Chapter 1
Introduction

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1.1 Water Disinfection

The last 50 years have witnessed a growing awareness of the fragile state of most of the planets' drinking water resources. Access to freshwater will become even more important in the near future, as the world's population rises from 7 billion today to 9 billion by 2050. The World Health Organization (WHO) has estimated that 80 % of illnesses in the developing world are water related, resulting from poor water quality and lack of sanitation [1]. There are 3.3 million deaths each year from diarrheal diseases caused by bacteria such as *Escherichia coli*, *Salmonella* sp. and *Cholera* sp., parasites and viral pathogens. In the 1990s, the number of children who died of diarrhoea was greater than the sum of people killed in conflicts since World War II [2]. It is also estimated that around 4 billion people worldwide experience to have no or little access to clean and sanitized water supply, and millions of people died of severe waterborne diseases annually [3, 4].

Waterborne diseases are caused by pathogenic microorganisms that most commonly are transmitted in contaminated freshwater. The pathogenic microorganisms responsible for these diseases include a variety of helminthes, protozoa, fungi,

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bacteria, rickettsiae, viruses and prions [1, 5], many of which are intestinal parasites or invade the tissues or circulatory system through walls of the digestive tract. Water disinfection means the removal, deactivation or killing of pathogenic microorganisms, resulting in termination of growth and reproduction. Problems with waterborne diseases are expected to grow worse in the future, both in developing and industrialized nations. Therefore, effective and lower-cost methods to disinfect microorganism-contaminated waters are urgently needed, without further stressing the environment or endangering human health by the treatment itself [6].

1.2 Traditional Water Disinfection Methods

The existing drinking water pretreatment processes, such as coagulation, flocculation and sedimentation, can remove a maximum of 90 % of bacteria, 70 % of viruses and 90 % of protozoa [4]. Filtration for drinking water treatment (e.g. sand and membrane filtration), with proper design and adequate operation, can act as a consistent and effective barrier for microbial pathogens leading to about 90 % removal of bacteria. However, the remaining bacteria might still be able to cause disease, which makes filtration a good pretreatment, but not a completely safe disinfection technique [7]. The most commonly used drinking water disinfection techniques after pretreatment include chlorination (chlorine and derivates), ozonation and UVC irradiation.

1.2.1 Chlorination

Chlorine is a very effective disinfectant for most microorganisms. It is reported that 99 % of bacterial cells can be killed with chlorine of 0.08 mg/min/L at 1–2 °C under neutral pH condition. In addition, 99 % of viruses can be killed by 12 mg/min/L chlorine at 0–5 °C under neutral pH condition. However, the protozoa including *Cryptosporidium*, *Giardia* and *Acanthamoeba* are quite resistant to chlorination and cannot be effectively inactivated [7]. Another major disadvantage of chlorination is the formation of potentially mutagenic and carcinogenic disinfection byproducts (DBPs) during water chlorination, which can lead to the problems of recontamination and salting of freshwater sources [8, 9]. The DBPs are formed from the reaction of chlorine with natural organics in water and include trihalomethanes (THMs) and haloacetic acids (HAAs). US Environmental Protection Agency (USEPA) regulations have further limited THMs, HAAs and other DBPs (including chlorite and bromate) in drinking water [10]. As a result, many water systems now limit the use of chlorine to high-quality groundwater or reduce total organic carbon prior to disinfection.

1.2.2 Ozonation

The application of ozone is another widespread disinfection method for drinking water treatment throughout the world [11]. Similar to chlorination, ozone is unstable in water and undergoes reactions with some water matrix components. However, the unique feature of ozone is its decomposition into hydroxyl radicals (•OH), which are the strongest oxidants in water [12]. While disinfection occurs dominantly through ozone, oxidation processes may occur through both ozone and •OH [13], making the ozonation even more effective than Cl_2 in destroying bacterial cells and viruses [14, 15]. It is reported that 99 % of bacterial cells can be removed with 0.02 mg/min/L ozone at 5 °C under neutral pH condition. For the disinfection of protozoa *Cryptosporidium*, the required ozone concentration is suggested to be 40 mg/min/L at 1 °C [16]. Despite its highly efficient inactivation of all microorganisms, ozonation can also produce DBPs, such as aldehydes, carboxylic acids and ketones, in the presence of dissolved organic matter [17]. However, as ozonation is usually followed by biological filtration, some organic compounds can be mineralized microbiologically. Thus, the most important ozonation DBP regulated in drinking waters today is bromate, which is formed during ozonation of bromide-containing waters and cannot be degraded in biological filtration process [18, 19]. In addition, ozonation is a more complex technology than chlorination and is often associated with increased costs and process complexity [20].

