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1 *Review*

2 **Photocatalytic oxidation of natural organic matter in** 3 **water**

4 **Dan C.A Gowland** ¹, **Neil Robertson** ² and **Efthalia Chatzisymeon** ^{1,*}

5 ¹ School of Engineering, Institute for Infrastructure and Environment, The University of Edinburgh,
6 Edinburgh EH9 3JL, United Kingdom; d.c.a.gowland@sms.ed.ac.uk

7 ² EaStCHEM School of Chemistry, Joseph Black Building, King's Buildings, Edinburgh, United Kingdom,
8 EH9 3FJ; neil.robertson@ed.ac.uk

9 * Correspondence: e.chatzisymeon@ed.ac.uk; Tel.: +44 (0)1316505711

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

26 **Keywords:** DBPs; AOPs; Advanced oxidation processes; Fulvic acid; Humic acid; Wastewater
27 treatment
28

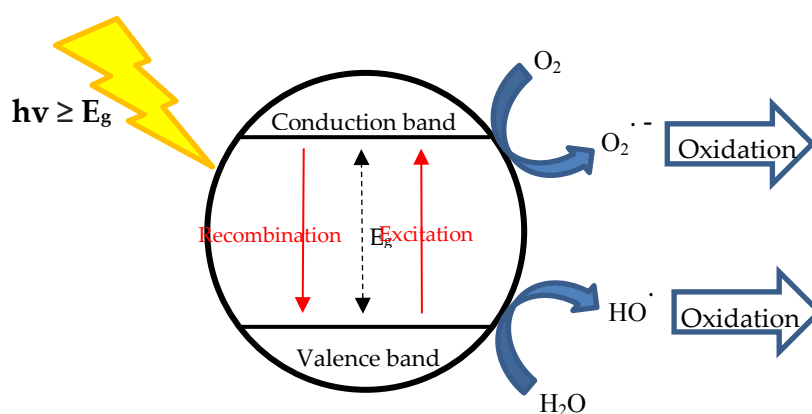
29 **1. Introduction**

30 Natural organic matter (NOM) poses a significant threat to the treatment of drinking water by
31 adding several complications to standard processing methods as well as presenting a substantial risk
32 to public health. NOM is a complex matrix of organic compounds mostly made up of a mixture of
33 humic and fulvic substances including anionic macromolecules of various molecular weights with
34 both aromatic and aliphatic components. Humic acids are mostly made up of larger (10,000 to
35 100,000 Da), alkaline soluble molecules that vary greatly on the source of material they decay from
36 whereas fulvic acids (fulvates, molecules bound to minerals, and free-form fulvic acids) are usually
37 smaller than humic acids (1,000 to 10,000 Da) and are soluble at most pH levels. NOM levels found
38 in most natural waters range from 0.1 to 20 mg/L,¹⁻³ however an increase in its concentration in
39 environmental water matrices has been observed recently,^{4,6} presenting a strain on current water
40 treatment infrastructure and local ecosystems. This increase in NOM concentration can be attributed
41 to several drastic changes to climate conditions.⁷⁻⁹ For example, there is a correlation between
42 intensity of precipitation and NOM concentration discharged from forested sites, giving rise to
43 increased runoff intensities and therefore increased discharge from soils rich in soil organic matter
44 (SOM). Decreased retention time in lake waters, due to climate change induced precipitation, may
45 further cause decreased photochemical degradation of coloured NOM, decreased microbial

46 degradation of complex organic compounds, and decreased in-lake NOM coagulation and
 47 sedimentation.¹⁰ Additionally, apparent changes in colour and UV absorption relative to total
 48 organic carbon (TOC)¹¹ also imply a change in NOM characteristics and therefore treatability
 49 meaning diversification of NOM removal is needed now more than ever.¹² High NOM
 50 concentrations can cause aesthetic problems, such as colour and taste¹³ in drinking water, as well as
 51 higher maintenance and treatment costs of water and wastewater.¹⁴⁻¹⁵ Most importantly, recent
 52 studies show that certain classes of NOM can react with chemicals (e.g. chlorine) used in the water
 53 treatment process, leading to the formation of carcinogenic disinfection by-products (DBPs) and
 54 trihalomethanes (THMs).¹⁶⁻¹⁸ Since the discovery of DBP formation, several studies have outlined
 55 associations between consumption of chlorinated tap water containing elevated THM
 56 concentrations and adverse health outcomes, including bladder cancer,¹⁹ children born small for
 57 gestational age,²⁰⁻²¹ and miscarriages.²² Another adverse effect indirectly caused by the presence of
 58 NOM in surface waters is the observed interference humic substances have on water treatment
 59 processes that are targeting toxic compounds or heavy metals. For example, there has been a
 60 significant amount of investigation on the inhibitory effects of NOM on targeted wastewater
 61 treatments for residual pharmaceuticals which has been shown to significantly decrease the
 62 efficiency of such processes.²³⁻²⁸

63 Current alternative treatment techniques for NOM removal, such as coagulation,²⁹ adsorption,³⁰
 64 membrane filtration,³¹⁻³² flotation,³³ biological¹⁵ and ion exchange (IE)³⁴ processes also bring their
 65 own set of problems. For example, the pre-treatment for micro/ultrafiltration systems using
 66 conventional treatment processes such as coagulation/flocculation which can partially remove
 67 NOM, show low removal efficiency at lower NOM concentrations. Nanofiltration is also sometimes
 68 used as a method of NOM removal but additionally comes with the problem of significant
 69 membrane fouling.³⁵ These problems all show a clear need for an alternative method of removing
 70 NOM from water resources.

