DISINFECTION FOR WATER SYSTEM USING NEW ELECTROLYTIC SYSTEM

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CERTIFICATION OF ORIGINALITY

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_____(Signed)

PAN YUELING (Name of the student)

ABSTRACT

The land area of Hong Kong is 1104 km^2 and the population reaches nearly 7 million. Severe environmental problems raised up because of concentrated economic activities, population growth, and lack of pollution control. In this paper, a theoretical basis and practical evidence for the application of new electrolytic system on the water treatment are provided. These experimental results are expected to be helpful for the process design of water treatment system and reduction of the water pollution.

This thesis compiles the works carried out to develop a RuO_2 electrolytic and TiO_2 photocatalytic system for water disinfection system. A RuO_2 electrolytic and TiO_2 photocatalytic integrated water disinfection system was developed to disinfect swimming pool water, fountain water and flashing water. This relatively compact system enables water disinfection without having to resort to conventional chlorine dosing, which is costly and poses potential health hazards to the public. The electrolytically generated free chlorine could achieve a stable 1-3 mg/L residual level that could effectively produce a bacterial reduction which was equivalent to more than 99 % bacterial removal as required by local

legislation. These results, when translated into absolute figures for specific pathogenic bacteria, represented an extremely promising 99.9 % of *Escherichia coli* and a 100 % *Cholera vibrio* removal. Furthermore, a stable 100 % pathogenic destruction was achieved at a relatively short treatment time of 60 minutes and relatively low operational electro-potential of 30 volts. The pilot-scale system was installed, monitored and assessed on a long-term basis at Harbour Place, Hung Hom. The technology for water treatment was tested on-site rigorously in order to demonstrate its stable treatment performances, long-term reliabilities and maintenance requirements.

The Ruthenium Dioxide coated electrolytic disinfection system has been very effective in treating and disinfecting water in water features in residential estates. The effectiveness and stability of electrolytic disinfection mechanism and process have been optimized. The system will also be tested and proven in treating saline water, domestic and commercial toilet flushing water to remove the pathogens.

Keywords: Electro-photo disinfection system; Water treatment; Free chlorine; Bacterial removal

LIST OF PUBLICATIONS

Journal

[1] C.W. Kan, Y.N. Pan and H. Chua, "Effect of Electric Voltage on the Photocatalytic Oxidation Disinfection of Water Used in Real Estate", *International Journal of Environmental Science and Development*, Vol. 6, No. 2., 118-121, April (2015).

Conference

[1] C.W. Kan, Y.L. Pan and H. Chua, "Effect of Operating Parameters on the Photocatalytic Oxidation Disinfection of Swimming Pool Water", *Book of Abstract of 2014 International Conference on Energy and Environmental Engineering (ICEEE 2014),* Regal Riverside Hotel, Hong Kong, May 20-21, 2014, pp.2.

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ABBREVIATION	DESCRIPTION
AOPs	Advanced Oxidation Processes
COD	Chemical oxygen demand
D.C.	Direct Current
DO	Dissolved oxygen
EA	Electron acceptor
INETI	Instituto Nacional de Engenharia, Technologia Industrial
LeH	LangmuireHinshelwood
LCA	Life cycle assessment
MPG	Methyphenylglycerine
MF	Microfiltration
MV	Multi-variable
NTU	Nephalometric turbidity units

NF	Nanofiltration
PMRs	Photocatalytic membrane reactors
PCO	Photocatalytic oxidation
PZC	Point of zero charge
PSA	Plataforma Solar de Almeria
SODIS	Solar disinfection
TOC	Total organic carbon
UF	Ultrafiltration
UV	Ultraviolet
WPCO	Water Pollution Control Ordinance

Chapter 1: Introduction

1.1 Water Environment in HK

Hong Kong has a high population density, especially around the Victoria Harbour, which is 1000 residents per hectare. BecauNose of the economic activities, population growth, and ignorance of pollution control in the past, severe environmental problems have raised up. In the beginning of 1990s, less than 50% waste water received proper treatment and entered the coastal waters either directly or indirectly via stream. Pollutions such as oil, persistent, grease, recalcitrant synthetic materials, and heavy metal pollutants accumulated, which had negative effects on aquatic and marine ecological system.

In order to reverse this situation, Hong Kong has made a lot of efforts to improve its water quality. A series of ordinances and management plans have been established to fight against water pollution, such as the Water Pollution Control Ordinance (WPCO). Nowadays, 98% of the waste water generated in Hong Kong have been treated. The deterioration in water environment is efficiently controlled in the whole territory.

1.2 Current Water Treatment Technologies

In order to treat waste water more effectively, more reliably, more economically and safely, many novel water treatment technologies have been developed. The conventional ceramic and polymeric water treatment membrane materials can be enhanced by nanotechnology. There have been a lot of concepts proposed, including hybrid inorganic–organic nanocomposite membranes, aligned nanotube membranes, isoporous block copolymer membranes, and catalytic nanoparticle coated ceramic membranes. The new technologies are proposed to improve water permeability and operational robustness, while reduce the scalability, costs, and compatibility. The problems lies in that, some kinds of improved membranes offer excellent performance enhancements but seems be quite far from commercial reality.

In comparison with some tradition water treatment technologies, such as disinfection and distillation, which have chemical additives and thermal inputs, membrane treatment has its unique advantages. The membrane treatment can offer selective, efficient, and reliable separations

In the past few decades, many methods have been developed to drive the membrane separation processes, such as evaporation, electrochemical and pressure-driven membrane processes. For water treatment applications, pressure-driven membrane processes is the most commonly used membrane technologies. According to pore size or intended applications, the membranes are classified into several types. Microfiltration

(MF) is used for the removal of suspended solids, protozoa, and bacteria removal, ultrafiltration (UF) is used for virus and colloid removal, nanofiltration (NF) is used the removal of dissolved organic matter, heavy metals, and hardness, and reverse osmosis (RO) is used for ultrapure water production, water reuse and desalination. In order to improve the treatment effectiveness and economy of the membranes for water, their selectivity, stability available, productivity, fouling resistance should be further enhanced and the fabricating cost and manufacturing defects should be further reduced.

1.3 New Disinfection System

In order to destruct disease-causing organisms, disinfection is one of the indispensable processes in water treatment system. There are a few methods to accomplish disinfection including physical membrane filtration methods, microwave radiation, chemical disinfection agents, and mechanical ultrasonic means. Because of the high disinfection power and relatively low costs, chlorine disinfection is the most traditional and commonly used water treatment technology all around the world. Chlorine has been widely used for disease-causing organisms destruction. Chlorine gas, chlorine dioxide, sodium hypochlorite, and calcium hypochlorite are the most common used chlorine compounds in water treatment process. Previous studies have proved the high biocidal efficiency of chlorine against bacterial pathogens and viral.

There was Sodium-chloride (NaCl) in the water, reaction take place:

$NaCl+H_2O<=>Na^+ + OH^- + Cl_2 + H_2$

When chlorine in the form of Cl_2 gas is added to water, two reactions take place: ionization and hydrolysis:

$Cl_2 + H_2O <=> HOCl + H^+ + Cl^-$

$HOCl <=> H^+ + OCl^-$

The quantity of OCl^- and HOCl in water is the free chlorine and is the primary disinfectant employed. The disinfection efficiency of HOCl is about 40 to 80 times compared with OCl^-.

When water and waste water contain nitrogen in the form of ammonia and various combined organic forms, HOCl will react with ammonia in the water and three types of chloramines will form as follows:

$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$

$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$

$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$

These chloramines also serve as disinfectants, although they are extremely slow-reacting compared to hypochlorous acid. Common disadvantages of using chlorine for

disinfection include high operating and chemical costs, uncontrolled accumulation of ionic chemicals in the pool water, and potential health hazards (suspected carcinogenicity and mutagenicity) of tri-halomethanes.

Though chlorine gas (Cl_2), sodium hypochlorite (NaOCl), and calcium hypochlorite ($Ca(OCl)_2$) are the common disinfectant used in water and waste water disinfection, aqueous solution of sodium hypochlorite has more and more applications in water treatment, considering the safety for usage, storage and transportation of the disinfectant.

Basically, an industrial grade of sodium hypochlorite solution is used for the chlorine disinfection in fountain water system and flushing water system, the maximum concentrations of the solution is up to 12 % by weight chlorine. However, there are some problems using sodium hypochlorite solution, the problems include the accessibility of sodium hypochlorite in some places and expensive transportation costs. Moreover, the high concentration of sodium hypochlorite solution is lack of stability, the higher hypochlorite concentration and storage temperature is, the higher rate of concentration decays will be. In order to mitigate the problem of decay of concentration, the solution can be diluted to low-concentration solution (0.8% chlorine concentration).

Chlorine disinfection disadvantage:

1. Accessibility of sodium hypochlorite in some places and expensive transportation costs.
2. High concentration of sodium hypochlorite solution is lack of stability, the higher hypochlorite concentration and storage temperature is, the higher rate of concentration decays will be.
3. High operating and chemical costs, uncontrolled accumulation of ionic chemicals in the pool water, and potential health hazards of tri-halothanes.

Photocatalytic oxidation (PCO) disinfection:

The electro-activation technology capitalizes on a special coating technique of a specifically designed formula of ornamented titanium dioxide on D.C. electrodes. The electrically activated coated surfaces transform naturally occurring chloride ions in water into activated chlorine with effective disinfecting power. This technology has been modified into a compact system that has small footprint, low power consumption, no chemical addition requirement, fully automatic operation, stable and reliable water disinfection system.

Secondly, photocatalytic oxidation (PCO) component in the system utilizes TiO_2 as a photocatalyst to generate oxidation/reduction reactions. When a photo catalyst medium is exposed to radiation of ultraviolet rays, electrons will be set free from the TiO_2 coating

and positively charged pockets called “positive holes” will generate. The hydroxide ions (OH^-) will be attracted by positive holes from ambient water. The hydroxide ions will give out electrons to the positive holes and turn into an extremely unstable hydroxyl radicals. The hydroxyl radicals will take electrons from nearby organic pollutants. This process breaks up organic compounds, including viruses and bacteria, and degrades them into carbon and water.

1.4 Objectives

Most current research on treating drinking water by AOPs is limited to theoretical research and lack of enlarged experimental progress. This thesis focused on the optimal treatment condition, the optimal treatment time and some important factors that could possibly affect the reaction process in an enlarged experimental treatment system and aims to provide data for the application of AOPs in drinking water disinfection field. Artificial water experimental water and natural water of various quality are being treated by disinfection under different reaction path, reaction time and concentration of reactant.

The objective of this study is to assess the formation and the disinfection efficiency of the free chlorine, which is generated by a novel integrated water disinfection system electrolytic system.

The specific objectives of this study are as follows,

1. To determine disinfection efficiency of electrolytic system and TiO_2 photocatalytic system;

2. To determine the effects of various operating parameters on the treatment performances and optimize the parameter;

3. To study the treatment performances and long term stability of the system in onsite operations.

1.5 Organization of the Thesis

This thesis is divided into six chapters. The present chapter includes introduction of water environment in Hong Kong, current water treatment technology, and objectives of this study. A detailed literature review is presented in Chapter Two. Chapter Three introduces the methodology of this research. Chapter Four studies the effects of various operating parameters on the treatment performances and optimize the parameter. Chapter Five concentrates on the study of treatment performances and long term stability of the system in onsite operations. Finally, Chapter Six gives a general conclusion of this study.

Chapter 2: Literature review

2.1 Background

With growing of population worldwide, the shortage of water resource become more and more critical. For this reason, various practical strategies have been adopted to get access more viable water resources. Researches have reported that around 4 billion people all around the world have no or little access to clean water. Every year, millions of people died because of severe waterborne diseases (Malato *et al*., 2009). The situations are expected to become worse in the future, as the continuous discharge of micropollutants and contaminants into the natural water bodies (Wintgens *et al*., 2008; Richardson, 2008; Suarez *et al*., 2008). In order to reverse this condition, it is critical to develop advanced water treatment technologies, which should both meet high efficiency and economy.

The reuse of treated rural municipal wastewater for the use of agricultural and industrial activities becomes one of a few attractive options (Bradley *et al*., 2002). Among the various water treatment technologies, disinfection was one of the most important one, which could ensure the effluent quality.

There are two kinds of disinfection methods such as chemical and physical processes. The chemical and physical disinfection processes have their own advantages and disadvantages. For the chemical disinfection, it has been proved to have a higher reliability and efficiency. It ensures extermination of microorganisms and prevents the

disinfected water from recontamination for a certain time. However, the chemical disinfection has also some non-ignorable drawbacks. The side-reactions between the disinfectants and some pollutions in water and the disinfection byproducts are unwanted. Moreover, producing, handling and transporting a large quantity of disinfectants such as ozone and chlorine have also potential danger.

For physical disinfection processes, membrane separation filtration, ultrasound, irradiation and heating are adopted to remove or kill microorganisms in water. The physical disinfection has no side-reactions and no byproducts will be produced. However, the disinfection effect cannot last and the microorganisms could obviously emerge again soon.

In order to conquer the disadvantages of chemical disinfection, electro-disinfection has been developed as a technology to sanitize wastewater. It could also inactivate microorganisms with lower chlorine concentration and produce less chlorinated disinfection byproducts (Issa-Zacharia 2010). Originally, the primary interest of the electrochemical technology for the sewage treatment was deodorizing and disinfection wastewater by electrolytic generated chlorine.

The electrochemical water disinfection has arrived at technical maturity only recently because of a few reasons. Firstly, sufficiently stable and efficient electrode materials such

as titanium electrodes with mixed oxide coatings based on iridium and/or ruthenium oxide, doped diamond electrodes for electrochemical water disinfection have been developed and optimised only in the last forty years. Secondly, the effects of chloride concentration in the water, electrode material, current, current density and water quality on disinfecting action have been investigated in detail only recently. Thirdly, only a few electrochemists have been interested in this topic. The mechanism of the process is usually lack of scientific explanations. (Bradley *et al*., 2002)

Although there is no addition of chemical compounds added into water during electrochemical disinfection, the mechanism of disinfection is nevertheless founded on the biocidal effects of various chemical substances. Previous study has proved that, *E. coli* cells are killed electrochemically while no noticeable chlorine species are induced (Matsunaga *et al*., 1985).

As mentioned above, water is an important resource for the subsistence of the mankind. While safe drinking water, in particular, imposes direct influence on our health. Faced with increasingly serious water pollution, current regular treatment on drinking water usually cannot handle issues such as low killing rate of micro-organism, side effects of disinfectant on human health and secondary pollution caused by disinfection process. "Advanced Oxidation Processes (AOPs)" are new oxidation technologies which take advantage of highly activated Hydroxyl Radical (·OH) to analyze harmful subsistence. This technology has broad-spectrum bactericidal features, the speed of killing

microorganism is extremely fast. It is a new generation disinfection technique for drinking water that avoids by-products and secondary pollution.

2.2 Electrochemical Disinfection

There are different types of electrochemical disinfection. Alternating current (AC) with a frequency of 0.5 to 800 Hz as well as direct current (DC) has been used (Patermarakis and Fountoukidis, 1990). Diffrent kinds of electrode such as titanium, diamond, carbon-cloth, silver, stainless steel, platinum, and graphite fibers were in a polymer matrix. In order to increase the effectiveness of disinfection, additives such as NaCl and NaBr will be sometimes added.

There are some parameters that could affect the effectiveness of electrochemical disinfection, such as energy input, water quality, and nature of the electrodes. Previous studies have demonstrated a high disinfection efficiency of the electro-disinfection process within a short contact time for treated wastewater effluent, raw water supply, and potable water (Li *et al*., 2012).

During the electrochemical disinfection, microorganisms can be inactivated through the electric fields as well as the generated active chemical species, including $OH^{\cdot}$, $HO_2^{\cdot}$, Cl_2, OCl^-, etc. The inactivation by electric fields is based on its destruction effect to

microorganisms' cells and electrosorption of bacteria on the electrode surface and their subsequent destruction (Drees *et al*., 2003). At the same time, the electric current could produce disinfecting species such as ozone from the water itself, and free chlorine, which is the oxidative product of dissolved chloride in the water at the phase boundary between the electrodes and the water.

Previous studies also found that the two kinds of electrochemical disinfection, namely direct and indirect routes cannot always be separated during disinfection process. Electro-disinfection is actually quite complex and both parts play significant role. The different kinds of disinfective process are as the followings (Patermarakis and Fountoukidis, 1990).

1. When the adopted voltage is low (5-15V), the disinfection effect may be achieved by generated active chemical species, such as $OH^{\cdot}$, $HO_2^{\cdot}$, Cl_2, OCl^{-}, etc. Hydroperoxide ions and hydroxyl radicals are very unstable but very effective for disinfection.

2. The effect of electric fields: the electrical field directly could causes the electrocution of microorganisms. The electrochemical oxidation can destruct intracellular Coenzyme A (CoA) and decrease their respiration to kill them (Matsunaga *et al.*, 1985).

3. When carbonate and sulphate ions contain in the water, they could be oxidized at to form percarbonate and persulphate. They are also very effective for the disinfection.

4. When transition metal ions such as copper and silver are used as the electrode material, they may be dissolved into the solution and be responsible for disinfection.

The active oxygen compounds produced at the electrodes is also the effective disinfectant. Moreover, it help to reduce the formation of disinfection byproducts (DBP) such as THM, which are formed during the conventional chlorine disinfection. The mechanism of advanced oxidation processes (AOP) in drinking water treatment to oxidize DBP precursors is shown in Fig. 2.1.

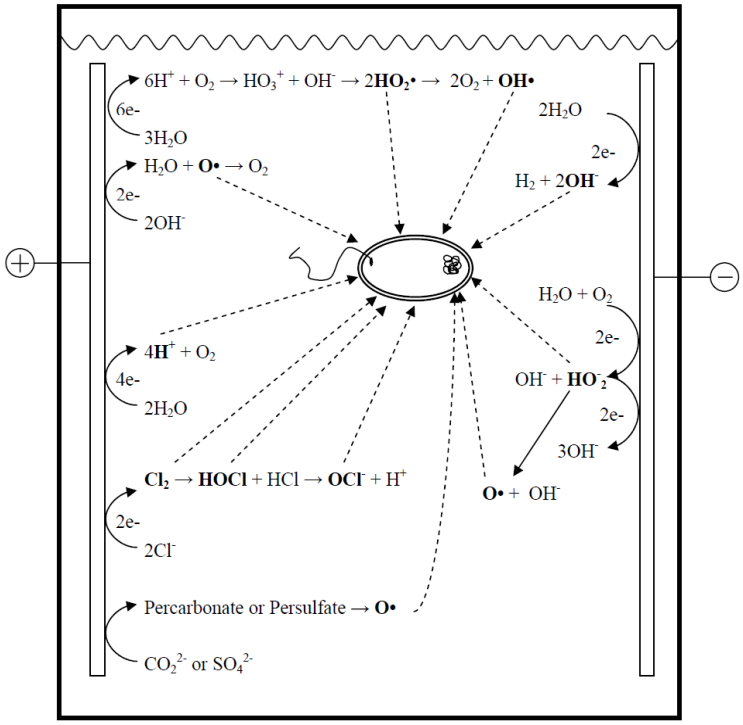


Figure 2.1 Mechanism of advanced oxidation processes (AOP) with the presence of water pollutant (P) (Drees *et al*. 2003)

When the chloride content exists in the water, the productions through electrochemical reaction is hypochlorite and/or hypochlorous acid, which is the active substance for

disinfection. The hypochlorous acid/hypochlorite is produced at the anode in a side reaction to oxygen evolution. The reaction mechanism is as follows:

1. The chloride ions dissolved in the water are electrochemically oxidised and the chlorine is produced:

$2Cl^- \rightarrow Cl_2 + 2e^-$

2. Chlorine hydrolyses in water and then hypochlorous acid (HClO) is formed:

$Cl_2 + H_2O \rightarrow HClO + HCl$

3. A pH-dependent equilibrium is formed between hypochlorous acid and the hypochlorite anion:

$HClO \leftrightarrow ClO^- + H^+$

In the nomenclature of water disinfection, the sum of concentrations is usually termed. The “free chlorine” or “active chlorine”, which is consist of hypochlorous acid and hypochlorite, will release atomic oxygen, and it is responsible for disinfection. The reactions are as follows

$HClO \rightarrow O + Cl^- + H^+$

$ClO^- \rightarrow O + Cl^-$

As shown in the above mentioned reactions, the chloride ions will be consumed and the free chlorine or active chlorine will be reproduced during the disinfection. Therefore, the chemical compositions in the treated water will not change dramatically.

When drinking water is disinfected by electrochemical process, the current efficiency of the electrode material is of great importance, considering that the concentration of chloride in the water is low and it is relatively difficulty to produce the free chlorine. A lot of materials can be used as the electrode materials. Stainless steel, carbon reticulated vitreous, graphite, carbon cloth, and copper are suitable for Cathode; Tantalum, platinized titanium or niobium, nickel, graphite, silver, carbon, metal oxides, copper, and monel are suitable for anode. Moreover, Electrocatalytic materials, such as titanium oxide (TiO_2), mixed iridium oxide (MIO), ruthenium oxide (RuO_2), can be incorporated into electrodes (Fernández et al., 2003).

There have already been some electrochemical disinfection systems that are currently available in the market. Among them e-GreenWater is an electrolytic disinfection system which enables the reuse of the process water (drain water) with nutrients in greenhouses. By using this system, effective inactivation of germs, virus and fungi can be achieved without disinfectant addition. Thus the treated water is especially suitable for irrigation of the plants considering their roots and leaves are sensitive to chemical disinfectants or biocides. However, in order to broaden its application in greenhouses for vegetables and

floriculture, there is still a long way to go. More e-GreenWater systems are expected to be installed in the future.

OMNIPURE™ Series 55/64 systems could be adopted for the marine sewage treatment. This system oxidizes sewage through an electrolytic process as well as generates sodium hypochlorite for the disinfection of the sewage streams. It offer effective electrolytic treatment of both black and gray water while providing a safe and sanitary method of handling solids. The treatment capacity of this system reaches 65 m^3/day in maximum and increased capacity can be achieved by combination of the system. The water quality of treated wastewater by the system reaches the MEPC.227(64) requirements. Moreover, this system is Easy to install, operate and service, has lightweight package, and requires no additional tanks or filtration equipment.

Figure 2.2 OMNIPURE™ Series 55/64 systems

A micro-electrolysis system for swimming pool disinfection has been developed by Shanghai Sciyee Water Sci.&Tech. Co.,Ltd. This system can achieve water sterilization and purification without any chemical disinfectants. The micro-electrolyzed water have sustainable bacteriostatic effect. The bacteriostatic action can last 48 hours, because of the oxidizing material in the outlet of the generator and the physical change of the water molecule under the lower electric field. Such technology can thus perfectly substitute the ozone and disinfector.

Takenaka Corporation has developed a practical automatically controlled hot spring water electrolysis disinfection system, which was shown in Figure 2.3.

