Photocatalytic oxidation of natural organic matter in water

Citation for published version:
Gowland, D, Robertson, N & Chatzisymeon, E 2021, 'Photocatalytic oxidation of natural organic matter in water', Water, vol. 13, no. 3, 288. https://doi.org/10.3390/w13030288

Digital Object Identifier (DOI):
10.3390/w13030288

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Water

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.
Photocatalytic oxidation of natural organic matter in water

Dan C.A Gowland 1, Neil Robertson 2 and Efthalia Chatzisymeon 1,*

1 School of Engineering, Institute for Infrastructure and Environment, The University of Edinburgh, Edinburgh EH9 3JL, United Kingdom; d.c.a.gowland@sms.ed.ac.uk
2 EaStCHEM School of Chemistry, Joseph Black Building, King’s Buildings, Edinburgh, United Kingdom, EH9 3JF; neil.robertson@ed.ac.uk
* Correspondence: e.chatzisymeon@ed.ac.uk; Tel.: +44 (0)1316505711

Received: date; Accepted: date; Published: date

Abstract: Increased concentrations of natural organic matter (NOM), a complex mixture of organic substances found in most surface waters, have recently emerged as a substantial environmental issue. NOM has a significant variety of molecular and chemical properties, which in combination with its varying concentrations both geographically and seasonally, introduce the opportunity for an array of interactions with the environment. Due to an observable increase in amounts of NOM in water treatment supply sources, an improved effort to remove naturally-occurring organics from drinking water supplies, as well as from municipal wastewater effluents, is required to continue the development of highly efficient and versatile water treatment technologies. Photocatalysis has received increasing interest from around the world, especially during the last decade, as several investigated processes have been regularly reported to be amongst the best performing water treatment technologies to remove NOM from drinking water supplies and mitigate the formation of disinfection by products. Consequently, this overview highlights recent research and developments on the application of photocatalysis to degrade NOM by means of TiO2-based heterogeneous and homogeneous photocatalysts. Analytical techniques to quantify NOM in water and hybrid photocatalytic processes are also reviewed and discussed.

Keywords: DBPs; AOPs; Advanced oxidation processes; Fulvic acid; Humic acid; Wastewater treatment

1. Introduction

Natural organic matter (NOM) poses a significant threat to the treatment of drinking water by adding several complications to standard processing methods as well as presenting a substantial risk to public health. NOM is a complex matrix of organic compounds mostly made up of a mixture of humic and fulvic substances including anionic macromolecules of various molecular weights with both aromatic and aliphatic components. Humic acids are mostly made up of larger (10,000 to 100,000 Da), alkaline soluble molecules that vary greatly on the source of material they decay from whereas fulvic acids (fulvates, molecules bound to minerals, and free-form fulvic acids) are usually smaller than humic acids (1,000 to 10,000 Da) and are soluble at most pH levels. NOM levels found in most natural waters range from 0.1 to 20 mg/L, however an increase in its concentration in environmental water matrices has been observed recently, presenting a strain on current water treatment infrastructure and local ecosystems. This increase in NOM concentration can be attributed to several drastic changes to climate conditions. For example, there is a correlation between intensity of precipitation and NOM concentration discharged from forested sites, giving rise to increased runoff intensities and therefore increased discharge from soils rich in soil organic matter (SOM). Decreased retention time in lake waters, due to climate change induced precipitation, may further cause decreased photochemical degradation of coloured NOM, decreased microbial
degradation of complex organic compounds, and decreased in-lake NOM coagulation and sedimentation.\textsuperscript{10} Additionally, apparent changes in colour and UV absorption relative to total organic carbon (TOC)\textsuperscript{11} also imply a change in NOM characteristics and therefore treatability meaning diversification of NOM removal is needed now more than ever.\textsuperscript{12} High NOM concentrations can cause aesthetic problems, such as colour and taste\textsuperscript{13} in drinking water, as well as higher maintenance and treatment costs of water and wastewater.\textsuperscript{14-15} Most importantly, recent studies show that certain classes of NOM can react with chemicals (e.g. chlorine) used in the water treatment process, leading to the formation of carcinogenic disinfection by-products (DBPs) and trihalomethanes (THMs).\textsuperscript{16-18} Since the discovery of DBP formation, several studies have outlined associations between consumption of chlorinated tap water containing elevated THM concentrations and adverse health outcomes, including bladder cancer,\textsuperscript{19} children born small for gestational age,\textsuperscript{20-21} and miscarriages.\textsuperscript{22} Another adverse effect indirectly caused by the presence of NOM in surface waters is the observed interference humic substances have on water treatment processes that are targeting toxic compounds or heavy metals. For example, there has been a significant amount of investigation on the inhibitory effects of NOM on targeted wastewater treatments for residual pharmaceuticals which has been shown to significantly decrease the efficiency of such processes.\textsuperscript{23-28}

Current alternative treatment techniques for NOM removal, such as coagulation,\textsuperscript{29} adsorption,\textsuperscript{30} membrane filtration,\textsuperscript{31-32} flotation,\textsuperscript{33} biological\textsuperscript{15} and ion exchange (IE)\textsuperscript{34} processes also bring their own set of problems. For example, the pre-treatment for micro/ultrafiltration systems using conventional treatment processes such as coagulation/flocculation which can partially remove NOM, show low removal efficiency at lower NOM concentrations. Nanofiltration is also sometimes used as a method of NOM removal but additionally comes with the problem of significant membrane fouling.\textsuperscript{35} These problems all show a clear need for an alternative method of removing NOM from water resources.

Advanced oxidation processes (AOPs) are widely applied methods for removal of NOM and water treatment.\textsuperscript{36} Within the area of AOPs, photocatalysis is an up and coming area of research due to its, until recently, untapped wide potential for possible environmental engineering applications. Ongoing research on photocatalytic NOM removal is based around the use of semiconductors (e.g. TiO\textsubscript{2} and ZnO) as sensitizers for light-induced redox processes. When illuminated with a photon of energy greater than the bandgap energy, these semiconductors form an electron/hole pair. These electron/hole pairs are powerful redox species which many organic photodegradation reactions utilize either directly or indirectly via formation of hydroxyl radicals in solution,\textsuperscript{37-38} as shown in figure 1. Early research tested the capabilities of these reactions using low efficiency UV lamps as TiO\textsubscript{2}, the most commonly used photocatalyst, has a fairly low visible light absorption. Whereas current work has shifted over to the use of solar and high efficiency light emitting diodes (LEDs) as sustainable photocatalytic irradiation sources.\textsuperscript{39-44}

![Figure 1 – Principle Mechanism of Photocatalysis](image)
Photocatalysis is commonly categorised into either heterogeneous or homogeneous depending on whether the catalyst is in a different phase from the reactants (heterogeneous) or in the same phase (homogeneous). Most common heterogeneous photocatalysts are transition metal oxides and semiconductors, TiO$_2$ being the most researched due to its high photocatalytic activity, excellent physical and chemical stability, low cost, and nontoxicity to humans and the environment. Other common heterogeneous photocatalysts include zinc oxide (ZnO), which also shows great photocatalytic activity, and graphitic carbon nitride (g-C$_3$N$_4$), which is being increasingly used because of its preferable bandgap for visible light reactions. Heterogeneous photocatalysis gives practical advantages as it allows easy separation of the reaction media from the catalyst as well as high levels of chemical stability and reusability with many new compounds being developed each day. Alternatively, homogeneous photocatalysis may require more complicated steps for catalyst removal but has shown very high photocatalytic activity. The most commonly used homogeneous systems are based on the photo-Fenton process (Fe$^{2+}$/H$_2$O$_2$) where the hydroxy radicals produced are the reactive species.

Increased NOM concentrations in aqueous environment and their adverse effects on human health and ecosystems have been extensively reported. In addition, there are several publications demonstrating that photocatalytic oxidation is a very promising process to remove NOM from water. Nevertheless, a systematic review of all these studies that will be able to summarize all previous research findings, highlight important issues and research areas for further study, as well as suggest new ways to increase the effectiveness and sustainability of existing practices in water and wastewater treatment plants is still missing from literature. Therefore, the aim of this study is to provide a comprehensive review of the work surrounding the photocatalytic treatment and removal of NOM in water resources. Publications on TiO$_2$-based heterogeneous and homogeneous photocatalytic oxidation are systematically presented and discussed. Recommendations for future research directions and approaches that show promise in advancing these areas are made.

2. Materials and Methods

"Natural organic matter", "water", and "wastewater" were used as topic words in searching for papers and patents in Web of Science, Scopus, and Google Scholar (as supplementary) without restriction on publication date. Related documents (>100) were selected to summarize research findings on NOM treatment using photocatalytic degradation as well as other current methods for NOM treatment.

3. Results and Discussion

3.1. Analytical techniques to detect and quantify NOM in water

The type and amount of NOM in water substantially varies among different environmental matrices, as it strongly depends on climatic conditions, hydrological regime as well as other environmental factors. Therefore, to monitor NOM concentration during treatment at lab-scale and improve reproducibility of results, synthetic NOM solutions are commonly used. Common procedures involve dissolving humic and/or fulvic acids in ultrapure water and using them to mimic NOM, as humic and fulvic acids represent up to 80% of the dissolved organics in natural waters and have been shown to be DBP precursors. The reduction of DBP from drinking water is the subject of many NOM related projects, therefore simple, refined humic and fulvic acid samples that are commercially available are typically used by researchers, at least in preliminary testing. More complex NOM samples extracted from water (e.g. International Humic Substances Society (IHSS) samples from the Suwannee River and Mississippi River) have also been known to be used to simulate surface waters as they can give results that more accurately reflect the conditions of certain waters in a controlled manner, although they are more expensive than simpler synthetic NOM varieties.