71 Advanced oxidation processes (AOPs) are widely applied methods for removal of NOM and
 72 water treatment.³⁶ Within the area of AOPs, photocatalysis is an up and coming area of research due
 73 to its, until recently, untapped wide potential for possible environmental engineering applications.
 74 Ongoing research on photocatalytic NOM removal is based around the use of semiconductors (e.g.
 75 TiO₂ and ZnO) as sensitizers for light-induced redox processes. When illuminated with a photon of
 76 energy greater than the bandgap energy, these semiconductors form an electron/hole pair. These
 77 electron/hole pairs are powerful redox species which many organic photodegradation reactions
 78 utilize either directly or indirectly via formation of hydroxyl radicals in solution,³⁷⁻³⁸ as shown in
 79 figure 1. Early research tested the capabilities of these reactions using low efficiency UV lamps as
 80 TiO₂, the most commonly used photocatalyst, has a fairly low visible light absorption. Whereas
 81 current work has shifted over to the use of solar and high efficiency light emitting diodes (LEDs) as
 82 sustainable photocatalytic irradiation sources.³⁹⁻⁴⁴



93 Figure 1 – Principle Mechanism of Photocatalysis
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96 Photocatalysis is commonly categorised into either heterogeneous or homogeneous depending
97 on whether the catalyst is in a different phase from the reactants (heterogeneous) or in the same
98 phase (homogeneous). Most common heterogeneous photocatalysts are transition metal oxides and
99 semiconductors, TiO₂ being the most researched due to its high photocatalytic activity, excellent
100 physical and chemical stability, low cost, and nontoxicity to humans and the environment. Other
101 common heterogeneous photocatalysts include zinc oxide (ZnO), which also shows great
102 photocatalytic activity,⁴⁵⁻⁴⁸ and graphitic carbon nitride (g-C₃N₄), which is being increasingly used
103 because of its preferable bandgap for visible light reactions.⁴⁹ Heterogeneous photocatalysis gives
104 practical advantages as it allows easy separation of the reaction media from the catalyst as well as
105 high levels of chemical stability and reusability with many new compounds being developed each
106 day.⁵⁰⁻⁵² Alternatively, homogeneous photocatalysis may require more complicated steps for catalyst
107 removal but has shown very high photocatalytic activity. The most commonly used homogeneous
108 systems are based on the photo-Fenton process (Fe²⁺/H₂O₂) where the hydroxy radicals produced are
109 the reactive species.⁵³⁻⁵⁶

110 Increased NOM concentrations in aqueous environment and their adverse effects on human
111 health and ecosystems have been extensively reported. In addition, there are several publications
112 demonstrating that photocatalytic oxidation is a very promising process to remove NOM from
113 water.⁵⁷ Nevertheless, a systematic review of all these studies that will be able to summarize all
114 previous research findings, highlight important issues and research areas for further study, as well
115 as suggest new ways to increase the effectiveness and sustainability of existing practices in water
116 and wastewater treatment plants is still missing from literature. Therefore, the aim of this study is to
117 provide a comprehensive review of the work surrounding the photocatalytic treatment and removal
118 of NOM in water resources. Publications on TiO₂-based heterogeneous and homogeneous
119 photocatalytic oxidation are systematically presented and discussed. Recommendations for future
120 research directions and approaches that show promise in advancing these areas are made.

121 2. Materials and Methods

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

127 3. Results and Discussion

128 3.1. Analytical techniques to detect and quantify NOM in water

129 The type and amount of NOM in water substantially varies among different environmental
130 matrices, as it strongly depends on climatic conditions, hydrological regime as well as other
131 environmental factors. Therefore, to monitor NOM concentration during treatment at lab-scale and
132 improve reproducibility of results, synthetic NOM solutions are commonly used. Common
133 procedures involve dissolving humic and/or fulvic acids in ultrapure water and using them to
134 mimic NOM, as humic and fulvic acids represent up to 80% of the dissolved organics in natural
135 waters and have been shown to be DBP precursors. The reduction of DBP from drinking water is the
136 subject of many NOM related projects, therefore simple, refined humic and fulvic acid samples that
137 are commercially available are typically used by researchers, at least in preliminary testing.⁵⁸ More
138 complex NOM samples extracted from water (e.g. International Humic Substances Society (IHSS)
139 samples from the Suwannee River and Mississippi River) have also been known to be used to
140 simulate surface waters as they can give results that more accurately reflect the conditions of certain
141 waters in a controlled manner, although they are more expensive than simpler synthetic NOM
142 varieties.⁵⁹


143 Different methods are applied to quantify NOM in water: Specific UV absorbance at $\lambda = 254$ nm
144 (SUVA),⁶⁰⁻⁶³ chemical oxygen demand (COD),⁶⁴ total organic carbon analyser (TOC),⁶⁵⁻⁶⁶ fluorescence

145 spectroscopy,⁶⁷⁻⁷⁰ high performance liquid chromatography (HPLC),⁷¹⁻⁷² and mass spectrometric
146 methods (MS).⁷³⁻⁷⁴ The pros and cons of these commonly used methods are weighed up in Table 1.
147 UV-Vis spectroscopy, in the range of 254–280 nm, is commonly used to measure the presence of
148 unsaturated double bonds and π - π electron interactions typically found in aromatic compounds
149 such as humic acid. Measuring SUVA is fast, simple, and does not require complicated equipment or
150 chemical reagents making it a popular analytical method in NOM related research. Chemical oxygen
151 demand (COD), utilises an oxidising agent to measure the amount of oxygen needed to oxidise
152 organic matter in solution (Permanganate Index). This method has been used for a long time due to
153 its simplicity but the many hazardous chemicals (i.e., mercury, hexavalent chromium, sulfuric acid,
154 and silver) involved in the process mean more complex waste management is required than most
155 other methods. Standard COD methods also only allow for COD concentrations that are > 50 mg/L
156 with alterations to allow for COD detection from 5 to 50 mg/L⁷⁵ making its applications in
157 wastewater management very limited. TOC analysis, considered the main indicator of NOM in the
158 drinking water, determines the organic carbon present in solution by using infrared (IR)
159 spectroscopy to measure the carbon dioxide produced by heat catalysed chemical oxidation with a
160 persulfate solution. Although, compared to UV254 spectroscopy, TOC analysis requires a slightly
161 longer runtime and a more complex preparation, it is still a relatively quick and simple method for
162 quantifying NOM in water with many different available conditions to allow for the tailoring of
163 specific test environments. The chemicals generally required in TOC also have low toxicity and are
164 cheaply available compared to other methods available. Other analytical methods to detect and
165 quantify NOM are also widely used across various disciplines. The complexity of these methods is
166 increased as more information about the NOM's profile is afforded.⁷⁶⁻⁸²

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199**Table 1.** Table presenting the main analytical techniques for NOM detection and quantification in water.