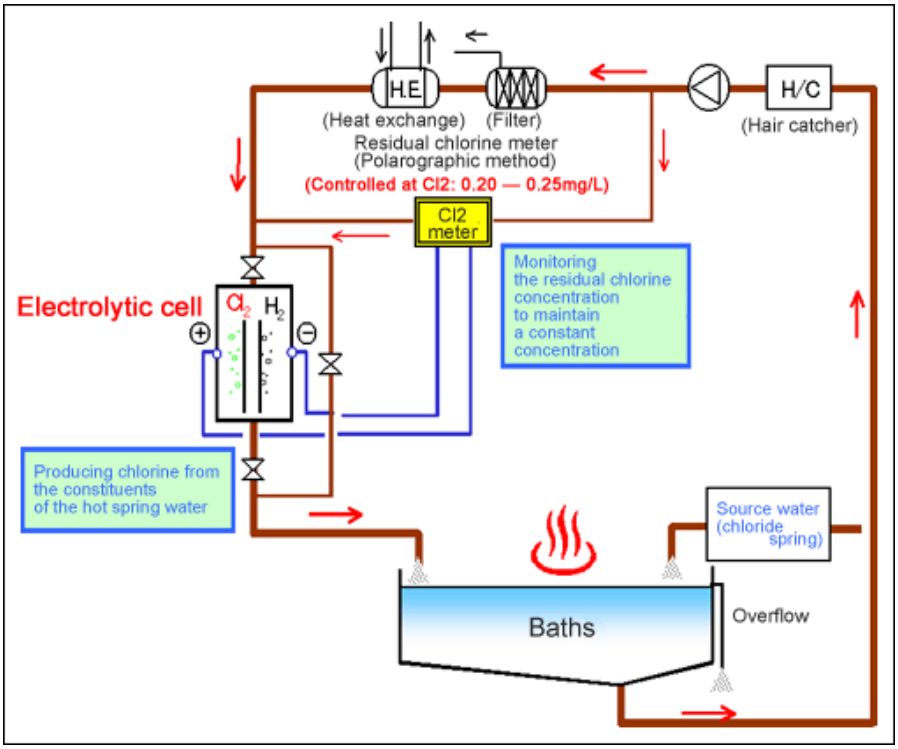


Figure 2.3 Automatically controlled hot spring water electrolysis disinfection system

The system automatically controls the residual chlorine concentration at a uniform level, simplifying operation and maintenance, and holding down the running costs, electricity charges, etc. It has been installed at the Atami Korakuen Hotel and operated for more than three years. It has been proved that the system effectively disinfects the hot spring water while maintaining the residual chlorine concentration between 0.2 and 0.4 mg/L.

2.3 Photocatalytic Disinfection

2.3.1. Fundamentals and Mechanism of TiO_2 Photocatalysis

As already mentioned, more and more countries nowadays have irrigation and drinking water supply problems. The water bodies are polluted by hazardous chemicals as well as by pathogenic microorganisms. The water has to be disinfected before use. Chlorination, which is the mostly used technology has also some negative effect. For example, the free chlorine can react with organic matter in water and trihalomethanes (THMs) as byproducts will be produced. THMs makes drinking water unpleasant to taste. In addition, chlorine is often phytotoxic when the treated water is used for irrigation. Under this circumstance, heterogeneous photocatalysis with TiO_2 as the photocatalysis, which is clean, low-cost, can offer us an additional option for water disinfection. (Akira *et al*., 2000)

Most of the knowledge about TiO_2 photocatalysis was gained during the development of semiconductor photoelectrochemistry during the 1970 and 1980s. As far as we know, during the photocatalytic processes, the oxygen plays a role as oxidizing agent and the semiconductor metal oxide as the catalyst. The photocatalytic reaction mechanism was shown in figure 2.2. Intensive researches have been carried out to obtain modified semiconductor metal oxide with higher quantum yield and broader absorption spectrum. Among the variety of catalyst, titanium dioxide could be one of the most important in environmental photocatalysis because of its availability, economy, highly chemical stability, and high efficiency.

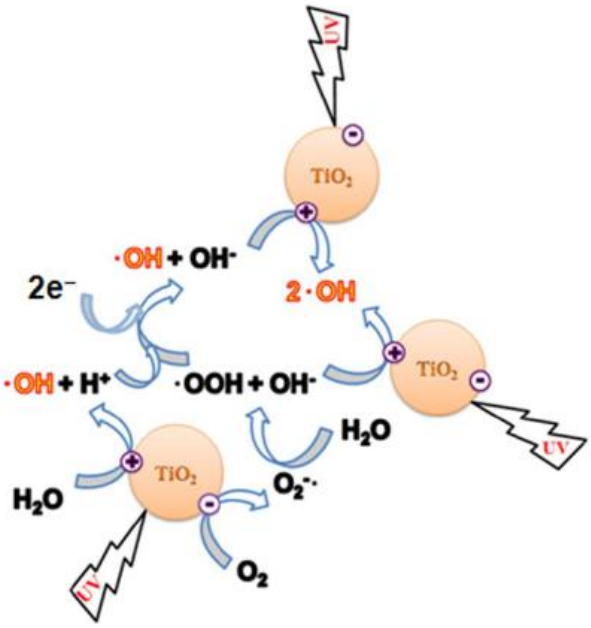


Figure 3.4 Photocatalytic generation of hyfroxyl radicals (Lazar *et al.*, 2012)

In recent years, TiO_2 photocatalysis for disinfection has attracted much attention. Previous works found that the hydroxyl radicals produced during the photocatalysis reaction will attack the cell membrane by peroxidation of the polyunsaturated

phospholipid component of the lipid cell membrane leading to a loss of essential cell functions, e.g., respiratory activity, and in the end, to cell death (Sichel *et al*., 2007).

Photocatalytic disinfection can be affected by light intensity, catalyst physicochemical properties and concentration, temperature, microorganism type and concentration, and exposure time. (Fujishima *et al*., 1972).

2.3.2. Advancements in Photocatalyst Immobilization and Supports

Since the discovery of great photocatalytic performance using TiO_2 electrode to water disinfection, a lot of works has been done to prepare TiO_2 catalyst. The physical properties and photooxidation performances were also determined (Fujishima and Honda, 1972; Hosono *et al*., 2004; Joo *et al*., 2005). The nano-scale TiO_2 catalyst, which has a large surface area-to-volume ratio, has normally better photocatalytic performance (Nagaveni *et al*., 2004a,b). However, The post-treatment separation is needed, which is quite expensive on a large scale (Li *et al*., 2012). Loading TiO_2 film on a substrate is an option to avoid the expensive and inconvenient post-treatment process. The substrates can be variety such as graphite (Rahmawati *et al*. 2011), titanium plate and titanium metal mesh (Harper *et al*. 2001), activated carbon (Viessman, 1998), or titanium foil (Dunlop *et al*. 2002).

2.3.2.1. Nano-size TiO_2 for water and wastewater treatment

There are lots of studies reported the use of nano-size TiO_2 as the photocatalysts. During the photooxidation process, continuous stirring of the TiO_2 suspensions is required to ensure effective contact between TiO_2 and target species. This method has been proven to be effective in inactivation of a variety of bacteria and viruses, such as *MS2 bacteriophage, hepatitis B virus, poliovirus 1,* and *herpes simplex virus*. Considering the different sizes of the particles, the intensity and wavelength of the light used, the dosage of TiO_2 usually varied between 100 and 1000 ppm in order to disinfect efficiently. Wong et al. have adopted commercial TiO_2 (Degussa, P25) as photocatalysts and disinfectants to kill four Legionella pneumophila serogroup 1 strains (Strain 977, Strain 1009, Strain 1014 and ATCC 33153). The experiment was undertaken with four 43 cm 15 W Cole Parmers UV lamps with the maximum emission at 365 nm as the light source. They found that the strains was susceptible to photocatalytic oxidation inactivation except for ATCC strain, which has the different fatty acid profiles. They concluded that the amount of saturated16-carbon branched-chain fatty acid might be the key factor for PCO disinfection. Moreover, photocatalytic disinfection using fluorescence as the light source and P25 as the photocatalyst was found to be feasible and effective for marine bacteria such as *Alteromonas alvinellae* and *Photobacterium phosphoreum*. The regrowth of the bacteria could be study found that completely inhibited by this method, which is difficult for the traditional disinfection methods. When using Sonication of TiO_2 suspensions, the effectiveness of disinfection could be further improved, because more active sites on the

catalytic surface were produced and thus the reaction rate will be increased. (Zhang *et al*. 2010)

Although the suspended TiO_2 powder has preferable disinfection performance in photoreaction system compared with immobilized TiO_2 catalysts, the disadvantages of the suspension system are also obvious. The UV light penetration will be reduced by catalyst powders and the post-treatment is indispensable, in order to remove the nano-size TiO_2 after treatment. The greatest limitation of the nano-size TiO_2 in practice was the difficulties for its separation and reuse. There are two ways to solve this problem, namely reducing the difficulty of recycle for nano-size TiO_2 and improving the disinfection performance of the immobilized TiO_2 catalysts.

Amounts of works have been done to reduce the difficulty of recycle for nano-size TiO_2. Li et al. (2000) have developed a new type of nano-size TiO_2 microsphere, which was prepared via sol-spraying calcination method. This kind of microsphere can easily be seperated under gravity. Its physical characteristics were observed by SEM and XRD, which were shown in Figure 2.3.

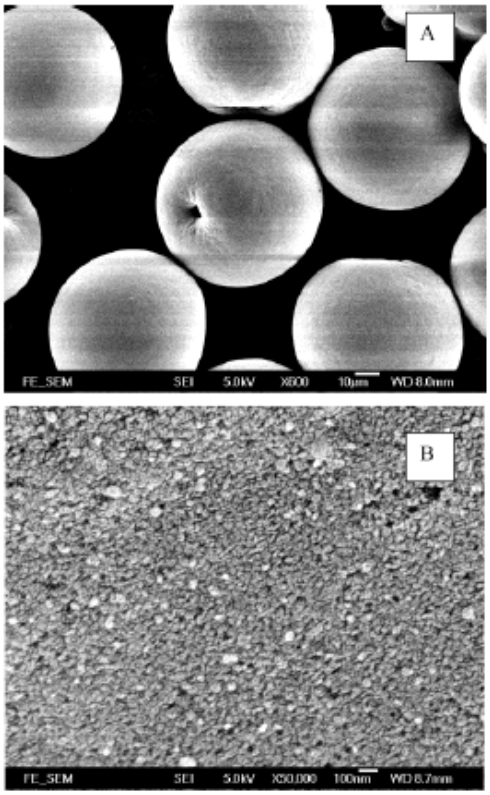


Figure 2.5 SEM image of the TiO_2 microsphere samples (Li *et al*. 2000)

As shown in Figure 2.3, the nano-size TiO_2 microsphere was almost sphere and the particle size range from 30 nm to 160 nm. Compared with the normal TiO_2 powders, this material had a higher specific surface area and pore volume, which ensured the stronger adsorption ability. The photocatalytic activity of the nano-size TiO_2 microspheres was evaluated in a designed photoreactor system, which was shown in Figure 2.4. The result showed a favourable photodegradations performance for salicylic acid (SA) and sulfosalicylic acid (SSA) and the TiO_2 microsphere could be readily recycled (Li *et al*. 2000).

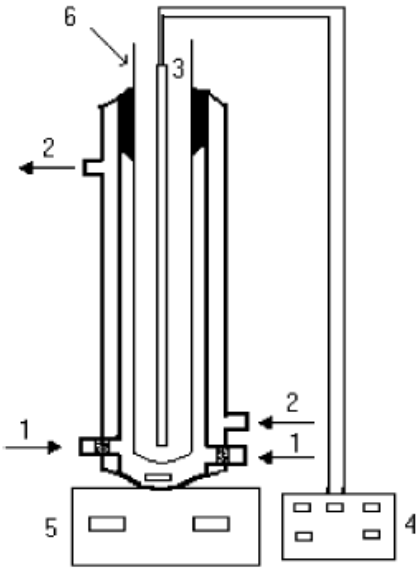


Figure 2.6 One designed photoreactor system (1-air, 2-water, 3-UV lamp, 4- timer, 5-stirrer, 6-quartz jacket) (Li *et al*. 2000)

In order to improve the treatment efficiency, heterogeneous photocatalysis can be considered to be combined with adsorption. Lazar *et al* (2012) have studied the applicability of this idea to degrade 2-CP. The result showed that the target pollutant could be efficiently enriched, removed and degraded. The combined process was a promising water treatment technology (Lazar *et al*.).

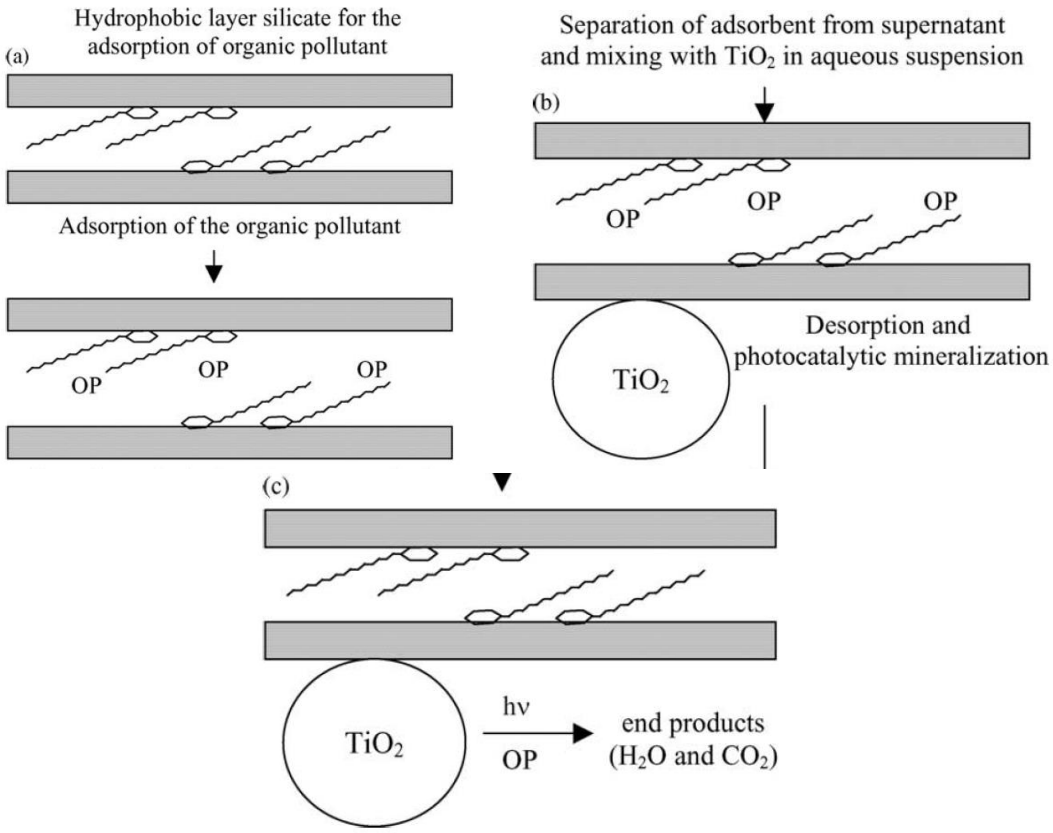


Figure 2.7 Schematic diagram for the photocatalytic degradation with the existence of adsorbent (Lazar *et al*., 2012)

Compositing TiO_2 with some substrates could not only decrease the difficulty of the recycle process, but also sometimes improve the photocatalytic performance. Wang *et al*. (2008) have prepared the MWCNT-TiO_2 composite materials through an acid modified sol–gel method. The SEM and TEM analysis showed that MWCNT was homogeneously covered by TiO_2 and there were hardly any TiO_2 nanoparticles agglomerated on MWCNT surface. Moreover, the synergy effect on the photocatalytic removal of phenol was noticed, especially in using visible light as the light resource, which related to the UV–vis absorption shift of the material to the longer wavelengths. This phenomenon was inferred to be derived from the strong interphase structure effect of both phases in the

composite material. Deshalb, the MWCNT was not only a dispersing and adsorbent agent, but also a photosensitizer. This synergy effect was proved to happen only when MWCNT and TiO_2 were successfully composited and mechanical mixture of them would not have this synergy effect. The morphology of MWCNT-TiO_2 composite materials were shown in Figure 2.6 and Figure 2.7.

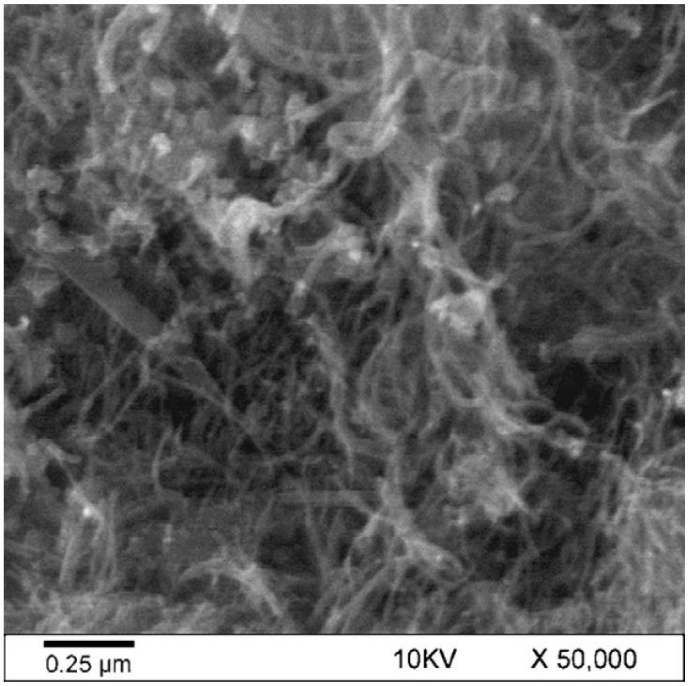


Figure 2.8 SEM image of composite material of MWCNT and TiO_2 (Wang *et al.*, 2008)

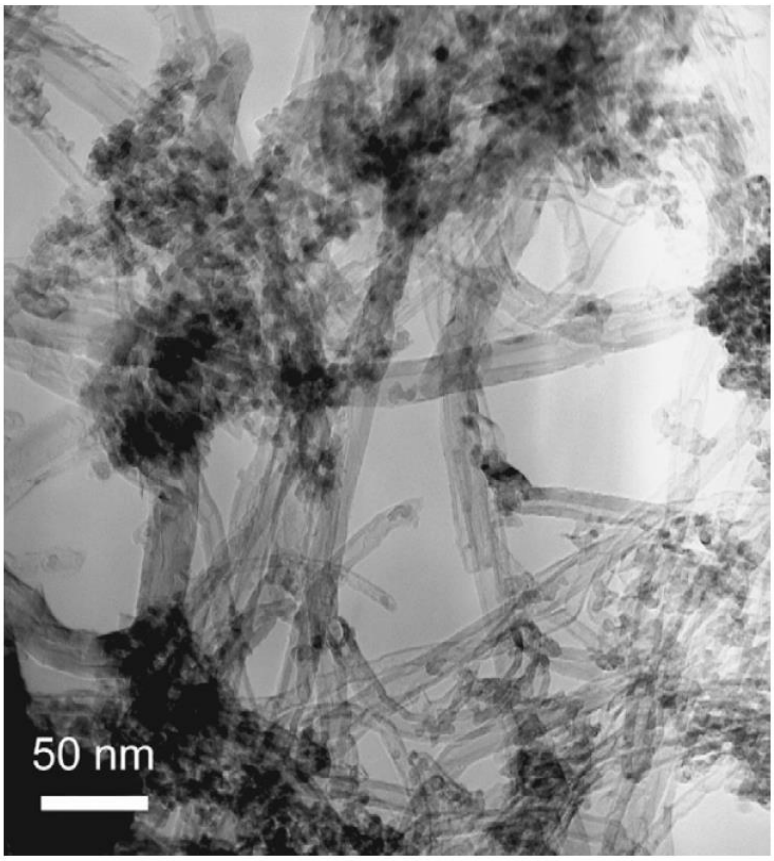


Figure 2.9 TEM image of composite material of MWCNT and TiO_2 (Wang *et al.*, 2008)

Cao *and Zhu* (2008) has prepared the R-Fe_2O_3 hierarchically nanostructured hollow spheres by thermal decomposition of a precursor, which was obtained by a facile microwave-assisted solvothermal method. The morphology of the R-Fe_2O_3 was shown in Figure 2.8. Researchers have found that this material showed a favorable photocatalytic performance for methyl orange. The enhancement of the photocatalytic property was considered to be due to the unique hierarchically nanostructured hollow structures, which were different from the ringlike nanoparticles.

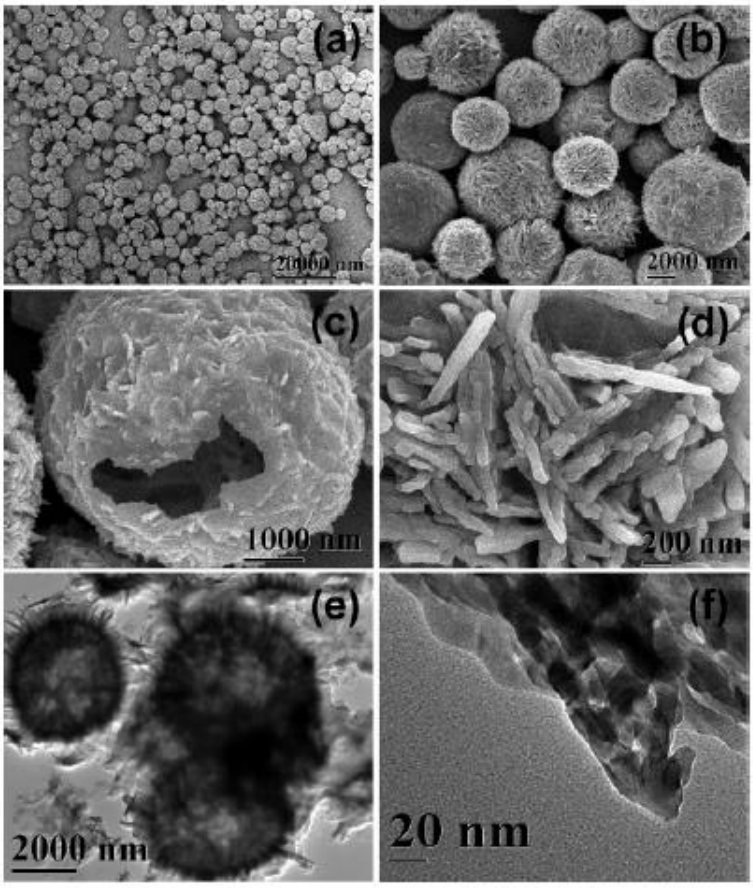


Figure 2.10 (a-d) SEM micrographs (e, f) TEM micrographs of hierarchically nanostructured R-Fe_2O_3 hollow spheres (*Cao and zhu., 2008)*

2.3.2.2. Nanochains and nanowires

Because of the favorable chemical stability and photocatalytic performance, nano-sized TiO_2 is a promising catalyst for water and wastewater treatment. However, there are some significant problems for its practical use. The nano-sized TiO_2 particles are hard to be separated, recovered and reused of because of their ultrafine particle size. Although membrane filtration such as microfiltration (MF) or ultrafiltration membrane can separate the nano-sized TiO_2 from treated water, the TiO_2 nanoparticles will soon block the pores

of the membranes and cause serious fouling of the membranes (Huang *et al*., 2007). In order to avoid this problem, a lot of works have been done to improve the practicability of TiO_2. Coating TiO_2 on inorganic membrane is one of the important improvement (Choi *et al*., 2007). Some advanced technologies have been adopted to enhance the photocatalytic activity of the immobilized TiO_2.

Zhang *et al*. (2009) have prepared two types of TiO_2 nanowires, TNW10 and TNW20 to degrade humic acid. The FESEM and TEM images of the two kinds of nanowires are shown in Figure 2.9.