Different methods are applied to quantify NOM in water: Specific UV absorbance at $\lambda = 254$ nm (SUVA), chemical oxygen demand (COD), total organic carbon analyser (TOC), fluorescence
spectroscopy, high performance liquid chromatography (HPLC), and mass spectrometric methods (MS). The pros and cons of these commonly used methods are weighed up in Table 1. UV-Vis spectroscopy, in the range of 254–280 nm, is commonly used to measure the presence of unsaturated double bonds and π–π electron interactions typically found in aromatic compounds such as humic acid. Measuring SUVA is fast, simple, and does not require complicated equipment or chemical reagents making it a popular analytical method in NOM related research. Chemical oxygen demand (COD), utilises an oxidising agent to measure the amount of oxygen needed to oxidise organic matter in solution (Permanganate Index). This method has been used for a long time due to its simplicity but the many hazardous chemicals (i.e., mercury, hexavalent chromium, sulfuric acid, and silver) involved in the process mean more complex waste management is required than most other methods. Standard COD methods also only allow for COD concentrations that are > 50 mg/L with alterations to allow for COD detection from 5 to 50 mg/L making its applications in wastewater management very limited. TOC analysis, considered the main indicator of NOM in the drinking water, determines the organic carbon present in solution by using infrared (IR) spectroscopy to measure the carbon dioxide produced by heat catalysed chemical oxidation with a persulfate solution. Although, compared to UV254 spectroscopy, TOC analysis requires a slightly longer runtime and a more complex preparation, it is still a relatively quick and simple method for quantifying NOM in water with many different available conditions to allow for the tailoring of specific test environments. The chemicals generally required in TOC also have low toxicity and are cheaply available compared to other methods available. Other analytical methods to detect and quantify NOM are also widely used across various disciplines. The complexity of these methods is increased as more information about the NOM’s profile is afforded.
| Method                        | Advantages                                                                 | Disadvantages                                                                 | Complexity of method |
|-------------------------------|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------|---------------------|
| Adsorption at 254 nm          | - Ease of use                                                                | - Measurement of unsaturated organics in water (not only NOM/humic acid)       | Low                 |
|                               | - Very fast measurement                                                      | - High nitrate content in low dissolved organic carbon (DOC) waters may interfere the measurement |                     |
|                               | - Cheap                                                                     |                                                                               |                     |
| COD                           | - Simple                                                                     | - Toxic treatment chemicals                                                    | Low                 |
|                               | - Well known method                                                          | - Low accuracy                                                                |                     |
|                               |                                                                               | - High minimum detection limit                                                 |                     |
| TOC                           | - Fast measurement                                                           | - Expensive specialised equipment                                             |                     |
|                               | - Tailorable modes of detection for specific experiments                     | - Measurement of total organics in water (not only NOM/humic acid)             |                     |
| Fluorescence spectroscopy     | - No pre-treatment required                                                  | - Only detects fluorescent NOM molecules                                      |                     |
|                               | - Gives information on specific NOM                                          | - Sensitive to chemical environment, e.g. pH                                 |                     |
| FTIR                          | - Good signal to noise ratio                                                 | - Can see large water band interference                                        |                     |
|                               | - Extensive libraries of humic substances to identify specific compound characteristics | - Pre-treatment could alter chemical makeup of NOM                              |                     |
| HPLC                          | - Good separation of NOM compounds                                          | - Requires expensive, high purity solvents, columns etc.                       | High                |
|                               |                                                                               | - NOM can have unwanted interactions with the stationary phase                 |                     |
| GC-MS                         | - Accurate detection of all substances found in water                       | - Cost of reagents, columns, etc                                               |                     |
|                               |                                                                               | - Difficulty in analysing and interpreting results                              |                     |
3.2. NOM photocatalytic treatment

3.2.1. Heterogeneous TiO$_2$ photocatalysis

Table 2 shows all publications focusing on treatment of NOM in water by means of heterogeneous TiO$_2$ photocatalysis. Some of the earliest work on the photocatalytic degradation of NOM was done by Bekbölet et al.\textsuperscript{83,84} where slurries of P25 − TiO$_2$ were used to explore the limitations and general trends observed when changing the reaction conditions in standard photocatalytic procedures. Although these early papers reported on the most favourable conditions for photocatalytic NOM removal, much more work has been done since on optimizing the resultant degradation of NOM by altering basic operational parameters.
| Water matrix                  | Catalyst type       | Reaction time | Irradiation source | Other operating parameters | Removal efficiency | Other important findings | Reference                        |
|------------------------------|---------------------|---------------|--------------------|-----------------------------|--------------------|--------------------------|----------------------------------|
| Humic acid solution          | P25 – TiO₂          | 120 min       | UVA – 125 W        | Ambient pH [HA] = 50 mg/L \[TiO₂] = 1 g/L | 88% TOC 99% Vis₄₀₀ | THMFP* = 14.5 μg/L         | Bekböl et al. (1996)³³¹          |
| Humic acid solution          | P25 – TiO₂, UV100 - TiO₂ | 60 min       | UVA – 125 W \(\lambda = 300-420 \text{ nm}) | Ambient pH [HA] = 10 mg/L \[TiO₂] = 0.25 g/L | P25: 70% TOC UV100: 50% TOC | NOM removal rate constant: P25 = 1.9x10⁻² min⁻¹ UV100 = 1.2x10⁻² min⁻¹ | Bekböl et al. (2002)³³²          |
| Reservoir water: M-Myponga site W-Woronora site | P25 – TiO₂ | 150 min       | UVA – 20 W \(\lambda = 365 \text{ nm}) | pH ~ 7 TOC₄₀ = 10.6 mg/L TOC₃₅ = 3.5 mg/L \[TiO₂] = 0.1 g/L | M: 80% TOC 100% UV₅₄ W: 80% TOC 100% UV₅₄ | THMFP: M = <20 μg/L W = <20 μg/L | Liu et al. (2010)³³³          |
| Sand filtered treatment plant water | N-Pd-TiO₂  | 120 min       | Solar simulator 500 W | pH ~ 6.73 TOC = 2.38 mg/L \[N-Pd-TiO₂] = 5 g/L | HPO** = 71% HPI** = 35% TPI** = 15% UV₅₄ |                           | Nkambule et al. (2012)³³⁴ |
| Reverse osmosis isolate & Alginic acid solution | AgSiO₂-TiO₂ | 30 min       | Solar simulator \(\lambda = 400-1100 \text{ nm}) | pH ~ 8.2 TOC = 3.7 mg/L \[TiO₂] = 0.1 g/L | 20% TOC 42% UV₅₄ | 219 ± 40 μg THMFP per g TiO₂ | Gora et al. (2018)³³⁵          |

*THMFP: Trihalomethanes Formation Potential
Humic acid solution  | Al:Fe-TiO2 (1%) | 15 min | UVC – 37 W  
| |  | λ = 254 nm | pH ~ 7  
| | [HA] = 10 mg/L  
| | [TiO2] = 0.1 g/L  
| | O3 | 63.2% TOC  
| | 79.4% UV254 | Increasing HCO3- concentration decrease NOM reduction rate | Yuan et al. (2013)

Reservoir water: MV-Midvaal  
P-Plettenberg bay | MWCNT/N, Pd-TiO2** | 120 min | Solar simulator  
| |  | 300 W | MV: 69.4% P: 97.7% UV254  
| | [MWCNT/N, Pd-TiO2] = 1 g/L  
| |  | pH ~ 7 | Ndlangamandla et al. (2018)

Humic acid solution | TiO2 nanotubes | 120 min | UVC – 11 W  
| |  | λ = 254 nm | [HA] = 50 mg/L  
| | [TiO2] = 0.5 g/L  
| |  | 98.27% DOC  
| | 100% UV436 | Humic acid removal rate: 0.0607 mol/m^3 s^-1 | Zhang et al. (2009)

Landscape surface water | Bi2O3-TiO2 | 10 min | Vis – 300 W  
| |  | λ = 400-780 nm | pH ~ 6.13  
| | TOC = 2.2 mg/L  
| | [Bi2O3-TiO2] = 2 g/L  
| |  | 20.2% TOC  
| | 24.4% UV254 | Wang et al. (2019)

Pre-treated (coagulation-flocculation) water | P25 - TiO2, TiO2/β-SiC | 220 min | Solar simulator – 1500 W  
| | P25: TOC = 7.8 mg/L  
| | [TiO2] = 0.5 g/L  
| | β-SiC: TOC = 5.5 mg/L  
| | [TiO2] = 0.5 g/L  
| | pH ~ 7 | P25: 80% TOC  
| |  | β-SiC: 80% TOC | Ayekoe et al. (2017)

Treatment plant inlet water in immersed ultrafiltration module | P25 - TiO2 | 120 min  
| | Irradiation 43 hour total treatment | UVC – 15 W  
| | λ = 254 nm | pH ~ 7  
| | DOC = 5.48 mg/L  
| | [TiO2] = 0.1 g/L | 60% DOC  
| | 90% UV254 | THMFP* = 25 μg/L | Rajca et al. (2016)

Humic acid solution | LiCl-TiO2 doped PVDF*** membrane | 30 min | UVA – 100 W  
| |  | λ = 365 nm | pH ~ 7.5  
| | [HA] = 2 mg/L  
| |  | 80-84% UV254 | Song et al. (2014)

Extracted river NOM | P25 - TiO2 | 120 min | UVC – 8 W  
| |  | λ = 254 nm | pH ~ 8.2  
| | TOC = 10 mg/L  
| |  | 80% TOC  
| | 100% UV254 | NOM degradation rate constant: 0.0163 min^-1 | Huang et al. (2008)
|                | Methodology                                                                 | Conditions                                                                 | Results                                                                 | References |
|----------------|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------|-------------------------------------------------------------------------|------------|
| River water    | Nano-TiO2 on diatomite                                                      | 360 min 3x UVC lamps – 16 W λ = 254 nm pH ~ 8.0-8.5 TOC = 9.84–13.18 mg/L [TiO2] = 1 g/L | 28.5% TOC 40% UV254                                                    | Sun et al. (2014)
| Humic acid solution | TiO2 nanoparticles/ granular activated carbon (GAC) | 180 min UVA – 500 W λ = 365 nm pH ~ 4.2 TOC = 5.04 mg/L [TiO2/GAC] = 2 g/L | 99.5% UV254 Significantly lower degradation (70% UV254) at pH = 11 | Xue et al. (2011) |
3.2.1.1. Catalyst and NOM concentration

The concentration of catalyst is an important parameter for photocatalytic oxidation processes. In general, photocatalytic oxidation is enhanced when catalyst concentration is increased up to a value at which removal rate reaches a plateau. Bekbölet et al.\textsuperscript{83} observed that an optimal catalyst concentration for NOM removal is 1 g/L and this is high enough to provide a large surface area to adsorb NOM but not so high that the slurry significantly reduces the availability of light throughout the reaction mixture. This upper limit has been noted to depend on the geometry and on the working conditions of the photoreactor.\textsuperscript{39} This same study evaluated the trihalomethane formation potential (THMFP) of various humic acid concentrations with respect to time, which also opened up the possibility for more research on the area by showing up to 94% reductions in THMFP (below United States Environmental Protection Agency limits) after 120 min of photocatalytic treatment. A similar experiment by Maleki et al.\textsuperscript{47} investigated the effects of catalyst concentration on humic acid degradation using Cu-doped ZnO nanoparticles. The same characteristic rise and plateau in degradation rate was observed when increasing the catalyst concentration from 1.5 g/L to 2 g/L, which was attributed to partial catalyst agglomeration and a consequent decrease in the active catalyst surface at higher dosages of catalysts. Additionally, early work from Palmer et al.\textsuperscript{89} on the operational conditions of photocatalytic NOM degradation using TiO\textsubscript{2} showed that the rate of initial degradation increased with increasing concentration until the concentration of 30 ppm of carbon, after which, the rate decreased. This trend is seen in several other studies of NOM degradation above 30 ppm of C.\textsuperscript{100-102}