Method	Advantages	Disadvantages	Complexity of method
Adsorption at 254 nm	<ul style="list-style-type: none"> - Ease of use - Very fast measurement - Cheap 	<ul style="list-style-type: none"> - Measurement of unsaturated organics in water (not only NOM/humic acid) - High nitrate content in low dissolved organic carbon (DOC) waters may interfere the measurement 	Low
COD	<ul style="list-style-type: none"> - Simple - Well known method 	<ul style="list-style-type: none"> - Toxic treatment chemicals - Low accuracy - High minimum detection limit 	
TOC	<ul style="list-style-type: none"> - Fast measurement - Tailorable modes of detection for specific experiments 	<ul style="list-style-type: none"> - Expensive specialised equipment - Measurement of total organics in water (not only NOM/humic acid) 	
Fluorescence spectroscopy	<ul style="list-style-type: none"> - No pre-treatment required - Gives information on specific NOM 	<ul style="list-style-type: none"> - Only detects fluorescent NOM molecules - Sensitive to chemical environment, e.g. pH 	
FTIR	<ul style="list-style-type: none"> - Good signal to noise ratio - Extensive libraries of humic substances to identify specific compound characteristics 	<ul style="list-style-type: none"> - Can see large water band interference - Pre-treatment could alter chemical makeup of NOM 	
HPLC	<ul style="list-style-type: none"> - Good separation of NOM compounds 	<ul style="list-style-type: none"> - Requires expensive, high purity solvents, columns etc. - NOM can have unwanted interactions with the stationary phase 	
GC-MS	<ul style="list-style-type: none"> - Accurate detection of all substances found in water 	<ul style="list-style-type: none"> - Cost of reagents, columns, etc - Difficulty in analysing and interpreting results 	

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206 3.2. NOM photocatalytic treatment

207 3.2.1. Heterogeneous TiO₂ photocatalysis

208 Table 2 shows all publications focusing on treatment of NOM in water by means of
209 heterogeneous TiO₂ photocatalysis. Some of the earliest work on the photocatalytic degradation of
210 NOM was done by Bekbölet et al.⁸³⁻⁸⁴ where slurries of P25 – TiO₂ were used to explore the
211 limitations and general trends observed when changing the reaction conditions in standard
212 photocatalytic procedures. Although these early papers reported on the most favourable conditions
213 for photocatalytic NOM removal, much more work has been done since on optimizing the resultant
214 degradation of NOM by altering basic operational parameters.

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Table 2. publications on heterogeneous photocatalytic treatment of NOM.

Water matrix	Catalyst type	Reaction time	Irradiation source	Other operating parameters	Removal efficiency	Other important findings	Reference
Humic acid solution	P25 – TiO ₂	120 min	UVA – 125 W	Ambient pH [HA] = 50 mg/L [TiO ₂] = 1 g/L	88% TOC 99% Vis ₄₀₀	THMFP* = 14.5 µg/L	Bekbölet et al. (1996) ⁸³
Humic acid solution	P25 – TiO ₂ , UV100 - TiO ₂	60 min	UVA – 125 W λ = 300-420 nm	Ambient pH [HA] = 10 mg/L [TiO ₂] = 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	Bekbölet et al. (2002) ⁸⁴
Reservoir water: M-Myponga site W-Woronora site	P25 – TiO ₂	150 min	UVA – 20 W λ = 365 nm	pH ~ 7 TOC _M = 10.6 mg/L TOC _W = 3.5 mg/L [TiO ₂] = 0.1 g/L	M: 80% TOC UV ₂₅₄ W: 80% TOC 100% UV ₂₅₄	THMFP: M = <20 µg/L W = <20 µg/L	Liu et al. (2010) ⁸⁵
Sand filtered treatment plant water	N-Pd-TiO ₂	120 min	Solar simulator 500 W	pH ~ 6.73 TOC = 2.38 mg/L [N-Pd-TiO ₂] = 5 g/L	HPO** = 71% HPI** = 35% TPI** = 15% UV ₂₅₄		Nkambule et al. (2012) ⁸⁶
Reverse osmosis isolate & Alginic acid solution	AgSiO ₂ -TiO ₂	30 min	Solar simulator λ = 400-1100	pH ~ 8.2 TOC _I = 3.7 mg/L [TiO ₂] = 0.1 g/L	20% TOC 42% UV ₂₅₄	219 ± 40 µg THMFP per g TiO ₂	Gora et al. (2018) ⁸⁷

				nm				
Humic acid solution	Al:Fe-TiO ₂ (1%)	15 min	UVC – 37 W λ = 254 nm	pH ~ 7 [HA] = 10 mg/L [TiO ₂] = 0.1 g/L O ₃	63.2% TOC 79.4% UV ₂₅₄	Increasing HCO ₃ - concentration decrease NOM reduction rate	Yuan et al. (2013) ⁸⁸	
Reservoir water: MV-Midvaal P-Plettenberg bay	MWCNT/N, Pd-TiO ₂ **	120 min	Solar simulator 300 W	[MWCNT/N, Pd-TiO ₂] = 1 g/L	MV: 69.4% P: 97.7% UV ₂₅₄		Ndlangamandla et al. (2018) ⁸⁹	
Humic acid solution	TiO ₂ nanotubes	120 min	UVC – 11 W λ = 254 nm	[HA] = 50 mg/L [TiO ₂] = 0.5 g/L	98.27% DOC 100% UV ₄₃₆	Humic acid removal rate: 0.0607 molm ⁻³ s ⁻¹	Zhang et al. (2009) ⁹⁰	
Landscape surface water	Bi ₂ O ₃ -TiO ₂	10 min	Vis – 300 W λ = 400-780 nm	pH ~ 8.13 TOC _i = 2.2 mg/L [Bi ₂ O ₃ -TiO ₂] = 2 g/L	20.2% TOC 24.4% UV ₂₅₄		Wang et al. (2019) ⁹¹	
Pre-treated (coagulation-flocculation) water	P25 - TiO ₂ , TiO ₂ /β-SiC	220 min	Solar simulator – 1500 W	pH ~ 6.7 P25: TOC _i = 7.8 mg/L [TiO ₂] = 0.5 g/L β-SiC: TOC _i = 5.5 mg/L [TiO ₂] = 0.5 g/L	P25: 80% TOC β-SiC: 80% TOC		Ayekoe et al. (2017) ⁹²	
Treatment plant inlet water in immersed ultrafiltration module	P25 - TiO ₂	120 min irradiation 43hour total treatment	UVC – 15 W λ = 254 nm	pH ~ 7 DOC = 5.48 mg/L [TiO ₂] = 0.1 g/L	60% DOC 90% UV ₂₅₄	THMFP* = 25 µg/L	Rajca et al. (2016) ⁹³	
Humic acid solution	LiCl- TiO ₂ doped PVDF*** membrane	30 min	UVA – 100 W λ = 365 nm	pH ~ 7.5 [HA] = 2 mg/L	80-84% UV ₂₅₄		Song et al. (2014) ⁹⁴	
Extracted river NOM	P25 - TiO ₂	120 min	UVC – 8 W λ = 254 nm	pH ~ 8.2 TOC _i = 10 mg/L	80% TOC 100% UV ₂₅₄	NOM degradation rate constant: 0.0163 min ⁻¹	Huang et al. (2008) ⁹⁵	

