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Perspective

The Effect of Mineral Ions Present in Tap Water on Photodegradation of Organic Pollutants: Future Perspectives

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Abstract: Photodegradation is the chemical conversion of large, toxic, and complex molecules into non-toxic, simpler, and lower molecular weight species due to light exposure. Heterogeneous photocatalysis has sufficient potential to degrade toxic organic pollutants present in wastewater. As industries discharge their effluents containing organic pollutants into natural water bodies, which penetrate into the subsurface through connected pores it is necessary to study this process in natural or tap water. Tap water (TW) is mainly obtained from underground wells having inorganic salts in a minute quantity with a conductivity of 500 µS/cm. TW contains inorganic anions, which affect the photocatalytic activity and photocatalysis process. The aim of this review is to evaluate the effect of TW on the photo-degradation of organic pollutants such as dyes, pharmaceutical products, pesticides, etc., with the support of the literature. The TW had a diverse effect on the photodegradation of organic pollutants; either it may enhance or decrease the rate of pollutants' photodegradation.

Keywords: tap water; photodegradation; dyes; pharmaceutical products; pesticides; environmental monitoring

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1. Introduction

Organic pollutants are toxic compounds that can cause different health problems in humans when they surpass their permitted levels. Various industrial products, e.g., petroleum hydrocarbons, detergents, plastics, dyes, pesticides, and organic solvents, are the major sources of organic compounds [1]. Toxic organic pollutants cause a serious threat to the environment and ecological existence. Organic pollutants have a harmful effect on human health and thus have received researchers' attention to degrade them by applying novel approaches and developing new protocols [2]. Various physical, chemical, and biological approaches were employed for the removal of organic pollutants, such as adsorption [3], flocculation [4], coagulation [5], biodegradation [6], phytoremediation [7], electrochemical degradation [8] heterogenous photocatalysis [9], etc. With increased environmental awareness, an environmentally friendly approach to eliminating organic pollutants from municipal and industrial wastewater is required [10]. Advanced oxidation processes (AOPs) are well-documented and viable chemical methods for the wastewater treatment and production of potable water via oxidation. AOP is an aqueous phase oxidation technique that incorporates the insitu generation of strong oxidizing agents such as hydroxyl radicals and sulfate radicals that facilitate the oxidation of polluting molecules found in wastewater [11]. Among the AOPs, photocatalysis is a sustainable and eco-friendly treatment process and has been demonstrated to have considerable potential for the removal of dyes from wastewater [12]. This potential process is mainly performed for the remediation of dyes [9,13–15]. Heterogeneous photocatalysis has sufficient potential to degrade toxic organic dyes present in wastewater [16]. In this method, the wastewater contaminated with dye is treated with catalysts composed of semiconducting materials and irradiated under light [17]. This process is commonly reported for the photodegradation of dyes [18], antibiotics [19], pesticides [20], volatile organic pollutants [21], solvents [22], polycyclic aromatic hydrocarbons [23], etc. For the enhancement of efficiency, the process is performed in the presence of heterogeneous photocatalysts such as MoO_2 nanocrystals [24], ZnO/CdS nanocomposite [25], NiO–$CuFe_2O_4$ nano-heterostructure [26], g-C_3N_4 nanosheets/carbon dot/FeOCl nanocomposites [27], oxidized graphitic carbon nitride [28], Z-scheme Bi_2WO_6-P25 heterojunction [29], Fe_2O_3 multi-walled carbon nanotube [30], CoP/ZnSnO3 composite [31], etc. Nanoparticles (NPs) have displayed broad applications in the municipal and industrial wastewater treatment sectors [32].

The mechanism of photodegradation is that as light falls upon a photocatalyst, electrons are excited from the valence band (VB) to the conduction band (CB) and create positive holes (h^+) in the VB. The electron in the VB reacts with O_2 to produce a superoxide anion radical ($^{\bullet}O_2{}^-$), while the h^+ of the VB reacts with H_2O and generates hydroxyl radicals ($^{\bullet}OH$). Both of these radicals are very reactive and take part in the photodegradation of organic pollutants [33]. This process is normally carried out in an aqueous medium, which is usually purified water [34–37].

The organic pollutants contained in industrial effluents are impure and contain various other impurities. These impurities are mostly inorganic anions and cations, which are also present in tap water (TW) obtained from different sources, and thus it is necessary to study the effect of these mineral ions on the photodegradation of organic pollutants such as dyes, pesticides, antibiotics, etc. Such assessment will also lead to applying the process to real water samples, which will ultimately pave the way for the practical implementation of this process for pollutant remediation. The occurrence of dissolved inorganic ions is rather common in dye-containing industrial wastewater, which may compete for the active sites on the photocatalyst's surface or deactivate the photocatalyst and, subsequently, decrease the degradation rate of the target dyes [38]. The photodegradation of some dyes also generates some inorganic anions [39], whose presence in the solutions may also affect the photodegradation process. These inorganic ions are present in TW. TW usually comes from water treatment plants and is originally from artesian wells or rivers [40]. TW is mainly obtained from underground wells having inorganic salts in minute quantities such as Na, Ca, Mg, sulfates, chlorides, and hydrocarbonates. Mineral content in drinking water is essential for human health [41]. Groundwater is sometimes regarded as the finest and most essential source of drinking water. Groundwater reserves have significantly declined in quality as well as quantity in several arid and semi-arid regions around the world. In recent years, groundwater contamination has increased dramatically in arid and semi-arid regions of the world. Hydrocarbons, synthetic organic compounds, anionic and cationic minerals, viruses, and radionuclides are the major pollutants reported in groundwater. Apart from these, nitrite and nitrate ions also occur naturally as part of the nitrogen cycle [42]. TW is contaminated by pipe leaks as well as corrosion in pipes [43]. The literature shows that the TW which is mostly used in household activities, contains carbonates, bicarbonates, chlorides, oxides, sulfates, and phosphates of different metal ions such as Fe^{2+}, Mg^{2+} $Ca^{2+,}$ and Si^{2+} [44]. The levels of different cations in TW can be determined by applying atomic absorption spectroscopy. Nano-Fe-bearing particles have been reported in TW [45,46]. Bicarbonate and carbonate ions are also commonly found in groundwater, surface water, and wastewater. Carbonate and bicarbonate ions are known as hydroxyl radical scavengers in certain processes such as pulse radiolysis and flash photolysis [46]. The taste of water depends on the chemical composition of the salt content, with both anions and cations [47]. The cations and anions content of TW can both positively and negatively affect the taste, with undesirable taste resulting from anions and cations levels that are above or below regulatory limits [48]. TW has a 500 µS/cm conductivity and its pH range is 7–8, which is a very suitable pH for ·OH radical formation [49]. According to the WHO standard specifications, the total dissolved solids in TW is 1000 mg/L and its pH range is 6.5–8.5 [50].