3.2.1.2. UV-light driven TiO\textsubscript{2} catalysts

Another early paper by Bekbölet et al.\textsuperscript{84} investigated the differences in performance between; the standard P25 – TiO\textsubscript{2}, a 20:80 mix of rutile: anatase titania, and another commercially available HOMBIKAT UV 100 – TiO\textsubscript{2} made entirely of anatase phase. Here it was shown that P25 – TiO\textsubscript{2} showed better photocatalytic activity when it came to humic acid degradation. This correlated with the adsorption experiments also performed, which revealed that the P25 adsorbed 3 times as much humic acid at a set loading than the UV100 despite having a much lower BET surface area. Due to its proven high-performance rate P25 – TiO\textsubscript{2} is often the comparative standard used in NOM photocatalytic degradation studies of various semiconductor loadings. Huang et al.\textsuperscript{90} in 2008 studied the photocatalysis’ effect on NOM by analysing its compositions in water before and after irradiation. There was observed preferential removal of high molecular weight, hydrophobic NOM molecules, which are the major NOM fraction responsible for membrane fouling.\textsuperscript{85,86} Further research by Valencia et al.\textsuperscript{103} using size-exclusion chromatography with respect to operating pH levels during photocatalytic degradation showed that changes in pH values affected the adsorption of NOM onto TiO\textsubscript{2}. It was established that the pH determines the mechanism, but not the sequence of the photocatalytic degradation and therefore, regardless of pH, the degradation of the NOM preferentially removed the larger molecular size fraction in comparison to the middle and small fractions. Other comprehensive work on operating parameters includes that done by Espinoza et al.\textsuperscript{104} on the effect of metal ions (Cu\textsuperscript{2+}, Fe\textsuperscript{3+}, Zn\textsuperscript{2+}, Mn\textsuperscript{2+}) in solution on the photocatalytic degradation of NOM. Photocatalytic degradation experiments with and without the addition of various combinations of CuSO\textsubscript{4} or CuCl\textsubscript{2}-2H\textsubscript{2}O, FeCl\textsubscript{3}, ZnCl\textsubscript{2}, and MnCl\textsubscript{2} solutions revealed an apparent reduction in photoactivity and prevention of certain degradation products when in the presence of added Cu\textsuperscript{2+} ions (10μM). The addition of Mn\textsuperscript{2+} was observed to change the magnitude of the effect of added Cu\textsuperscript{2+} a larger inhibiting effect from added Cu\textsuperscript{2+} was observed in the absence of added Mn\textsuperscript{2+} during the degradation of large molecular weight NOM. It was suggested by Espinoza et al. that these observations could be explained by a stabilization of the NOM against degradation by HO\textsuperscript{-} by complexation with Cu\textsuperscript{2+}, which would increase the longevity of NOM in aquatic systems. Adding Fe\textsuperscript{3+} and Zn\textsuperscript{2+} to the experiments showed no significant effects.
3.2.1.3. Visible light driven modified TiO$_2$ catalysts

Many investigations on photocatalytic reactions are performed under UV light due to the band gap energy of pure TiO$_2$ (3 or 3.2 eV in rutile or anatase phase), which means that there is very limited photocatalytic activity in the visible range. On top of this, unmodified TiO$_2$ can be characterised with a high recombination rate for the photo-produced electron and hole pairs, and a significant difficulty to strongly bind to some support materials.\textsuperscript{105} Therefore, a significant amount of research surrounding the photocatalytic degradation of NOM is focussed on improving the photo-efficiency of TiO$_2$ and its degradation efficiency of organic compounds. Various approaches to do so consist of chemical and structural modification of TiO$_2$, in order to enable light absorption in the visible region. These studies include several chemical modification schemes that report promising options to improve photocatalytic activity. Chemical modifications to TiO$_2$ involve the addition of various other species, typically involving: metals (such as Fe, Pd or Ag)\textsuperscript{86, 88, 106-107/metal oxides (such as Bi$_2$O$_3$)\textsuperscript{108-111} which can either facilitate electron–hole separation and promote interfacial electron transfer or decrease the TiO$_2$ band gap. This promotes electron transfer from the valence band to the conduction band, facilitating the formation of oxidative species such as hydroxyl radicals.\textsuperscript{112}

Other chemical modifications include the addition of non-metals (such as C, N, S or F) which have also been shown to form new impurity levels close to the valence or conduction band of TiO$_2$, thereby lowering the optical gap and shifting the absorption edge to the visible light region.\textsuperscript{113} Nkambules\textsuperscript{\textsuperscript{86} 2012 work focuses on N-doped TiO$_2$, a growing area of photocatalysis which has been shown to increase visible light photocatalytic activity when coupled with co-dopant metals by reducing the band gap of TiO$_2$ and shifted the absorption into the visible light region.\textsuperscript{89, 114} The Pd-modified N-doped TiO$_2$ catalyst synthesised by Nkambule et al. in 2012 showed a particularly successful shift in titania’s visible light absorption with an over 70% removal in hydrophobic NOM fractions using a solar simulator. A drawback to these N-doped TiO$_2$ species would be that the doping of N into the lattice of TiO$_2$ usually results in the formation of oxygen vacancies in the bulk material.\textsuperscript{115} These defects can act as recombination centres for carriers and therefore, compared to pure TiO$_2$, a loss of UV-activity is usually found for N-doped TiO$_2$, which is due to the rapid recombination rate of generated electrons and holes introduced by the impurity level. The addition of non-metals to metal doped TiO$_2$ can also be utilised to improve the stability of the photocatalyst, for example forming a thin layer of SiO$_2$ around a catalyst’s surface to prevent oxidation of metal nanoparticles like Gora et al. in their 2018 investigation on modified TiO$_2$ for solar photocatalysis.\textsuperscript{87} This work saw a Ag$_2$ TiO$_3$ nanoparticle co-catalyst reduce NOM levels by 42% UV$_{254}$ only 30 min of treatment time. This study also found significant changes to the disinfectant by-product formation potential (DBPFP) of NOM wherein the different modifications to TiO$_2$ followed the same trend in DBPFP level changes but by differing amounts.

3.2.1.4. Immobilized catalysts

Alongside the chemical changes, various nano structured TiO$_2$ materials have been tested with enhanced visible light photoactivity such as nanoparticles,\textsuperscript{116} nanotubes,\textsuperscript{90} nanowires\textsuperscript{117} and nanofilms.\textsuperscript{118} As well as affecting the photoactivity of TiO$_2$, many of these structurally modified materials combat the problems faced by loose slurry reactions such as catalyst separation, recovery and reuse which bring about significant obstacles for practical applications of TiO$_2$ powder heterogeneous photocatalysis due to its small particle size.\textsuperscript{119} Many researchers apply membrane filtration for the separation of nanosized TiO$_2$ from treated water however, as mentioned previously, serious membrane fouling usually occurs as the TiO$_2$ forms a cake layer and blocks membrane pores. Work done by Zhang et al.\textsuperscript{90} showed that creating titania nanotubes can not only improve upon P25 – TiO$_2$’s ability to photocatalytically degrade NOM, most likely due to increased surface area, but also significantly reduces the amount of membrane fouling caused by catalyst separation. Another approach to reducing the need for catalyst separation when photocatalytically degrading NOM is producing hybrid materials by combining TiO$_2$ with carbon materials such as multiwalled carbon nanotubes\textsuperscript{90} and activated carbons.\textsuperscript{97} A particularly successful example of this is the work done by
Xue et al. where a TiO$_2$ nanoparticle/ granular activated carbon composite (GAC) was prepared by a sol-dipping–gel process. This investigation displayed a synergetic relationship between adsorption upon GAC and degradation involving TiO$_2$ where a humic acid removal of 99.5% UV$_{254}$ was achieved as well as improved filterability. Hybrid membranes combining TiO$_2$ with various polymeric compounds such as polyvinylalcohol, pyrrolidone$^{120}$ and poly (amide–imide)$^{121}$ also show a solution to catalyst separation. These hybrid membranes exhibit great potential for water treatment since they combine filtration and photo degradation in a single unit. Although blending photocatalytic nanoparticles into polymeric thin film can cause the entrapped photocatalyst to show reduced catalytic activity due to the agglomeration and shielding effects in the polymer matrix.$^{122}$

### 3.2.1.5 Hybrid processes

The most widely used processes for the removal of NOM from water sources are separation and purification technologies including (micro, ultra and nano) membrane filtration, reverse or forward osmosis, and coagulation. One approach to improving the overall efficiency of water treatment facilities is combining one or more of these technologies with heterogeneous photocatalysis. This includes the combining of photocatalysts with membrane filtration$^{83,95,120,123-125}$ and adsorption,$^{126}$ as well as coagulation systems.$^{91}$ An example of such systems would be Wang et al.$^{91}$ whose work which showed pre-treatment by photocatalysis with Bi$_2$O$_3$–TiO$_2$(4%) could improve the removal of organic matter compared to polyaluminium chloride (PACl) coagulation treatment alone. This study saw removal rates of 20.2% and 24.4% UV$_{254}$ after just 10 min of photocatalytic treatment which increased to 37.93% TOC and 58.75% UV$_{254}$. Photocatalytic oxidation prior to coagulation has been observed to decrease coagulation efficiency by 15%, most likely because the oxidation changes the characteristics of NOM and degrades NOM molecules towards smaller molecular mass fractions.$^{127}$ However, when oxidation was performed after coagulation, about 32% DOC and 33% UV$_{254}$ enhancements to the removal of NOM occurred.$^{128}$

These hybrid processes can also work in tandem to help reduce the inherent downfalls of photocatalytic systems. For example, to ensure an efficient rate of photocatalytic reaction, it is recommended that water turbidity should not exceed 5 NTU.$^{129-130}$ Although it has been observed that the 5 NTU limit is subjective and differs for each water source and desired treatment level,$^{131}$ this limitation on photocatalytic efficiency set by water turbidity means that conventional treatments (ie sieving, filtration, sedimentation, coagulation and flocculation) may be an appropriate industrial pre-treatment for many photocatalytic processes.

### 3.2.2. Homogeneous photocatalysis

#### 3.2.2.1. Photo-Fenton

Recent interest in homogeneous photocatalytic NOM removal has increased due to reports of lower chemical doses, and therefore lower residual levels of chemicals post treatment, when compared to conventional NOM removal methods such as coagulation.$^{132}$ Although heterogeneous photocatalysis, such as a standard TiO$_2$/UV NOM removal mentioned previously, has the added benefit of easy separation after treatment is completed, homogeneous photocatalysis reactions have the advantage of providing a greater degree of interaction between the catalyst and the specified target due to the increased accessibility of the catalytic sites whilst in solution. The homogeneous photocatalytic degradational removal of organic compounds from water is mainly based on the generation of high amounts of hydroxyl radicals from either ozone or hydrogen peroxide. These generated hydroxyl radicals can degrade the organic matter commonly through hydrogen abstraction from aliphatic carbon atoms and electrophilic addition to double bonds or aromatic rings.$^{133}$ This is ideal for the degradation of the large hydrophobic NOM fractions which are major precursors for DBP formation.$^{63}$

---

*Xue et al. Water, 2020, 12, x FOR PEER REVIEW*
Table 3. Publications on homogeneous photocatalytic treatment of NOM.