River water	Nano- TiO ₂ on diatomite	360 min	3x UVC lamps – 16 W λ = 254 nm	[TiO ₂] = 1 g/L pH ~ 8.0-8.5 TOC _i = 9.84–13.18 mg/L [TiO ₂] = 0.5 g/L	28.5% TOC 40% UV ₂₅₄		Sun et al. (2014) ⁹⁶
Humic acid solution	TiO ₂ nanoparticles/ granular activated carbon (GAC)	180 min	UVA – 500 W λ = 365 nm	pH ~ 4.2 TOC _i = 5.04 mg/L [TiO ₂ /GAC] = 2 g/L	99.5% UV ₂₅₄	Significantly lower degradation (70% UV ₂₅₄) at pH = 11	Xue et al. (2011) ⁹⁷

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220 3.2.1.1. Catalyst and NOM concentration

221 The concentration of catalyst is an important parameter for photocatalytic oxidation processes.
222 In general, photocatalytic oxidation is enhanced when catalyst concentration is increased up to a
223 value at which removal rate reaches a plateau. Bekbölet et al.⁸³ observed that an optimal catalyst
224 concentration for NOM removal is 1 g/L and this is high enough to provide a large surface area to
225 adsorb NOM but not so high that the slurry significantly reduces the availability of light throughout
226 the reaction mixture. This upper limit has been noted to depend on the geometry and on the
227 working conditions of the photoreactor.⁹⁸ This same study evaluated the trihalomethane formation
228 potential (THMFP) of various humic acid concentrations with respect to time, which also opened up
229 the possibility for more research on the area by showing up to 94% reductions in THMFP (below
230 United States Environmental Protection Agency limits) after 120 min of photocatalytic treatment. A
231 similar experiment by Maleki et al.⁴⁷ investigated the effects of catalyst concentration on humic acid
232 degradation using Cu-doped ZnO nanoparticles. The same characteristic rise and plateau in
233 degradation rate was observed when increasing the catalyst concentration from 1.5 g/L to 2 g/L,
234 which was attributed to partial catalyst agglomeration and a consequent decrease in the active
235 catalyst surface at higher dosages of catalysts. Additionally, early work from Palmer et al.⁹⁹ on the
236 operational conditions of photocatalytic NOM degradation using TiO₂ showed that the rate of initial
237 degradation increased with increasing concentration until the concentration of 30 ppm of carbon,
238 after which, the rate decreased. This trend is seen in several other studies of NOM degradation
239 above 30 ppm of C.¹⁰⁰⁻¹⁰²

240 3.2.1.2. UV-light driven TiO₂ catalysts

241 Another early paper by Bekbölet et al.⁸⁴ investigated the differences in performance between;
242 the standard P25 – TiO₂, a 20:80 mix of rutile: anatase titania, and another commercially available
243 HOMBIKAT UV 100 – TiO₂, made entirely of anatase phase. Here it was shown that P25 – TiO₂
244 showed better photocatalytic activity when it came to humic acid degradation. This correlated with
245 the adsorption experiments also performed, which revealed that the P25 adsorbed 3 times as much
246 humic acid at a set loading than the UV100 despite having a much lower BET surface area. Due to its
247 proven high-performance rate P25 – TiO₂ is often the comparative standard used in NOM
248 photocatalytic degradation studies of various semiconductor loadings. Huang et al.⁹⁵ in 2008 studied
249 the photocatalysis' effect on NOM by analysing its compositions in water before and after
250 irradiation. There was observed preferential removal of high molecular weight, hydrophobic NOM
251 molecules, which are the major NOM fraction responsible for membrane fouling.⁸⁵⁻⁸⁶ Further
252 research by Valencia et al.¹⁰³ using size-exclusion chromatography with respect to operating pH
253 levels during photocatalytic degradation showed that changes in pH values affected the adsorption
254 of NOM onto TiO₂. It was established that the pH determines the mechanism, but not the sequence
255 of the photocatalytic degradation and therefore, regardless of pH, the degradation of the NOM
256 preferentially removed the larger molecular size fraction in comparison to the middle and small
257 fractions. Other comprehensive work on operating parameters includes that done by Espinoza et
258 al.¹⁰⁴ on the effect of metal ions (Cu²⁺, Fe³⁺, Zn²⁺, Mn²⁺) in solution on the photocatalytic degradation
259 of NOM. Photocatalytic degradation experiments with and without the addition of various
260 combinations of CuSO₄ or CuCl₂·2H₂O, FeCl₃, ZnCl₂, and MnCl₂ solutions revealed an apparent
261 reduction in photoactivity and prevention of certain degradation products when in the presence of
262 added Cu²⁺ ions (10µM). The addition of Mn²⁺ was observed to change the magnitude of the effect of
263 added Cu²⁺ a larger inhibiting effect from added Cu²⁺ was observed in the absence of added Mn²⁺
264 during the degradation of large molecular weight NOM. It was suggested by Espinoza et al. that
265 these observations could be explained by a stabilization of the NOM against degradation by HO· by
266 complexation with Cu²⁺, which would increase the longevity of NOM in aquatic systems. Adding
267 Fe³⁺ and Zn²⁺ to the experiments showed no significant effects.
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269 3.2.1.3. Visible light driven modified TiO₂ catalysts