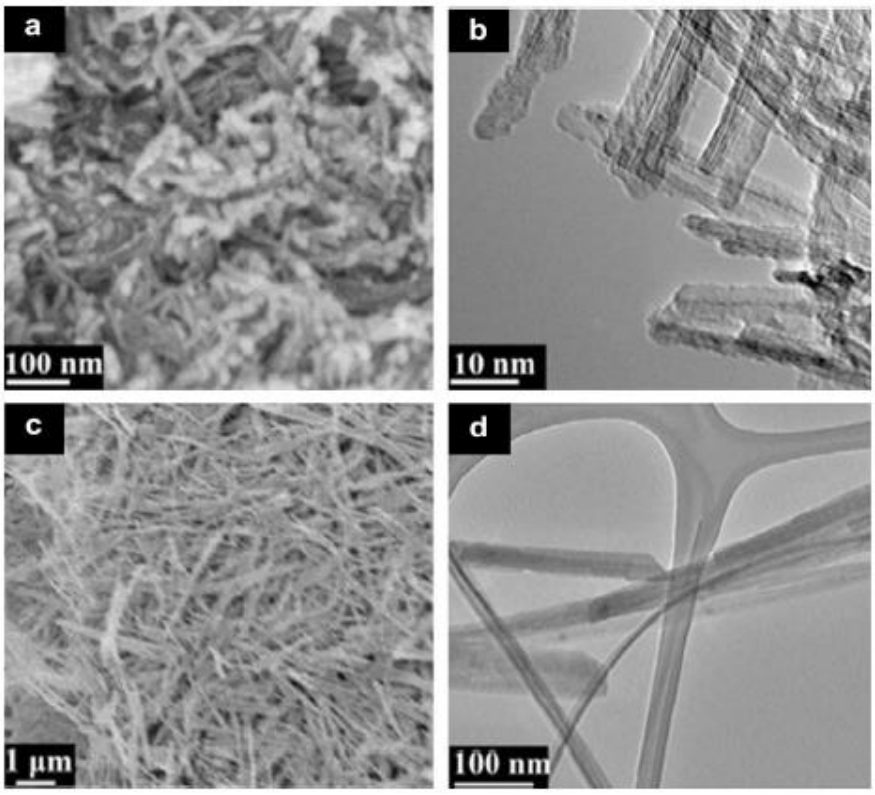


Figure 2.11 (a) FESEM and (b) TEM images of TNW10, (c) FESEM and (d) TEM images of TNW20 (Zhang *et al*., 2009)

The photocatalytic degradation results showed an excellent photocatalytic activity of the two kinds of nanowires. Almost all humic acid could be degraded using TNW10 and TNW20 as the catalyst, which indicated by the TOC removal rate as figure 2.10 showed. Moreover, the two materials showed good stability on photocatalytic activity. In additional, compared with conventional nano-sized TiO_2 particles, the nanowires were easier to be separated and recovered by membrane filtration and could cause less membrane fouling, which was very important for practical use.

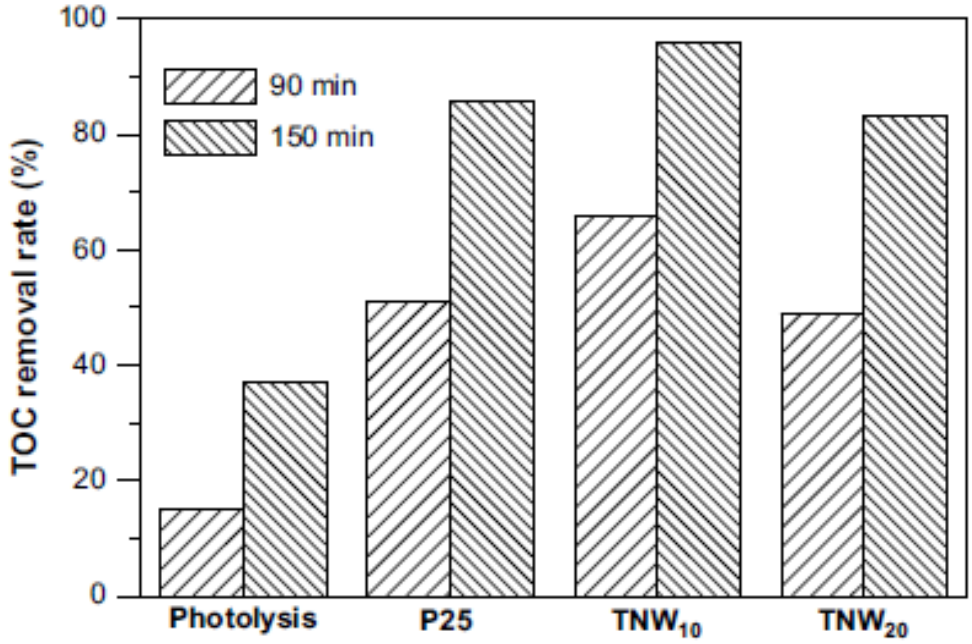


Figure 2.12 TOC removal rate by P25, TNW10 and TNW20 photocatalytic oxidation and photolysis (Zhang *et al*., 2009)

Liu *et al*. (2011) prepared a functional 1D pearl chain-like Fe_3O_4/C/CdS coaxial nanostructures, which was synthesize by the methods of magnetic field-induced assembly and microwaveassisted deposition. The morphology of the nanostructures were shown in Figure 2.11.

These materials showed favorable photocatalytic performance for RhB dye even under visible-light irradiation instead of UV irradiation. Moreover, the photocatalysts had good stability and reusability, which were important for practical use in water and wastewater treatment.

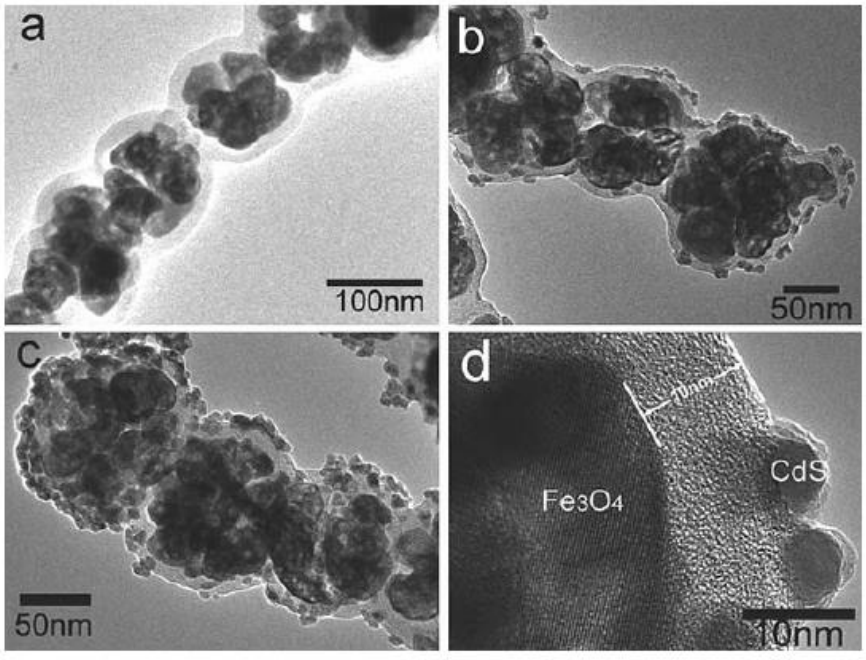


Figure 2.13 TEM images of as-prepared (a) 1D chain-like Fe_3O_4/C core–shell nanostructures, and Fe_3O_4/C/CdS composites prepared with an irradiation time of (b) 5 min and (c) 20 min. (d) HRTEM image of 1D chain-like Fe_3O_4/C/CdS nanostructures (Liu *et al*., 2011)

Zhang *et al*. (2008) have prepared TiON/PdO fibers and the morphology was shown in Figure 2.12. The material was proved to have favorable photoelectrocatalytic inactivation performance for *Escherichia coli.* The result showed that there were no bacteria surviving after 60 min of treatment, when the photocatalytic process was assisted by a 0.6 V

positive potential. During the reaction, bacterial which were negatively charged, would transfer to the positive photoanode..

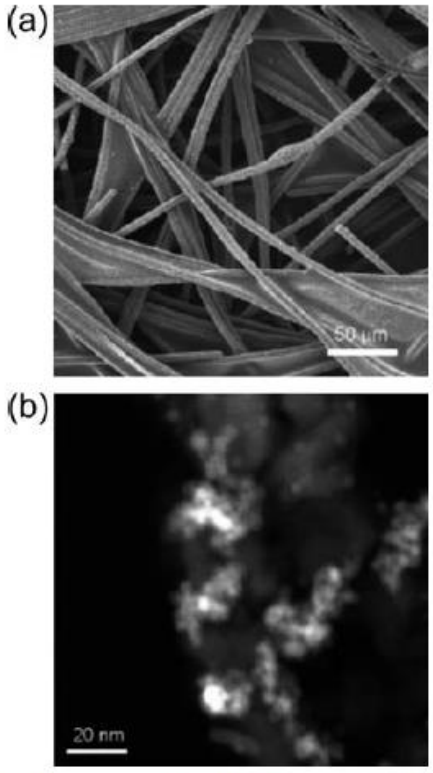


Figure 2.14 (a) SEM image, and (b) STEM image of TiON/PdO fibers (Zhang *et al*., 2008)

2.3.2.3. Photocatalytic film

Beside the nanochains and nanowires, photocatalytic film is also an effective method for the immobilisation of powder TiO_2 in order to decease the difficulties of recovery and reusability of the catalyst for industrial scale use. Through the immobilization of some catalysts with high photocatalytic activity on the inexpensive support substrates, the

material owned a favorable photocatalytic performance and could be easily separated from treated water. The common support substrates is ceramic membrane, which owns a good stability under UV irradiation and reactive oxygen species.

Zhang *et al*. (2010) have fabricated transparent TiO_2 films on stainless steel. Half of the *Bacillus pumilus* could be killed in two hours by using the materials as the catalyzer. Moreover, the research found that the iron dopants could improve the photocatalytic activity of the TiO_2 films.

Byrne et al. have coated TiO_2 powder on the substrate to immobilize them in order to avoid the difficulty of their recycle. The device was designed for the treatment of polluted water. Its configuration was shown in figure 2.13.

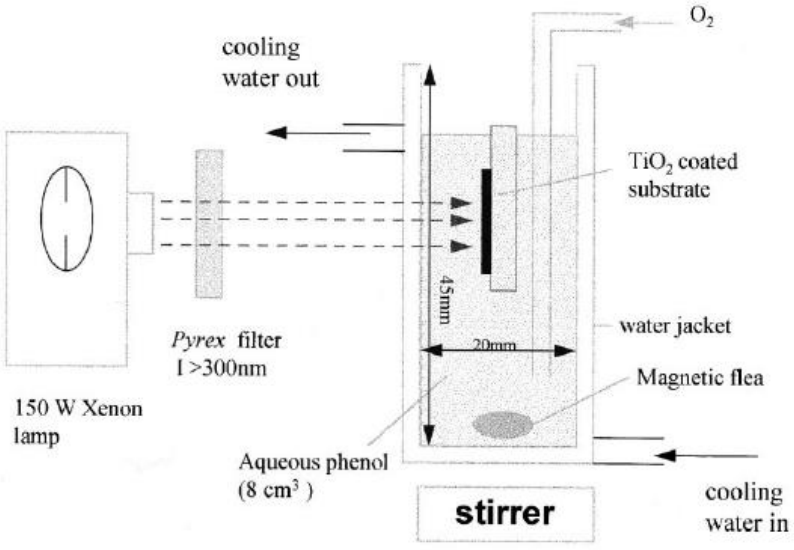


Figure 2.15 Quartz water jacketed photocatalytic reactor (Byrne et al., 1998)

Han *et al*. (2011) have successfully prepared the sulfur doped TiO_2 films, which were visible light-activated. H_2SO_4 was used as a sulfur source and sulfur was doped via sol–gel method. Significant shift of the optical absorption edge toward the visible region was detected and thus calbiochem could be degraded under visible light irradiation. Considering their preferable economy, this nanostructured sulfur doped TiO_2 thin films are a promising photocatalyst for environmental practical applications.

Choi *et al*. (2005) have synthesized the TiO_2 films and membranes via modified sol–gel method. The films had favorable nanostructures, such as high pore volume, controlled pore size distribution, and homogeneity. At the same time, they also had a preferable photocatalytic activity because of their small crystal size, high surface area, and active anatase phase. The results showed that these materials could effectively kill a variety of pathogenic microorganisms.

2.3.2.4. Solar photocatalytic disinfection

As we discussed above, the traditional photocatalytic process requires vast energy for irradiating the catalyst, which hindered its practical use in water treatment. In order to reduce the energy demand, solar induced photocatalytic catalysts attract a lot of attention nowadays.

Sichel *et al*. (2007) have reported research on disinfection of *Escherichia coli K12* in a compound parabolic collector (CPC) solar reactor. The TiO_2 coated paper was set on a tubular support in the middle of the CPC. The structure of the CPC was shown in Figure 2.14 and Figure 2.15.

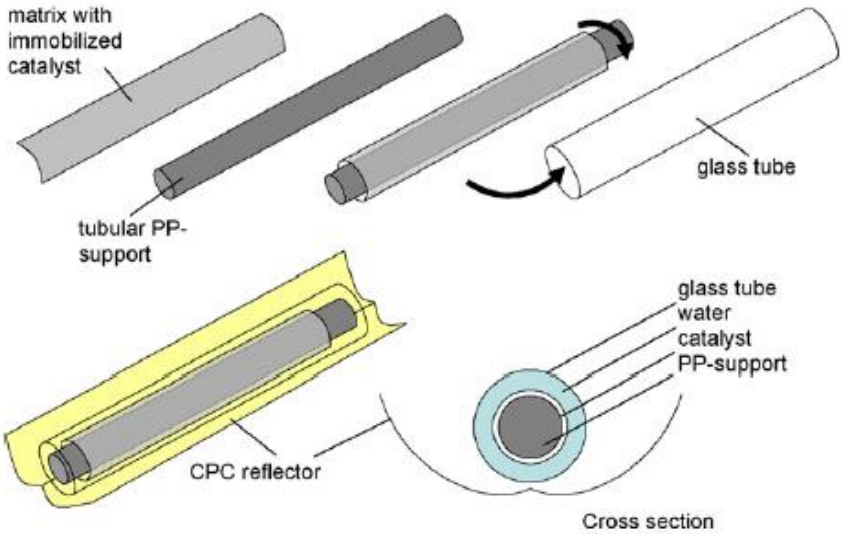


Figure 2.16 Schematic diagram of the CPC reactor configuration (Sichel *et al.*, 2007)

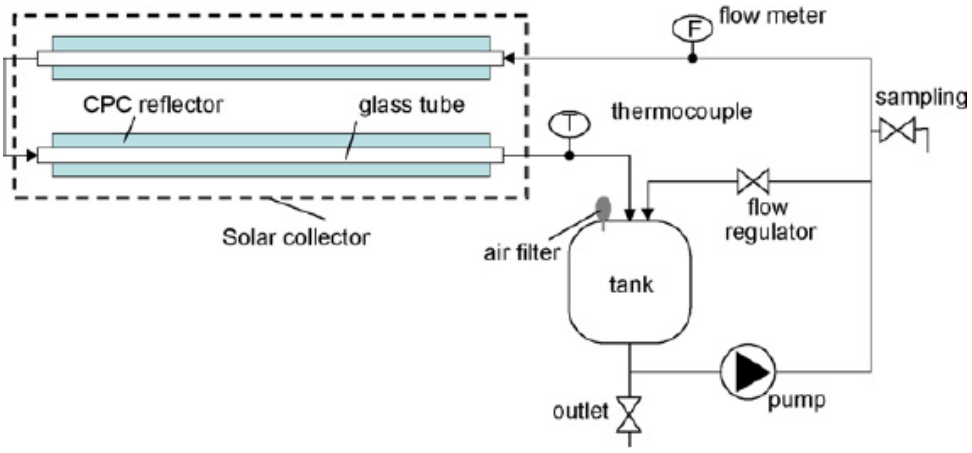


Figure 2.17 Flow diagram of the solar CPC photoreactor (Sichel *et al*., 2007)

The effects of operating parameters such as bacterial concentration, water quality, and flow rate on disinfection, have been studied. The results showed that the disinfection effectiveness was strongly influenced by flow rates and almost all the *E. coli* cells were inactivated after 90 min of treatment at a flow rate of 10 L/min in the CPC reactor. (Sichel *et al*., 2007)

Solar photocatalytic disinfection has been used in pilot plant test. (Bahnemann, 2004). As shown in Figure 2.16, the plant included two thin film fixed bed reactors (TFFBR), which have a total effective illuminated area of 50m^2. The reactors can be operated in different modes depending on the reaction kinetics, namely in parallel or as a cascade flow and in a continuous or a recycling mode. Before and after this structures were the sequencing batch reactors (SBR) for pre- and posttreatment. Long term experiments are being undertaken to evaluate its effectiveness and stability.

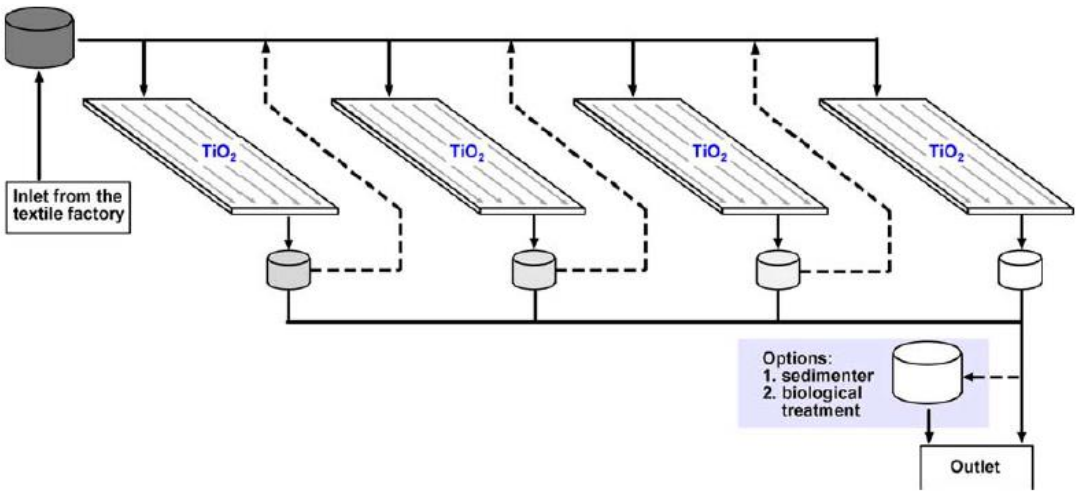


Figure 2.18 Flow chart of a TFFBR pilot plant (Bahnemann, 2004)

2.3.2.5. Photocatalytic Reactor Configuration

The scaling up photocatalytic reactors are much complex than the one just for study, for many practical parameters have to be considered. Besides, they are also complex than the homogeneous photoreactors, for the solid catalyst should be properly added in the reactor to achieve the best performance. Many parameters such as good contact between reactants and catalysts, preferable exposure of the catalyst to light irradiation, flow patterns of the treated water, reaction temperature control, etc., should be taken into consideration. Among these factors, illumination time of the catalyst is the most important one, because without illumination photons of appropriate energy content will not be generated and the catalyst thus shows no activity. Moreover, the design of the reactor should achieve the best reaction kinetics, mass transport, and illumination at the same time, which is definitely not an easy work. (Preety and Ajay, 1999).

Chen *et al*. (2003) have designed a novel composite reactor with nano TiO_2 as the photocatalyst and a UV lamp as the light source for degradation of organic pollutants. An electrolysis system was also adopted to accumulate H_2O_2 to improve the photocatalytic process. The result showed that rhodamine 6G (R-6G) could be effectively degraded by this reactor. Moreover, this reactor could also be used to treat the effluent from dyeing and printing process. The quantity of bacteria, the biochemical oxygen demand, the chemical oxygen demand, and the ammonia nitrogen of the effluent decreased by 99.9%, 87.6%, 93.9%, and 67.5%, respectively, after 0.5 h of treatment.

Ochiai *et al*. (2010) have developed a water treatment system combined electrochemical with a photocatalytic oxidation unit, which was totally driven by solar energy and thus had a favorable economy. The boron-doped diamond (BDD) was adopted as the electrode and TiO_2 as the photocatalyst. The configuration of this system is shown in Figure 2.17.

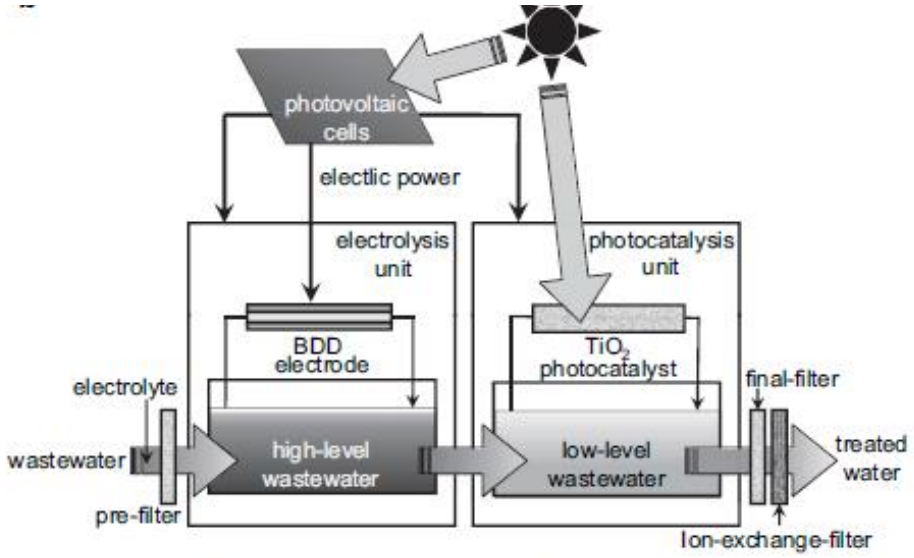


Figure 2.19 Schematic diagram of the wastewater treatment system (Ochiai *et al*., 2010)

This system had also been proven to be effective for wastewater treatment. Firstly, high-loaded wastewater was treated by electrolysis on BDD electrode and was converted to low-loaded wastewater. The COD and BOD of the low-loaded wastewater was then degraded by photocatalysis on TiO_2 to achieve a satisfied effect. It could be concluded that this system is suitable for some area where is short of energy supply.

Nickels *et al*. **(**2012) have assembled a UV-LED photoreactor, which consisted of an LED lamp, a liquid flow cell with transparent windows, a microcirculating fluid pump, and a photodiode monitor. It owned many advantages such as flexibility, low production cost, and light weight. The schematic diagram was shown in Figure 2.18.

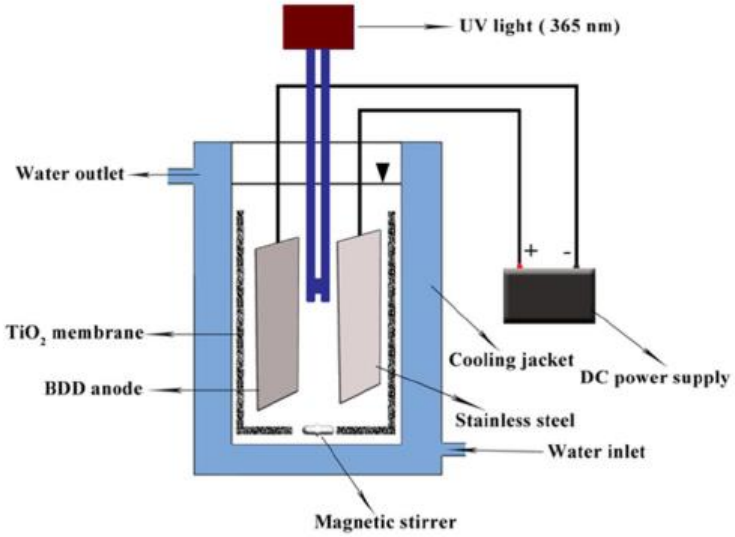


Figure 2.20 Schematic diagram of photocatalytic reactor arrangement (Nickels *et al*., 2012)

Through the photodiode monitor, the concentration decrease of methyl orange dye could be evaluated in real time and the study result showed that this application was suitable for both laboratory and field work.