| Homogeneous processes | Water matrix | Catalyst type | Reaction time | Irradiation source | Other operating parameters | Removal efficiency | Reference |
|-----------------------|--------------|---------------|---------------|-------------------|---------------------------|-------------------|-----------|
| Hybrid Photolysis     | Reservoir water | O₃/UV         | 60 min        | UVA lamp          | pH ~ 6.6                  | 50% TOC           | Chin & Bérubé (2005)¹³⁴ |
|                       | River water | H₂O₂/UV       | 30 min        | UVA lamp – 43W    | TOC = 3.1 mg/L            | H₂O₂ only: 3-23% DOC | Lamsal et al. (2011)¹³⁵ |
|                       |             | O₃/UV         |               |                   |                          | O₃ only: 60% UV₂₅₄ |           |
|                       |             |               |               |                   |                          | O₃ dosage = 4 mg/L  |           |
|                       | Reservoir water | H₂O₂/UV       |               | UVC lamp          | [H₂O₂] = 23 mg/L         | H₂O₂ only: 88% UV₂₅₄ |           |
|                       |             |               |               |                   | [Cat] = 5.65mg/L         |                   |           |
|                       |             |               |               |                   | pH ~ 4                   |                   |           |
|                       | Inlet water to water treatment works | FeSO₄·7H₂O+H₂O₂ | 20 min | 4x UVA lamps - 25W | DOC = 9.6 mg/L           | 90% DOC           | Murray et al. (2002)¹³² |
|                       |             |               |               |                   | λ = 365 nm               |                   |           |
|                       |             |               |               |                   |                           |                   |           |
|                       | Water treatment works reservoir water | FeSO₄·7H₂O+H₂O₂ | 30 min | 4x UVA lamps - 25W | DOC = 7.5 mg/L           | 90% DOC           | Murray et al. (2004)¹³⁷ |
|                       |             |               |               |                   | λ = 365 nm               |                   |           |
|                       | Reservoir water | FeSO₄·7H₂O+H₂O₂ | 1 min | 4x UVC lamp – 12W | pH ~ 4.5                 | FeSO₄·7H₂O+H₂O₂   | Goslan et al. (2006)¹³⁸ |
|                       |             |               |               |                   | λ = 254 nm               | Fe₂⁺ = 4:1        |           |
|                       | River water | FeCl₃·7H₂O+    | After 6.5 KJ/L | Solar CPC         | pH ~ 5                   | 90% DOC           | Moncayo-Lasso   |
|                       |             |               |               |                   |                           |                   |           |
| pre-treated with slow sand filtration | H₂O₂ of solar energy | DOC = 2.7–3.1 mg/L | 95% UV<sub>254</sub> | et al. (2008)<sup>139</sup>
|---|---|---|---|---|
| River water | FeCl₃·7H₂O + H₂O₂ + H₂O₂ of solar energy | Solar CPC | pH ~ 6.5 | 55% DOC 75% UV<sub>254</sub> | Moncayo-Lasso et al. (2009)<sup>128</sup> |
A comparative study by Goslan et al.\textsuperscript{138} showed that the addition of Ferrous sulphate increased UV/H$_2$O$_2$ ability to remove NOM from reservoir water by forming a photo-Fenton reaction.

\[
\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + \text{H}^+
\]

(1)

\[
\text{Fe(OH)}_2 + \text{hv} \rightarrow \text{Fe}^{2+} + \cdot \text{OH}
\]

(2)

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \cdot \text{OH}
\]

(3)

During the photo-Fenton process, in addition to equations (2) and (3), hydroxyl radical formation can also occur via the following reactions:

\[
\text{Fe}^{2+} + \text{H}_2\text{O} + \text{hv} \rightarrow \text{Fe}^{2+} + \cdot \text{H} + \cdot \text{OH}
\]

(4)

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\cdot \text{OH}
\]

(5)

In the photo-Fenton process (equations (1) and (2)), the Fenton reaction rates are strongly increased by irradiation with UV--vis light. The positive effect of irradiation on the degradation rate is due to the photo-chemical regeneration of ferrous iron (Fe$^{2+}$) by photo-reduction of ferric complexes, which leads to additional -OH generation.\textsuperscript{140-143} The ferrous iron generated in solution reacts with H$_2$O$_2$ yielding a second -OH radical and ferric iron (equation (3)), and the cycle continues.

A major advantage of the photo-Fenton reagent is that the reactions light absorption maximum wavelength is roughly 600 nm which gives a much larger absorption overlap with natural sunlight compared to many other common photocatalysts.

Although the exact mechanism used for degradation of NOM using photo-Fenton processes is not presently clear, work from Fukushima et al.\textsuperscript{141} has shed some light on possible processes occurring during these degradation reactions. Fukushima’s 2001 work on the degradation products produced from degrading several different NOM fractions in a photo-Fenton solution showed that the TOC decreased dependent on increasing irradiation time, indicating mineralisation of the HA to CO$_2$ during this process. Analysis on different molecular weight fractions of HA also suggested that the degradation of high molecular weight fractions of HA results in a lowering in molecular size during photo-Fenton processes.

3.2.2.2. Hybrid photolytic oxidation processes

An interesting comparison to homogeneous photocatalysis is the work done with homogeneous hybrid photolysis for NOM treatment by enhancing the oxidative capabilities of common oxidising species (e.g. ozone and peroxides) with light. The advantages of these hybrid processes, as well as other AOPs including O$_3$/UV, H$_2$O$_2$/UV and H$_2$O$_2$/O$_3$, was explored by Lamsal et al.\textsuperscript{135} in 2011. This study specifically investigated the treatment process impact on the change of molecular weight distribution (MWD) and disinfection by-product formation potential (DBPFP) with the UV/ozone hybrid showing a significantly improved removal of NOM and reduced DBPFP when compared to UV or ozone treatment alone.

3.2.2.2.1. Hydrogen peroxide based photocatalysis

Many factors decide on the optimum H$_2$O$_2$ dosage in UV degradation reactions. For UV / H$_2$O$_2$ NOM removal, the characteristics and concentration of the organic compounds can directly influence the overall mineralisation ability. The amount of hydroxyl radicals produced upon UV irradiation depends on the H$_2$O$_2$ concentration whilst H$_2$O$_2$ can also react with these radicals and inhibit hydroxyl radical evolution. Additionally, H$_2$O$_2$ absorbs UV energy therefore reducing the availability of UV photons for oxidising pollutants at higher H$_2$O$_2$ concentrations. Wang et al.\textsuperscript{145} found, for the oxidation of humic acid, that the hydroxyl radical scavenging effect (the production and then combination of HO$_2$ into H$_2$O and O$_2$) became significant when the H$_2$O$_2$ concentration was higher than 0.1% making this the optimum dosage. This study also noted that the presence of bicarbonate/carbonate species has a negative effect on NOM degradation due to causing competition for hydroxyl radicals, especially at high concentrations of H$_2$O$_2$. 

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \cdot \text{OH}
\]
Ozone can degrade NOM directly through ozonolysis which has been found to be fairly selective and relatively slow\(^{146-147}\) so most NOM degradation research is focussed on increasing the generation of hydroxyl radicals from the decomposition of ozone in water. This includes the combination of ozone with UV irradiation to degrade NOM through quick, non-selective ozonation. Study results from Ratpukdi et al.\(^{148}\) on the optimal operating conditions for UV/ozone hybrid photolysis procedures revealed that the mineralization rate of DOC provided by the processes tested ranked in the following order: vacuum ultraviolet (VUV)/ozone > VUV > UV/ozone > ozone > UV. The study also showed that the highest DOC mineralisation rate and biodegradability increase was at a neutral pH 7 rather than in a basic environment (pH 9 and pH 11) with extremely basic conditions (pH 11) showing no synergistic hybrid effect from combining UV and ozone at all.

Research comparing O\(_3\)-NOM degradation with and without the addition of UVC shows a clear enhancement effect from UV light. Work by Chin & Bérubé\(^{134}\) concluded that the combined UV/O\(_3\) treatment is more effective at reducing organic constituents, as well as the DBP-FP, in raw water than either the ozone or UV treatment alone. Lamsal et al.\(^{139}\) investigated this hybrid effect further by showing how several AOP treatment processes impacted the change of molecular weight distribution (MWD) and disinfection by-product formation potential (DBPFP). The UV/ozone hybrid in this side by side study showed a significantly improved removal of NOM and reduced DBPFP when compared to UV or ozone treatment alone. It was also noted that this UV/ozone process induced a near complete alteration of the molecular weight of NOM from >900 Da to <300 Da.

### 3.2.2.2. Ozone based photocatalysis

A significant area of interest surrounding UV photocatalysis is the energy consumption, and associated operating costs, of artificial lighting. The electric energy per order, \(E_{\text{EO}}\) value was introduced by Bolton et al.,\(^{149}\) and is used to estimate the energy consumption of photocatalytic reactors. \(E_{\text{EO}}\) is defined as the energy required for 90% degradation of a pollutant per cubic meter of contaminated water. \(E_{\text{EO}}\) (kWh/m\(^3\)/order), for a batch-operated reactor, is calculated from the following equation (6):

\[
E_{\text{EO}} = \frac{P \times t \times 1000}{V \times 60 \times \log (C_i/C_f)}
\]  
(6)

where \(P\) is the electrical power of the irradiation source (kW), \(t\) is the irradiation time (min), \(V\) is the volume of the treated effluent (L), and \(C_i\) and \(C_f\) are the initial and final pollutant concentrations (mg L\(^{-1}\)), respectively. The \(E_{\text{EO}}\) of selected significant publications are displayed in table 4 to give an example of the relative energy efficiencies of various photocatalytic NOM treatments.

An interesting observation from the data displayed in table 4 is the significance the electrical power of the irradiation source (P) plays in the energy efficiency of a reaction. For example, for electrical power \(\geq 0.125\) kW the \(E_{\text{EO}}\) is at the order of \(10^3\) (process types 1\(^{st}\) and 3\(^{rd}\) as shown in table 4), while this decreases to the order of 10 for \(P\leq 0.1\) kW. This is due to the position of \(P\) on the numerator of equation 6 which is then multiplied by 1000, making relatively small differences in the power inputs of irradiation sources result in large disparities in \(E_{\text{EO}}\). Also, when process types with similar \(P\), for example types 1\(^{st}\) and 6\(^{th}\) are compared (as shown in table 4), it can be observed that short treatment time (i.e. 30 min) is also important to keep the \(E_{\text{EO}}\) at the low order of 10 kWh m\(^3\) order\(^{-1}\).

This shows the significance that recent advancements in LED technology have had for the prospects of industrial scale photocatalytic water treatment due to the drastically improved efficiency when compared to conventional mercury black lights.
Table 4. Energy efficiency comparison of photocatalytic treatments of NOM.

| Process type            | Water matrix                      | Catalyst type | Electrical power of the irradiation source (P) / kW | Reaction time (t) / min | Volume (V) / L | TOC % | EKWh m⁻³ order⁻¹ | Reference                          |
|-------------------------|-----------------------------------|---------------|----------------------------------------------------|-------------------------|----------------|-------|------------------|------------------------------------|
| Heterogeneous           | Humic acid solution               | P25-TiO₂      | 0.125                                              | 120                     | 0.05           | 88    | 5,430            | Bekbolet et al. (1996)              |
| Heterogeneous           | Reservoir water                   | P25-TiO₂      | 0.02                                               | 150                     | 0.8            | 100   | 15.625           | Liu et al. (2010)                   |
| Heterogeneous           | Pre-treated (coagulation-flocculation) water | P25-TiO₂/βSiC | 1.5                                                | 220                     | 0.1            | 80    | 78,687           | Ayekoe et al. (2017)                |
| Homogeneous             | River water                       | H₂O₂/UV       | 0.043                                              | 30                      | 3              | 23    | 63.137           | Lamsal et al. (2010)               |
| Homogeneous             | River water                       | O₃/UV         | 0.043                                              | 30                      | 3              | 31    | 44.472           | Lamsal et al. (2011)               |
| Homogeneous             | Water treatment works             | FeSO₄.7H₂O₂ + H₂O₂ | 0.1                                                | 30                      | 1              | 90    | 50               | Murray et al. (2004)               |
4. Conclusions and Considerations for Future Research

The removal of NOM from drinking water presents a great challenge that will require the application of efficient and flexible water treatment technology or more likely a combination of synergistic technologies. A crucial process towards achieving this is the proper characterisation of NOM and its various fractions in order to accurately estimate their reactivity with the utilised treatment system. This procedure is critical in the selection and application of the most suitable process by achieving the highest removal efficiency, the greatest reduction in disinfection by-product formation potential, and the best possible cost efficiency. Photocatalysis is highly regarded amongst NOM removal researchers due to the quick and nonselective character of the hydroxyl radicals produced during processing. This makes the measured differences of NOM in water less of an issue in photocatalysis when compared to other conventional NOM removal treatments. Although, various studies reported that photocatalysis can tend to have more impact on NOM’s hydrophobic and higher MW compounds. The non-specificity of hydroxy radicals can also be a disadvantage to photocatalytic methods in that the highly reactive HO· can also interact with ions and other dissolved organics in waters which could reduce the overall efficiency of NOM removal. These unintentional side reactions have been observed during the removal of humic acid in the presence of bicarbonate (HCO₃⁻) and halide (Cl⁻ and Br⁻) ions.