1.2.3 UV Irradiation

Water disinfection utilizing germicidal UV irradiation has become more and more important in recent years, as the low-pressure UV produces almost no disinfection byproducts [21]. In addition, unlike chemical disinfectants, the biological stability of the water is not affected by low-pressure lamps. In Europe, UV has been widely applied for drinking water disinfection since the 1980s, for the control of incidental contamination of vulnerable groundwater and for the reduction of heterotrophic plate counts [22]. Depending on irradiation wavelengths, UV can be divided into UVA (315–400 nm), UVB (280–315 nm), UVC (200–280 nm) and vacuum UV (VUV) (100–200 nm). In particular, UVC is the most effective wavelength for microorganism inactivation, as UVC light will damage irradiated DNA, directly inducing pyrimidine and purine dimers and pyrimidine adducts. For water disinfection, 99 % inactivation of bacterial cells can be achieved at UVC intensity of 7 mJ/cm^2. The susceptibility of protozoa to UVC damage is very similar to that of bacteria; thus, the 99 % inactivation for *Cryptosporidium* can be achieved at 5 mJ/cm^2 [23]. However, due to the weak penetration power, UV disinfection can only inactivate bacterial cells on the surface of the wastewater [24], and the treated cells can often regrowth after removal of UV irradiation [25]. General application of UV

disinfection was further hampered because of high costs, poor equipment reliability and maintenance problems [26, 27].

Therefore, although traditional disinfection methods can be effectively applied in water disinfection, the disadvantages of these methods must be considered when selecting suitable disinfection methods for water treatment, and alternative technologies are needed.

1.3 Advanced Oxidation Process

Advanced oxidation processes (AOPs) are defined as the processes that generate hydroxyl radicals (•OH) in sufficient quantities to be able to oxidize the majority of the complex chemicals present in the effluent water [28]. AOPs have been receiving increasing attention to be effectively applied in the near-ambient total degradation of soluble organic contaminants from waters and soils, as the produced •OH would be able to oxidize almost all organic compounds to carbon dioxide and water because of its powerful redox potential (2.8 V vs. NHE) [29]. These processes include cavitation [30, 31], photo-Fenton [32, 33], photocatalytic oxidation [34] and other combination methods, such as H_2O_2/UV, O_3/UV and H_2O_2/O_3/UV, which utilize the photolysis of H_2O_2 and O_3 to produce •OH [35]. In particular, heterogeneous photocatalysis based on the use of a semiconductor with suitable energy band gap (Eg) is the most interesting and promising advanced oxidation technology that has received much attention in the past few decades for a variety of photochemical applications, including water splitting, organic compounds degradation and CO_2 reduction, as well as water disinfection.

1.4 Photocatalysis

With respect to the generally accepted definition of thermal catalysis, photocatalysis can be defined as "acceleration of a photoreaction by the presence of a catalyst", which indicates both light and a catalyst are necessary to bring about or to accelerate a chemical transformation [36]. As the photoreaction takes place in more than one homogeneous medium, it is usually called "heterogeneous photocatalysis" [37, 38].

Fujishima and Honda (1972) [39] discovered the photocatalytic splitting of water on TiO_2 electrodes, which has marked the beginning of heterogeneous photocatalysis [40]. Since then, tremendous research efforts have been devoted into understanding the fundamental process of heterogeneous photocatalysis, thus enhancing the photocatalytic efficiencies [41–44]. Photocatalysis was initially applied in hydrogen evolution by splitting water, with intention to address the energy crisis [45–48]. Research activities were soon extended to photocatalytic oxidation of organic pollutants [49, 50], CO_2 reduction [51] and the disinfection of microorganisms in contaminated water [52, 53]. Although an early study

demonstrated that there was no improved antimicrobial activity of TiO_2 for the disinfection of primary wastewater effluent [54], a number of subsequent studies have shown the effectiveness of TiO_2 photocatalysis for water disinfection [55, 56], including inactivation of bacterial cells [57] and viruses from contaminated water [58], tertiary treatment of wastewater [59], purifying drinking water [60], treatment of wash waters from vegetable preparation [61] and in bioreactor design to prevent biofilm formation [62].