Dyeing wastewater also contains large amounts of inorganic ions because the dyeing process requires the addition of inorganic ions for various purposes. Both Cl- and SO42- are common inorganic ions used in textile dyeing as promoters, exhausting, retarding, or leveling agents. These ions that remain in the wastewater may have significant impacts on the degradation process of organic pollutants. Therefore, it is necessary to investigate the roles of inorganic ions during the dye degradation process [51]. Along with inorganic ions, wastewater also contains natural organic matter, which can also influence the photodegradation of organic pollutants in several ways [52,53]. Natural organic matter ranges from aliphatic to highly colored and aromatic compounds, and from highly charged to uncharged, with different molecular sizes and a wide variety of chemical compositions [40].

Various reviews are reported, containing the factors affecting the rate of photodegradation of dyes as a portion [17,54–59], however, no review reports on assessing the effect of TW on the photodegradation of dyes. Although there is limited research on TW's impact on the photocatalytic degradation of dyes and other organic pollutants such as pharmaceuticals, pesticides, and so on, an attempt was made to synthesize the existing information in this study and evaluate the influence of TW on the photo-degradation of dyes as well as other organic pollutants.

According to the Scopus database, research on the effect of TW on the photodegradation of organic pollutants is limited. As shown in Figure 1, the number of research papers published on the photodegradation of organic pollutants has increased steadily from 2010 to 2022.

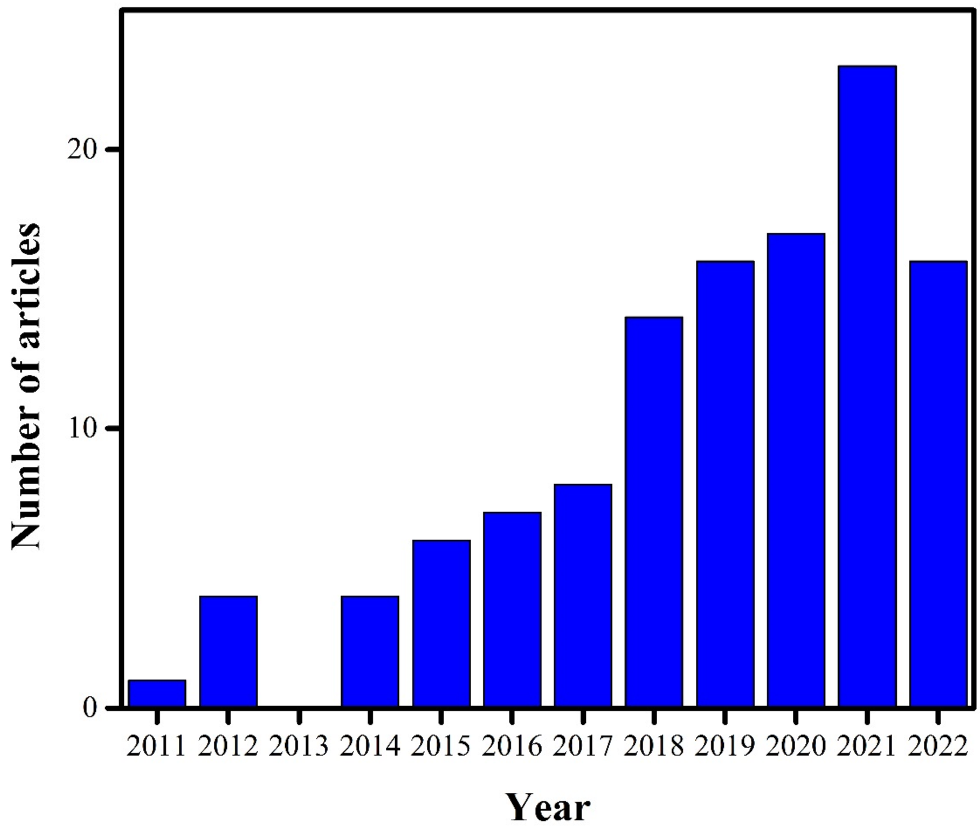

Figure 1. Annual article frequency extracted from the Scopus database at date 26 June 2022 (Searched with the keyword 'effects of tap water on pollutants degradation').

The effects of TW on the photo-degradation of some organic pollutants are summarized below.