The electrical bias was adopted to prepare electrodes, on which the TiO_2 powder (Aldrich and Degussa P25) was immobilized (Dunlop *et al*., 2002). The configuration of the device was shown in Figure 2.19.

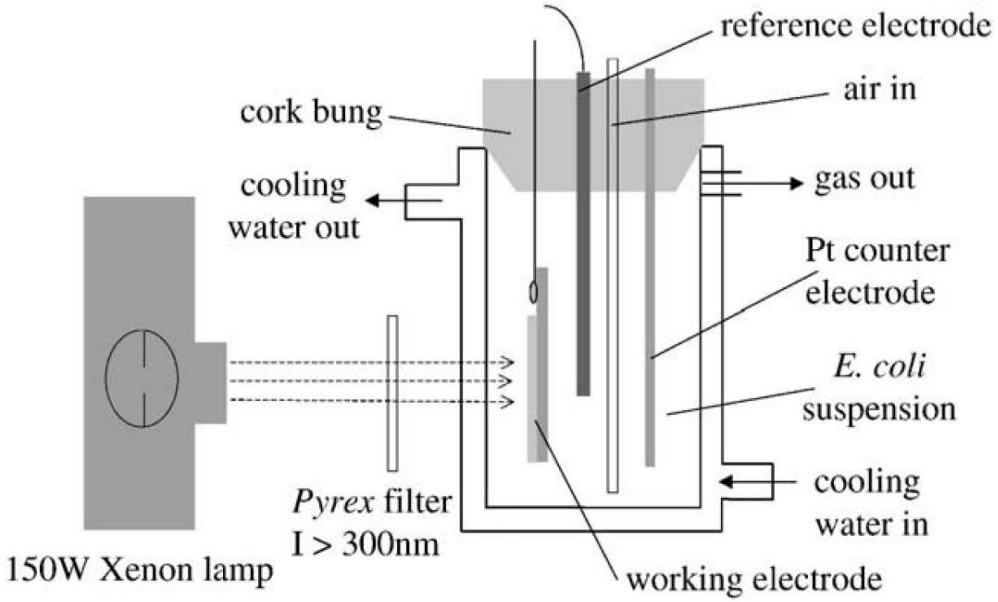


Figure 2.21 Quartz water jacketed photocatalytic reactor (Dunlop *et al*., 2002)

The electrodes were used for disinfection. It could enhance the disinfection performance by about 40% and 80% compared with sole Degussa P25 TiO_2 powder and Aldrich TiO_2 powder. The disinfection effect could last for at least 2 days, which means the bacteria would not occur up within 48h after disinfection.

Byrne *et al*. (2002) have developed one-compartment and two-compartment photoelectrochemical flow cell. The electrodes were prepared by the immobilisation of nano-sized TiO_2 on tin oxide coated glass. The second cell was for the simultaneous photocatalytic oxidation and the recovery of copper ions from solution. The configurations of the devices were shown in Figure 2.20 and Figure 2.21.

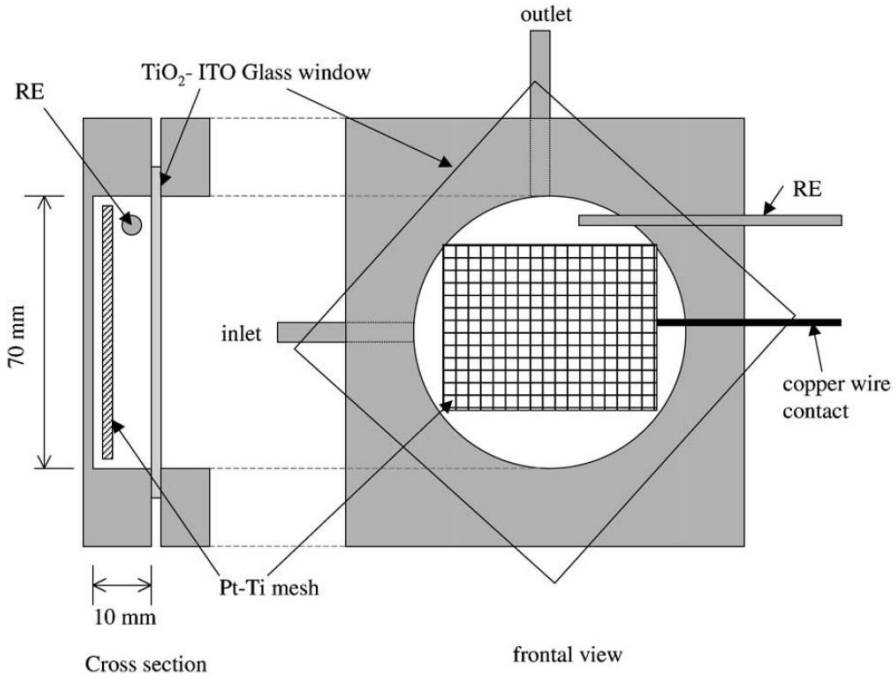


Figure 2.22 Schematic diagram of the one-compartment flow cell (Byrne *et al*., 2002)

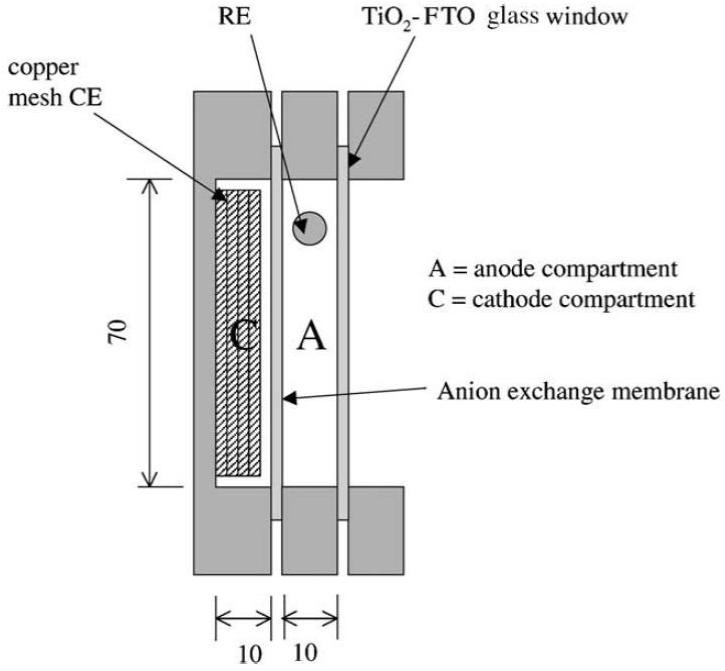


Figure 2.23 Schematic diagram of the two-compartment flow cell (Byrne *et al*., 2002)

The devices were used for degradation of formic acid. The result showed that the formic acid could be effectively and rapidly degraded under anaerobic and air sparged conditions when the voltage was set to +1.0V (SCE). The second cathode compartment could effectively achieve the recovery of copper ions from solution and the degradation of formic acid at the same time, which was critical for the continuous operation of this unit.

2.4. Summary

With the increasing water pollution, more and more advanced water and wastewater treatment technologies have been developed. Among a variety technologies, photocatalytic water treatment has drawn a lot of attention. Since the 1970s, the nano-sized TiO_2 has been proved to have the ability to completely mineralize a wide spectrum of pollutants and disinfect the water with the relatively simple experimental design and cheap operating costs. Through the review of their recent developments, there are some conclusions that can be made.

1. There are a huge gap between the laboratory-scale study and commercialized use of the developed devices. A large number of pollutants have been successfully but individually tested for photocatalytic disinfection or degradation. However, there is still a long way to realize commercialization of these technology. In addition, in order to degrade some trace pollutants, which is highly toxic, selective photocatalysis and selective degradation is becoming a research hotspot.

2. There are quite a few methods that have been developed to enhance catalytic activity and recovery performance of TiO_2, such as surface treatment, metals and non-metals doping, immobilization, coating etc.

3. The parameters of photocatalytic reactors design are complex and interacted. A satisfied photocatalytic reactor should have a favorable effectiveness, stability, simplicity and economy. In the practical use, a lower operating cost is of great importance. Hence, studies on reactors using solar radiation as the energy source and do not require pre- and post-treatment have a lot of opportunities.

4. Doping by metals and non-metals is a common used method for photocatalytic materials treatment because it can reduce the band gap of the catalyst and make them active under visible light irradiation. However, there is still no satisfied doped catalyst in water treatment that is efficient for practical with sole visible light as the light source. Moreover, the possibility of dopant leaching also limits its development.

5. A more practical use of photocatalysis may probably combine it with other common treatment technologies, such as membrane filtration, UV disinfection, biodegradation etc. Study on the optimal combination and the optimal operating parameters of these treatment technologies have great potential in large-scale water treatment.

Chapter 3: Materials and Methodology

3.1 System Operations

The novel method developed in this project is an electrolytic-photocatalytic method. Low levels of sodium hypochlorite, free chlorine, or hypochlorous acid can be produced in situ in the NaCl-containing solutions by this method. The electro-photo-disinfection system emerges as a superior option in water disinfection. This technology capitalizes on a special coating technique of a specifically designed formula of ornamented ruthenium dioxide on D.C. electrodes. The electrically activated coated surfaces transform naturally occurring chloride ions in water into activated chlorine with effective disinfecting power. Over, the years, we have developed and employed this technology into a compact system that has small footprint, low power consumption, no chemical addition required, and fully automatic, stable and reliable water disinfection system.

Various operating parameters, including chloride concentration, electric potential and organic substance content, of the lab-scale compact reactor were comprehensively studied at the Water and Waste Laboratory in the Department of Civil and Structural Engineering at the Hong Kong Polytechnic University. The schematic diagram of the electro-activation and PCO components was shown in Figure 3.1. Operation performance of this integrated disinfection system was studied according to the formation of free

chlorine, the deactivation of total bacteria and the disinfection efficiency of the pathogenic microorganisms.

A pilot-scale electrolytic disinfection simulator adjoined with 80M PCO unit was designed and fabricated. Part of the water leaving the sand filter was diverted to the electro-photocatalytic disinfection system. The electrolytic component contains a stainless steel container, water circulation pump, electrolysis device and a set of PVC pipe lines (Figure 3.1).

The PCO unit with effective titanium dioxide coated surface of area of 2,850 cm^2. The UV lamp wave length was 254 nm with UV lamp length of 29 cm. The PCO unit was constructed by stainless steel, grade SUS304/SUS316. Figure 3.2 shows the cut-open view of the TiO_2 panel.

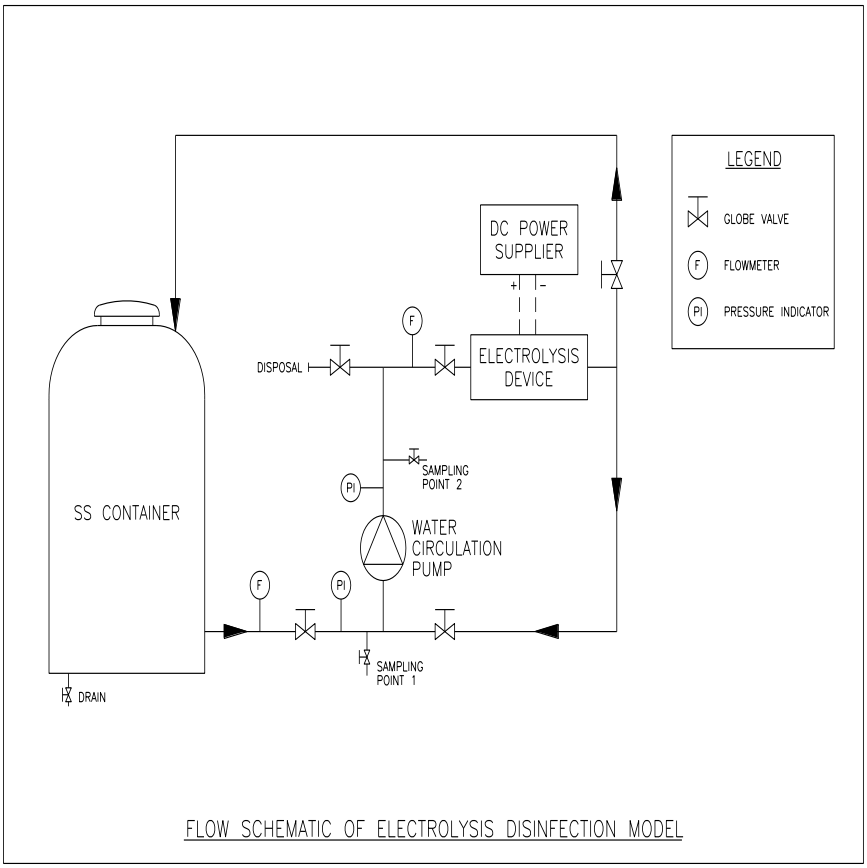
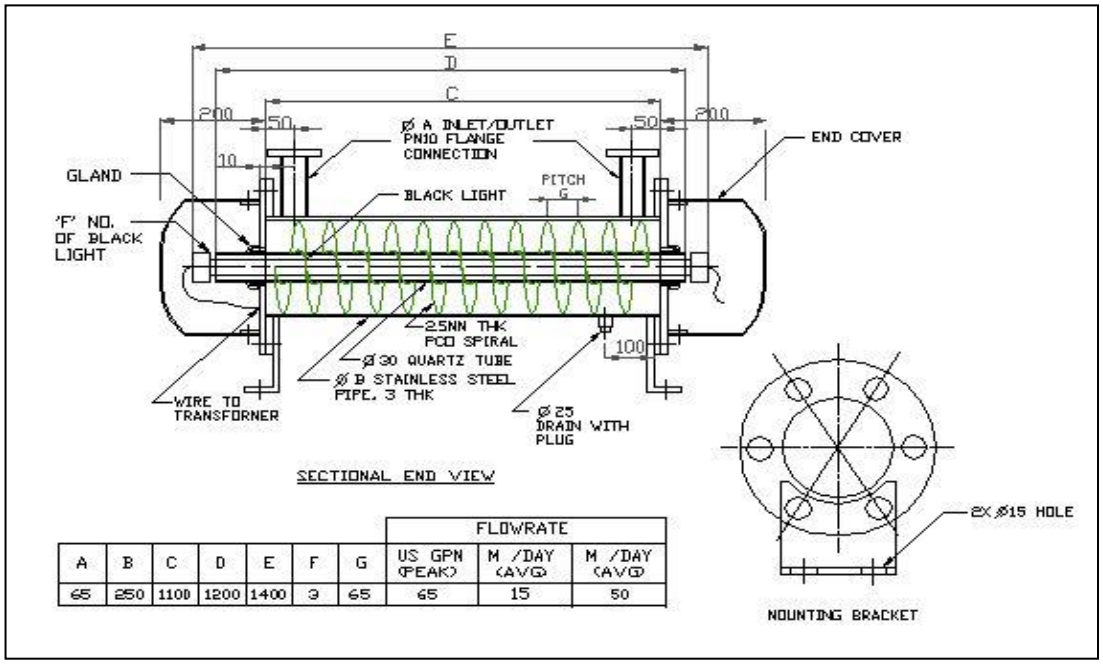


Figure 3.1 Schematic diagram of the electrolytic component and the recirculation tank

After passing the sand filter, a portion of the water was drained into the system from the main stream of flow to the chlorination process. The water pass the electro-activation component before passing the photocatalytic oxidation unit and recycled at the flow rate of 2 m^3/h.



A	B	C	D	E	F	G	FLOWRATE US GPN (PEAK)	FLOWRATE M /DAY (AVG)	FLOWRATE M /DAY (AVG)
65	250	1100	1200	1400	3	65	65	15	50

Figure 3.2 A pilot-scale electrolytic disinfection simulator system with PCO unit on site (upper). The cut-open view of TiO2 panel in the water disinfection system (lower)

The flow rate was controlled by a series of control valves and internal recirculation circuits. The concentration of free chlorine and the concentration of *E. coli* were monitored during the processes of electrolysis and photocatalysis at each 15 min interval.

The free chlorine concentrations and *E. coli* count in three sampling points were analysed. The three sampling points are 1) at the entrance of flow to the tank, 2) outlet from the electro-activation unit and 3) outlet from the photocatalytic oxidation unit (Figure 3.3.)

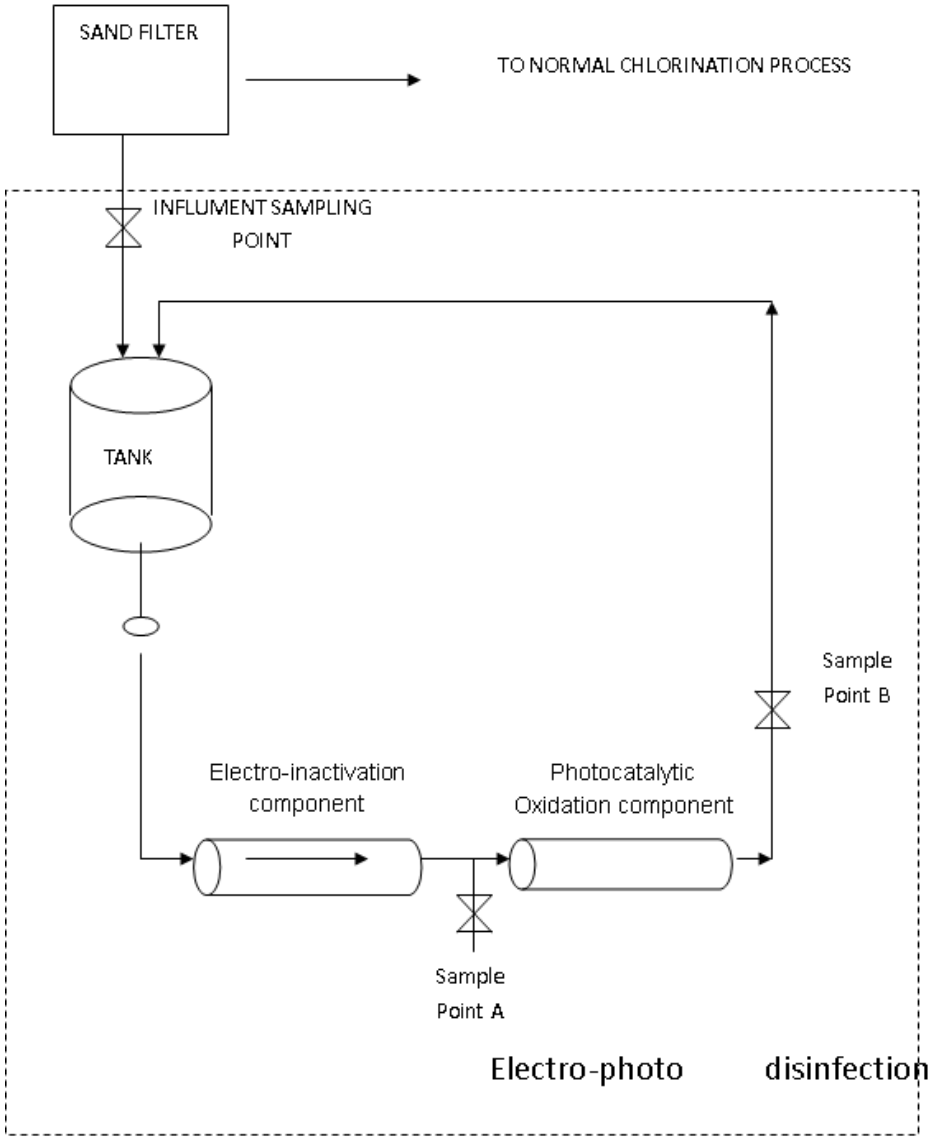


Figure 3.3 Bench-scale electro-photo disinfection system

3.2 Water Sample Analysis

Three kinds of raw water, namely swimming pool water, fountain water and toilet flushing water were taken from different places. The swimming pool water was taken from the swimming pool at the Royal Peninsula, Hung Hom. The fountain water was taken from the Fountain of the Tower 4, Harbor Place (A private estate in Hong Kong). And the flushing water was taken from Flushing water tank in the 37/F of Tower 4, Harbor Place. The effectiveness of this process was quantified by measuring the free chlorine concentrations in the water and evaluating the *E. coli* concentration that were removed in the process. Chloride concentrations in the circulating water and the voltage applied to the system were also monitored in the experiment. Total organic carbon was also measured to identify the concentration of organic pollutants in the water on-site.

The free chlorine in the water sample was measured by using HACH Colorimeter Model 46700. In order to determine free chlorine, a N,N-diethyl-p-phenylenediamine namely DPD Free Chlorine tablet was added with stirring until dissolved. When there is chlorine, the solution will turn red. Concentration of free chlorine will be displayed in the unit of mg/L. On the other hand, NaCl was added into the circulating water in each test. The concentration of total chloride was measured by using Chloride meter (Model: EA940 of Orion).

The method for bacterial enumeration was as follows: The microbial culture media, glassware, deionised water were sterilized in an autoclave at 121 ℃ for 15 min. Dilutions of microbial samples were carried out using sterilized deionised water. An appropriate sample volume was filtered through a sterile membrane filter. The filter papers were then placed on the surface of a plate containing agar medium for determining total bacteria content, and were incubated at 38 ℃ for 48 hours. The colonies were counted in a standard microbial counter after the complete cycle of incubation.

3.3 Electrolytic System

A bench-scale electrolytic disinfection simulator system was designed and fabricated. A total volume of 70L tap water was filled in the equalizing tank in each test. The electric voltage applied in water electrolysis processes was maintained at 30 V. The amount of chloride ion in the tap water was adjusted by adding sodium chloride. In this study, chloride concentrations of 0, 10, 50, 75, 100 mg/L were added in the tap water, respectively. Concentrations of organic substance (urea) that represents the common contaminants/pollutants in swimming pools, in the tank were controlled at 0, 5, 10, 20, 40 mg/L, respectively.

The water samples in the tank were pumped to pass the electrolytic-photocatalytic device, then returned to the tank and recycled at the flow rate of $2m^3/h$. Flow rate was controlled

by a series of control valves and internal recirculation circuits. Flow rate, pH and temperature were measured during the test. The concentration of free chlorine was monitored during the process of electrolysis at each 5 min interval. The free chlorine concentration shown in the following report was regarded as the free chlorine in the water tank.

The effectiveness of this process was quantified by evaluating the total bacteria that were removed in the process. The method for bacterial enumeration was as follows: The microbial culture media, glassware, deionised water were sterilized in an autoclave at 121 ℃ for 15 min. The colonies were counted in a standard microbial counter after the complete cycle of incubation.

3.4 Outside Study

The system was installed and assessed on a long-term basis at the swimming pool at the Royal Peninsula, Hung Hom. The technology for water treatment was tested on-site rigorously for its treatment performances, long-term reliabilities and maintenance requirements.

Figure 3.4 The fountain of Tower 4

The outside study about the fountain water was in Fountain of the Tower 4, Harbor Place (A private estate in Hong Kong) as shown in Figure 3.4.

We had chosen the place and put machine in the pump house, the arrangement was shown in Figure 3.5.

Figure 3.5 Arrangement of the equipment

Flushing water tank was in the 37/F of Tower 4. Figure 3.6 and Figure 3.7 were the photos showing the outside and inside views of flushing water tank, respectively.

Figure 3.6 Flushing water tank (outside view)

Figure 3.7 Flushing water tank (inside view)

A total volume of 70 L tap water was filled in the equalizing tank in each test. We used TiO_2 with UV lamp to disinfection; the UV lamp wavelength was 254 nm with UV lamp length of 29 cm take loop round in the tank. Sample was taken every 15 min and the effectiveness of this process was quantified by evaluating the total bacteria that were removed in the process. The work loop of the electro-photo disinfection system was shown in Figure 3.8.