Currently, the coupling of photocatalysis with other water treatment technologies is being investigated as a viable option to overcome the inadequacies of photocatalysis and the selected technology alone. As there is no standalone water treatment technique that is able to optimally remove NOM by itself, numerous integrated processes for the removal of NOM have been studied, such as the combination of photocatalysis with; membrane filtration and adsorption, coagulation, and biodegradation.

When focussing on heterogeneous photocatalysis, most research tends to either focus on the optimisation of the photocatalytic activity of TiO₂ or to synthesise novel photocatalysts able to compete with TiO₂. The improved degradation capabilities of TiO₂ is commonly explored via structural modifications (nanocrystals, nanoparticles, nanotubes, nanowires and nanofilms.) and/or combination with other catalysts (ZnO) or materials (polymers, multiwalled carbon nanotubes and activated carbons). Alternatively, novel photocatalysts are regularly chosen based on their superior photocatalytic activity under near visible or solar light when compared to a TiO₂ standard.

Due to large amounts of research focussing on lab scale efficiency, there is an apparent lack of focus on the economics of applying various photocatalytic treatments for the removal of NOM from drinking water sources. This step is crucial to giving a more well-rounded comparison of photocatalytic water treatment with current, well established procedures for NOM removal. Very few publications have evaluated the cost of applying selected photocatalysts for other pollutants, such as immobilised TiO₂ for the treatment of industrial wastewaters. Another important factor to consider is the environmental impact of such photocatalytic treatments, life cycle assessments including a goal and scope definition, inventory analysis and life cycle impact assessment (LCIA) would need to be done to properly predict the implications of using these systems on an industrial scale.

Owing to the high energy demand of traditional UV-lamps, alternative sources of UV-light are being investigated. One obvious choice of reducing energy demand of UV-light is the use of sunlight for a lower environmentally impacting and cheap light source. The downside of this being that using solar light is typically less effective as an energy source as its emission spectrum has a relatively small overlap with the absorbance of many common photocatalysts, such as TiO₂. This is reflected by the large volume of interest in increasing/red shifting the absorbance wavelength range of TiO₂ by doping it with different elements such as nitrogen and carbon. Another possible alternative method of UV illumination is the use of light emitting diodes (LED) reactors due to their high efficiency and durability.
Developing and applying efficient photocatalysis based technologies to remove NOM and mitigate DBP formations is a promising start and making them more efficient and cost-effective for large scale application in integration with other advanced water treatment technologies is the next crucial step to advancing water treatment engineering.

**Author Contributions:** Conceptualization, E.C.; methodology, D.G. investigation, D.G.; writing—original draft preparation, D.G.; writing—review and editing, E.C. and N.R.; supervision, E.C. and N.R. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Scottish Water, grant number EP/R513209/1.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Volk, C.; Wood, L.; Johnson, B.; Robinson, J.; Zhu, H. W.; Kaplan, L., Monitoring dissolved organic carbon in surface and drinking waters. *Journal of Environmental Monitoring* 2002, 4 (1), 43-47.

2. Bolto, B.; Dixon, D.; Eldridge, R.; King, S.; Linge, K., Removal of natural organic matter by ion exchange. *Water Research* 2002, 36 (20), 5057-5065.

3. Reyes, T. G.; Crisosto, J. M., Characterization of Dissolved Organic Matter in River Water by Conventional Methods and Direct Sample Analysis-Time of Flight-Mass Spectrometry. *Journal of Chemistry* 2016, 2016, 1537730.

4. Worrall, F.; Harriman, R.; Evans, C.; Watts, C.; Adamson, J.; Neal, C.; Tipping, E.; Burt, T.; Grieve, I.; Monteith, D.; Naden, P.; Nisbet, T.; Reynolds, B.; Stevens, P., Trends in Dissolved Organic Carbon in UK Rivers and Lakes. *Biogeochemistry* 2004, 70, 369-402.

5. Zhang, J.; Hudson, J.; Neal, R.; Sereda, J.; Clair, T.; Turner, M.; Jeffries, D.; Dillon, P.; Molot, L.; Somers, K.; Hesslein, R., Long-term patterns of dissolved organic carbon in lakes across eastern Canada: Evidence of a pronounced climate effect. *Limnology and Oceanography* 2010, 55 (1), 30-42.

6. Dong, Q.; Li, P.; Huang, Q.; Abdelhafiz, A. A.; Chen, L., Occurrence, polarity and bioavailability of dissolved organic matter in the Huangpu River, China. *Journal of Environmental Sciences* 2014, (26), 1843-1850.

7. Eikebrokk, B.; Vogt, R. D.; Liltved, H., NOM increase in Northern European source waters: discussion of possible causes and impacts on coagulation/contact filtration processes. *Water Supply* 2004, 4 (4), 47-54.

8. Kaal, J.; Plaza, C.; Nierop, K.; Pérez-Rodriguez, M.; Biester, H., Origin of dissolved organic matter in the Harz Mountains (Germany): A thermally assisted hydrolysis and methylation (THM-GC–MS) study. *Geoderma* 2020, 378, 114635.

9. Selle, B.; Knorr, K.-H.; Lischeid, G., Mobilisation and transport of dissolved organic carbon and iron in peat catchments - insights from the Lehstenbach stream in Germany using Generalised Additive Models. *Hydrological Processes* 2019, 33.

10. Korth, A.; Fiebig, C.; Bornmann, K.; Schmidt, W., NOM increase in drinking water reservoirs - Relevance for drinking water production. *Water Science and Technology: Water Supply* 2004, 4.

11. Grunewald, K.; co-author, a., Increase in colour and amount of organic matter in surface waters. 2003.

12. Ritson, J. P.; Graham, N. J. D.; Templeton, M. R.; Clark, J. M.; Gough, R.; Freeman, C., The impact of climate change on the treatability of dissolved organic matter (DOM) in upland water supplies: A UK perspective. *Science of The Total Environment* 2014, 473-474, 714-730.

13. Leenheer, J. A.; Croué, J.-P., Peer Reviewed: Characterizing Aquatic Dissolved Organic Matter. *Environmental Science & Technology* 2003, 37 (1), 18A-26A.

14. Costa, A. R.; de Pinho, M. N., Performance and cost estimation of nanofiltration for surface water treatment in drinking water production. *Desalination* 2006, 196 (1), 55-65.
15. Krzeminski, P.; Vogelsang, C.; Meyn, T.; Köhler, S. J.; Poutanen, H.; de Wit, H. A.; Uhl, W., Natural organic matter fractions and their removal in full-scale drinking water treatment under cold climate conditions in Nordic capitals. *Journal of Environmental Management* **2019**, *241*, 427-438.

16. Tian, C.; Liu, R.; Liu, H.; Qu, J., Disinfection by-products formation and precursors transformation during chlorination and chloramination of highly-polluted source water: Significance of ammonia. *Water Research* **2013**, *47*(15), 5901-5910.

17. Yang, X.; Guo, W.; Lee, W., Formation of disinfection byproducts upon chlorine dioxide preoxidation followed by chlorination or chloramination of natural organic matter. *Chemosphere* **2013**, *91*(11), 1477-1485.

18. Pan, Y.; Wang, Y.; Li, A.; Xu, B.; Xian, Q.; Shuang, C.; Shi, P.; Zhou, Q., Detection, formation and occurrence of 13 new polar phenolic chlorinated and brominated disinfection byproducts in drinking water. *Water Research* **2017**, *112*, 129-136.

19. Costet, N.; Villanueva, C. M.; Jaakkola, J. J. K.; Kogevinas, M.; Cantor, K. P.; King, W. D.; Lynch, C. F.; Nieuwenhuijsen, M. J.; Cordier, S., Water disinfection by-products and bladder cancer: is there a European specificity? A pooled and meta-analysis of European case–control studies. *Occupational and Environmental Medicine* **2011**, *68*(5), 379-385.

20. Wright, J. M.; Evans, A.; Kaufman, J. A.; Rivera-Núñez, Z.; Narotsky, M. G., Disinfection By-Product Exposures and the Risk of Specific Cardiac Birth Defects. *Environmental Health Perspectives* **2017**, *125*(2), 269-277.

21. Grellier, J.; Bennett, J.; Patelarou, E.; Smith, R. B.; Toledano, M. B.; Rushton, L.; Briggs, D. J.; Nieuwenhuijsen, M. J., Exposure to Disinfection By-products, Fetal Growth, and Prematurity: A Systematic Review and Meta-analysis. *Epidemiology* **2010**, *21*(3), 300-313.

22. Waller, K.; Swan, S. H.; DeLorenze, G.; Hopkins, B., Trithalomethanes in Drinking Water and Spontaneous Abortion. *Epidemiology* **1998**, *9*(2), 134-140.

23. De Vietro, N.; Tursi, A.; Beneduci, A.; Chidichimo, F.; Milella, A.; Fracassi, F.; Chatzisymeon, E.; Chidichimo, G., Photocatalytic inactivation of Escherichia coli bacteria in water using low pressure plasma deposited TiO2 cellulose fabric. *Photochemical & Photobiological Sciences* **2019**, *18*(9), 2248-2258.

24. Davididou, K.; McRitchie, C.; Antonopoulou, M.; Konstantinou, I.; Chatzisymeon, E., Photocatalytic degradation of saccharin under UV-LED and blacklight irradiation. *Journal of Chemical Technology & Biotechnology* **2018**, *93*(1), 269-276.

25. Davididou, K.; Nelson, R.; Monteagudo, J. M.; Durán, A.; Expósito, A. J.; Chatzisymeon, E., Photocatalytic degradation of bisphenol-A under UV-LED, blacklight and solar irradiation. *Journal of Cleaner Production* **2018**, *203*, 13-21.

26. Sounthararajah, D. P.; Loganathan, P.; Kandasamy, J.; Vigneswaran, S., Effects of Humic Acid and Suspended Solids on the Removal of Heavy Metals from Water by Adsorption onto Granular Activated Carbon. *Int J Environ Res Public Health* **2015**, *12*(9), 10475-10489.

27. Wang, L.; Wei, S.; Jiang, Z., Effects of humic acid on enhanced removal of lead ions by polystyrene-supported nano-Fe (0) nanocomposite. *Scientific Reports* **2020**, *10*(1), 19663.