2. Effect of TW on Photodegradation of Dyes

About 1–20% of the total dyes are lost during the dyeing process and are released into the environment in textile effluents [60]. The dyes released in wastewater are highly toxic, xenobiotic, teratogenic, and carcinogenic to living organisms [61]. Dyes are the emergent pollutants responsible for various severe deleterious effects such as drinking water poisoning, death of aquatic life, and the ruining of soil [62]. Organic dyes in water have caused a major problem owing to their huge burden on both the environment and the economy [63]. According to the literature, TW represents a dual effect: either a decrease or an increase in photocatalysts activity and efficiency of dye degradation [49]. The photodegradation of methylene blue (MB) in wastewater and TW by Ag NPs/TiO_2/Ti_3C_2Tx was compared and it was observed that the degradation of MB was a little slower in the wastewater than in the TW, which might be due to other competing organic species present in the wastewater. However, in both the mediums, MB dye is completely degraded in 30 min in wastewater and TW, while in deionized water it rapidly degrades in the first 15 min under UV light [64]. Similarly, the photodegradation of MB dye without a catalyst in TW is higher than that occurring in distilled water, which might be due to the presence of a small Fe concentration that can create the photo-Fenton system with H_2O_2 and generate ·OH having a high oxidizing capacity. In the presence of 0.02% nanoTiO_2 stabilized by 1% CMBCD-P (carboxymethyl β-cyclodextrin polymer) catalyst, the degradation of MB is faster in distilled water than TW which is due to the presence of dissolved organic components in TW which have an initial inhibiting effect [65]. In the Fenton process, ferrous ions (Fe^{2+}) react with H_2O_2 in the acidic media and oxidize Fe^{2+} to ferric ions (Fe^{3+}) which generates $^{\bullet}$OH, which degrades the organic contaminants [66].

The methyl violet photo-degradation by TiO_2/Pd and TiO_2/Pt in TW was found to be less in TW as compared to deionized water, applying the same experimental parameters. The reasonable causes explained for such decreases are the presence of additional species in TW e.g., organic, inorganic, and metallic ions, which adsorb on the catalyst's active sites and hence decrease its activity [67]. Fe_3O_4–TiO_2 nanoparticles (NPs) photocatalytically degraded a food dye, Brilliant Blue FCF in the presence of peroxymonosulfate, distilled water, TW, river water, and filtrated raw municipal wastewater in the UVA system. The degradation results show that the rate of photocatalytic degradation of dye in distilled water and TW is almost the same, while river water and filtrated raw municipal wastewater decrease the photocatalytic efficiency [68]. Similarly, the diazo reactive red 120 and triazo direct blue 71 dyes in the presence of Au–Nx-TiO_2 nanospheres under sunlight irradiation demonstrate a 10% lower degradation than the degradation occurring in milli-Q water, and the reason is the presence of organic, inorganic, and metal ions in TW [69]. The degradation of methyl orange dye using ZnO NPs loaded on activated carbon in TW was very good due to the common ions and other impurities [70]. The photocatalysts degraded Fe_3O_4 NPs and Fe_3O_4/ZrO_2 NPs degraded methyl red dye very efficiently in TW than degraded in distilled water, as shown in Figure 2 [71]. It is reported that natural organic matter sometimes acts as a photosensitizer for a large variety of chemical reactions that are produced by singlet oxygen, energy transfer, and radical species generation [72]. The effects of TW on the photodegradation of some dyes are summarized in Table 1.

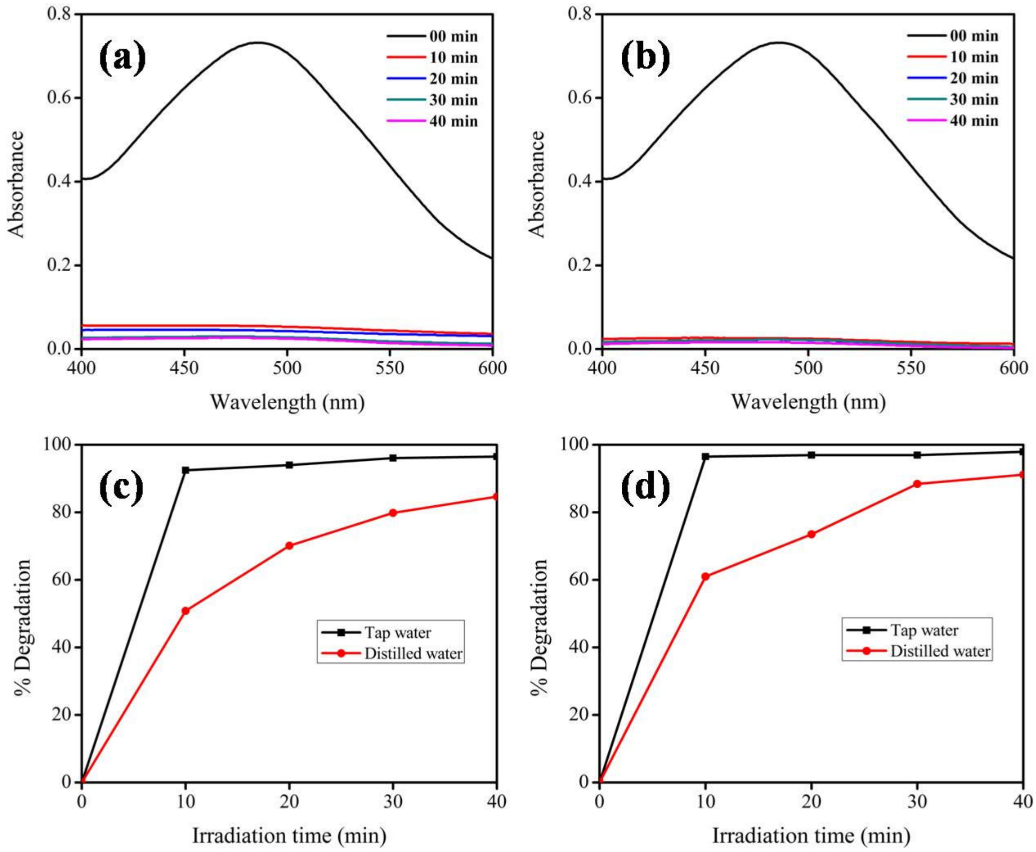

Figure 2. U.V./Vis spectra of methyl red dye in TW before and after reaction using (**a**) Fe_3O_4 NPs, (**b**) Fe_3O_4/ZrO_2 NPs, (**c**) %degradation comparison of methyl red dye in distilled and TW photodegraded by Fe_3O_4 NPs, and (**d**) %degradation comparison of methyl red dye in distilled and TW photodegraded by Fe_3O_4/ZrO_2 NPs [71].