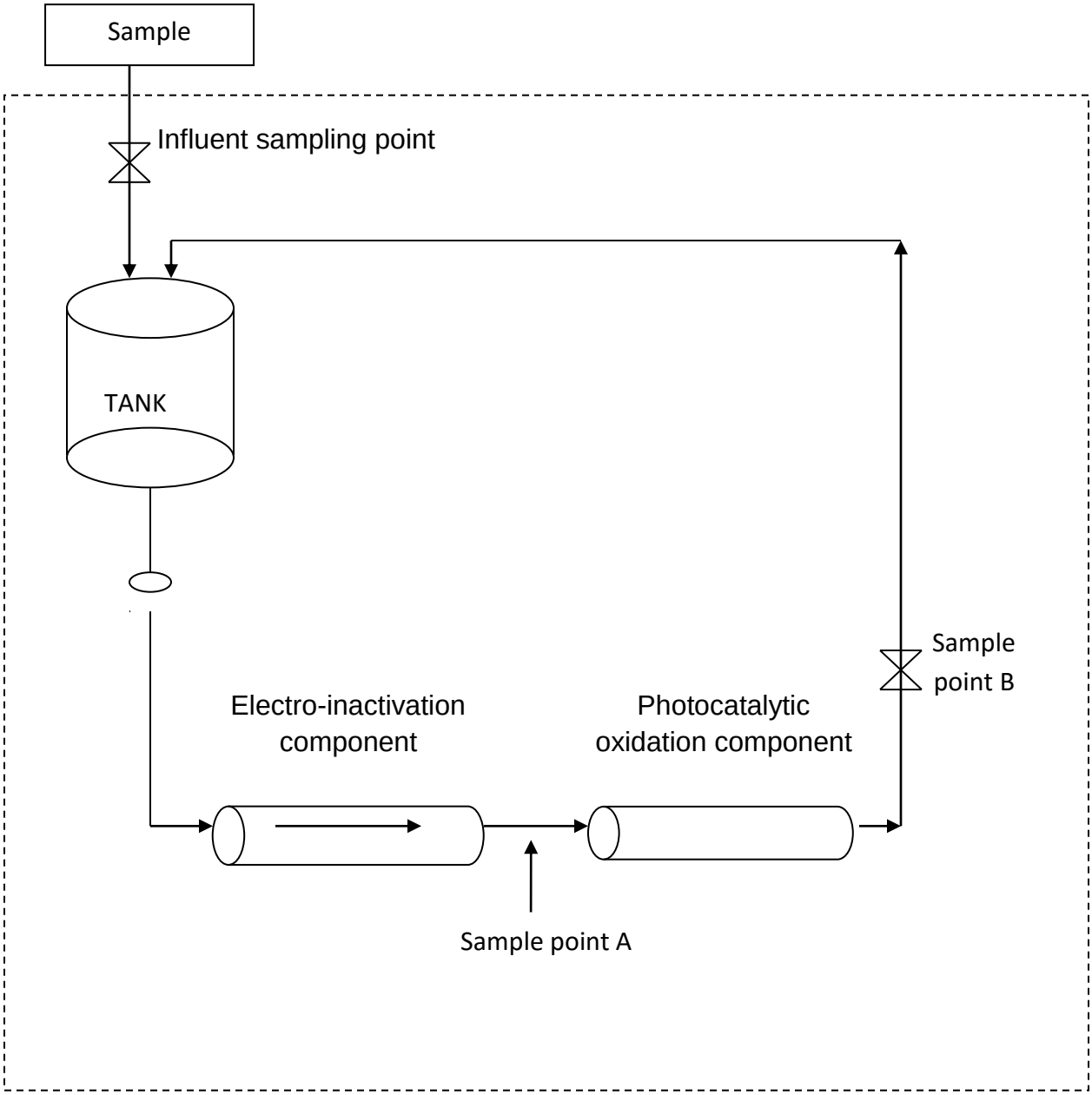


Figure 3.8 On-site pilot-scale electro-photo disinfection system

The sampling procedure was shown as Figure 3.9. The samples were taken and the microbial culture media were made. Glassware, and deionised water used in the experiments were sterilized in an autoclave at 121 ℃ for 15 min. Dilutions of microbial

samples were carried out using sterilized deionised water. An appropriate sample volume was filtered through a sterile membrane filter. The filter papers were then placed on the surface of a plate containing agar medium for determining total bacteria content, and were incubated at 32 ℃ for 48 hours. Finally, data were collected and analysed.

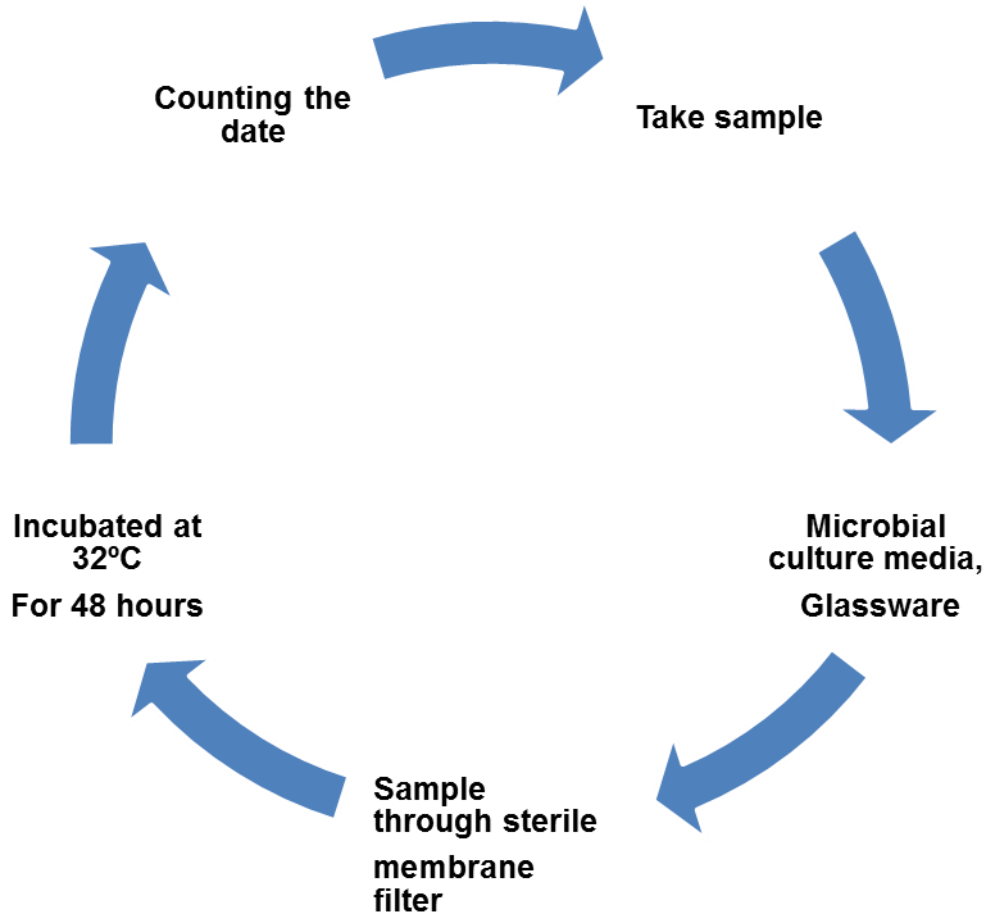


Figure 3.9 Experimental procedures

3.5 Method of Microbiology

3.5.1 Microbial isolation

The microorganisms in the water samples were isolated by plate cultures, which contains Czapek's agar and added with 0.4% yeast extract. The microorganisms are then incubated at 28ºC for 3 weeks. The isolated bacteria were cultured in 500 mL flasks with 100 mL sterilized LB medium, on an orbital shaker at 28ºC and 200 rpm for 120 hours.

3.5.2 Culture medium

The culture medium consisted of minimal salt medium (MSM) that contained: KH_2PO_4 2.796 g/L, Na_2HPO_4 2.834 g/L, nitrilotriactic acid 0.200 g/L, $MgSO_4$ 0.289 g/L, $CaCl_2.2H_2O$ 0.067 g/L, $(NH_4)_2Mo_7O_{24}.4H_2O$ 0.185 mg/L, $FeSO_4.7H_2O$ 2.480 mg/L, EDTA 0.250 mg/L, $ZnSO_4.7H_2O$ 1.095 mg/L, $MnSO_4.4H_2O$ 0.203 mg/L, $CuSO_4$ 0.020 mg/L, $CoSO_4.7H_2O$ 0.024 mg/L, and $Na_2B_4O_7.10H_2O$ 0.018 mg/L. Papermaking effluent, which contained a lot of lignin and had a COD_{Cr} value of more than 200mg/L, was used as sole carbon source. The pH of the minimal salt medium was adjusted to 6.5. Papermaking effluent was filtered through a 0.45 μm membrane filter and sterilized.

3.5.3 Inoculum

The seed was preserved in on yeast-extract-glucose agar slants at 4^{o}C. The inoculum was grown in the same medium as described above. *Escherichia coli* (*E. Coli*) and *Cholera vibrio* were transferred from agar slants into separate flasks containing required volume of medium and incubated for 72 and 24 hours, respectively on an orbital shaker at 200 rpm at 30°C.

3.5.4 Culture conditions

Shake flask culture was grown in 500mL baffled conical flasks, on orbital shaker at 200 rpm, with 90mL of MSM, 10 of ml papermaking effluent and 5mL of inoculum, at 30 ℃ and initial pH 6.5 for a period required to enter the stationary phase.

3.5.5 Total bacteria count

Plate counting method was used to obtain the total bacteria. The sample was inoculated onto the aerobic plate count agar that will be incubated at 30 ℃ for 48 hours in PolyU CSE Water Laboratory. Colonies formed on the strips were counted, recorded and converted into colony forming units per cubic meter (CFU/m^3). The sample method was taken with reference to the "Field Guide for the Determination of Biological Contaminants in Environmental Samples" published by the American Industrial Hygiene Association in 1996. The removal efficiencies were calculated by (C_{in}–C_{out}) / C_{in}x 100%.

3.5.6 Colonies counting

After the total bacteria experiment, the pour plates to be counted had been inoculated with bacterial cells and incubated for 48 hours. When the colonies were counted in the pour plate, Quebec colony counter was used. The first part to note was the adjustable magnifying glass. It could be moved closer or further away from the ruled area, depending on whether to reduce or increase the magnification. This magnifying glass could also be swung out of the way by moving it to the right or left. The in-line switch in the electrical cord was used to control the light in the counting area. This light would make it easier to see the colonies.

3.6 Effect of organic substance content

The effect of organic substance on the formation of free chlorine was examined by varying the concentration of organic substance. Urea was selected as a simulated organic matter commonly introduced by swimmers and the system operated at different concentration of urea (0, 5, 10, 20 and 40 mg/L).

3.7 Effect of the concentration of chloride added

The effect of the concentration of chloride on the generation of chlorine was evaluated. Analysis of free chlorine formation was conducted under different concentrations of chloride of 20 mg/L, 50 mg/L and 100 mg/L. Each test was operated with 60 minutes and water sample was taken at every 15 minutes. Moreover, the effectiveness and stability of the pilot-scale water disinfection system was studied under different concentration of NaCl from 1.5 % to 3.5 %

3.8 Effect of electric potential

The effect of electric potential on the rate of bacterial disinfection and chloride ion content by the electro-photo-disinfection system was determined by varying the voltage from 10 to 30 V at defined time intervals from 0 to 60 min. The samples were taken and analysed.

3.9 Effect of operation time on bacterial disinfection

The water samples were taken at certain time interval to evaluate the removal efficiency of bacterial during the operation of the system. The removal efficiency of the bacterial was determined by measuring the quantity of bacterial in the samples collected from the tank before and after the disinfection process.

3.10 Treatment Performances and Long Term Stability of the System in Onsite Operations

The operation parameters such as concentration of chloride, electric voltage and temperature were varied to test the stability of the system in onsite operations. The variation of pH, temperature, bacteria and free chlorine of the treated swimming pool water, fountain water and flushing water was tested. Moreover, for the on-site pilot-scale testing of swimming pool water, the effectiveness of this system were examined at different concentrations of chloride (20 mg/L, 50 mg/L and 100 mg/L) with fixed electrical supply (DC 30 V) and under different electric voltages (10 V, 20 V and 30 V) with fixed NaCl concentration (100 mg/L). For the on-site pilot-scale testing of flushing water, the effect of temperature and salinity on bacterial disinfection was studied under different temperature (10 ℃, 20 ℃ and 35 ℃) and different concentration of NaCl (1.5%, 2.0%, 2.5% and 3.0%).

Chapter 4: Effects of Various Operating Parameters on the Treatment Performances in the bench-scale water disinfection system

4.1 Disinfection of Swimming Pool Water

The objective of this part study is to evaluate the formation and the disinfection efficiency of the free chlorine generated by a bench-scale water disinfection system under different chloride concentrations, electric potentials, and contents of organic substance.

A bench-scale electrolytic disinfection simulator system was designed and fabricated. This system is a cut-open view of RuO_2 electrodes and TiO_2 panels.

A total volume of 70L tap water was filled in the equalizing tank in each test. The amount of chloride ion in the tap water was adjusted by adding sodium chloride. In this study, chloride concentrations of 0, 10, 50, 75, 100 mg/L were added in the tap water, respectively. Concentrations of organic substance (urea) that represents the common

contaminants/pollutants in swimming pools, in the tank were controlled at 0, 5, 10, 20, 40 mg/L, respectively.

The free chlorine generated by the electro-photo-disinfection system in the voltage of 10V, 15V, 20V and 25V at different dosage of NaCl was tested to evaluate the effect of electric potential.

The water samples in the tank were pumped to pass the electrolytic-photocatalytic device, then returned to the tank and recycled at the flow rate of $2m^3/h$. Flow rate was controlled by a series of control valves and internal recirculation circuits. The concentration of free chlorine was monitored during the process of electrolysis at each 5 mins interval. The free chlorine concentration shown in the following report was regarded as the free chlorine in the water tank.

The effectiveness of this process was quantified by evaluating the total bacteria that were removed in the process.

4.1.1 Effect of chloride concentration on the formation of free chlorine

The production of free chlorine over the period of 40-minute operation under different chloride concentrations is shown in Figure 4.1 and 4.2. The results indicated that free

chlorine was not formed during the electrolysis process under either no NaCl or 10 mg/L NaCl addition. It is due to the low chloride concentration in the tap water. This was attributed to both low chloride concentration and low electric current (2.2A) set in this test. Low electrolyte concentration (the simulated swimming pool water) results in poor conductivity of the solution. In addition, the decline of free chlorine is due to the water motion in the system, which was somewhat like the effect of aeration in the water that purges out free chlorine.

Figure 4.2 shows the free chlorine concentration under operation with 50, 75 and 100 mg/L chloride ion added. The results showed that free chlorine was formed during the electrolysis process depending on the how many chloride ions existing in the water. Less than 10 mins operation was required to generate more than 1 mg/L of free chlorine when more than 50 mg/L of NaCl was used. The concentration of free residual chlorine reached the requirement of the standard of public and private swimming pools in Hong Kong (> 1 mg/L). The formation of free chlorine in the water was obvious and substantial during the electrolysis process when chloride concentration reached a higher level of 75 and 100 mg/L. About 5 min after the beginning of the electrolysis process, free chlorine in the water reached 1 mg/L. In addition, the process period for sufficient free Cl generation could be shortened by increasing the NaCl dosage.

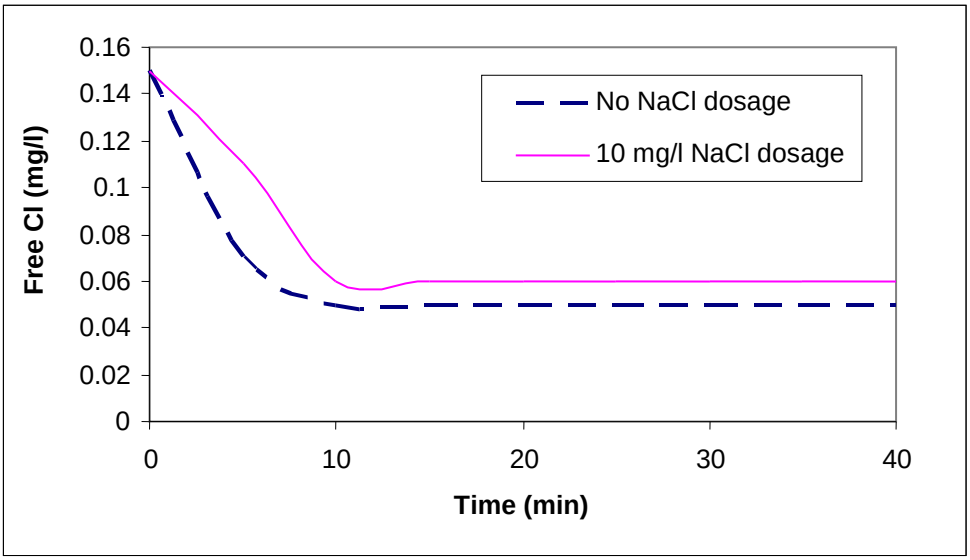


Figure 4.1 Free Cl concentrations under the operation without NaCl addition and with 10 mg/L NaCl addition

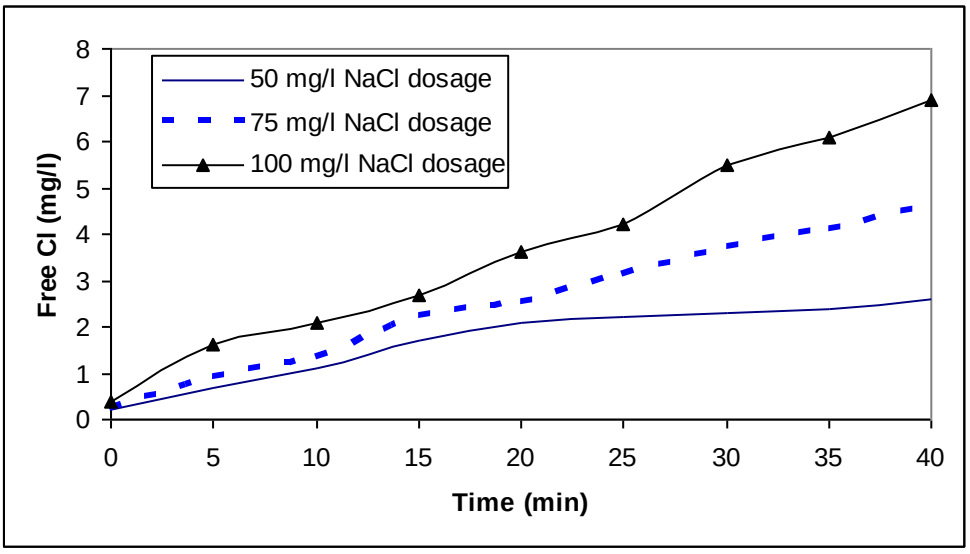


Figure 4.2 Free Cl concentrations under the operation with 50, 75, and 100 mg/L NaCl addition

According to the test results, the chloride concentration in water should be maintained at around 50 mg/L, which is the optimum dosage under the electric voltage of 30 V, in order to generate sufficient free chlorine (1 to 3 mg/L) for legislative requirements and effective disinfection.

4.1.2 Effect of electric potential on the formation of free chlorine

The effect of electric potential on the generation of free chlorine by the electro-photo-disinfection system was determined by varying the voltage from 10 to 25 V at different NaCl dosage. The results of free chlorine generation at different voltages and 50 mg/L NaCl dosage are illustrated in Figure 4.3. The concentrations of initial free chlorine at time of zero were different because the water samples we used were taken at different time and the concentrations of existing residue chlorine of different water samples also varied.

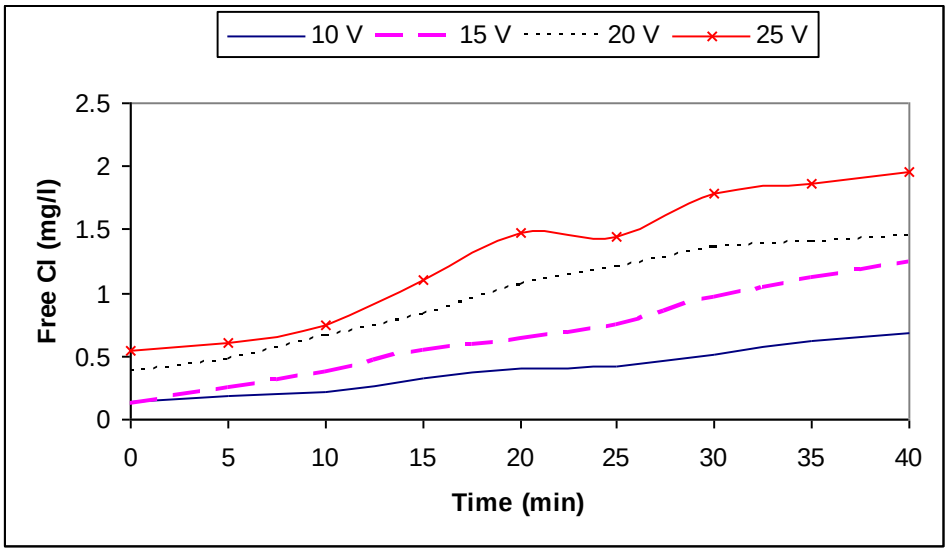


Figure 4.3 Free Cl generation under different voltages and at 50 mg/L NaCl dosage

As shown in Figure 4.3, the rate of free chlorine formation was also very slow under lower voltage (10 V) because of the relatively smaller current in the system. When the voltage was increased to 15 V, the rate of chlorine generation was significantly increased. The concentration of free chlorine in the water reached 1 mg/L after 30-minute operation.

As the electric voltage was further increased to 20 and 25 V, the formation of free chlorine was substantially increased due to the higher current applied. The reaction time required to generate 1 mg/L free chlorine was shortened to 20 mins and 15 mins for 20 V and 25 V, respectively. As the electrolysis went on, the concentration of free chlorine accumulated. This indicated that the system is capable of generating a free chlorine production rate that reaches a dynamic equilibrium with the rate of chlorine consumption in the pool water disinfection process.

The concentrations of free chlorine formed under various electrode potentials and externally-dosed chloride concentrations were studied and the results were presented in Table 4.1.

Table 4.1 Formation of free chlorine under various conditions after 30min operation

Quantity of chloride concentration added in the water (mg/L)	Electric potential applied the electrode (V)			
	10	15	20	25
10	0.05	0.05	0.05	0.05
20	0.09	0.36	0.67	1.20
50	0.51	0.98	1.40	1.78
75	0.71	1.44	2.12	2.88
100	1.01	1.98	3.30	4.67

As shown in table 4.1, when chloride concentration was controlled above a certain value, the formation of free chlorine was positive and was proportional to the electric voltage applied across the electrodes. The higher the voltage applied in electrode, the higher rate of free chlorine formation in the water. The electric potential should be applied to the system for effective disinfection is shown in Table 4.1 (the underline values), in order to

acquire sufficient free chlorine (1 to 3 mg/L) in the pool water for effective disinfection. The optimum operational condition of this system is 50 mg/L NaCl dosage and 20 V to 25 V.

4.1.3 Effect of organic substance content on the formation of free chlorine

The effect of organic substance on the formation of free chlorine was examined by varying the concentration of organic substance with 75 mg/l of external NaCl addition and at 30 V electric potential. Urea was selected as a simulated organic matter commonly introduced by swimmers.