270 Many investigations on photocatalytic reactions are performed under UV light due to the band
271 gap energy of pure TiO₂ (3 or 3.2 eV in rutile or anatase phase), which means that there is very
272 limited photocatalytic activity in the visible range. On top of this, unmodified TiO₂ can be
273 characterised with a high recombination rate for the photo-produced electron and hole pairs, and a
274 significant difficulty to strongly bind to some support materials.¹⁰⁵ Therefore, a significant amount of
275 research surrounding the photocatalytic degradation of NOM is focussed on improving the
276 photo-efficiency of TiO₂ and its degradation efficiency of organic compounds. Various approaches to
277 do so consist of chemical and structural modification of TiO₂, in order to enable light absorption in
278 the visible region. These studies include several chemical modification schemes that report
279 promising options to improve photocatalytic activity. Chemical modifications to TiO₂ involve the
280 addition of various other species, typically involving: metals (such as Fe, Pd or Ag)^{86, 88, 106-107}/metal
281 oxides (such as Bi₂O₃)¹⁰⁸⁻¹¹¹ which can either facilitate electron-hole separation and promote
282 interfacial electron transfer or decrease the TiO₂ band gap. This promotes electron transfer from the
283 valence band to the conduction band, facilitating the formation of oxidative species such as hydroxyl
284 radicals.¹¹²

285 Other chemical modifications include the addition of non-metals (such as C, N, S or F) which
286 have also been shown to form new impurity levels close to the valence or conduction band of TiO₂,
287 thereby lowering the optical gap and shifting the absorption edge to the visible light region.¹¹³
288 Nkambules⁸⁶ 2012 work focuses on N-doped TiO₂, a growing area of photocatalysis which has been
289 shown to increase visible light photocatalytic activity when coupled with co-dopant metals by
290 reducing the band gap of TiO₂ and shifted the absorption into the visible light region.^{89, 114} The
291 Pd-modified N-doped TiO₂ catalyst synthesised by Nkambule et al. in 2012 showed a particularly
292 successful shift in titania's visible light absorption with an over 70% removal in hydrophobic NOM
293 fractions using a solar simulator. A drawback to these N-doped TiO₂ species would be that the
294 doping of N into the lattice of TiO₂ usually results in the formation of oxygen vacancies in the bulk
295 material.¹¹⁵ These defects can act as recombination centres for carriers and therefore, compared to
296 pure TiO₂, a loss of UV-activity is usually found for N-doped TiO₂, which is due to the rapid
297 recombination rate of generated electrons and holes introduced by the impurity level. The addition
298 of non-metals to metal doped TiO₂ can also be utilised to improve the stability of the photocatalyst,
299 for example forming a thin layer of SiO₂ around a catalyst's surface to prevent oxidation of metal
300 nanoparticles like Gora et al. in their 2018 investigation on modified TiO₂ for solar photocatalysis.⁸⁷
301 This work saw a Ag- TiO₂ nanoparticle co-catalyst reduce NOM levels by 42% UV₂₅₄ only 30 min of
302 treatment time. This study also found significant changes to the disinfectant by-product formation
303 potential (DBPFP) of NOM wherein the different modifications to TiO₂ followed the same trend in
304 DBPFP level changes but by differing amounts.

305 3.2.1.4. Immobilized catalysts

306 Alongside the chemical changes, various nano structured TiO₂ materials have been tested with
307 enhanced visible light photoactivity such as nanoparticles,¹¹⁶ nanotubes,⁹⁰ nanowires¹¹⁷ and
308 nanofilms.¹¹⁸ As well as affecting the photoactivity of TiO₂, many of these structurally modified
309 materials combat the problems faced by loose slurry reactions such as catalyst separation, recovery
310 and reuse which bring about significant obstacles for practical applications of TiO₂ powder
311 heterogeneous photocatalysis due to its small particle size.¹¹⁹ Many researchers apply membrane
312 filtration for the separation of nanosized TiO₂ from treated water however, as mentioned previously,
313 serious membrane fouling usually occurs as the TiO₂ forms a cake layer and blocks membrane pores.
314 Work done by Zhang et al.⁹⁰ showed that creating titania nanotubes can not only improve upon P25
315 – TiO₂'s ability to photocatalytically degrade NOM, most likely due to increased surface area, but
316 also significantly reduces the amount of membrane fouling caused by catalyst separation. Another
317 approach to reducing the need for catalyst separation when photocatalytically degrading NOM is
318 producing hybrid materials by combining TiO₂ with carbon materials such as multiwalled carbon
319 nanotubes⁸⁹ and activated carbons.⁹⁷ A particularly successful example of this is the work done by

320 Xue et al. where a TiO₂ nanoparticle/granular activated carbon composite (GAC) was prepared by a
321 sol-dipping–gel process. This investigation displayed a synergetic relationship between adsorption
322 upon GAC and degradation involving TiO₂ where a humic acid removal of 99.5% UV₂₅₄ was
323 achieved as well as improved filterability. Hybrid membranes combining TiO₂ with various
324 polymeric compounds such as polyvinylalcohol, pyrrolidone¹²⁰ and poly (amide–imide)¹²¹ also show
325 a solution to catalyst separation. These hybrid membranes exhibit great potential for water
326 treatment since they combine filtration and photo degradation in a single unit. Although blending
327 photocatalytic nanoparticles into polymeric thin film can cause the entrapped photocatalyst to show
328 reduced catalytic activity due to the agglomeration and shielding effects in the polymer matrix.¹²²