28. Męczykowska, H.; Stepnowski, P.; Caban, M., Impact of humic acids, temperature and stirring on passive extraction of pharmaceuticals from water by trihexyl(tetradecyl)phosphonium dicyanamide. *Microchemical Journal* **2019**, *144*, 500-505.

29. Matilainen, A.; Vepsäläinen, M.; Sillanpää, M., Natural organic matter removal by coagulation during drinking water treatment: A review. *Advances in Colloid and Interface Science* **2010**, *159*(2), 189-197.
30. Velten, S.; Knappe, D. R. U.; Traber, J.; Kaiser, H.-P.; von Gunten, U.; Boller, M.; Meylan, S., Characterization of natural organic matter adsorption in granular activated carbon adsorbers. *Water Research* **2011**, *45*(13), 3951-3959.

31. Petala, M. D.; Zouboulis, A. I., Vibratory shear enhanced processing membrane filtration applied for the removal of natural organic matter from surface waters. *Journal of Membrane Science* **2006**, *269*(1), 1-14.

32. Winter, J.; Barbeau, B.; Bérubé, P., Nanofiltration and Tight Ultrafiltration Membranes for Natural Organic Matter Removal- Contribution of Fouling and Concentration Polarization to Filtration Resistance. *Membranes (Basel)* **2017**, *7*(3), 34.

33. Zouboulis, A. I.; Jun, W.; Katsoyiannis, I. A., Removal of humic acids by flotation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2003**, *231*(1), 181-193.

34. Boyer, T. H., Removal of Dissolved Organic Matter by Magnetic Ion Exchange Resin. *Current Pollution Reports* **2015**, *1*(3), 142-154.

35. Li, Q.; Elimelech, M., Synergistic effects in combined fouling of a loose nanofiltration membrane by colloidal materials and natural organic matter. *Journal of Membrane Science* **2006**, *278*(1), 72-82.

36. Alrousan, D.; Afkhami, A.; Bani-Melhem, K.; Dunlop, P., Organic Degradation Potential of Real Greywater Using TiO2-Based Advanced Oxidation Processes. *Water Research* **2020**, *12*(10), 2811.

37. Westerhoff, P.; Aiken, G.; Amy, G.; Debroux, J., Relationships between the structure of natural organic matter and its reactivity towards molecular ozone and hydroxyl radicals. *Water Research* **1999**, *33*(10), 2265-2276.

38. Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.; Bahnemann, D. W., Understanding TiO2 Photocatalysis: Mechanisms and Materials. *Chemical Reviews* **2014**, *114*(19), 9919-9986.

39. Moreira, N. F. F.; Sousa, J. M.; Macedo, G.; Ribeiro, A. R.; Barreiros, L.; Pedrosa, M.; Faria, J. L.; Pereira, M. F. R.; Castro-Silva, S.; Segundo, M. A.; Manaia, C. M.; Nunes, O. C.; Silva, A. M. T., Photocatalytic ozonation of urban wastewater and surface water using immobilized TiO2 with LEDs: Micropollutants, antibiotic resistance genes and estrogenic activity. *Water Research* **2016**, *94*, 10-22.

40. Jallouli, N.; Pastre-Ramirez, L. M.; Ribeiro, A. R.; Moreira, N. F. F.; Faria, J. L.; Hentati, O.; Silva, A. M. T.; Ksibi, M., Heterogeneous photocatalytic degradation of ibuprofen in ultrapure water, municipal and pharmaceutical industry wastewaters using a TiO2/UV-LED system. *Chemical Engineering Journal* **2018**, *334*, 976-984.

41. Gao, Y.; Li, S.; Li, Y.; Yao, L.; Zhang, H., Accelerated photocatalytic degradation of organic pollutant over metal-organic framework MIL-53(Fe) under visible LED light mediated by persulfate. *Applied Catalysis B: Environmental* **2017**, *202*, 165-174.

42. Martín-Sómer, M.; Pablos, C.; van Grieken, R.; Marugán, J., Influence of light distribution on the performance of photocatalytic reactors: LED vs mercury lamps. *Applied Catalysis B: Environmental* **2017**, *215*, 1-7.

43. Casado, C.; Timmers, R.; Sergejevs, A.; Clarke, C. T.; Allsopp, D. W. E.; Bowen, C. R.; van Grieken, R.; Marugán, J., Design and validation of a LED-based high intensity photocatalytic reactor for quantifying activity measurements. *Chemical Engineering Journal* **2017**, *327*, 1043-1055.

44. Ye, Y.; Feng, Y.; Bruning, H.; Yntema, D.; Rijnaarts, H. H. M., Photocatalytic degradation of metoprolol by TiO2 nanotube arrays and UV-LED: Effects of catalyst properties, operational parameters, commonly present water constituents, and photo-induced reactive species. *Applied Catalysis B: Environmental* **2018**, *220*, 171-181.

45. Lee, K. M.; Lai, C. W.; Ngai, K. S.; Juan, J. C., Recent developments of zinc oxide based photocatalyst in water treatment technology: A review. *Water Research* **2016**, *88*, 428-448.
46. Maleki, A.; Safari, M.; Rezaee, R.; Cheshmeh Soltani, R. D.; Shahmoradi, B.; Zandsalimi, Y., Photocatalytic degradation of humic substances in the presence of ZnO nanoparticles immobilized on glass plates under ultraviolet irradiation. *Separation Science and Technology* **2016**, *51* (14), 2484-2489.

47. Maleki, A.; Safari, M.; Shahmoradi, B.; Zandsalimi, Y.; Daraei, H.; Ghariﬁ, F., Photocatalytic degradation of humic substances in aqueous solution using Cu-doped ZnO nanoparticles under natural sunlight irradiation. *Environmental Science and Pollution Research* **2015**, *22* (21), 16875-16880.

48. Birben, N. C.; Paganini, M. C.; Calza, P.; Bekbolet, M., Photocatalytic degradation of humic acid using a novel photocatalyst: Ce-doped ZnO. *Photochemical & Photobiological Sciences* **2017**, *16* (1), 24-30.

49. Wen, J.; Xie, J.; Chen, X.; Li, X., A review on g-C3N4-based photocatalysts. *Applied Surface Science* **2017**, *391*, 72-123.

50. Ioannidi, A.; Petala, A.; Frontistis, Z., Copper phosphide promoted BiVO4 photocatalysts for the degradation of sulfamethoxazole in aqueous media. *Journal of Environmental Chemical Engineering* **2020**, *8* (5), 104340.

51. Tomara, T.; Frontistis, Z.; Petala, A.; Mantzavinos, D., Photocatalytic performance of Ag2O towards sulfamethoxazole degradation in environmental samples. *Journal of Environmental Chemical Engineering* **2019**, *7* (3), 103177.

52. Kumaravel, V.; Rhatigan, S.; Mathew, S.; Bartlett, J.; Nolan, M.; Hinder, S. J.; Sharma, P. K.; Singh, A.; Byrne, J. A.; Harrison, J.; Pillai, S. C., Indium-Doped TiO2 Photocatalysts with High-Temperature Anatase Stability. *The Journal of Physical Chemistry C* **2019**, *123* (34), 21083-21096.

53. Wu, C.-H.; Chang, C.-L., Decolorization of Reactive Red 2 by advanced oxidation processes: Comparative studies of homogeneous and heterogeneous systems. *Journal of Hazardous Materials* **2006**, *128* (2), 265-272.

54. Peternel, I. T.; Koprivanac, N.; Božić, A. M. L.; Kušić, H. M., Comparative study of UV/TiO2, UV/ZnO and photo-Fenton processes for the organic reactive dye degradation in aqueous solution. *Journal of Hazardous Materials* **2007**, *148* (1), 477-484.

55. Liu, X.; Zhou, Y.; Zhang, J.; Luo, L.; Yang, Y.; Huang, H.; Peng, H.; Tang, L.; Mu, Y., Insight into electro-Fenton and photo-Fenton for the degradation of antibiotics: Mechanism study and research gaps. *Chemical Engineering Journal* **2018**, *347*, 379-397.

56. Vorontsov, A. V., Advancing Fenton and photo-Fenton water treatment through the catalyst design. *Journal of Hazardous Materials* **2015**, *372*, 103-112.

57. Byrne, J. A.; Dunlop, P. S. M.; Hamilton, J. W. J.; Fernández-Ibáñez, P.; Polo-López, I.; Sharma, P. K.; Vennard, A. S. M., A Review of Heterogeneous Photocatalysis for Water and Surface Disinfection. *Molecules* **2015**, *20* (4), 5574-5615.

58. Duarte, R. M. B. O.; Santos, E. B. H.; Duarte, A. C., Spectroscopic characteristics of ultrafiltration fractions of fulvic and humic acids isolated from an eucalyptus bleached Kraft pulp mill effluent. *Water Research* **2003**, *37* (17), 4073-4080.

59. Ye, Y.; Bruning, H.; Liu, W.; Rijnaarts, H.; Yntema, D., Effect of dissolved natural organic matter on the photocatalytic micropollutant removal performance of TiO2 nanotube array. *Journal of Photochemistry and Photobiology A: Chemistry* **2019**, *371*, 216-222.

60. Korshin, G. V.; Benjamin, M. M.; Li, C.-W., Use of differential spectroscopy to evaluate the structure and reactivity of humics. *Water Science and Technology* **1999**, *40* (9), 9-16.

61. Ates, N.; Kitis, M.; Yetis, U., Formation of chlorination by-products in waters with low SUVA—correlations with SUVA and differential UV spectroscopy. *Water Research* **2007**, *41* (18), 4139-4148.
62. Sambo, S. P.; Marais, S. S.; Msagati, T. A. M.; Mamba, B. B.; Nkambule, T. T. L., Quantification of biodegradable natural organic matter (NOM) fractions and its impact on bacterial regrowth in a South African Water Treatment Plant. *Journal of Water Process Engineering* **2020**, *36*, 101332.

63. Hua, L.-C.; Chao, S.-J.; Huang, K.; Huang, C., Characteristics of low and high SUVA precursors: Relationships among molecular weight, fluorescence, and chemical composition with DBP formation. *Science of the Total Environment* **2020**, *727*, 138638.

64. Walton, J.; Labine, P.; Reidies, A., The chemistry of permanganate in degradative oxidations. In *Chemical oxidation*, Technomic Publishing Co. Inc. Lancaster, Basel: 1991; pp 205-219.

65. Wallace, B.; Purcell, M.; Furlong, J., Total organic carbon analysis as a precursor to disinfection byproducts in potable water: Oxidation technique considerations. *Journal of Environmental Monitoring: JEM* **2002**, *4*, 35-42.

66. Kiashemshaki, H.; Mahvi, A. H.; Najafpoor, A. A.; Hosseinzadeh, A., Investigation of the Efficiency of the Conventional Water Treatment Processes Employed to Eliminate TOC in Jalaliyeh Water Treatment Plant, Tehran. *Health Scope* **2017**, *6* (4), e61907.

67. Baker, A.; Tipping, E.; Thacker, S. A.; Gondar, D., Relating dissolved organic matter fluorescence and functional properties. *Chemosphere* **2008**, *73* (11), 1765-1772.

68. Bieroza, M.; Baker, A.; Bridgeman, J., Relating freshwater organic matter fluorescence to organic carbon removal efficiency in drinking water treatment. *Science of the Total Environment* **2009**, *407* (5), 1765-1774.