According to the result shown in Figure 4.4, the effect of organic contents on the formation of free chlorine was significant. Higher organic concentration obviously reduced the quantity of free chlorine formed in the water solution. This is because the free chlorine was consumed in the oxidation-reduction reactions with oxidizable organics (e.g. urea). However, the concentrations of organic substances are usually very low in the swimming pools, the presence of organic substances have little effects on the formation of free chlorine under normal circumstances (less than few ppm of organic matters) and normal operations.

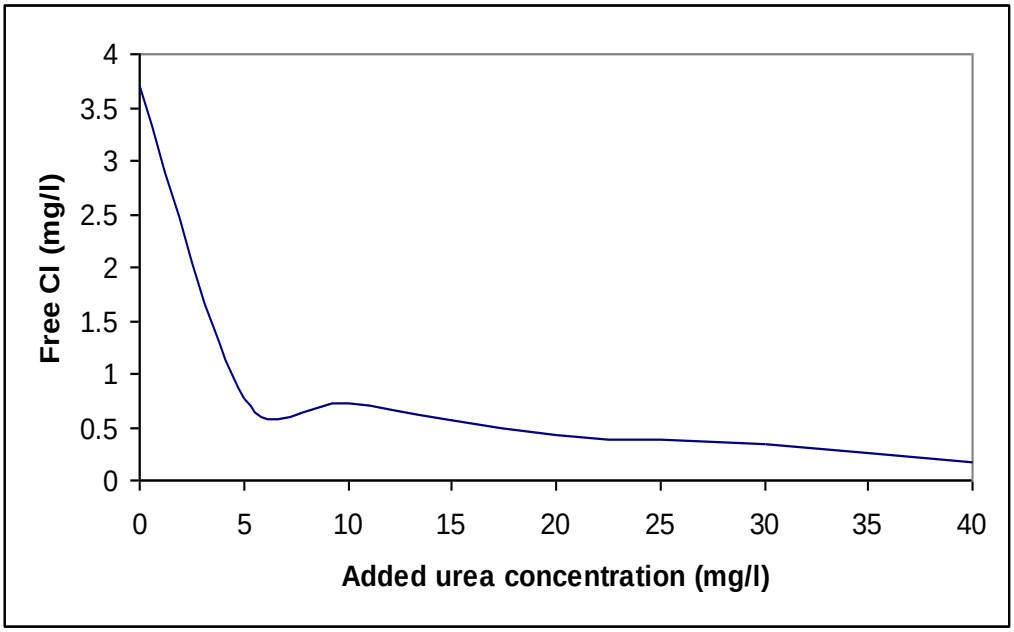


Figure 4.4 Free Cl generation at various urea concentrations

4.1.4 Effect of free chlorine on disinfection

4.1.4.1 Formation and disinfection efficiency of free chlorine

The microbial inactivation efficacy of the electrolysis system at an electrode potential 30 V with 50 mg/L NaCl addition is shown in Figure 4.5. The removal of total bacteria (*E. Coli*) was increased with increasing chlorine generation. After 25 mins operation (free Cl>2 mg/L), which is well above the legislative requirements, 7 logarithmic reduction of total bacteria was achieved. These results illustrated the effectiveness of electrochemically generated chlorine species for disinfection.

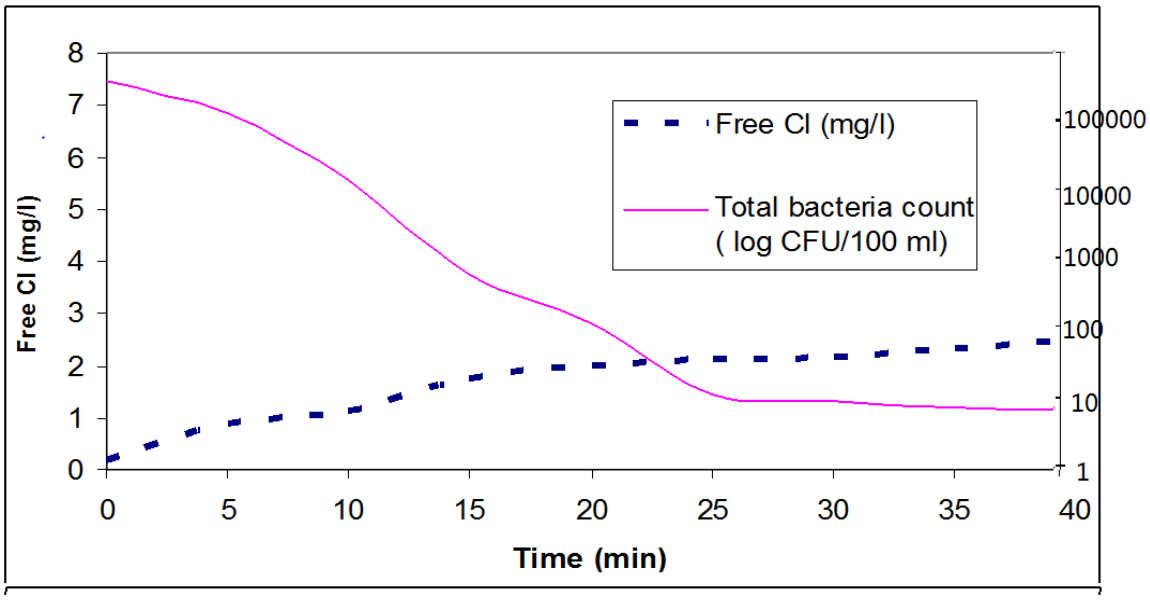


Figure 4.5 Microbial inactivation efficiency under the operation at 30 V and 50 mg/L NaCl addition

4.1.4.2 Effects of free chlorine concentration and contact time on the inactivation efficiency

The effects of Cl concentration and contact time on the disinfection performance are assessed by varying the free chlorine concentration from 0.5 to 4.0 mg/L and the contact time from 5 to 20 mins, respectively. According to the results, the germicidal efficiency of disinfection, as a measurement of bacteria survival, depends primarily on the concentration of free chlorine and contact time. The result of inactivation efficiency under various operating conditions is presented in the Table 4.2. The contact time is recommended between 15 to 20 mins according to the desirable contact time values and

the ratio of total bacteria survival (< 0.01). This superior results show that this novel electro-photo- disinfection system is suitable for the application in swimming pools. The optimum contact time, which is about 15 to 20 mins, is long enough is the normal swimming pool operation with a close loop recirculation flow system. These results (desirable contact time values) can establish a database which is important for the process scale up in full scale applications.

Table 4.2 Ratio of total bacteria (*E. Coli*) survival in a batch reactor (value less than 0.01 represents 2 log bacteria reduction)

Contacting time (min)	Concentration of free chlorine used (mg/L)				
	0.5	1.0	2.0	3.0	4.0
5	0.48	0.31	0.015	0.009	0.0056
10	0.33	0.02	0.0061	0.0005	0.0004
15	0.21	0.008	0.0007	0.0003	0.0002
20	0.015	0.007	0.0003	0.0002	0.0001

4.1.4.3 Disinfection efficiency of the pathogenic microorganisms

The disinfection efficiency of the pathogenic microorganisms of this system is evaluated by the removal of the two selected pathogens (*Escherichia coli* and *Cholera vibrio*). The removal efficiency of these two pathogenic microbes is determined by measuring the quantity of microbes in the samples collected from the tank before and after the disinfection process. The excellent performance (99.96 % and 100 removal efficiencies on *E. coli* and *Cholera vibrio*, respectively) on the treatment of pathogenic microbes was observed by the system operated under the optimum conditions (Figure 4.6).

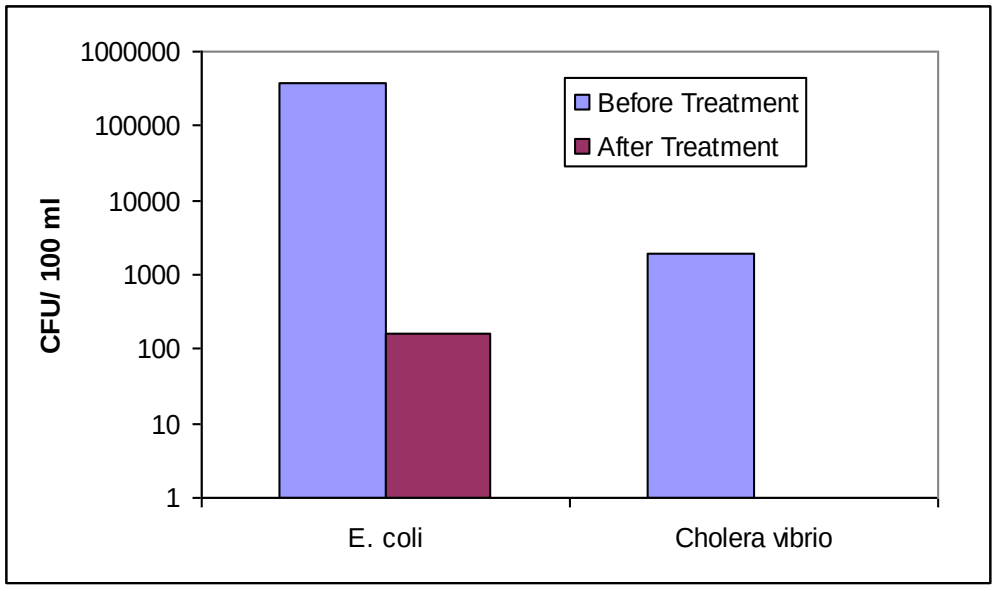


Figure 4.6 The bacteria count (CFU/ 100 ml) of samples collected before and after the disinfection

4.1.5 Discussion on swimming pool water

This part was designed to develop and carry out a laboratory study on a novel RuO_2 electrolysis and TiO_2 photocatalytic water disinfection system. The optimum condition for disinfection was as follows: chloride concentration 50 mg/L; electric voltage 25V; contact time 15 mins. The similar system would be used in the subsequent full-scale water disinfection that will be arranged for installation and on-site testing at a selected SHK-managed residential estate (Royal Peninsula) swimming pool.

4.2 Fountain Water

4.2.1 The effect of electric potential on bacterial content

The effect of electric potential on the rate of bacterial disinfection by the electro-photo-disinfection system was determined by varying the voltage from 10 to 30 V at defined time intervals from 0 to 60 min. The samples were taken and analysed by bacterial enumeration. The method for bacterial enumeration was as follows: The microbial culture media, plasticsware, deionised water were sterilized in an autoclave at 121℃ for 15 min. Dilutions of microbial samples were carried out using sterilized deionised water. An appropriate sample volume was filtered through a sterile membrane filter. The filter papers were then placed on the surface of a plate containing agar medium for determining total bacteria content, and were incubated at 32℃ for 48 hours. The colonies were

counted in a standard microbial counter after the complete cycle of incubation. The results of free bacterial disinfection at different voltage were shown in Table 4.3.

Table 4.3 Bacteria (*E. Coli*) variation with time and voltage (Fountain Water)

Time (min)	Bacteria (/plate)		
	10V	20V	30V
0	34~35	32~33	30~33
15	33~34	30~31	23~25
30	27~29	17~19	2~4
45	18~20	10~11	0
60	11~13	3~5	0

It could be found from the results that the rate of bacterial disinfection was also very slow under lower voltage (10 V). When the voltage was increased to 20 V, the rate of bacterial disinfection was significantly increased. There were 3~5 clones on a plate after 60 minute operation. As the electric voltage was further increased to 30 V, the formation of free chlorine was substantially increased due to the higher current applied. The reaction time required to kill the bacterial to 3~5 clones was shortened to 30 min. Therefore, the voltage of 25V or 30V is the best voltage that we need and we set 25V or 30V as the work condition.

4.2.2 The effect of electric potential on chlorine concentration

The effect of electric potential on the generation of free chlorine by the electro-photo-disinfection system was determined by varying the voltage from 10 to 30 V at different contact time. The results of free chlorine generation at different voltage and different contact time were shown in Table 4.4.

It could be found that the rate of free chlorine formation was also very slow under lower voltage (10 V) because the current was small in the system. When the voltage was increased to 20 V, the rate of chlorine generation was significantly increased. The concentration of free chlorine in the water reached about 1.9 mg/L after 60-minute operation.

Table 4.4 Chlorine concentration variation with time and voltage (Fountain Water)

Time intervals (min)	Chlorine concentration(ppm)		
	10V	20V	30V
0	1.53	1.55	1.51
15	1.51	1.57	1.92
30	1.53	1.67	2.17
45	1.54	1.77	2.15
60	1.55	1.86	2.22

As the electric voltage was further increased to 30 V, the formation of free chlorine was substantially increased due to the higher current applied. The reaction time required to generate 1.9 mg/L free chlorine was shortened to 15 min for 30 V. As the electrolysis went on, the concentration of free chlorine accumulated. This indicated that the system is capable of generating a free chlorine production rate that reaches a dynamic equilibrium with the rate of chlorine consumption in the fountain water disinfection process.

Moreover, the formation of free chlorine was positive and was proportional to the electric voltage applied across the electrodes, when the chloride concentration was controlled above a certain value. The higher the voltage applied in electrode, the higher rate of free chlorine formation in the water. The electric potential should be applied to the system for

effective disinfection is shown in Table 4.4, in order to acquire sufficient free chlorine (1 to 3 mg/L) in the fountain water for effective disinfection.

4.2.3. Discussion on fountain water

This part was designed to develop and carry out a laboratory study on a novel RuO_2 electrolysis and TiO_2 photocatalytic water disinfection system. The optimum operational condition of this system was as follows: electric voltage 30 V and contact time 60 mins. The similar system would be used in the subsequent full-scale water disinfection that will be arranged for installation and on-site testing at Fountain of the Tower 4, Harbor Place.

4.3 Flushing Water

4.3.1 The effect of electric potential on bacterial content

The effect of electric potential on the generation of free chlorine by the electro-photo-disinfection system was determined by varying the voltage from 10 to 30 V at different contact time. The results of free bacterial disinfection at different voltage were presented in Table 4.5.

Table 4.5 Bacteria (*E. Coli*) variation with time and voltage (Flushing water)

Time (min)	Bacteria (/plate)		
	10V	20V	30V
0	29	28	28
15	26	25	22
30	26	17	5
45	25	13	0
60	23	5	0

It could be found from Table 4.5 that the rate of bacterial disinfection was very slow under lower voltage (10 V) because the current was small in the system. When the voltage was increased to 20 V, the rate of bacterial disinfection was significantly increased. There were 5 clones on a plate after 60 minute operation. As the electric voltage was further increased to 30 V, the formation of free chlorine was substantially increased due to the higher current applied. The reaction time required to kill the bacterial to 5 clones was shortened to 30 min. Therefore, the voltage of 25V or 30V is the best voltage that we need and we then set 25V or 30V as the work condition.

4.3.2 The effect of electric potential on free chlorine formation

The effect of electric potential on the generation of free chlorine by the electro-photo-disinfection system was determined by varying the voltage from 10 to 30 V at different contact time. The results of free chlorine generation at different voltage and different contact time were illustrated in Figure 4.7.

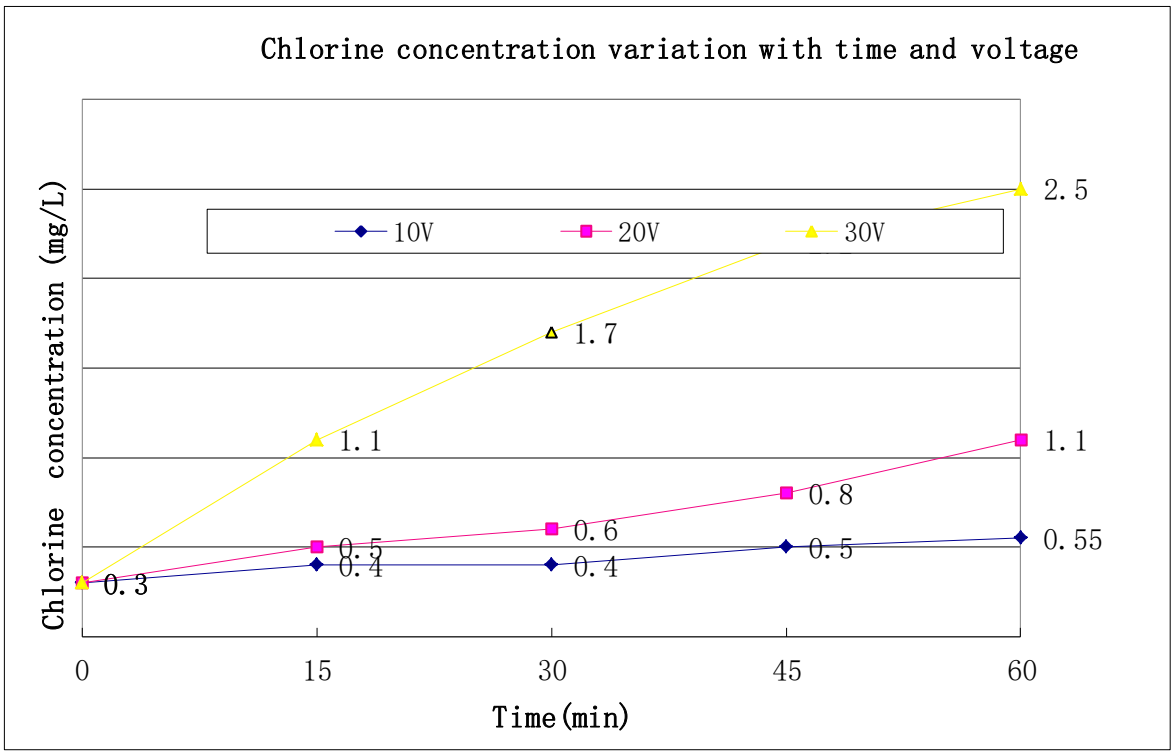


Figure 4.7 The effect of electric potential on free chlorine formation

As demonstrated in Figure 4.7, the rate of free chlorine formation was also very slow under lower voltage (10 V) because the current was small in the system. When the voltage was increased to 20 V, the rate of chlorine generation was significantly increased. The concentration of free chlorine in the water reached about 1.1 mg/L after 60-minute

operation. As the electric voltage was further increased to 30 V, the formation of free chlorine was substantially increased due to the higher current applied. The reaction time required to generate 1.1 mg/L free chlorine was shortened to 15 min for 30 V. As the electrolysis went on, the concentration of free chlorine accumulated. This indicated that the system is capable of generating a free chlorine production rate that reaches a dynamic equilibrium with the rate of chlorine consumption in the flushing water disinfection process.

Moreover, the formation of free chlorine was positive and was proportional to the electric voltage applied across the electrodes when chloride concentration was controlled above a certain value. The higher the voltage applied in electrode, the higher rate of free chlorine formation in the water.

4.3.3 Discussion on flushing water

In this section, the effect of electric potential on bacterial content and effect of electric potential on chlorine concentration for flushing water were studied. The optimum operational condition of this system is 30 V. In order to acquire sufficient free chlorine (1 to 3 mg/L) in the fountain water for effective disinfection, we then set 30V as the work condition.

4.4 Summary

The laboratory study on a novel RuO_2 electrolysis and TiO_2 photocatalytic water disinfection system for swimming pool water, fountain water and flushing water was developed and carried out in chapter 4. The optimum operational condition of this system for each type of water was obtained. For the disinfection of swimming pool water, the optimum condition is the followings: electric voltage of 25 V, contact time of 15 mins, and chloride concentration of 50 mg/L. For flushing water disinfection, the optimum condition is the followings: electric voltage of 30 V. For fountain water treatment, the optimum condition is the followings: electric voltage of 30 V, and the contact time of 60 mins. The similar system would be used in the subsequent full-scale water disinfection that will be arranged for installation and on-site testing.

Chapter 5: Treatment Performances and Long Term Stability of the System in Onsite Operations

This part includes the on-site pilot-scale testing of the electro-photo-disinfection system. The operation parameters were varied to test the stability of the system in onsite operations. Results demonstrated the effectiveness of the system. The RuO_2 electrolytic and TiO_2 photocatalytic water disinfection system was capable of ensure the quality of swimming pool water, flushing water and fountain water. This relative compact system enables water disinfection without having to resort to chlorine dosing, which is costly and poses potential health hazards to the public. This novel RuO_2 electrolytic and TiO_2 photocatalytic technology may also be useful for safe and cost-effective disinfection in potable water tanks, ornamental pools, air-con cooling towers, wastewater treatment, etc.

5.1 On-site Pilot-scale Testing of Swimming Pool Water

The pilot-scale system was installed and assessed on a long-term basis at the swimming pool at the Royal Peninsula, Hung Hom. The technology for water treatment was tested on-site rigorously for its treatment performances, long-term reliabilities and maintenance requirements.

5.1.1 System Operations

A pilot-scale electrolytic disinfection simulator adjoined with 80M PCO unit was designed and fabricated. Part of the swimming pool water leaving the sand filter was diverted to the electro-photocatalytic disinfection system. The electrolytic component contains a stainless steel container, water circulation pump, electrolysis device and a set of PVC pipe lines.

The PCO unit with effective titanium dioxide coated surface of area of 2,850 cm^2. The UV lamp wave length was 254 nm with UV lamp length of 29 cm. The PCO unit was constructed by stainless steel, grade SUS304/SUS316.

After passing the sand filter, a portion of swimming pool water was drained into the system from the main stream of flow to the chlorination process. The water pass the electro-activation component before passing the photocatalytic oxidation unit and recycled at the flow rate of 2 m^3/h. Flow rate was controlled by a series of control valves and internal recirculation circuits. The concentration of free chlorine and the concentration of *E. Coli* were monitored during the processes of electrolysis and photocatalysis at each 15 min interval. The free chlorine concentrations and *E.Coli* count in three sampling points were analysed. The three sampling points are 1) at the entrance of flow to the tank, 2) outlet from the electro-activation unit and 3) outlet from the

photocatalytic oxidation unit. The chloride concentrations and the level of organic substance (urea) existed in the swimming pool water on-site was measured in advance.

5.1.2 Water sample analysis

The effectiveness of this process was quantified by measuring the free chlorine concentrations in the water and evaluating the *E. Coli* concentration that were removed in the process. Chloride concentrations in the circulating water and the voltage applied to the system were also monitored in the experiment. Total organic carbon was also measured to identify the concentration of organic pollutants in the swimming pool water on-site.

5.1.3 *E. Coli* concentrations

The pilot scale experiment was carried under the operating conditions showed in Table 5.1. And the initial chlorine concentration at the influent sampling point was 1.53 mg/L.

E. Coli concentrations in the swimming pool water throughout the experiment were analysed at every 15 min. The *E. Coli* concentrations at influent point, the outlet from the electro-activation unit (sampling point A) and outlet from the photocatalytic oxidation unit (sampling point B) were all found to be 0 mg/L in the experiment.

Table 5.1 Typical operating conditions of the on-site system

Parameters	Readings
TOC	4 mg/L
pH	6.5
Temperature	21 ℃

The absence of *E. Coli* in the water samples was because of the existing residue chlorine of 1.53 mg/L in the swimming pool water which circulated in the system. The background free chlorine concentration was effective to eliminate *E. Coli* from the swimming pool water.

5.1.4 Fixed electrical supply (DC 30 V) with different concentration of chloride added

The power voltage was kept at 30 VDC for evaluating the effect of concentration of chloride on the generation of chlorine. Analysis of free chlorine formation was conducted under different concentrations of chloride of 20 mg/L, 50 mg/L and 100 mg/L. Each test was operated with 60 minutes and water sample was taken at every 15 minutes.

5.1.4.1 20 mg/L of chloride added into electrolysis system

The production of free chlorine under the concentrations of chloride of 20 mg/L over the period was shown in Figure 5. 1.