Table 1. Effect of tap water on photodegradation of dyes.

Photocatalysts and Dye	%Degradation in Deionized Water	%Degradation in Tap Water	Conclusion and Reason	Ref
MnO_2/AC nanocomposite and MnO_2 NPs. Congo red dye	98.53% by MnO_2/AC and 66.57% by MnO_2 in 5 min under UV-light.	Dye almost completely (99%) degraded in 1 min under UV and visible light.	Dye degraded efficiently in TW. The presence of various mineral ions in the tap water enhanced the photocatalytic activity.	[73]
SnO_2/SiO_2 NPs and SnO_2 NPs	94.58% by SnO_2/SiO_2 NPs and 65.93% by SnO_2 NPs in 30 min under UV-light.	8.92% by SnO_2/SiO_2 NPs and 22.81% by SnO_2 NPs in 30 min under UV-light.	Dye degraded slowly in tap water. The presence of organic, inorganic and metallic ions present in TW serve as competing species for the active sites of photocatalysts and reduce their photocatalytic activity.	[74]
CuO/NC NPs and CuO NPs	97.18% by CuO/NC NPs and 68.22% by CuO NPs in 4 min under UV-light.	47.33% dye by CuO/NC NPs and 23.4% by CuO NPs in 4 min under UV-light.	Dye degraded slowly in TW. The presence of organic, inorganic and metallic ions in TW, serves as competitive species for the active sites of photocatalyst and reduce their photocatalytic activity.	[75]
Fe_3O_4/ZrO_2 NPs and Fe_3O_4 NPs. Methyl red	91% by Fe_3O_4/ZrO_2 NPs and 84% by Fe_3O_4 NPs within 40 min under UV-light.	97% by Fe_3O_4/ZrO_2 NPs and 96% by Fe_3O_4 NPs within 40 min under UV-light.	Dye degraded efficiently in TW. The presence of mineral ions in the TW enhances photocatalyst activity.	[71]

Table 1. *Cont.*

Photocatalysts and Dye	%Degradation in Deionized Water	%Degradation in Tap Water	Conclusion and Reason	Ref
Fe–TiO_2 nanotubes. Congo red	86% under visible light.	74% under visible light.	Dye degraded slowly in TW. Lower activity in tap water is due to the deactivating effects of organic, inorganic, and salt compounds.	[76]
Ag/P@BC. Rhodamine B	83.08% under visible light irradiation.	75.85% under visible light irradiation.	Some inorganic salts in TW slightly affected the process of adsorption and photodegradation.	[77]
Ag NPs/TiO_2/Ti_3C_2Tx	full degradation in 15 min under UV-light irradiation.	Lower photodegradation in tap water under UV-light irradiation.	Lower activity in TW. The presence of other competing organics in the wastewater.	[64]
TiO_2/Pd and TiO_2/Pt	78% and 95% in 20 min under UV-light.	62% and 47% in 20 min under UV-light.	Lower activity in TW. Presence of organic, inorganic, and metallic ions in TW, adsorbed on the catalyst active sites decreases its activity	[67]

In natural water and wastewater, different inorganic anions like Cl^-, SO_4^{2-}, and NO_3^- are present and may affect the degradation of organic pollutants. Inorganic anion tends to coexist with organic pollutants in wastewater effluent and can influence the separation and purification of substances represented in wastewater treatment. The inorganic ions such as SO_4^{2-}, HCO^{3-}, and Cl^- have a dual effect on the photodegradation of organic pollutants such as photocatalyst types and ion concentrations [78]. The presence of inorganic anions such as PO_4^{3-}, SO_4^{2-}, and F^- on the photocatalytic behaviors of TiO_2 are contradictory, mainly due to the various modification strategies and the reaction conditions [79]. In a Fe(III)/chlorine system for degradation of reactive green 12, $Cl_2^{\bullet-}$ was found to be primarily responsible for a huge reduction of dyes in the system, while $Cl^\bullet$ and $^\bullet OH$ participate with only ~5% in the overall removal efficiency [80]. In the mineralization of Reactive Orange 16 using TiO_2 NPs, the effect of mineral ions such as SO_4^{2-}, NO_3^-, HCO_3, and CO_3^{-2} have a detrimental effect on photocatalytic decolorization [81]. Similarly, in the ultrasound-assisted degradation of para-rosaniline and ethyl violet, the role of the carbonate ion on the degradation is captive, though the other ions such as chloride, nitrate, and sulfate had very little or no impact [82]. The effects of inorganic anions found in TW on the photodegradation of dyes are summarized in Table 2. The table shows that inorganic anions exhibited both positive and negative effects depending upon the nature of photocatalysts, dye, and their concentrations. Similarly, cations in wastewater also have a significant effect on the photodegradation of organic dyes.

Table 2. Effect of inorganic anions present in TW on photodegradation of dyes.