329 3.2.1.5 Hybrid processes

330 The most widely used processes for the removal of NOM from water sources are separation and
331 purification technologies including (micro, ultra and nano) membrane filtration, reverse or forward
332 osmosis, and coagulation. One approach to improving the overall efficiency of water treatment
333 facilities is combining one or more of these technologies with heterogeneous photocatalysis. This
334 includes the combining of photocatalysts with membrane filtration^{93-95, 120, 123-125} and adsorption,¹²⁶ as
335 well as coagulation systems.⁹¹ An example of such systems would be Wang et al.⁹¹ whose work
336 which showed pre-treatment by photocatalysis with Bi₂O₃-TiO₂(4%) could improve the removal of
337 organic matter compared to polyaluminium chloride (PACl) coagulation treatment alone. This study
338 saw removal rates of 20.2% and 24.4% UV₂₅₄ after just 10 min of photocatalytic treatment which
339 increased to 37.93% TOC and 58.75% UV₂₅₄. Photocatalytic oxidation prior to coagulation has been
340 observed to decrease coagulation efficiency by 15%, most likely because the oxidation changes the
341 characteristics of NOM and degrades NOM molecules towards smaller molecular mass fractions.¹²⁷
342 However, when oxidation was performed after coagulation, about 32% DOC and 33% UV₂₅₄
343 enhancements to the removal of NOM occurred.¹²⁸

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

351

352 3.2.2. Homogeneous photocatalysis

353 3.2.2.1. Photo-Fenton

354 Recent interest in homogeneous photocatalytic NOM removal has increased due to reports of
355 lower chemical doses, and therefore lower residual levels of chemicals post treatment, when
356 compared to conventional NOM removal methods such as coagulation.¹³² Although heterogeneous
357 photocatalysis, such as a standard TiO₂/UV NOM removal mentioned previously, has the added
358 benefit of easy separation after treatment is completed, homogeneous photocatalysis reactions have
359 the advantage of providing a greater degree of interaction between the catalyst and the specified
360 target due to the increased accessibility of the catalytic sites whilst in solution. The homogeneous
361 photocatalytic degradative removal of organic compounds from water is mainly based on the
362 generation of high amounts of hydroxyl radicals from either ozone or hydrogen peroxide. These
363 generated hydroxyl radicals can degrade the organic matter commonly through hydrogen
364 abstraction from aliphatic carbon atoms and electrophilic addition to double bonds or aromatic
365 rings.¹³³ This is ideal for the degradation of the large hydrophobic NOM fractions which are major
366 precursors for DBP formation.⁶³

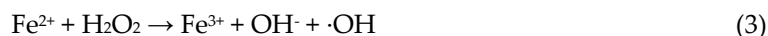
367

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	O ₃ /UV	60 min	UVA lamp Intensity = 9.7 mW/cm ²	pH ~ 6.6 TOC = 1.8 mg/L O ₃ dosage = 0.62 g/L	50% TOC	Chin & Bérubé (2005) ¹³⁴
	River water	H ₂ O ₂ /UV O ₃ /UV	30 min	UVA lamp – 43W	TOC = 3.1 mg/L [H ₂ O ₂] = 23 mg/L O ₃ dosage = 4 mg/L	H ₂ O ₂ only: 3-23% DOC 60% UV ₂₅₄ O ₃ only: 31% TOC 88% UV ₂₅₄	Lamsal et al. (2011) ¹³⁵
Photo-Fenton	Reservoir water	H ₂ O ₂ /UV	-	UVC lamp λ = 254 nm	[H ₂ O ₂] = 23 mg/L	-	Toor et al. (2005) ¹³⁶
	Inlet water to water treatment works	FeSO ₄ ·7H ₂ O + H ₂ O ₂	20 min	4x UVA lamps - 25W λ = 365 nm	pH ~ 4 DOC = 9.6 mg/L [Cat] = 5.65mg/L H ₂ O ₂ :Fe ²⁺ = 5:1	90% DOC 95% UV ₂₅₄	Murray et al. (2002) ¹³²
	Water treatment works reservoir water	FeSO ₄ ·7H ₂ O + H ₂ O ₂	30 min	4x UVA lamps - 25W λ = 365 nm	pH ~ 4 DOC = 7.5 mg/L [Fe ²⁺] = 0.1mM H ₂ O ₂ :Fe ²⁺ = 5:1	90% DOC 95% UV ₂₅₄	Murray et al. (2004) ¹³⁷
	Reservoir water	FeSO ₄ ·7H ₂ O + H ₂ O ₂ H ₂ O ₂ only	1 min	4x UVC lamp – 12W λ = 254 nm	pH ~ 4.5 DOC = 17.4 mg/L [H ₂ O ₂] = 2.0 mM H ₂ O ₂ :Fe ²⁺ = 4:1	Fe ₂ SO ₄ ·7H ₂ O + H ₂ O ₂ : 88% DOC 31% UV ₂₅₄ H ₂ O ₂ : 78% DOC 94% UV ₂₅₄	Goslan et al. (2006) ¹³⁸
	River water	FeCl ₃ ·7H ₂ O +	After 6.5 KJ/L	Solar CPC	pH ~ 5	90% DOC	Moncayo-Lasso

pre-treated with slow sand filtration	H ₂ O ₂	of solar energy			DOC = 2.7–3.1 mg/L [H ₂ O ₂] = 20 mg/L [Fe ³⁺] = 1 mg/L	95% UV ₂₅₄	et al. (2008) ¹³⁹
River water	FeCl ₃ ·7H ₂ O + H ₂ O ₂	After 20 KJ/L of solar energy	Solar CPC		pH ~ 6.5 DOC = 5.5 mg/L [H ₂ O ₂] = 10 mg/L [Fe ³⁺] = 0.6 mg/L	55% DOC 75% UV ₂₅₄	Moncayo-Lasso et al. (2009) ¹²⁸

369 A comparative study by Goslan et al.¹³⁸ showed that the addition of Ferrous sulphate increased
 370 UV/H₂O₂ ability to remove NOM from reservoir water by forming a photo-Fenton reaction.