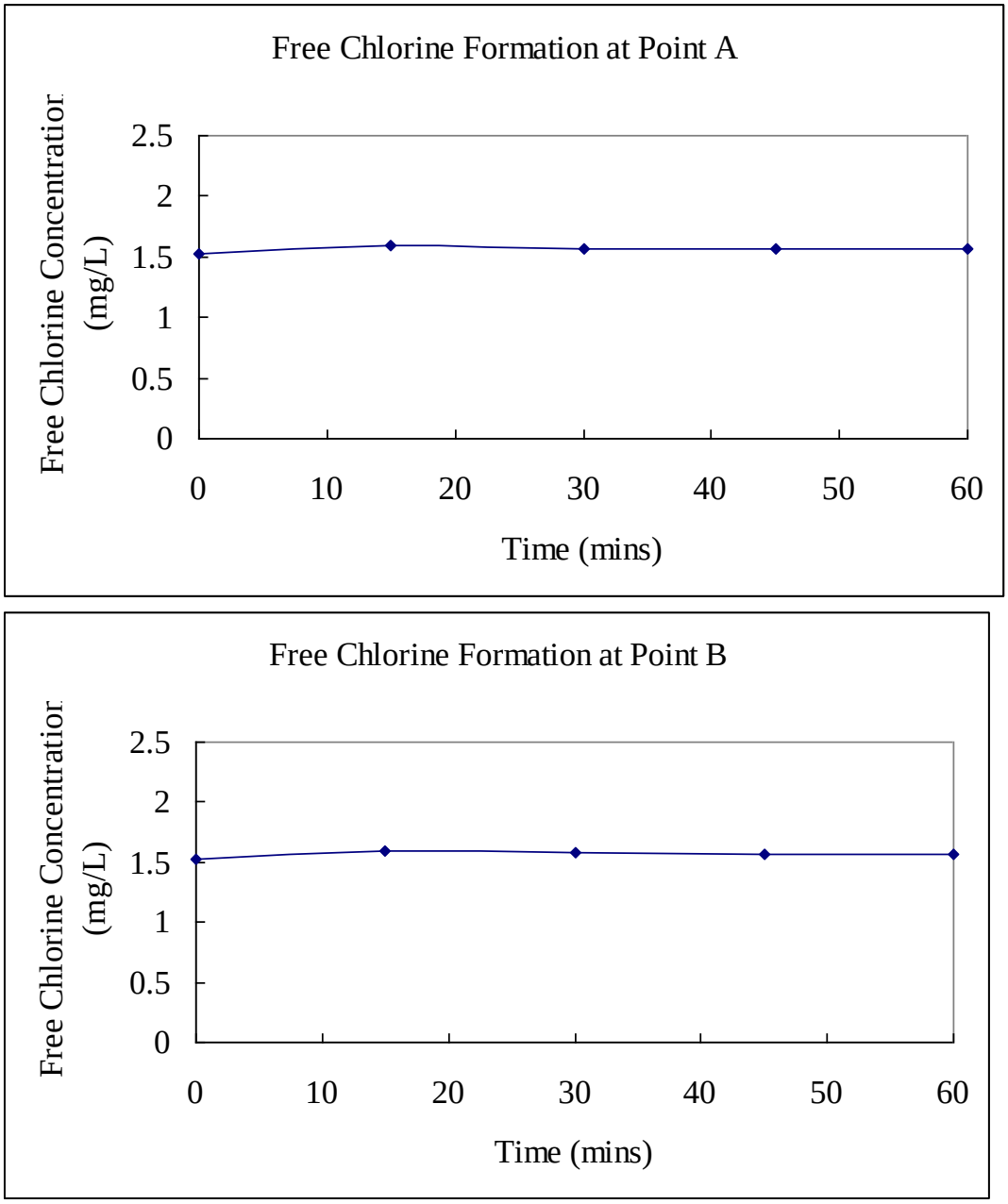


Figure 5.1 Free Chlorine concentrations at 30V and NaCl of 20 mg/L

Figure 5.1 showed that more than 1 mg/l of free chlorine was generated under operation with 20 mg/l chloride ion added at 30V, which reached the requirement of the standard of public and private swimming pools in Hong Kong (> 1 mg/l).Moreover, the free chlorine concentrations in sampling point A and sampling point B were almost the same, which suggested that the photocatalytic oxidation process hardly made the contribution to the formation of free chlorine.

5.1.4.2 50 mg/L of chloride added into electrolysis system

The production of free chlorine in the two sampling points under the concentrations of chloride of 50 mg/L over the period was shown in Figure 5. 2.

As shown in Figure 5.2, the free chlorine concentration increased to above 2 mg/L after 30-min operation. Moreover, the concentration of free chlorine accumulated when the electrolysis went on. This proved that the system was capable of generating a free chlorine production rate that reaches a dynamic equilibrium with the rate of chlorine consumption in the pool water disinfection process.

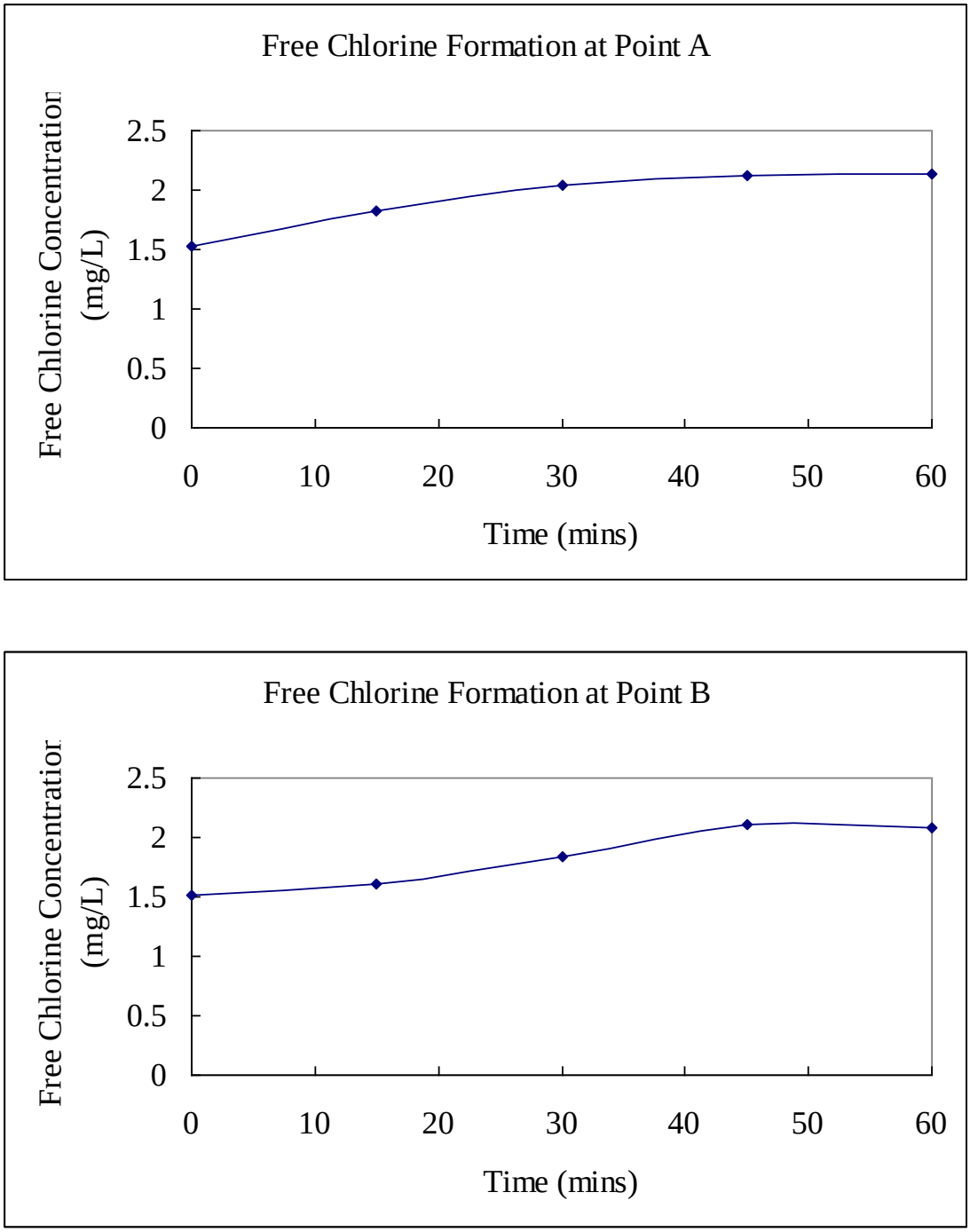
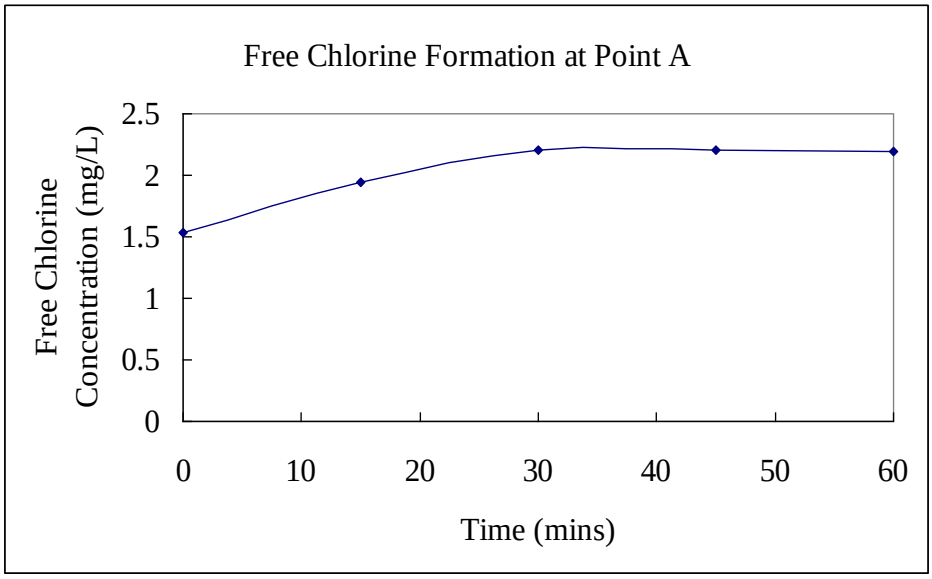


Figure 5.2 Free Chlorine concentration at 30V and NaCl of 50 mg/L

5.1.4.3 100 mg/L of chloride added into electrolysis system

The production of free chlorine in the two sampling points under the concentrations of chloride of 50 mg/L over the period was shown in Figure 5. 3.



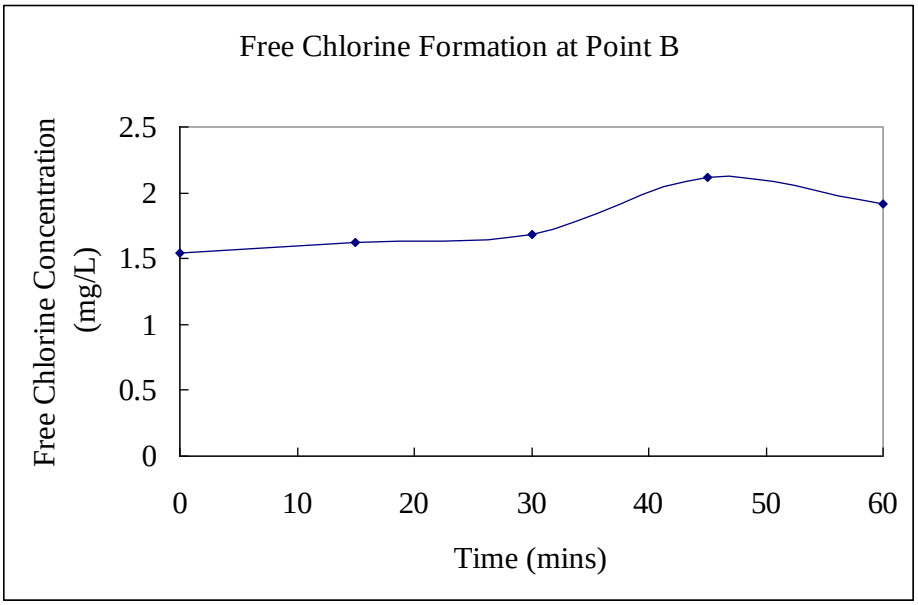


Figure 5.3 Free Chlorine concentrations at 30V and NaCl of 100 mg/L

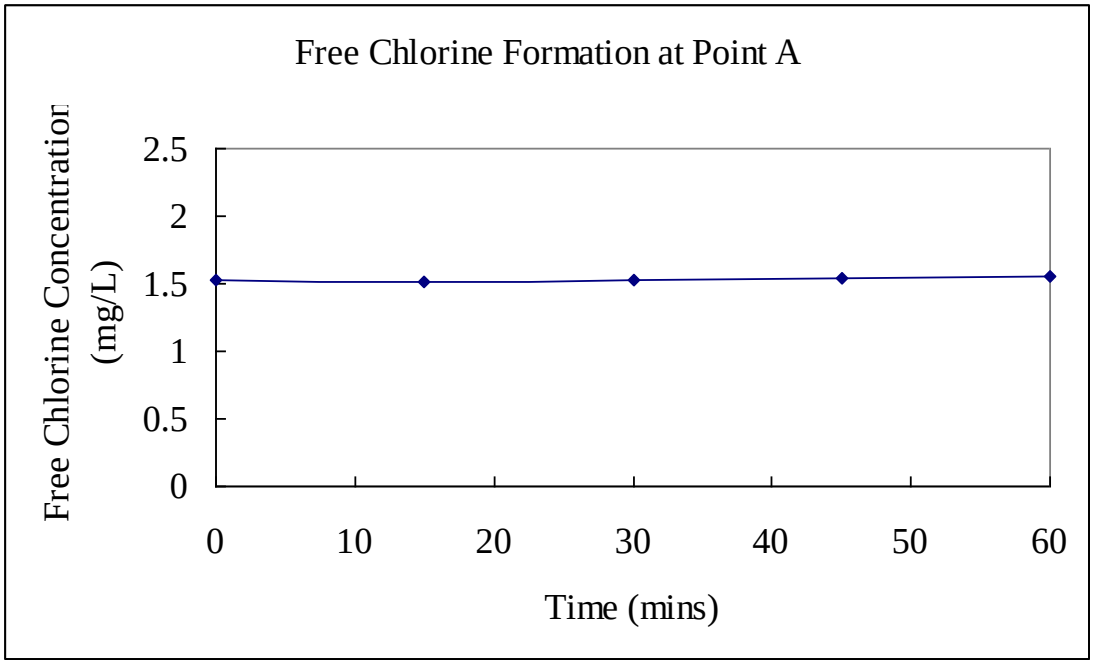
As shown in Figure 5.3, the free chlorine concentration increased to above 2 mg/L after 30-min operation. Comparing Figure 5.1, Figure 5.2 and Figure 5.3, it could be found that the more chloride added into electrolysis system, the higher concentration of free chlorine formation in the water because low electrolyte concentration resulted in poor conductivity of the solution. On the other hand, it could be found that the free chlorine concentrations in the two sampling points were slightly different. The decline of free chlorine might be due to the water motion in the system, which was somewhat like the effect of aeration in the water that purges out free chlorine.

5.1.5 Fixed NaCl concentration at 100 mg/L with different electric voltage

The chloride concentration was kept at 100 mg/L for evaluating the effect of electric voltage on the generation of chlorine in on-site pilot-scale swimming pool water. Analysis of free chlorine formation was conducted under different voltage values of 10 V, 20 V and 30 V. Each test was operated with 60 minutes and water sample was taken at every 15 minutes.

5.1.5.1 DC 10 V applied

The production of free chlorine under the electric voltage of 10V over the period was shown in Figure 5. 4.



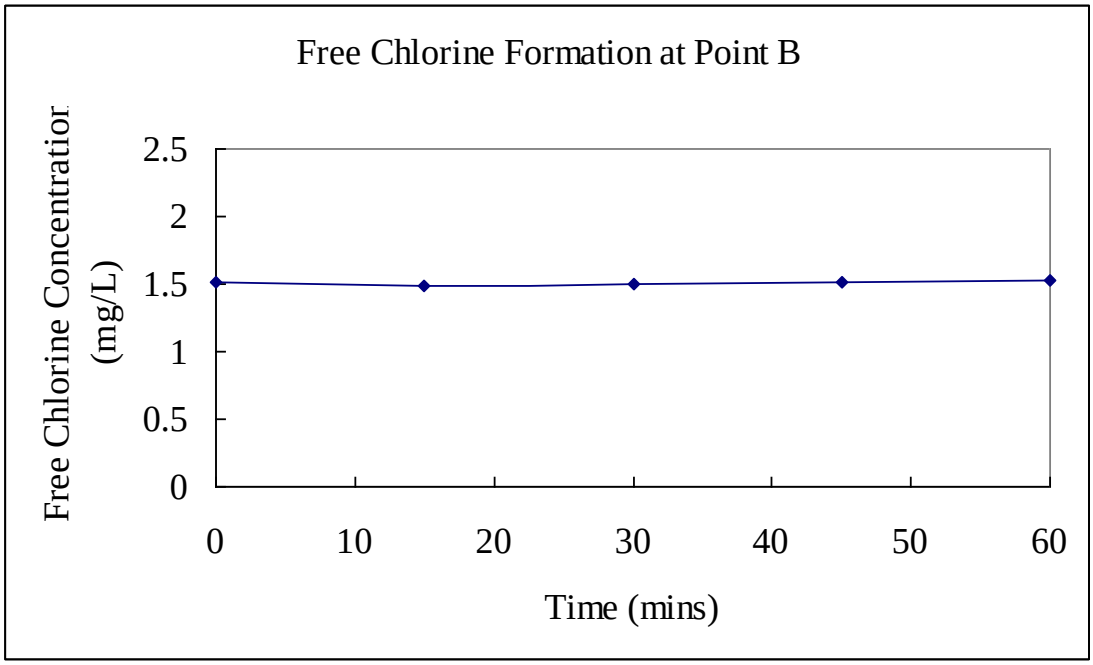


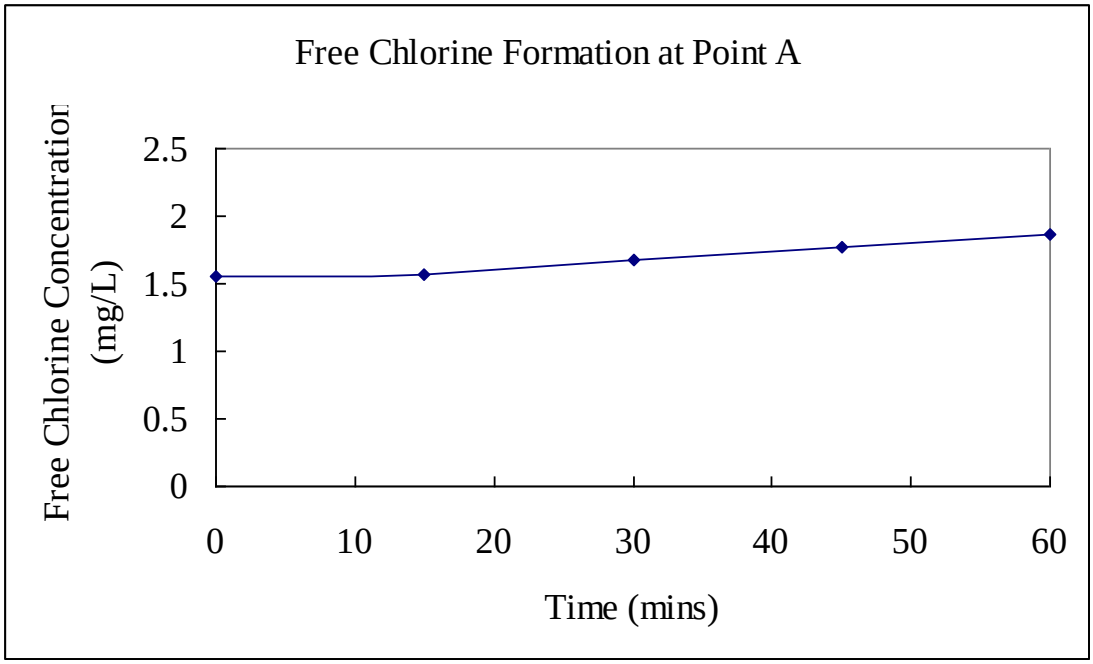
Figure 5.4 Free Chlorine concentration at 10V and NaCl of 100 mg/L

Figure 5.4 showed that the free chlorine concentration remained at about 1.5 mg/L under operation with 100 mg/L chloride ion added at 10V. Moreover, the free chlorine concentrations in sampling point A and sampling point B were almost the same, which proved that the photocatalytic oxidation process hardly made the contribution to the formation of free chlorine.

5.1.5.2 DC 20 V applied

The production of free chlorine under the electric voltage of 20V over the period was shown in Figure 5.5.

As shown in Figure 5.5, the free chlorine concentration increased from about 1.5 to 1.8mg/Lover the period. This proved that the system was capable of generating a free chlorine production rate that reaches a dynamic equilibrium with the rate of chlorine consumption in the pool water disinfection process under this condition.



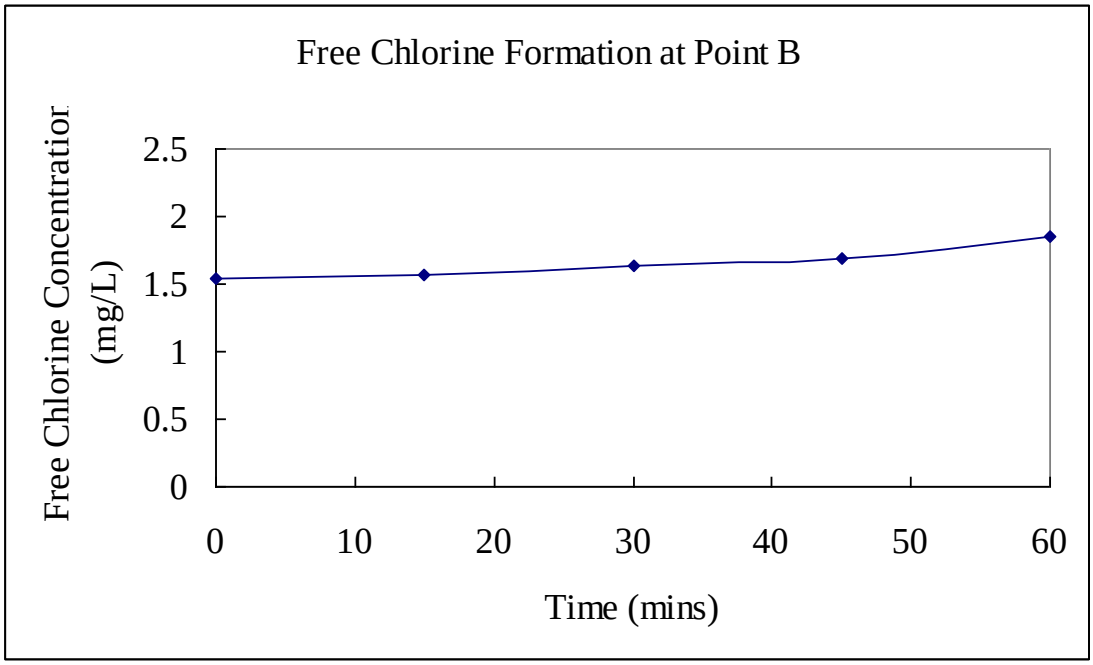


Figure 5.5 Free Chlorine concentration at 20V and NaCl of 100 mg/L

5.1.5.3 DC 30 V applied

The production of free chlorine under the electric voltage of 30V over the period was shown in Figure 5.6.