69. Peiris, R. H.; Hallé, C.; Budman, H.; Moresoli, C.; Peldszus, S.; Huck, P. M.; Legge, R. L., Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation-emission matrices. *Water Research* **2010**, *44* (1), 185-194.

70. Khamis, K.; Bradley, C.; Hannah, D. M., High frequency fluorescence monitoring reveals new insights into organic matter dynamics of an urban river, Birmingham, UK. *Science of the Total Environment* **2020**, *710*, 135668.

71. Allpike, B. P.; Heitz, A.; Joll, C. A.; Kagi, R. I., A new organic carbon detector for size exclusion chromatography. *Journal of Chromatography A* **2007**, *1157* (1), 472-476.

72. Brezinski, K.; Gorczyca, B., An overview of the uses of high performance size exclusion chromatography (HPSEC) in the characterization of natural organic matter (NOM) in potable water, and ion-exchange applications. *Chemosphere* **2019**, *217*, 122-139.

73. Mawhinney, D. B.; Rosario-Ortiz, F. L.; Baik, S.; Vanderford, B. J.; Snyder, S. A., Characterization of fulvic acids by liquid chromatography-quadrupole time-of-flight mass spectrometry. *Journal of Chromatography A* **2009**, *1216* (9), 1319-1324.

74. Zhang, X.; Han, J.; Zhang, X.; Shen, J.; Chen, Z.; Chu, W.; Kang, J.; Zhao, S.; Zhou, Y., Application of Fourier transform ion cyclotron resonance mass spectrometry to characterize natural organic matter. *Chemosphere* **2020**, *260*, 127458.

75. Huck, P. M., Measurement of Biodegradable Organic Matter and Bacterial Growth Potential in Drinking Water. *Journal AWWA* **1990**, *82* (7), 78-86.

76. Spencer, R. G. M.; Bolton, L.; Baker, A., Freeze/thaw and pH effects on freshwater dissolved organic matter fluorescence and absorbance properties from a number of UK locations. *Water Research* **2007**, *41* (13), 2941-2950.

77. Kanokkantapong, V.; Marhaba, T. F.; Panyapinyophol, B.; Pavasant, P., FTIR evaluation of functional groups involved in the formation of haloacetic acids during the chlorination of raw water. *J Hazard Mater* **2006**, *136* (2), 188-96.

78. Her, N.; Amy, G.; Chung, J.; Yoon, J.; Yoon, Y., Characterizing dissolved organic matter and evaluating associated nanofiltration membrane fouling. *Chemosphere* **2008**, *70* (3), 495-502.
Folhas, D.; Duarte, A. C.; Pilote, M.; Vincent, W. F.; Freitas, P.; Vieira, G.; Silva, A. M. S.; Duarte, R. M. B. O.; Canário, J., Structural Characterization of Dissolved Organic Matter in Permafrost Peatland Lakes. *Water* 2020, 12 (11), 3059.

Pelekani, C.; Newcombe, G.; Snoeyink, V. L.; Hepplewhite, C.; Assemi, S.; Beckett, R., Characterization of Natural Organic Matter Using High Performance Size Exclusion Chromatography. *Environmental Science & Technology* 1999, 33 (16), 2807-2813.

Zhou, Q.; Cabaniss, S. E.; Maurice, P. A., Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances. *Water Research* 2000, 34 (14), 3505-3514.

Wu, F. C.; Evans, R. D.; Dillon, P. J., Separation and Characterization of NOM by High-Performance Liquid Chromatography and On-Line Three-Dimensional Excitation Emission Matrix Fluorescence Detection. *Environmental Science & Technology* 2003, 37 (16), 3687-3693.

Bekebolet, M.; Özkoşemen, G., A preliminary investigation on the photocatalytic degradation of a model humic acid. *Water Science and Technology* 1996, 33 (6), 189-194.

Bekebolet, M.; Suphandag, A. S.; Uyguner, C. S., An investigation of the photocatalytic efficiencies of TiO2 powders on the decolourisation of humic acids. *Journal of Photochemistry and Photobiology A: Chemistry* 2002, 148 (1), 121-128.

Liu, S.; Lim, M.; Fabris, R.; Chow, C.; Drikas, M.; Amal, R., Comparison of photocatalytic degradation of natural organic matter in two Australian surface waters using multiple analytical techniques. *Organic Geochemistry* 2010, 41 (2), 124-129.

Nkambule, T. I.; Kuvarega, A. T.; Krause, R. W. M.; Haarhoff, J.; Mamba, B. B., Synthesis and characterisation of Pd-modified N-doped TiO2 for photocatalytic degradation of natural organic matter (NOM) fractions. *Environmental Science and Pollution Research* 2012, 19 (9), 4120-4132.

Gora, S.; Sokolowski, A.; Hatat-Fraile, M.; Liang, R.; Zhou, Y. N.; Andrews, S., Solar photocatalysis with modified TiO2 photocatalysts: effects on NOM and disinfection byproduct formation potential. *Environmental Science: Water Research & Technology* 2018, 4 (9), 1361-1376.

Yuan, R.; Zhou, B.; Hua, D.; Shi, C., Enhanced photocatalytic degradation of humic acids using Al and Fe co-doped TiO2 nanotubes under UV/ozonation for drinking water purification. *Journal of Hazardous Materials* 2013, 262, 527-538.

Ndlangamandla, N. G.; Kuvarega, A. T.; Msagati, T. A. M.; Mamba, B. B.; Nkambule, T. T. I., A novel photodegradation approach for the efficient removal of natural organic matter (NOM) from water. *Physics and Chemistry of the Earth, Parts A/B/C* 2018, 106, 97-106.

Zhang, X.; Pan, J. H.; Fu, W.; Du, A. J.; Sun, D. D., TiO2 nanotube photocatalytic oxidation for water treatment. *Water Supply* 2009, 9 (1), 45-49.

Wang, N.; Li, X.; Yang, Y.; Shang, Y.; Zhuang, X.; Li, H.; Zhou, Z., Combined process of visible light irradiation photocatalysis-coagulation enhances natural organic matter removal: Optimization of influencing factors and mechanism. *Chemical Engineering Journal* 2019, 374.

Ayekoe, C. Y. P.; Robert, D.; Lanciné, D. G., Combination of coagulation-flocculation and heterogeneous photocatalysis for improving the removal of humic substances in real treated water from Agbô River (Ivory-Coast). *Catalysis Today* 2017, 281, 2-13.

Rajca, M., The effectiveness of removal of NOM from natural water using photocatalytic membrane reactors in PMR-UF and PMR-MF modes. *Chemical Engineering Journal* 2016, 305, 169-175.
94. Song, H.; Shao, J.; Wang, J.; Zhong, X., The removal of natural organic matter with LiCl–TiO2-doped PVDF membranes by integration of ultrafiltration with photocatalysis. *Desalination* 2014, 344, 412-421.

95. Huang, X.; Leal, M.; Li, Q., Degradation of natural organic matter by TiO2 photocatalytic oxidation and its effect on fouling of low-pressure membranes. *Water Research* 2008, 42 (4), 1142-1150.

96. Sun, W.; Chu, H.; Dong, B.; Cao, D.; Zheng, S., The Degradation of Natural Organic Matter in Surface Water by a Nano-TiO2/Diatomite Photocatalytic Reactor. *CLEAN – Soil, Air, Water* 2014, 42 (9), 1190-1198.

97. Xue, G.; Liu, H.; Chen, Q.; Hills, C.; Tyrer, M.; Innocent, F., Synergy between surface adsorption and photocatalysis during degradation of humic acid on TiO2/activated carbon composites. *Journal of Hazardous Materials* 2011, 186 (1), 765-772.

98. Herrmann, J.-M., Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis Today* 1999, 53 (1), 115-129.

99. Palmer, F. L.; Eggins, B. R.; Coleman, H. M., The effect of operational parameters on the photocatalytic degradation of humic acid. *Journal of Photochemistry and Photobiology A: Chemistry* 2002, 148 (1), 137-143.

100. Joolaei, H.; Vossoughi, M.; Rashidi Mehr Abadi, A.; Heravi, A., Removal of humic acid from aqueous solution using photocatalytic reaction on perlite granules covered by Nano TiO2 particles. *Journal of Molecular Liquids* 2017, 242, 357-363.

101. Babel, S.; Sekartaji, P. A.; Sudrajat, H., TiO2 as an effective nanocatalyst for photocatalytic degradation of humic acid in water environment. *Journal of Water Supply: Research and Technology–Aqua* 2016, 66 (1), 25-35.

102. Song, L.; Zhu, B.; Jegatheesan, V.; Gray, S. R.; Duke, M. C.; Muthukumaran, S., Effect of Hybrid Photocatalysis and Ceramic Membrane Filtration Process for Humic Acid Degradation. In *Water Scarcity and Ways to Reduce the Impact: Management Strategies and Technologies for Zero Liquid Discharge and Future Smart Cities*, Pannirselvam, M.; Shu, L.; Griffin, G.; Philip, L.; Natarajan, A.; Hussain, S., Eds. Springer International Publishing: Cham, 2019; pp 95-113.

103. Valencia, S.; Marin, J.; Velásquez, J.; Restrepo, G.; Frimmel, F. H., Study of pH effects on the evolution of properties of brown-water natural organic matter as revealed by size-exclusion chromatography during photocatalytic degradation. *Water Research* 2012, 46 (4), 1198-1206.

104. Tercero Espinoza, L. A.; ter Haseborg, E.; Weber, M.; Karle, E.; Peschke, R.; Frimmel, F. H., Effect of selected metal ions on the photocatalytic degradation of bog lake water natural organic matter. *Water Research* 2011, 45 (3), 1039-1048.

105. Di Paola, A.; García-López, E.; Marci, G.; Palmisano, L., A survey of photocatalytic materials for environmental remediation. *Journal of Hazardous Materials* 2012, 211-212, 3-29.

106. Birben, N. C.; Uyguner-Demirel, C. S.; Kavurmaci, S. S.; Gürkan, Y. Y.; Turkten, N.; Cinar, Z.; Bekbolet, M., Application of Fe-doped TiO2 specimens for the solar photocatalytic degradation of humic acid. *Catalysis Today* 2017, 281, 78-84.

107. Sharma, P. K.; Cortes, M. A. L. R. M.; Hamilton, J. W. J.; Han, Y.; Byrne, J. A.; Nolan, M., Surface modification of TiO2 with copper clusters for band gap narrowing. *Catalysis Today* 2019, 321-322, 9-17.

108. Sood, S.; Mehta, S. K.; Sinha, A. S. K.; Kansal, S. K., Bi2O3/TiO2 heterostructures: Synthesis, characterization and their application in solar light mediated photocatalyzed degradation of an antibiotic, ofloxacin. *Chemical Engineering Journal* 2016, 290, 45-52.

109. Liu, Y.; Xin, F.; Wang, F.; Luo, S.; Yin, X., Synthesis, characterization, and activities of visible light-driven Bi2O3–TiO2 composite photocatalysts. *Journal of Alloys and Compounds* 2010, 498 (2), 179-184.
110. Geng, N.; Chen, W.; Xu, H.; Lin, T.; Ding, M.; Wang, Y.; Tao, H.; Hu, K., Preparation of Fe3O4/TiO2-N- GO sonocatalyst and using for humic acid removal with the assist of ultrasound. *Materials Science in Semiconductor Processing* 2019, 102, 104593.