Photocatalyst and Dye	Inorganic Anions	Positive Effect	Negative Effect	Negligible Effect	Reference
commercial TiO_2. Direct 80, Direct Blue, Reactive Yellow 2	SO_4^{2-}, Cl^- and NO_3^-		SO_4^{2-}, Cl^- and NO_3^-		[83]
TiO_2 dispersions. Procion Red MX-5B and Cationic Blue X-GRL	SO_4^{2-}, $H_2PO_4^-$, ClO_4^- and F^-	In acidic medium	In basic medium		[84]
Au-Fe_3O_4/ graphene composites. Methylene blue	NaCl, Na_2SO_4, NaH_2PO_4, $NaNO_3$, and Na_2CO_3		SO_4^{2-}, Cl^-, $H_2PO_4^-$, NO_3^-, CO_3^{2-}	Na^+	[85]
Ag_3PO_4. Methylene blue	NO_3^-, OH^-, NO_2^-, HCO_3^-, Cl^-, Br^-, CO_3^{2-}, SO_4^{2-}, SO_3^{2-}, S^{2-} and PO_4^{3-}	OH^-, Cl^-, Br^-, HCO−, CO_3^{2-}, SO_4^{2-}, SO_3^{2-}, S^{2-}	NO_2^-,	NO_3^-,	[86]

Table 2. *Cont.*

Photocatalyst and Dye	Inorganic Anions	Positive Effect	Negative Effect	Negligible Effect	Reference
CuO–Cu_2O nanocomposite. Methylene blue (MB) and Methyl orange (MO).	SO_4^{2-}, Cl^- and NO_3^-	Cl^- (0.5 mM) on MB	SO_4^{2-} on MB. Cl^- on MO	SO_4^{2-} on MO.	[87]
$ZnFe_2O_4$ Methylene blue	SO_4^{2-}, NO_3^-, Cl^-, CO_3^{2-}		SO_4^{2-}, NO_3^-, Cl^-, CO_3^{2-}		[88]
cerium-doped SiO_2/TiO_2 Methylene blue	NO_3^-, SO_4^{2-}, Cl^-		NO_3^-, SO_4^{2-}, Cl^-		[89]
Ag/Mn_3O_4 and Ag/Mn_3O_4/graphene with persulfate. Methylene blue	Cl^-, SO_4^{2-}, NO_3^-, $H_2PO_4^-$, CO_3^-		All ions have negative effect in the order $H_2PO_4^-$ > CO_3^{2-} > SO_4^{2-} > Cl^- > NO_3^-		[90]
silver ion-doped TiO_2 Methylene blue	Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}	Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}			[91]
ZnO nanorod. MB, Acid red, Remazol red, and Rhodamine B	PO_4^{3-}, Cl^-, SO_4^{2-}, NO_3^-,		All ions have negative effect in the order PO_4^{3-}, > Cl^-, > SO_4^{2-} ≈ NO_3^-		[92]
NiS/CuS-CdS composites. MB and MO	NaCl, K_3PO_4 and Na_2CO_3	K3PO4 for MO	NaCl and Na_2CO_3 both MB and MO. K_3PO_4 for MB.		[89]
TiO_2 NPs	SO_4^{2-}, NO_3^-, HCO_3, CO_3^{-2}		SO_4^{2-}, NO_3^-, HCO_3, CO_3^{-2}		[81]

The cations such as Mn^{2+}, Cu^{2+}, and Mg^{2+} are reported to inhibit the catalyst's activity [93]. $CaCO_3$ has also been extracted from TW as a white powder that was sintered at 900 °C and applied for the efficient adsorption/degradation of Rhodamine-B dye [94]. Inorganic cations, such as Na^+, K^+, Ca^{2+}, and Mg^{2+}, are also present in natural waters and affect the photocatalytic degradation of organic pollutants [95]. The effects of inorganic cations on the photodegradation of dyes are summarized in Table 3.

Table 3. Effect of inorganic salt cations present in TW on photodegradation of dyes.

Photocatalyst and Dye	Inorganic Anions	Positive Effect	Negative Effect	Negligible Effect	Reference
La/Bi_2WO_6 composite. Reactive brilliant red X-3B (X-3B) and rhodamine B (RhB)	Na^+, K^+, Ca^{2+} and Mg^{2+}	All cations promoted the removal of RhB	All cations inhibited the removal of X-3B		[96]
TiO_2/Electrochemically-assisted photodegradation. Methyl orange	Na^+, K^+, Ca^{2+}, NH_4^+ and Mg^{2+}	Na^+, K^+, Ca^{2+} and NH_4^+	Mg^{2+}		[97]
UV/TiO_2 system. Direct Red 23	Cu^{2+}, Al^{3+}, Cr^{3+}, Sn^{4+}		Cu^{2+}, Al^{3+}, Cr^{3+}, Sn^{4+}		[98]
NiS_2-rGO and CoS-rGO nanocomposite	Na^+, Mg^{2+} and Ca^{2+}	Positive effect at 0.1 M salt solution concentration		Negligible effect at 0.01 M salt solution concentration	[99]
Ag/rGO nanocomposite. congo red and bismarck brow	Ca^{2+}, Mg^{2+}, Na^+ and NH_4^+	Ca^{2+}, Mg^{2+}, Na^+ and NH_4^+			[100]
persulfate-assisted Ag/Mn_3O_4 and Ag/Mn_3O_4/graphene composites. methylene blue	K^+, Ca^{2+}, and Mg^{2+}		Inhibition effect in the order Ca^{2+} > Mg^{2+} > K^+		[90]

