.1% (in presence of UMR-NOM) and 62.5% (presence of SWR-NOM) MCPA removal was achieved within the same treatment time span. For bicarbonate, such mitigation on NOMs` inhibitory effects was also observed, but at weaker level (Fig. 8). With the presence of 100 mg/L bicarbonate, 73.1% and 62.5% MCPA removal was achieved with the presence of 15 mg/L SWR-NOM and UMR-NOM, respectively.

A similar phenomenon has been reported in TiO<sub>2</sub> slurry system in a recent study conducted by Long et al. [27]. The authors observed that phosphate counteracts the inhibitory effect of humic acids (an important constituent of NOM) on TiO<sub>2</sub> nanoparticles based system, and attributed such phenomenon to reduced humic acid adsorption (and therefore direct ROS scavenging upon adsorption) and enhanced electron transfer via changing the adsorption site of humic acid, by the presence of phosphate. Moreover, in another study conducted by Zhao et al. [40] on phosphate surface modification of TiO<sub>2</sub> nanoparticles, it was found that the adsorption of phosphate ions on the catalyst surface would lead to enhanced photocatalytic degradation of target pollutants by promoting the separation of  $e^-/h^+$  pairs via introducing an electrostatic field on the catalyst surface.

The effect of competitive adsorption between phosphate anions and NOMs was investigated using a transient photo-electrolysis technique [41] (Text SI 1). The time-dependent photocurrent curves are shown in Fig. 9b. Upon UV irradiation, the photocurrent increased to a peak value and would then decay gradually to a steady state. The decay curves (5 s-10 s) fits well with a double-exponential model ( $\text{R}^2 > 0.99$ ), where the two exponential decay terms reveal both surface and interfacial photocatalytic reactions (in this case, NOM oxidation). The

relevant rate constants were calculated and shown in Table 1. The obtained results suggest that the presence of phosphate anions can indeed reduce the NOM oxidation on TNA surface.

For bicarbonate, its role observed in the present work is rather different from a previously reported paper on TiO<sub>2</sub> slurry systems. It is reported that the alkalinity impose significant inhibitory effects on the performance of TiO<sub>2</sub> slurry system mainly due to formation of larger TiO<sub>2</sub> aggregates [24]. However, such mechanism can be neglected in the present work because TNA, instead of TiO<sub>2</sub> nanoparticles, was employed. In addition, quenching of conduction band electrons by bicarbonate can be a major factor that contributes to the mitigation effect of their presence on the NOMs' inhibitory effect. According to our previous study [12], bicarbonate anions can act as conduction band electrons quencher [42] upon adsorption on the TiO<sub>2</sub> surface, which decreases the recombination of  $e^{-}/h^{+}$  pairs and can in turn enhance the generation of ROS. In addition, competitive adsorption of bicarbonate against NOMs was also observed, which can reduce the h<sup>+</sup> scavenging effect of NOMs (Fig. 9b). The photocurrent tests results support that the presence of bicarbonate anions can greatly reduce the surface related NOM oxidation: the surface oxidation related photocurrent decay rate constants were much lower with the presence of bicarbonate (Table 1).

Unlike phosphate and bicarbonate, the presence of sulfate, nitrate, and chloride anions imposes no mitigation effect on NOMs' inhibitory effects (Figs. 10–12). This is due to the fact that these anion species can likely enhance the adsorption of NOMs (especially the humic acid components) on the catalyst [43].

## 4. Conclusions

In the present work, we demonstrate the effects of two aquatic NOMs collected from large rivers, i.e. SWR-NOM and UMR-NOM, on the photocatalytic micropollutant removal performance of TNA. For the micropollutant tested herein, main findings can be concluded as below:

- Both types of tested NOMs impose inhibitory effect on MCPA removal performance of TNA, even at low concentration level;
- Acidic pH counteracts the inhibitory effect of NOM, because of enhanced interaction between MCPA and the TNA surface, and strengthened photosensitization effect of NOMs; Under alkaline conditions, NOMs impose a slightly positive impact on MCPA removal, due to photosensitization effect of NOMs and mitigated competitive adsorption of NOMs;
- The presence of a certain level of phosphate and bicarbonate anions can mitigate the inhibitory effect of NOM, while the presence sulfate, nitrate and chloride does not have such mitigation effect.
- The transient photo-electrolysis measurement results demonstrate that the presence of bicarbonate and phosphate anions can reduce the h<sup>+</sup> scavenging effect of NOMs.

## Acknowledgements

This work was performed in the cooperation framework of Wetsus, European Centre of Excellence for Sustainable Water Technology (www.wetsus.eu). Wetsus is co-funded by the Dutch Ministry of Economic Affairs and Ministry of Infrastructure and Environment, the Province of Fryslân, and the Northern Netherlands Provinces. The authors would like to thank the participants of the research theme "Advanced water treatment" for the fruitful discussions and their financial support. The authors gratefully thank Ton van der Zande and Mieke Kersaan-Han for the realization of the instrumental analysis.

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2018.11. 012.

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