111. Khan, S.; Kim, J.; Sotto, A.; Van der Bruggen, B., Humic acid fouling in a submerged photocatalytic membrane reactor with binary TiO2-ZrO2 particles. *Journal of Industrial and Engineering Chemistry* 2015, 21, 779-786.

112. Kumar, S. G.; Devi, L. G., Review on Modified TiO2 Photocatalysis under UV/Visible Light: Selected Results and Related Mechanisms on Interfacial Charge Carrier Transfer Dynamics. *The Journal of Physical Chemistry A* 2011, 115 (46), 13221-13241.

113. Dozzi, M. V.; Selli, E., Doping TiO2 with p-block elements: Effects on photocatalytic activity. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 2013, 14, 13-28.

114. Zhang, J.; Wu, Y.; Xing, M.; Lehari, S. A. K.; Sajjad, S., Development of modified N doped TiO2 photocatalyst with metals, nonmetals and metal oxides. *Energy & Environmental Science* 2010, 3 (6), 715-726.

115. Sakthivel, S.; Janczarek, M.; Kisch, H., Visible Light Activity and Photoelectrochemical Properties of Nitrogen-Doped TiO2. *The Journal of Physical Chemistry B* 2004, 108 (50), 19384-19387.

116. Gora, S. L.; Andrews, S. A., Adsorption of natural organic matter and disinfection byproduct precursors from surface water onto TiO2 nanoparticles: pH effects, isotherm modelling and implications for using TiO2 for drinking water treatment. *Chemosphere* 2017, 174, 363-370.

117. Zhang, X.; Pan, J. H.; Du, A. J.; Fu, W.; Sun, D. D.; Leckie, J. O., Combination of one-dimensional TiO2 nanowire photocatalytic oxidation with microfiltration for water treatment. *Water Research* 2009, 43 (5), 1179-1186.

118. Rizzo, L.; Uyguner, C. S.; Selcuk, H.; Bekbolet, M.; Anderson, M., Activation of solgel titanium nanofilm by UV illumination for NOM removal. *Water Science and Technology* 2007, 55 (12), 113-118.

119. Lee, S.-A.; Choo, K.-H.; Lee, C.-H.; Lee, H.-A.; Hyeon, T.; Choi, W.; Kwon, H.-H., Use of Ultrafiltration Membranes for the Separation of TiO2 Photocatalysts in Drinking Water Treatment. *Industrial & Engineering Chemistry Research* 2001, 40 (7), 1712-1719.

120. Ng, H. K. M.; Sabran, A. H.; Leo, C. P.; Ahmad, A. L.; Abdullah, A. Z., Photocatalysts in polysulfone membrane for the removal of humic acid: The effects of PVP and PVA on membrane morphology, separation performance and catalytic hindrance. *Journal of Membrane Science and Research* 2016, 2, 95-101.

121. Rajesh, S.; Senthilkumar, S.; Jayalakshmi, A.; Nirmala, M. T.; Ismail, A. F.; Mohan, D., Preparation and performance evaluation of poly (amide-imide) and TiO2 nanoparticles impregnated polysulfone nanofiltration membranes in the removal of humic substances. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2013, 418, 92-104.

122. Ballari, M. d. l. M.; Brandi, R.; Alfano, O.; Cassano, A., Mass transfer limitations in photocatalytic reactors employing titanium dioxide suspensions: II. External and internal particle constrains for the reaction. *Chemical Engineering Journal* 2008, 136 (2), 242-255.

123. Yao, P.; Choo, K.-H.; Kim, M.-H., A hybridized photocatalysis–microfiltration system with iron oxide-coated membranes for the removal of natural organic matter in water treatment: Effects of iron oxide layers and colloids. *Water Research* 2009, 43 (17), 4238-4248.

124. Athanasekou, C. P.; Morales-Torres, S.; Likodimos, V.; Romanos, G. E.; Pastrana-Martinez, L. M.; Falaras, P.; Dionysiou, D. D.; Faria, J. L.; Figueiredo, J. L.; Silva, A. M. T., Prototype composite membranes of partially reduced graphene oxide/TiO2 for photocatalytic ultrafiltration water treatment under visible light. *Applied Catalysis B: Environmental* 2014, 158-159, 361-372.
125. Pastrana-Martínez, L. M.; Morales-Torres, S.; Figueiredo, J. L.; Faria, J. L.; Silva, A. M. T., Graphene oxide based ultrafiltration membranes for photocatalytic degradation of organic pollutants in salty water. Water Research 2015, 77, 179-190.

126. Kaplan Bekaroglu, S. S.; Yigit, N. O.; Harman, B. I.; Kitis, M., Hybrid Adsorptive and Oxidative Removal of Natural Organic Matter Using Iron Oxide-Coated Pumice Particles. Journal of Chemistry 2016, 2016, 3108034.

127. Uyguner, C. S.; Suphandag, S. A.; Kerc, A.; Bekbolet, M., Evaluation of adsorption and coagulation characteristics of humic acids preceded by alternative advanced oxidation techniques. Desalination 2007, 210 (1), 183-193.

128. Moncayo-Lasso, A.; Sanabria, J.; Pulgarin, C.; Benítez, N., Simultaneous E. coli inactivation and NOM degradation in river water via photo-Fenton process at natural pH in solar CPC reactor. A new way for enhancing solar disinfection of natural water. Chemosphere 2009, 77 (2), 296-300.

129. Gelover, S.; Gómez, L. A.; Reyes, K.; Teresa Leal, M., A practical demonstration of water disinfection using TiO2 films and sunlight. Water Research 2006, 40 (17), 3274-3280.

130. Fernández-Ibáñez, P.; Sichel, C.; Polo-López, M. I.; de Cara-García, M.; Tello, J. C., Photocatalytic disinfection of natural well water contaminated by Fusarium solani using TiO2 slurry in solar CPC photo-reactors. Catalysis Today 2009, 144 (1), 62-68.

131. Chong, M. N.; Jin, B.; Chow, C. W.; Saint, C., Recent developments in photocatalytic water treatment technology: a review. Water Res 2010, 44 (10), 2997-3027.

132. Murray, C. A.; Parsons, S. A., Advanced oxidation processes: flowsheet options for bulk natural organic matter removal. Water Supply 2004, 4 (4), 113-119.

133. Legrini, O.; Oliveros, E.; Braun, A. M., Photochemical processes for water treatment. Chemical Reviews 1993, 93 (2), 671-698.

134. Chin, A.; Bérubé, P. R., Removal of disinfection by-product precursors with ozone-UV advanced oxidation process. Water Research 2005, 39 (10), 2136-2144.

135. Lamsal, R.; Walsh, M. E.; Gagnon, G. A., Comparison of advanced oxidation processes for the removal of natural organic matter. Water Research 2011, 45 (10), 3263-3269.

136. Toor, R.; Mohseni, M., UV-H2O2 based AOP and its integration with biological activated carbon treatment for DBP reduction in drinking water. Chemosphere 2007, 66 (11), 2087-2095.

137. Murray, C. A.; Parsons, S. A., Removal of NOM from drinking water: Fenton’s and photo-Fenton’s processes. Chemosphere 2004, 54 (7), 1017-1023.

138. Goslan, E. H.; Gurses, F.; Banks, J.; Parsons, S. A., An investigation into reservoir NOM reduction by UV photolysis and advanced oxidation processes. Chemosphere 2006, 65 (7), 1113-1119.

139. Moncayo-Lasso, A.; Pulgarin, C.; Benítez, N., Degradation of DBPs’ precursors in river water before and after slow sand filtration by photo-Fenton process at pH 5 in a solar CPC reactor. Water Research 2008, 42 (15), 4125-4132.

140. Zepp, R. G.; Faust, B. C.; Hoigne, J., Hydroxyl radical formation in aqueous reactions (pH 3-8) of iron(II) with hydrogen peroxide: the photo-Fenton reaction. Environmental Science & Technology 1992, 26 (2), 313-319.

141. Wardman, P.; Candia, L. P., Fenton Chemistry: An Introduction. Radiation Research 1996, 145 (5), 523-531.

142. Park, S.; Yoon, T.-i., The effects of iron species and mineral particles on advanced oxidation processes for the removal of humic acids. Desalination 2007, 208 (1), 181-191.

143. Clarizia, L.; Russo, D.; Di Somma, I.; Marotta, R.; Andreozzi, R., Homogeneous photo-Fenton processes at near neutral pH: A review. Applied Catalysis B: Environmental 2017, 209, 358-371.
Angford, C. H., Application of Photocatalysts and LED Light Sources in Drinking Water Treatment. *ACS Sustainable Chemistry & Engineering* **2013**, 3 (3), 726-743.

Bircher, K.; Tumas, W.; Tolman, C., Figures-of-Merit for the Technical Development and Application of Advanced Oxidation Technologies for Both Electric- and Solar-Driven Systems – (IUPAC Technical Report). *Pure and Applied Chemistry* - *PURE APPL CHEM* **2001**, 73, 627-637.

Carr, S. A.; Baird, R. B., Mineralization as a mechanism for TOC removal: study of ozone/ozone–peroxide oxidation using FT-IR. *Water Research* **2000**, 34 (16), 4036-4048.

Gottschalk, C.; Libra, J.; Saupe, A., Ozonation of Water and Waste Water: A Practical Guide to Understanding Oxygen and Its Application. 2000; p 189.

Grebel, J. E.; Pignatelto, J. J.; Mitch, W. A., Effect of Halide Ions and Carbonates on Organic Contaminant Degradation by Hydroxyl Radical-Based Advanced Oxidation Processes in Saline Waters. *Environmental Science & Technology* **2010**, 44 (17), 6822-6828.

Treguer, R.; Tatin, R.; Couvert, A.; Wolbert, D.; Tazi-Pain, A., Ozonation effect on natural organic matter adsorption and biodegradation – Application to a membrane bioreactor containing activated carbon for drinking water production. *Water Research* **2010**, 44 (3), 781-788.

Yan, W.-Y.; Zhou, Q.; Chen, X.; Yang, Y.; Zhang, Y.; Huang, X.-J.; Wu, Y.-C., Size-Controlled TiO2 nanocrystals with exposed [001] and [101] facets strongly linking to graphene oxide via p-Phenylenediamine for efficient photocatalytic degradation of fulvic acids. *Journal of Hazardous Materials* **2016**, 314, 41-50.

Turkten, N.; Bekbolet, M., Photocatalytic performance of titanium dioxide and zinc oxide binary system on degradation of humic matter. *Journal of Photochemistry and Photobiology A: Chemistry* **2020**, 401, 112748.

Valencia, S.; Marin, J.; Restrepo, G., Photocatalytic Degradation of Humic Acids with Titanium Dioxide Embedded into Polyethylene Pellets to Enhance the Postrecovery of Catalyst. *Environmental Engineering Science* **2017**, 35 (3), 185-193.

Asha, R. C.; Vishnuganth, M. A.; Remya, N.; Selvaraju, N.; Kumar, M., Livestock Wastewater Treatment in Batch and Continuous Photocatalytic Systems: Performance and Economic Analyses. *Water, Air, & Soil Pollution* **2015**, 226 (5), 132.
161. Tokode, O.; Prabhu, R.; Lawton, L.; Robertson, P., UV LED Sources for Heterogeneous Photocatalysis. 2014.

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© 2020 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).