3. Effect of TW on Photodegradation of Pharmaceutical Products

The increased global production of drugs has caused an increase in pharmaceutical contaminants in our natural water bodies. Great amounts of these drugs consumed by the population are discharged into the environment and finally cause contamination of ground and surface water bodies [101]. Human as well as veterinary pharmaceuticals offer many benefits, but also pose risks to both public health and the environment [102]. Antibiotics have various adverse effects on human health as well as aquatic life [103]. Pharmaceutical pollution is an emerging issue that has the potential to unbalance ecosystems [104]. One of the most significant public health and environmental concerns is related to the active pharmaceutical ingredients (APIs) and medicines discharged into bodies of water [105]. The disposed of wastewater contains antibiotics, and TW is susceptible to antibiotics contamination, ranging from a few to hundreds of nanograms per liter in different countries [106], and detected in some countries experimentally in TW [107,108]. To simulate the actual situation, it is essential to consider the effect of inorganic ions as the real water types include a large number of different ions [109]. The effect of TW on the photo-degradation of pharmaceutical products is of great importance. Photocatalysis is an advanced oxidation process (AOP) that has been potentially applied in the treatment of antibiotic residues and this technology has recently become the focus of much attention [110]. Bismuth oxyiodide (BiOI) materials were prepared for the photocatalytic degradation of oxytetracycline (OTC) in which BiOI microspheres were found to be the most active in removing the antibiotic under visible light. BiOI microspheres degraded 84% OTC in pure water and 92% in TW after 5 h of visible light irradiation. In terms of mineralization of the dissolved organic matter, BiOI microspheres photocatalytically converted 77.1% of pure water and 82% of TW to CO_2. The higher rate of degradation in TW might be attributed to the dissolved components such as nitrate ions in the TW [111]. The photolysis of nitrate can significantly improve the production of hydroxyl radicals [112], which are highly reactive toward the photodegradation of organic pollutants [113]. The photo-degradation of metoprolol (MTP) through TiO_2 nanotube arrays demonstrates that the photocatalysts degraded 87.09% of MTP in Milli-Q water and 62.05% of MTP in TW. The decrease was attributed to the presence of organic species competing with the target MTP for oxidizing species, adsorbing onto the photocatalyst surface, and screening UV irradiation [114]. Similarly, TW also reduced the rate of photodegradation of paracetamol and aspirin by applying a micro-sized TiO_2 catalyst owing to the presence of a large number of inorganic anions in TW. These anions play a significant deactivating role in the adsorption efficiency of the catalyst. The SO_4^{2-} present in TW reacts with the photo-generated holes (h^+) and the bicarbonate anions react with $^{\bullet}OH$ radicals to generate carbonate radicals which are less reactive [115]. The photodegradation of naproxen shows a remarkable enhancement in TW compared to ultrapure water in the presence of g-C_3N_4 both under natural sunlight and visible light as shown in Figure 3 [116]. The photodegradation of sulfonamides by TiO_2 is significantly suppressed by SO_4^{2-} ions generated by the addition of Na_2SO_4 [117]. The photodegradation of oxolinic acid and oxytetracycline by solar-assisted TiO2 is hindered by PO_4^{3-} while other inorganic ions (Cl^-, SO_4^{2-}, NO_3^-, NH_4^{+}, and HCO_3^-) did not substantially alter the antibiotics' photodegradation [118]. The inorganic anions present in water did not significantly influence sulfadiazine degradation using N-doped coconut-shell biochar as a catalyst [119]. Similarly, dissolved organic matter, phosphate, and ferrous ions inhibit the degradation of Diclofenac, which becomes stronger when the concentrations of dissolved organic matter, phosphate, and ferrous ions increase [120].