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



373 In the photo-Fenton process (equations (1) and (2)), the Fenton reaction rates are strongly
 374 increased by irradiation with UV–vis light. The positive effect of irradiation on the degradation rate
 375 is due to the photo-chemical regeneration of ferrous iron (Fe²⁺) by photo-reduction of ferric
 376 complexes, which leads to additional ·OH generation.¹⁴⁰⁻¹⁴³ The ferrous iron generated in solution
 377 reacts with H₂O₂ yielding a second ·OH radical and ferric ion (equation (3)), and the cycle continues.
 378 A major advantage of the photo-Fenton reagent is that the reactions light absorption maximum
 379 wavelength is roughly 600 nm which gives a much larger absorption overlap with natural sunlight
 380 compared to many other common photocatalysts.

381 Although the exact mechanism used for degradation of NOM using photo-Fenton processes is
 382 not presently clear, work from Fukushima et al.¹⁴⁴ has shed some light on possible processes
 383 occurring during these degradation reactions. Fukushima's 2001 work on the degradation products
 384 produced from degrading several different NOM fractions in a photo-Fenton solution showed that
 385 the TOC decreased dependent on increasing irradiation time, indicating mineralisation of the HA to
 386 CO₂ during this process. Analysis on different molecular weight fractions of HA also suggested that
 387 the degradation of high molecular weight fractions of HA results in a lowering in molecular size
 388 during photo-Fenton processes.

389 3.2.2.2. Hybrid photolytic oxidation processes

390 An interesting comparison to homogeneous photocatalysis is the work done with
 391 homogeneous hybrid photolysis for NOM treatment by enhancing the oxidative capabilities of
 392 common oxidising species (e.g. ozone and peroxides) with light. The advantages of these hybrid
 393 processes, as well as other AOPs including O₃/UV, H₂O₂/UV and H₂O₂/O₃, was explored by Lamsal
 394 et al.¹³⁵ in 2011. This study specifically investigated the treatment process impact on the change of
 395 molecular weight distribution (MWD) and disinfection by-product formation potential (DBPFP)
 396 with the UV/ozone hybrid showing a significantly improved removal of NOM and reduced DBPFP
 397 when compared to UV or ozone treatment alone.

398 3.2.2.2.1. Hydrogen peroxide based photocatalysis

399 Many factors decide on the optimum H₂O₂ dosage in UV degradation reactions. For UV/ H₂O₂
 400 NOM removal, the characteristics and concentration of the organic compounds can directly
 401 influence the overall mineralisation ability. The amount of hydroxyl radicals produced upon UV
 402 irradiation depends on the H₂O₂ concentration whilst H₂O₂ can also react with these radicals and
 403 inhibit hydroxyl radical evolution. Additionally, H₂O₂ absorbs UV energy therefore reducing the
 404 availability of UV photons for oxidising pollutants at higher H₂O₂ concentrations. Wang et al.¹⁴⁵
 405 found, for the oxidation of humic acid, that the hydroxyl radical scavenging effect (the production
 406 and then combination of HO₂· into H₂O₂ and O₂) became significant when the H₂O₂ concentration
 407 was higher than 0.1% making this the optimum dosage. This study also noted that the presence of
 408 bicarbonate/carbonate species has a negative effect on NOM degradation due to causing competition
 409 for hydroxyl radicals, especially at high concentrations of H₂O₂.

410 3.2.2.2.2. Ozone based photocatalysis

411 Ozone can degrade NOM directly through ozonolysis which has been found to be fairly
 412 selective and relatively slow¹⁴⁶⁻¹⁴⁷ so most NOM degradation research is focussed on increasing the
 413 generation of hydroxyl radicals from the decomposition of ozone in water. This includes the
 414 combination of ozone with UV irradiation to degrade NOM through quick, non-selective ozonation.
 415 Study results from Ratpukdi et al.¹⁴⁸ on the optimal operating conditions for UV/ozone hybrid
 416 photolysis procedures revealed that the mineralization rate of DOC provided by the processes tested
 417 ranked in the following order: vacuum ultraviolet (VUV)/ozone > VUV > UV/ozone > ozone > UV.
 418 The study also showed that the highest DOC mineralisation rate and biodegradability increase was
 419 at a neutral pH 7 rather than in a basic environment (pH 9 and pH 11) with extremely basic
 420 conditions (pH 11) showing no synergistic hybrid effect from combining UV and ozone at all.

421 Research comparing O₃ NOM degradation with and without the addition of UVC shows a clear
 422 enhancement effect from UV light. Work by Chin & Bérubé¹³⁴ concluded that the combined UV/O₃
 423 treatment is more effective at reducing organic constituents, as well as the DBP-FP, in raw water
 424 than either the ozone or UV treatment alone. Lamsal et al.¹³⁵ investigated this hybrid effect further by
 425 showing how several AOP treatment processes impacted the change of molecular weight
 426 distribution (MWD) and disinfection by-product formation potential (DBPFP). The UV/ozone
 427 hybrid in this side by side study showed a significantly improved removal of NOM and reduced
 428 DBPFP when compared to UV or ozone treatment alone. It was also noted that this UV/ozone
 429 process induced a near complete alteration of the molecular weight of NOM from >900 Da to <300
 430 Da.

431

432 3.2.3. Energy efficiency of NOM treatments

433 A significant area of interest surrounding UV photocatalysis is the energy consumption, and
 434 associated operating costs, of artificial lighting. The electric energy per order, E_{EO}, value was
 435 introduced by Bolton et al.,¹⁴⁹ and is used to estimate the energy consumption of photocatalytic
 436 reactors. E_{EO} is defined as the energy required for 90% degradation of a pollutant per cubic meter of
 437 contaminated water. E_{EO} (kWh/m³/order), for a batch-operated reactor, is calculated from the
 438 following equation (6):

$$439 \quad E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log (C_i/C_f)} \quad (6)$$

440

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

446 An interesting observation from the data displayed in table 4 is the significance the electrical
 447 power of the irradiation source (P) plays in the energy efficiency of a reaction. For example, for
 448 electrical power ≥0.125 kW the E_{EO} is at the order of 10³ (process types 1st and 3rd as shown in table 4),
 449 while this decreases to the order of 10 for P ≤0.1 kW. This is due to the position of P on the numerator
 450 of equation 6 which is then multiplied by 1000, making relatively small differences in the power
 451 inputs of irradiation sources result in large disparities in E_{EO}. Also, when process types with similar
 452 P, for example types 1st and 6th are compared (as shown in table 4), it can be observed that short
 453 treatment time (i.e. 30 min) is also important to keep the E_{EO} at the low order of 10 kWh m⁻³ order⁻¹.
 454 This shows the significance that recent advancements in LED technology have had for the prospects
 455 of industrial scale photocatalytic water treatment due to the drastically improved efficiency when
 456 compared to conventional mercury black lights.