1.4.1 Fundamental Mechanism for TiO_2 Photocatalysis

Semiconductors acting as the photocatalysts for the light-reduced redox processes, such as TiO_2, ZnO, Fe_2O_3, CdS and ZnS, are characterized by a filled valence band and an empty conduction band [63]. When the valence band receives a photon with energy bigger than the band gap, an electron (e^-) will be excited and promoted into the conduction band, leaving a hole (h^+) in the valence band. The photo-generated e^--h^+ pairs will subsequently migrate onto the surface of photocatalyst and undergo a variety of complicated reactions to produce reactive oxidative species (ROSs), which are potentially involved in the photocatalytic oxidation process. The most widely used photocatalyst is TiO_2, as it is nontoxic, low cost and highly efficient and has long-term photostability [64, 65]. The fundamental mechanism for TiO_2 photocatalysis under UV irradiation has been well established for photocatalytic oxidation process towards organic compounds degradation as well as microorganism inactivation (Fig. 1.1) [38, 66].

The primary photocatalytic oxidation mechanism includes the following four steps (Eqs. 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 1.10, 1.11 and 1.12):

1. Irradiation
   The first step is the light irradiation process for harvesting and conversion of light energy to chemical energy, thus leading to the generation of e^--h^+ pairs.

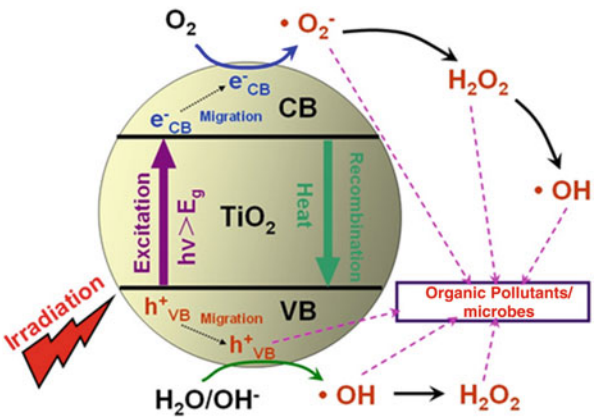

Fig. 1.1 A schematic diagram showing the photocatalytic oxidation mechanism of TiO_2 photocatalysis under UV irradiation

The requirement of this step is the incoming photon should have an energy of $h\nu$ that matches or exceeds the semiconductor band gap energy. For TiO_2, the light wavelength for fulfilment of the excitation process is restricted to the UV region because of its wide band gap (3.2 eV) [67].

2. Separation and recombination of e^--h^+ pairs
The photoexcited e^- is injected into the conduction band, leading to the separation of e^--h^+ pairs. However, the photo-generated e^- and h^+ can recombine in bulk or on surface of the semiconductor within extremely short time, releasing energy in the form of heat or photons (Eqs. 1.1 and 1.2) [68, 69].

$$TiO_2 + h\nu \rightarrow h_{vb}{}^+ + e_{cb}{}^- \tag{1.1}$$

$$h_{vb}{}^+ + e_{cb}{}^- \rightarrow \text{recombination} + \text{energy (heat/photons)} \tag{1.2}$$

The separated e^- and h^+ without recombination are migrated to the surface of TiO_2 and trigger photochemical reactions to produce secondary reactive species (i.e. ROSs) or directly oxidize/reduce the substrates adsorbed by the TiO_2.

3. h^+ trapping reactions
In the valence band, the separated h^+ is migrated to the surface and trapped by surface-adsorbed hydroxyl groups or water to produce trapped holes $\left(\equiv Ti^{IV}O\bullet\right)$ (Eq. 1.3), which is usually described as a surface-bound or surface-adsorbed hydroxyl radical ($\bullet OH_{ads}$) [70–72]. When electron donors (Red) (i.e. reductants) are available on the TiO_2 surface, the photocatalytic oxidation process thus happens by electron transferring from Red to trapped holes (Eq. 1.4). The subsequent release of $\bullet OH_{ads}$ to bulk solution, thus leading to the formation of bulk hydroxyl radical ($\bullet OH_{bulk}$), is suggested to contribute to the oxidation process (Eqs. 1.5, 1.6 and 1.7) [73]. On the other hand, h^+ can also be directly involved in oxidation of Red [74] and indirectly involved in production of H_2O_2 by coupling of two •OH (Eqs. 1.8 and 1.9) [75–77].