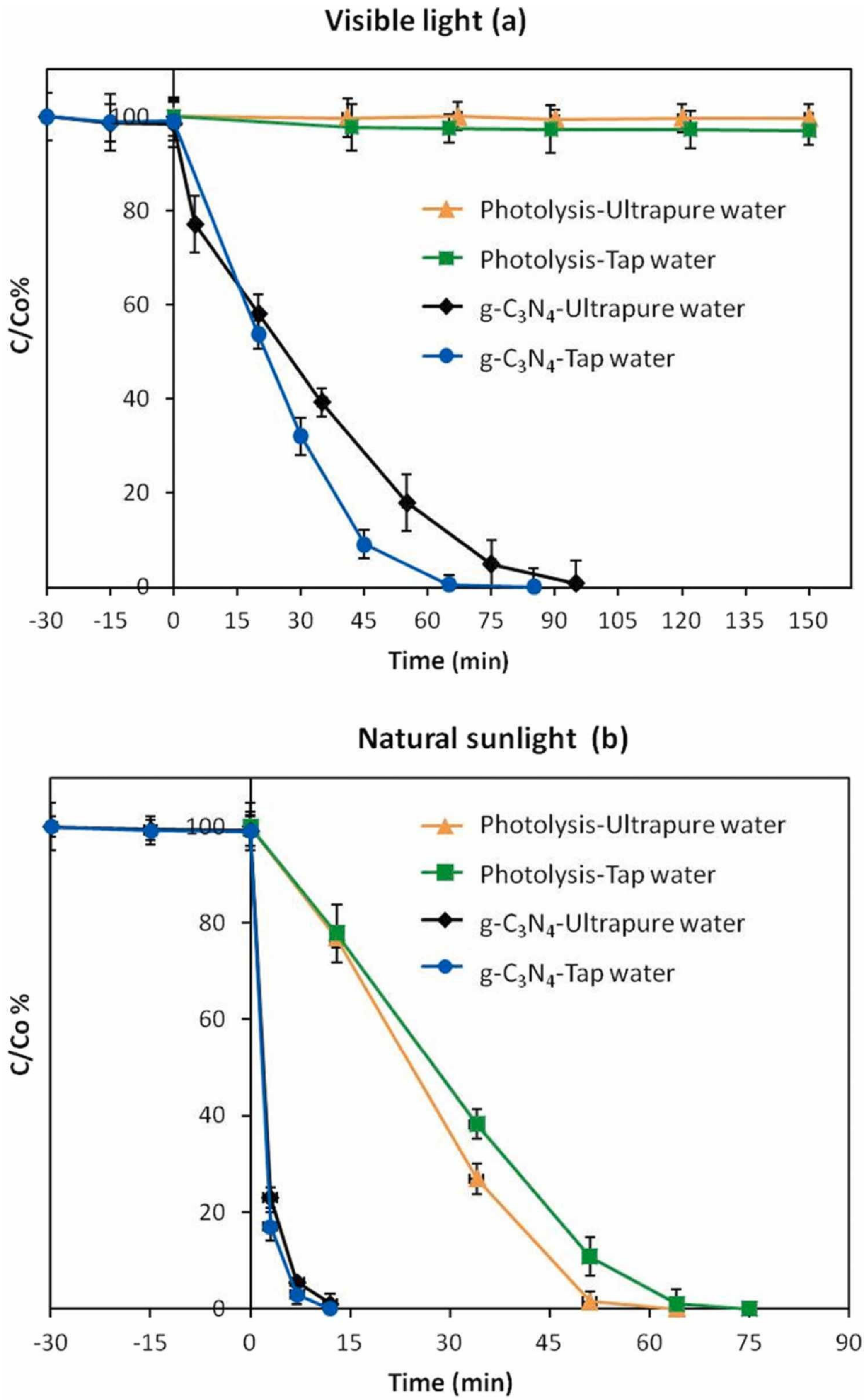

Figure 3. Photo-degradation of naproxen through g-C_3N_4 under (**a**) visible light radiation, and (**b**) and natural sunlight. Reprinted/adapted with permission from [116], 2022, Elsevier (License Number 5454330213985).

4. Effect of TW on Photodegradation of Pesticides

Pesticides are applied extensively in agriculture to protect crops from harmful pests. They are present in drinking water and have adverse health effects [121]. The extensive usage of pesticides has posed serious detrimental impacts on wild flora and fauna, including birds [122]. The residue of pesticides remain in plant parts, air, and soil, and even penetrate the water, and are considered one of the most destructive threats to the ecosystem. They can exist in the environment for a long time with carcinogenic effects [123]. Inorganic ions such as nitrate, sulfate, phosphate, ammonium, or copper are widely employed in agriculture, and others such as chloride, calcium, or sodium can be found in natural waters [124]. As pesticides are present in drinking water, assessing the TW effect on pesticide degradation is very important. The photo-degradation of four herbicides, namely clopyralid, amitrole, diuron, and fluroxypyr by UV-radiation revealed that the photodegradation rate is faster in ultrapure water than in TW and wastewater, as shown in Figure 4. Such behavior may be due to the absence of inorganic and organic compounds in ultrapure water, which consumes UV radiation [125]. Such results were also observed in the degradation of organophosphorus pesticides in water applying UV/H_2O_2 treatment. The rate of photodegradation followed the pattern: distilled water > TW > river water. The lower degradation in tap and river water is because the organic carbon present in this water absorbs most of the emitted photons and slows down the degradation of the pesticide [126]. The same results were also detected in the photodegradation of five insecticides such as imidacloprid, clothianidin, acetamiprid, thiamethoxam, and dinotefuran. The rate of photodegradation was faster in ultra-pure water than in tap and pond water [127]. In the photodegradation of Diazinon and Imidacloprid by TiO_2, Cl^- exhibited the strongest inhibition effect followed by NO_3^- and SO_4^{2-} ions, because these ions may compete for the TiO_2 active sites or deactivate the photocatalyst and, consequently, decrease the rate of the degradation of the pollutant. The inhibition effects of anions may be due to the reaction of h^+ and $^\bullet OH$ with anions that behave as h+ and $^\bullet OH$ scavengers, resulting in prolonged contaminant removal. The extremely reactive •OH also reacts with inorganic an-ions contained in water, resulting in a greater requirement for •OH to achieve the necessary degree of degradation or the full inhibition of the advanced oxidation process [128]. In the photodegradation of phosphamidon by TiO2, the Cl^-, PO_4^{3-}, and NO_3^- ions have no significant effect on degradation at low concentrations, but at higher concentrations, all these ions considerably inhibit degradation. This inhibition might be due to the competition of these ions for adsorption sites on the TiO_2 catalyst. The inhibition efficiency of the three anions follows the order $PO_4^{3-} > Cl^- > NO_3^-$ [129]. The same results of inhibition by Cl^-, SO_4^{2-}, NO_3^-, and F^- ions at higher concentrations were also observed in the photo-degradation of nicosulfuron using TiO_2 photocatalyst [130]. Similarly, the Cl^- and NO_3^- ions also displayed inhibitory effects in the degradation of terbufos using TiO_2 photocatalyst. Along with the competing mechanism, it was also stated that Cl^- may lead to the formation of f inorganic radical anions (e.g., $Cl^\bullet$, $ClOH^{-\bullet}$) as represented in the following equations.

$$Cl^- + h^+ \rightarrow Cl^\bullet$$

$$Cl^- + {}^\bullet OH \rightarrow ClOH^{-\bullet}$$

The reactivity of these radicals may be considered, but they are not as reactive as h^+ and $^\bullet OH$ [131].