457

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 %	E _{EO} KWh m ⁻³ order ⁻¹	Reference
Heterogeneous	Humic acid solution	P25-TiO ₂	0.125	120	0.05	88	5,430	Bekbolet et al. (1996) ⁸³
Heterogeneous	Reservoir water	P25-TiO ₂	0.02	150	0.8	100	15.625	Liu et al. (2010) ⁸⁵
Heterogeneous	Pre-treated (coagulation-flocculation) water	P25-TiO ₂ /βSiC	1.5	220	0.1	80	78,687	Ayekoe et al. (2017) ⁹²
Homogeneous	River water	H ₂ O ₂ /UV	0.043	30	3	23	63.137	Lamsal et al. (2010) ¹³⁵
Homogeneous	River water	O ₃ /UV	0.043	30	3	31	44.472	Lamsal et al. (2011) ¹³⁵
Homogeneous	Water treatment works reservoir water	FeSO ₄ .7H ₂ O + H ₂ O ₂	0.1	30	1	90	50	Murray et al. (2004) ¹³⁷

458

459

460

461 4. Conclusions and Considerations for Future Research

462 The removal of NOM from drinking water presents a great challenge that will require the
463 application of efficient and flexible water treatment technology or more likely a combination of
464 synergistic technologies. A crucial process towards achieving this is the proper characterisation of
465 NOM and its various fractions in order to accurately estimate their reactivity with the utilised
466 treatment system. This procedure is critical in the selection and application of the most suitable
467 treatment process by achieving the highest removal efficiency, the greatest reduction in disinfection
468 by-product formation potential, and the best possible cost efficiency. Photocatalysis is highly
469 regarded amongst NOM removal researchers due to the quick and nonselective character of the
470 hydroxyl radicals produced during processing. This makes the measured differences of NOM in
471 water less of an issue in photocatalysis when compared to other conventional NOM removal
472 treatments. Although, various studies reported that photocatalysis can tend to have more impact on
473 NOM's hydrophobic and higher MW compounds.¹⁵⁰ The non-specificity of hydroxy radicals can also
474 be a disadvantage to photocatalytic methods in that the highly reactive HO· can also interact with
475 ions and other dissolved organics in waters which could reduce the overall efficiency of NOM
476 removal. These unintentional side reactions have been observed during the removal of humic acid in
477 the presence of bicarbonate (HCO₃⁻) and halide (Cl⁻ and Br⁻)¹⁵¹⁻¹⁵³ ions.

478 Currently, the coupling of photocatalysis with other water treatment technologies is being
479 investigated as a viable option to overcome the inadequacies of photocatalysis and the selected
480 technology alone. As there is no standalone water treatment technique that is able to optimally
481 remove NOM by itself, numerous integrated processes for the removal of NOM have been studied,
482 such as the combination of photocatalysis with; membrane filtration and adsorption,⁹³ coagulation,⁹¹
483 and biodegradation.¹⁵⁴

484 When focussing on heterogeneous photocatalysis, most research tends to either focus on the
485 optimisation of the photocatalytic activity of TiO₂ or to synthesise novel photocatalysts able to
486 compete with TiO₂. The improved degradation capabilities of TiO₂ is commonly explored via
487 structural modifications (nanocrystals,¹⁵⁵ nanoparticles,¹¹⁶ nanotubes,⁹⁰ nanowires¹¹⁷ and
488 nanofilms.)¹¹⁸ and/or combination with other catalysts (ZnO)¹⁵⁶ or materials (polymers,¹⁵⁷
489 multiwalled carbon nanotubes⁸⁹ and activated carbons).⁹⁷ Alternatively, novel photocatalysts are
490 regularly chosen based on their superior photocatalytic activity under near visible or solar light
491 when compared to a TiO₂ standard.

492 Due to large amounts of research focussing on lab scale efficiency, there is an apparent lack of
493 focus on the economics of applying various photocatalytic treatments for the removal of NOM from
494 drinking water sources. This step is crucial to giving a more well-rounded comparison of
495 photocatalytic water treatment with current, well established procedures for NOM removal. Very
496 few publications have evaluated the cost of applying selected photocatalysts for other pollutants,
497 such as immobilised TiO₂ for the treatment of industrial wastewaters.¹⁵⁸ Another important factor to
498 consider is the environmental impact of such photocatalytic treatments, life cycle assessments
499 including a goal and scope definition, inventory analysis and life cycle impact assessment (LCIA)¹⁵⁹
500 would need to be done to more properly predict the implications of using these systems on an
501 industrial scale.

502 Owing to the high energy demand of traditional UV-lamps, alternative sources of UV-light are
503 being investigated. One obvious choice of reducing energy demand of UV-light is the use of sunlight
504 for a lower environmentally impacting and cheap light source. The downside of this being that using
505 solar light is typically less effective as an energy source as its emission spectrum has a relatively
506 small overlap with the absorbance of many common photocatalysts, such as TiO₂. This is reflected by
507 the large volume of interest in increasing/red shifting the absorbance wavelength range of TiO₂ by
508 doping it with different elements such as nitrogen and carbon.¹¹³ Another possible alternative
509 method of UV illumination is the use of light emitting diodes (LED) reactors due to their high
510 efficiency and durability.¹⁶⁰⁻¹⁶¹

511 Developing and applying efficient photocatalysis based technologies to remove NOM and
512 mitigate DBP formations is a promising start and making them more efficient and cost-effective for
513 large scale application in integration with other advanced water treatment technologies is the next
514 crucial step to advancing water treatment engineering.

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