$$h_{vb}{}^+ + \equiv Ti^{IV}OH \rightarrow \left[\equiv Ti^{IV}OH\bullet\right]^+ \rightarrow \equiv Ti^{IV}O\bullet + H^+ \tag{1.3}$$

$$\equiv Ti^{IV}O\bullet + \text{Red} + H^+ \rightarrow \equiv Ti^{IV}OH + \bullet Red^+ \tag{1.4}$$

$$h_{vb}{}^+ + H_2O \rightarrow \bullet OH_2{}^+ \rightarrow \bullet OH + H^+ \tag{1.5}$$

$$h_{vb}{}^+ + OH^- \rightarrow \bullet OH \tag{1.6}$$

$$\bullet OH + \text{Red} + H^+ \rightarrow \bullet Red^+ \tag{1.7}$$

$$h_{vb}{}^+ + \text{Red} \rightarrow \bullet Red^+ \tag{1.8}$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \tag{1.9}$$

4. e^- trapping reactions
In the conduction band, O_2 often acts as the electron acceptor to trap the photoexcited $e_{cb}{}^-$ in aerated systems, thus preventing the e^--h^+ recombination. In this process, $\bullet O_2{}^-$ is formed and undergoes a variety of reactions to produce H_2O_2 (Eqs. 1.10, 1.11, 1.12 and 1.13) [78, 79]. Meanwhile, the as-generated

H_2O_2 can also produce the highly reactive •OH by reduction or cleaving (Eqs. 1.14 and 1.15) [80–82].

$$O_2 + e_{cb}^- \rightarrow \bullet O_2^- \quad (1.10)$$

$$H_2O + \bullet O_2^- \rightarrow \bullet OOH + OH^- \quad (1.11)$$

$$2 \bullet OOH \rightarrow O_2 + H_2O_2 \quad (1.12)$$

$$\bullet OOH + H_2O + e_{cb}^- \rightarrow H_2O_2 + OH^- \quad (1.13)$$

$$H_2O_2 + e^- \rightarrow \bullet OH + OH^- \quad (1.14)$$

$$H_2O_2 \rightarrow \bullet OH + \bullet OH \quad (1.15)$$

During the overall photochemical process, the photo-generated e^-/h^+ and the produced ROSs such as •OH, $\bullet O_2^-$, •OOH and H_2O_2 are suggested to be responsible for the oxidation of organic pollutants, including synthetic dyes and pathogenic microorganisms in aqueous media. The importance of •OH as the oxidation agent was particularly attended by researchers in this typical mechanism model of photocatalytic oxidation in UV irradiation TiO_2 systems [38, 83, 84].

1.4.2 Photocatalytic Water Disinfection

Photocatalysis was first shown to be an effective disinfection process by Matsunaga et al. (1985) [53], who reported on the inactivation of *Lactobacillus acidophilus*, *Saccharomyces cerevisiae* and *Escherichia coli* by Pt-loaded TiO_2. Since then, a concerted range of research has been conducted on the development of photocatalysis for water disinfection. Photocatalytic disinfection of a wide range of bacteria and yeasts including *Escherichia coli* [85, 86], *Candida albicans* [87], *Enterococcus faecium*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* [24], *Streptococcus faecalis* [88], *Streptococcus mutans* [89], *Salmonella choleraesuis*, *Vibrio parahaemolyticus* and *Listeria monocytogenes* [90] as well as poliovirus [91] has been reported. The inactivation of the protozoan of *Cryptosporidium* and *Giardia*, known for their resistance to many chemical disinfectants, including chlorine, was also reported in recent years [92–94].

As the archetypical photocatalyst for water splitting and organic compounds degradation, TiO_2 also holds the preponderant position in water disinfection for destruction of various microorganism including bacteria (both Gram-negative and Gram-positive), fungi, algae, protozoa and viruses as well as microbial toxins [56]. Table 1.1 shows the typical examples of TiO_2 photocatalysis for microorganism inactivation. For all the inactivation of microorganism reported so far, only *Acanthamoeba* cysts and *Trichoderma asperellum* conidiospores were found to be resistant to photocatalysis [95, 96]. There are three crystal phases of TiO_2: anatase, rutile and brookite, in which anatase shows the highest photocatalytic activity [97].