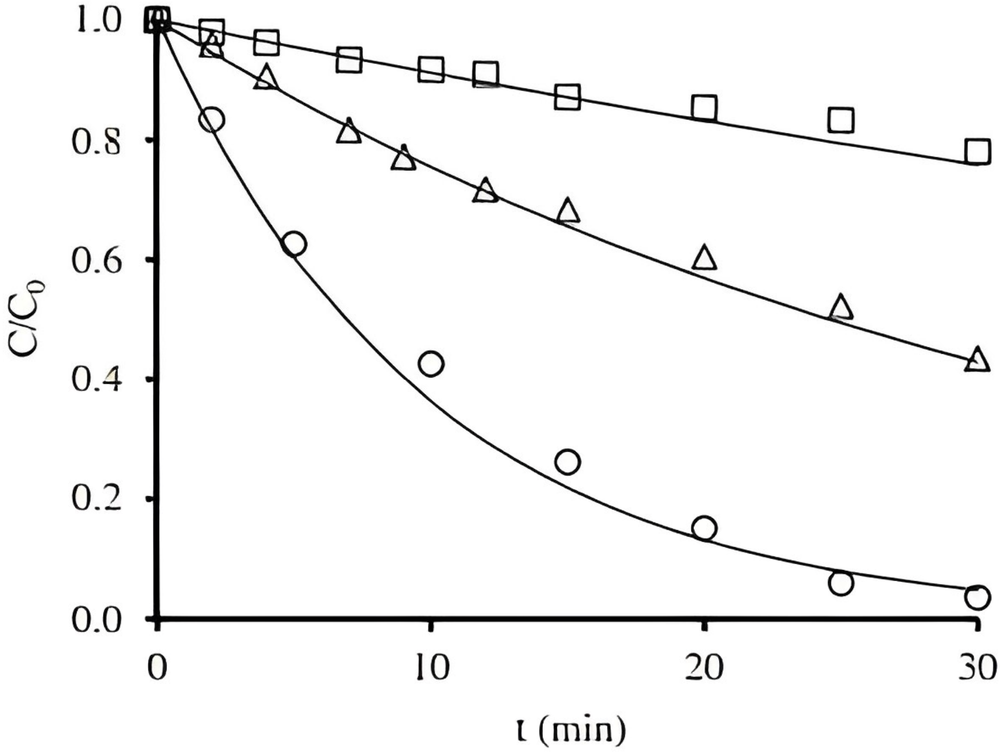

Figure 4. Influence of the type of water on the photodegradation of clopyralid (CLP) by UV radiation. $[CLP]_0$ = 25 mg/L. (□) wastewater, (△) tap water, and (○) ultrapure water. Reprined/Adapted with permission from [125], 2022, Elsevier (License Number 5336460765282).

5. Effect of TW on Photodegradation of Organic Solvents

Solvents are used widely in many sectors of industry as well as everyday life, like agrochemicals, detergents, pharmaceuticals, cosmetics, paints, inks, varnishes, etc. [132]. Despite their environmental toxicity, organic solvents are widely used [133]. Almost all of the solvents are hazardous to health if inhaled or swallowed in more than the allowed quantity and cause irritation when they come in contact with the skin [134]. Environmental pollution caused by the discharge of these organic solvents into aqueous solutions has become a major global issue of increasing concern [135]. A limited focus has been shifted to studying the effect of TW on the photodegradation of organic solvents. Sulfolane degradation was studied in milli-Q water, TW, and groundwater using TiO_2 and RGO-TiO_2 as photocatalysts and it was observed that in milli-Q water, sulfolane reached non-detectable levels in 3 h, while 32% and 29% of sulfolane remained in groundwater and TW at the end of the reaction time. The presence of SO_4^{2-}, HCO_3^- and Cl^- in high concentrations in tap and ground water coated on TiO_2 in the dark reaction time reduces the photocatalytic degradation of sulfolane [136].

6. Future Perspectives

In evaluating the TW effect, a few dimensions still require thorough investigations to clearly evaluate the dual effect of TW on the photodegradation of organic pollutants.

For the photo-degradation of organic pollutants, it is necessary to perform the experiment in TW and real water samples to approach the practical applicability of the process. It would also be beneficial to conduct the photodegradation experiment in other natural and running water sources.

It is necessary to individually evaluate the effect of organic and inorganic ions present in TW on the photodegradation of organic pollutants. It is also recommended to evaluate the effect of mineral ions present in TW on the mechanism of photodegradation of organic pollutants.

It is also necessary to evaluate the effect of common ions on the photodegradation of organic pollutants.

It is suggested to measure all the physicochemical properties such as pH, conductivity, types of ions, etc. of TW and real water samples utilized in photodegradation experiments.

It will also be useful to measure the surface charge of the photocatalysts before experiments because positive surface charge photocatalysts will display less activity in TW due to the strong electrostatic interaction with the inorganic anions present in TW, while negative surface charge photocatalysts will display maximum efficiency. This characterization will also help in the selection of organic pollutants such as dyes, antibiotics, and pesticides for photodegradation experiments.

Furthermore, it is highly recommended to perform theoretical studies along with experimental work, because density functional theory (DFT) calculations can predict in advance the effect of medium pH and particular minerals present in TW. DFT calculations will also suggest mechanisms and are also very helpful in supporting the experimental results.

7. Conclusions

Evaluating the effect of mineral ions present in TW on the photo-degradation of organic pollutants is very important for the practical applicability of the process. TW contains a minute quantity of inorganic salts and 7–8 pH, and this range of pH can enhance the formation of ·OH radicals. The enhancement or reduction of the photodegradation rate is due to the pH range and inorganic ions present in TW. Similarly, the reduction in the photodegradation rate is due to the presence of inorganic and metal ions in TW, which serve as competing species for the photocatalyst active sites and reduce their photocatalytic activity.

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