Table 1.1 Typical examples of microorganism inactivation caused by TiO_2 photocatalysis [56]

Microorganism	Photocatalysts	References
Bacteria (Gram-negative)		
Escherichia coli	Degussa P25 suspension	[98]
Escherichia coli	TiO_2-impregnated cloth filter	[99]
Enterobacter aerogenes	Degussa P25 suspension	[100]
Flavobacterium sp.	TiO_2-coated glass beads	[101]
Fusobacterium nucleatum	Anatase TiO_2 thin film	[102]
Pseudomonas aeruginosa	TiO_2-coated soda lime glass and silica tubing	[103, 104]
Legionella pneumophila	Degussa P25 suspension	[105]
Porphyromonas gingivalis	TiO_2 sol/gel-coated orthodontic wires	[106]
Vibrio vulnificus	TiO_2-impregnated steel fibres	[107]
Bacteria (Gram-positive)		
Actinobacillus actinomycetemcomitans	TiO_2 coated on Ti substrates	[102]
Bacillus cereus	TiO_2 suspension	[108]
Streptococcus cricetus	Kobe Steel TiO_2	[109]
Streptococcus mutans	TiO_2 thin film	[110]
Clostridium difficile	Evonik Aeroxide P25 thin film	[111]
Clostridium perfringens spores	Degussa P25 suspension	[112]
Bacillus subtilis endospore	TiO_2 coated on Al foil	[113]
Fungi		
Aspergillus niger	TiO_2 coated on wood	[114]
Aspergillus niger spores	Degussa P25 film on quartz discs	[62]
Candida famata	TiO_2-coated catheters	[115]
Candida albicans	TiO_2 thin film	[24]
Penicillium citrinum	TiO_2-coated air filter	[116]
Trichoderma asperellum	TiO_2-coated concrete	[96]
Protozoa		
Cryptosporidium parvum	Nanostructured TiO_2 films	[117]
Giardia sp.	Fibrous ceramic TiO_2 filter	[94]
Giardia lamblia	TiO_2 thin film	[118]
Acanthamoeba castellanii	Degussa P25 suspension	[95]
Algae		
Cladophora sp.	TiO_2-coated glass	[119]
Chroococcus sp.	Anatase TiO_2	[120]
Oedogonium sp.	TiO_2-coated concrete	[121]
Melosira sp.	TiO_2-coated glass	[122]
Virus		
Influenza A/H5N2	Degussa P25/TiO_2 Millennium PC500	[123]
E. coli coliphage	Degussa P25 suspension	[112]
E. coli MS2	TiO_2 suspension	[124]
E. coli λ vi	Degussa P25 suspension	[125]
Influenza A/H1N1	TiO_2 suspension	[126]

(continued)

Table 1.1 (continued)

Microorganism	Photocatalysts	References
Influenza A/H3N2	TiO_2/Pt-TiO_2	[127]
SARS coronavirus	Titanium apatite filter	[128]
Toxins		
Brevetoxins	Degussa P25 suspension	[129]
Microcystins LR, YR and YA	Degussa P25 suspension	[130]
Nodularin	Degussa P25 suspension	[131]

However, the most active and commercially available TiO_2 is P25 (Degussa Ltd., Germany), consisting of 80 % anatase and 20 % rutile. The improved activity of mixed crystal phases is generally ascribed to interactions between the two forms, thus preventing bulk recombination. For catalyst immobilization, TiO_2 is often coated on various supports, including glass plate, cloth filter, steel substrates, silica, wood, catheter, concrete, etc.

Although exciting progress has been made in TiO_2 photocatalysis for microorganism disinfection, challenges still pose in achieving photocatalytic water disinfection utilizing solar energy. Unfortunately, the most widely used TiO_2 is only active under UV irradiation which accounts for only 4 % of the sunlight spectrum, while 45 % of the sunlight spectrum is visible light. TiO_2 modification techniques have been attempted to shift its light absorption capacity towards visible wavelengths, while considerable scientific interests have been devoted to the development of new types of photocatalyst that is active under visible light irradiation. This opens avenue for designing and fabricating nanostructured materials that can be used in photocatalytic water disinfection by employing material science and nanotechnology [132–134].

1.4.3 Advances in Photocatalytic Disinfection

In this book, some of the key development of photocatalytic disinfection in the last decade will be presented and discussed. The use of naturally occurring minerals or novel synthetic catalysts for effective microbial disinfection will be compiled. In addition, the mechanism, catalysts and performance of microbial disinfection by photoelectrocatalytic process will be presented and discussed. Finally, how to apply modelling approaching to study the kinetics of the photocatalytic disinfection will be included in this book. With all these updated information, the useful information and data will be provided to the people in academic, engineering and technical sectors.

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