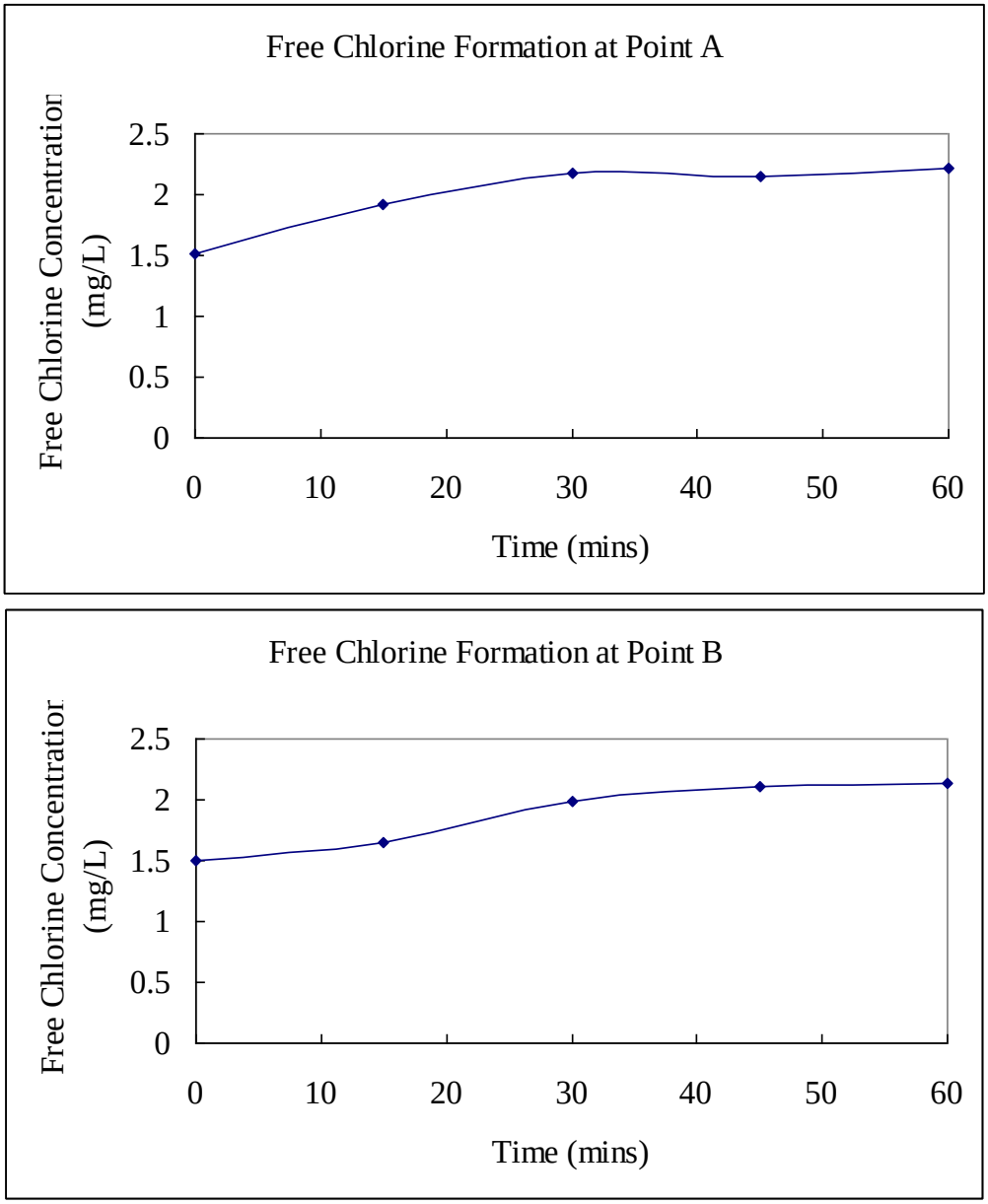


Figure 5.6 Free Chlorine concentrations at 30V and NaCl of 100 mg/L

As shown in Figure 5.6, the free chlorine concentration increased to above 2 mg/L after 30-min operation. Comparing Figure 5.4, Figure 5.5 and Figure 5.6, it could be found that the formation of free chlorine was substantially increased due to the higher voltage applied as the electric voltage was further increased from10 and 30V.On the other hand, it could also be found that the free chlorine concentrations in the two sampling points were different and this might be due to the chlorine decay during the photocatalytic oxidation process.

5.1.6 Formation of free chlorine solely with photocatalytic oxidation component

The effects of photocatalytic oxidation component to the concentration of free chlorine were also studied. Concentration of free chlorine in the water sample was monitored when no electric current was applied to the electro-activation component and only the PCO component was switched on. The production of free chlorine with NaCl concentration of 100mg/Lover the period was shown in Table 5.2.

Table 5.2 Free chlorine concentrations solely with PCO system

Time (mins)	Free Chlorine (mg/L) at sampling point A	Free Chlorine (mg/L) at sampling point B
0	1.52	1.54
15	1.43	1.41
30	1.39	1.39
45	1.26	1.25
60	1.24	1.25

It could be found that the rate of free chlorine formation was very slow solely with photocatalytic oxidation component. The PCO could break up organic compounds and kill most bacteria in the water, but it would not form the free chlorine solely. It confirmed the formation of free chlorine from the electrolytic activation component.

5.1.7 pH

The relationship between the pH and operation time was studied. The variation of pH over the period of 60-minute operation was monitored and the result was shown in Table 5.3.

Table 5.3 pH variation with time

Time (min)	0	15	30	45	60
pH	6.89	7.02	7.15	7.24	7.36

As shown in Table 5.3, the pH increased after the increase of the treatment time and the pH increased about 0.5 after 60 minutes. The pH value of the system reached a steady value upon prolongs treatment time. The pH reached in this system is in an acceptable range (4.0 to 9.0) (Chong *et al*., 2010)

5.1.8 Temperature

The variation of temperature over the period of 60-minute operation was also monitored to evaluate the effect of this water treatment system on the temperature. The result was shown in Table 5.4.

Table 5.4 Temperature variation during the process

Time (min)	0	15	30	45	60
Temperature (℃)	30.5	30.6	30.8	30.9	40.5

According to the results, it could be found that the temperature would increase with the increasing of operation time. But the temperature after 60mins operation was not very high and it increased only 10 ℃.One possible explanation for this could be that during the operation of the system, PCO destroy the stability of the molecules and a large number of molecules were colliding with each other and made heat. This process caused the temperature rising. The temperature of the system is steady within 0 to 45 minutes but greatly increases at 60 minutes. In fact, the temperature of the system is in an acceptable range (<80℃) (Chong *et al*., 2010).

5.1.9 Discussion on swimming pool water

The RuO_2 electrolytic and TiO_2 photocatalytic water disinfection system was designed and fabricated in our work. The water passed the electro-activation component first. Sufficient free chlorine was generated in the electro-activation component on the optimal condition. The free chlorineat a relatively high concentration would remove and deactivate red worm and red worm egg. After passing the electro-activation component, the water passed then the photocatalytic oxidation unit and the organic compounds, including bacteria and viruses would break up. The water recycled at a certain flow rate and the electrolysis and photocatalysis processes killed most bacteria in the water. It could be concluded that the RuO_2 electrolytic and TiO_2 photocatalytic water disinfection system was capable of ensure the swimming pool water quality.

In addition, this relative compact system enables water disinfection without having to resort to chlorine dosing, which is costly and poses potential health hazards to the public. This novel RuO_2 electrolytic and TiO_2 photocatalytic technology may also be useful for safe and cost-effective disinfection in potable water tanks, ornamental pools. The results obtained the pilot-scale experiment also provide reference for optimal operating conditions in different treatment demand.

5.2 Fountain Water

Our ultimate goal is to find out the disinfection effect on water quality of fountain water， so we have analyzed bacterial content, free chlorine concentration, pH and temperature (The data from the average of 20 times evidence). 30V is the working voltage; we maintain the voltage for the machine on 30V. The machine has two parts, namely, electro-activation component and photocatalytic oxidation component. The system for water treatment was tested for its treatment performances.

5.2.1 Only Photocatalytic Oxidation (PCO)

The effect of photocatalytic oxidation component to the removal of bacteria was studied. Bacteria (Escherichia coli) variation with time in the water sample was monitored when

no electric current was applied to the electro-activation component and only the PCO component was switched on. The result was shown in Table 5.5.

Table 5.5 Bacteria variation with time (only PCO)

Time（min）	0	15	30	45	60
Bacteria （/plate）	35~40	31~32	23~26	15~17	3~5

It could be found that bacteria (Escherichia coli) would decrease with the increasing of treatment time. However, there were still bacteria existed after 60 min treatment only with photocatalytic oxidation component. The PCO could break up organic compounds, including bacteria and viruses kill most bacteria in the water, but if with use the PCO only, it did not have strong efficiency.

5.2.2 Only electro-activation component

The effect of electro-activation component to the removal of bacteria was studied. Bacteria (Escherichia coli) variation with time in the water sample was monitored when the PCO component was switched off and only the electro-activation component was working. The result was shown in Table 5.6.

Table 5.6 Bacteria variation with time (only electro-activation)

Time（min）	0	15	30	45	60
Bacteria （/plate）	35~40	31~32	27~29	19~21	11~13

It could be found that bacteria would decrease with the increasing of treatment time. But after 60 min treatment there were still bacteria existed and the removal efficiency of bacteria was about 70% only with photocatalytic oxidation component. The electro-activation component could keep the chlorine ion in the water; it also had strong disinfection ability. But with use electro-activation component only, it did not have good efficiency.

5.2.3 Both PCO and electro-activation component

The effect of the combination of PCO and electro-activation component to the treatment of fountain water was studied. The variation of disinfection efficiency, free chlorine concentration, pH and temperature with time in the water sample was monitored and determined by using the RuO_2/TiO_2 water disinfection system.

5.2.3.1 The disinfection efficiency of the bacterial content

The disinfection efficiency of the microorganisms of this system was evaluated by the removal of *Escherichia coli*, which was a kind of common pathogen. The removal efficiency of the pathogenic microbe was determined by measuring the quantity of microbes in the samples collected from the tank before and after the disinfection process. The result was shown in Table 5.7.

Table 5.7 Bacteria variation with time

Time（min）	0	15	30	45	60
Bacteria（/plate）	35~40	29~30	15~17	3~5	0

According to the results, it could be found that the germicidal efficiency of disinfection, depended primarily on the treatment time and amount of bacteria would decrease with the increasing of treatment time. The amount of bacteria would be decrease to zero after 60 mins treatment. The excellent performance on the treatment of pathogenic microbes was observed by the system operated under the optimum conditions.

5.2.3.2 Free Chlorine Concentration

The relationship between the free chlorine concentration and operation time was studied by monitoring the chlorine concentration over the period of 60-minute operation. The result was shown in Table 5.8.

Table 5.8 Free chlorine concentration variations with time

Time(min)	Free chlorine conc. (mg/L)
0	1.3
15	1.58
30	1.73
45	1.84
60	1.97

It could be found that the free chlorine concentration would increase over the period of 60-minute operation. The free chlorine could be generated by electro-activation component and its concentration accumulated when the RuO_2/TiO_2 water disinfection system went on. This proved that the system was capable of generating a free chlorine production rate that reaches a dynamic equilibrium with the rate of chlorine consumption in the fountain water disinfection process.

5.2.3.3 pH

The relationship between the pH and operation time was studied. The variation of pH over the period of 60-minute operation was monitored and the result was shown in Table 5.9.

Table 5.9 pH variation with time

Time (min)	0	15	30	45	60
pH	7.14	7.65	7.75	7.85	7.95

As shown in Table 5.9, the pH increased as linear after treatment at the beginning. After 15 mins, the pH value would increase about 0.1 every 15 minutes and the pH approached by 8.0 after 60 minutes. However, after 60 minutes, the pH can be kept at acceptable level, i.e. 4.0 to 9.0 (Chong *et al*., 2010)

5.2.3.4 Temperature

The variation of temperature over the period of 60-minute operation was also monitored to evaluate the effect of this water treatment system on the temperature. The result was shown in Table 5.10.

Table 5.2 Temperature variation during the process

Time (min)	0	15	30	45	60
Temperature (℃)	28.2	28.3	28.6	29.4	30.6

According to the results, it could be found that the temperature would increase with the increasing of operation time. But the temperature after 60mins operation was not very high and it increased only 2.4 ℃.One possible explanation for this could be that during the operation of the system, PCO destroy the stability of the molecules and a large number of molecules were colliding with each other and made heat. This process caused the temperature rising. In fact the temperature of the system with 60 minutes operation time is kept within acceptable range, i.e. 20 to 80 ℃ (Chong *et al*., 2010).

5.2.3.5 Discussion on fountain water

The RuO_2/TiO_2 water disinfection system was capable of ensuring the fountain water quality in terms of pathogenic content. This relative compact system enables water disinfection without having to resort to chlorine dosing, which is costly and poses potential health hazards to the public. This system is promising in the practical use of the fountain water treatment.

5.3 Flushing Water

The technology for flushing water treatment was tested on-site for its treatment performances, reliabilities and maintenance requirements. We have studied the disinfection efficiency of the bacterial content and free chlorine concentration over the period of operation. In addition, the effect of salinity and temperature on bacterial disinfection was also studied.

5.3.1 The disinfection efficiency of the bacterial content

The disinfection efficiency of the microorganisms of this system was evaluated by the removal of *Escherichia coli,* which was a kind of common pathogen. The removal efficiency of the pathogenic microbe was determined by measuring the quantity of microbes in the samples collected from the tank before and after the disinfection process. The result was shown in Table 5.11.

Table 5.3 Bacteria content variation with time

Time（min）	0	15	30	45	60
Bacteria （/plate）	38~41	30~32	16~17	4~5	0

As shown in Table 5.11, it could be found that the germicidal efficiency of disinfection, depended primarily on the treatment time and amount of bacteria would decrease with the increasing of treatment time. The amount of bacteria would be decrease to zero after 60 mins treatment. The excellent performance on the treatment of pathogenic microbes was observed by the system operated under the optimum conditions.

5.3.2 Free Chlorine Concentration

The relationship between the free chlorine concentration and operation time was studied by monitoring the chlorine concentration over the period of 60-minute operation. The result was shown in Table 5.12.

Table 5.4 Free Chlorine concentration variation with time

Time(min)	Free chlorine conc. (mg/L)
0	1.5
15	1.7
30	1.9
45	2.0
60	2.1

According to the results, it could be found that the free chlorine concentration would increase over the period of 60-minute operation. The free chlorine could be generated by electro-activation component and its concentration accumulated when the RuO_2/TiO_2 water disinfection system went on. This proved that the system was capable of generating a free chlorine production rate that reaches a dynamic equilibrium with the rate of chlorine consumption in the flash water disinfection process.

5.3.3 The Effect of Temperature on Bacterial Disinfection

In order to evaluate the effectiveness and stability of this water disinfection system, the effect of temperature on bacterial disinfection was studied under different temperature.

5.3.3.1 Fixed temperature at 10 ℃.

The efficiency of disinfection at 10 ℃ by only the electro-activation component, only the PCO component and combination of electro-activation component and PCO component over the period of 60-minute operation was examined and the result was shown in Table 5.13.

Table 5.5 The efficiency of disinfection at 10 ℃

Time (min)	0	15	30	45	60
Only PCO	0	22%	40%	85%	90%
Only electro-activation component	0	25%	42%	85%	90%
Both	0	30%	50%	90%	100%

The result showed that the efficiency of disinfection would increase with the increasing of treatment time. However, the efficiency of disinfection could only reach 90% after 60 mins treatment only with photocatalytic oxidation component and only the electro-activation component. However, the efficiency of disinfection would reach 100%with the combination of electro-activation component and PCO component after 60 mins treatment. The excellent performance on the treatment of pathogenic microbes was observed by the system combined with electro-activation component and PCO component operated at 10 ℃.

5.3.3.2 Fixed temperature at 20 ℃

The efficiency of disinfection at 20 ℃ by only the electro-activation component, only the PCO component and combination of electro-activation component and PCO component

over the period of 60-minute operation was examined and the result was shown in Table 5.14.

Table 5.6 The efficiency of disinfection at 20 ℃

Time (min)	0	15	30	45	60
Only PCO	0	24%	42%	87%	92%
Only electro-activation component	0	26%	44%	88%	91%
Both	0	33%	52%	92%	100%

As shown in Table 5.14, the efficiency of disinfection would increase with the increasing of treatment time. The efficiency of disinfection was 92% and 91%, respectively, after 60 mins treatment only with photocatalytic oxidation component and only the electro-activation component, which were slightly higher than those at 10℃. Moreover, the efficiency of disinfection would reach 100% by the system combined with electro-activation component and PCO component after 60 mins treatment. The excellent performance on the treatment of pathogenic microbes was observed by the system in combination of electro-activation component and PCO component operated at 20 ℃.

5.3.3.3 Fixed temperature at 35 ℃

The efficiency of disinfection at 35℃ by only the electro-activation component, only the PCO component and combination of electro-activation component and PCO component over the period of 60-minute operation was examined and the result was shown in Table 5.15.

Table 5.7 The efficiency of disinfection at 35 ℃

Time (min)	0	15	30	45	60
Only PCO	0	26%	42%	87%	92%
Only electro-activation component	0	28%	45%	88%	92%
Both	0	35%	53%	92%	100%

It could be found that the efficiency of disinfection would increase with the increasing of treatment time. However, the efficiencies of disinfection were over 90% after 60 mins treatment only with photocatalytic oxidation component and only the electro-activation component. The efficiency of disinfection would reach 100% with the combination of electro-activation component and PCO component after 60 mins treatment. The excellent performance on the treatment of pathogenic microbes was observed by the system combined with electro-activation component and PCO component operated at 35℃.

5.3.4 pH

The relationship between the pH and operation time was studied. The variation of pH over the period of 60-minute operation was monitored and the result was shown in Table 5.16.

Table 5.8 pH variation with time

Time (min)	0	15	30	45	60
pH	7.21	7.25	7.34	7.52	7.69

As shown in Table 5.16, the pH increased continuously during the operation. After 60 minutes treatment, the pH increased about 0.5. In fact, the pH value of the system can be kept at acceptable level, i.e. 4.0 to 9.0 (Chong *et al*., 2010).

5.3.5 The effect of salinity

The salinity in the flushing water was not always stable. In order to evaluate the effectiveness and stability of this water disinfection system, the disinfection efficiency under different concentration of NaCl from 1.5 % to 3.5 %, which is the common salinity range in the flushing, was analyzed.

Table 5.9 The efficiency of disinfection with different salinity

Time(min) / NaCl (%)	0	15	30	45	60
1.5	0	39%	55%	87%	100%
2.0	0	39%	57%	89%	100%
2.5	0	41%	59%	90%	100%
3	0	40%	60%	91%	100%
3.5	0	42%	61%	93%	100%

It could be found that the efficiency of disinfection depended primarily on the operation time. The efficiencies of disinfection would all reach 100% under different concentrations of NaCl from 1.5 % to 3.5 %after 60 mins treatment. This superior result showed that the variation of salinity would not decrease efficiency of disinfection of this system. Therefore, our machine was reliable for the disinfection of flushing water.

5.3.6. Discussion on flushing water

It could be found from the results that our machine with the combination of electro-activation component and PCO component had high efficiency in different temperature on disinfection, which meant that our disinfection system had a high effectiveness and stability in four seasons. This system is promising in the practical use of the flushing water treatment.

5.4 Summary

The disinfection system has been established that the RuO_2/TiO_2 water disinfection system has been very effective in treating and disinfecting water in water features in residential estates. A SHK condominium estate (namely The Harbour Place) in the Hung Hom district has been selected for subsequent on-site testing of the system. This relative compact system enables water disinfection without having to resort to chlorine dosing, which is costly and poses potential health hazards to the public. The effectiveness and stability of disinfection mechanism and process has been optimized. The higher current applied as the electric voltage and the more chloride added into electrolysis system, the higher free chlorine concentration and disinfection efficiency would be achieved. Under optimum operational condition of this system, the water passed the electro-activation component first. Sufficient free chlorine was generated in the electro-activation component on the optimal condition. The free chlorine at a relatively high concentration

would remove and deactivate pathogens. After passing the electro-activation component, the water passed then the photocatalytic oxidation unit and the organic compounds, including bacteria and viruses would break up. The water recycled at a certain flow rate and the electrolysis and photocatalysis processes killed most bacteria in the water. Moreover, it had been proven in our work that the salinity and temperature would not decrease the disinfection efficiency, which indicated that this system designed and fabricated in work was stable and reliable for the water disinfection.

In conclusion, this compact electro-photo-disinfection system which has small footprint, low power consumption, no chemical addition requirement is a fully automatic, stable and reliable water disinfection system and it is promising in the practical use of the water treatment

Chapter 6: Conclusions and Recommendations

6.1 Conclusion

The novel method developed in this study is an electrolytic-photocatalytic technology in which low levels of free chlorine may be produced *in situ* in NaCl-containing solutions, without resorting to chemical dosing into the swimming pool, fountain water and toilet flushing system. The photocatalytic oxidation component in the system also provides extra disinfection capacity, thus securing in the swimming pool water, fountain water and toilet flushing water quality.

The study reported include the laboratory testing of the RuO_2/TiO_2 system for optimizing the operating conditions, and the on-site pilot-scale testing for the stability and reliability of the system for the intended applications. Results demonstrated that the system was effective in its respective intended purposes.

The electro-photo disinfection system is expected to emerge as a superior option in water disinfection. The electro-activation technology capitalizes on a special coating technique of a specifically designed formula of ornamented ruthenium dioxide on D.C. electrodes.

The electrically activated coated surfaces transform naturally occurring chloride ions in water into activated chlorine with effective disinfecting power. This technology has been modified into a compact system that has small footprint, low power consumption, no chemical addition requirement, fully automatic operation, stable and reliable water disinfection system.

Firstly, the RuO_2/TiO_2 water disinfection system was capable of ensuring the swimming pool water, fountain water and flushing water quality in terms of pathogenic content. This relative compact system enables water disinfection without having to resort to chlorine dosing, which is costly and poses potential health hazards to the public. A stable 100 % pathogenic destruction was achieved at a relatively short treatment time of 60 minutes and relatively low operational electro-potential of 30 volts. This novel RuO_2/TiO_2 technology may also be useful for safe and cost-effective disinfection in roof-top potable water tanks, cooling towers of central air conditioning systems, wastewater treatment, etc.

Secondly, photocatalytic oxidation (PCO) component in the system utilizes TiO_2 as a photocatalyst to generate oxidation/reduction reactions. When a photo catalyst medium is exposed to radiation of ultraviolet rays, active electrons will be set free from the TiO_2 coating and the positively charged pockets called “positive holes” will be generated. The hydroxide ions (OH-) is strongly attracted by positive holes from ambient water and then an electron is taken from an OH-. It turns into an extremely unstable OH hydroxyl radicals. The organic compounds and pollutants will give out electrons to hydroxyl

radicals. This reaction breaks up the water-borne organic compounds, including bacteria and viruses, and degrading them into carbon and water.

Comparing with the standard values, namely 1 to 3 mg/l, of free chlorine that should be dosed in the public swimming pools in Hong Kong in order to achieve acceptable disinfection, this study suggested that the added amount of common non-disinfecting chloride-ions to the pool water at a concentration of around 50 mg/l, could achieve comparable disinfection power.

Total bacteria count decreased with the increase of chlorine generation. Results from the tests illustrated that the electrochemically generated chlorine is useful and effective for water disinfection. According to the results, CT (contact time) value for the disinfection of chlorine was between 15 mins and 30 mins, which was comparable with conventional systems. Because of water recirculation pump, some chlorine would be purged and emitted to the air. So the actual formation and existing of free chlorine through the electrolysis process could be a little bit different compared with the above reported situation. When the electrolysis device is applied in full-scale swimming pools, the temperature factor will not take effect.

All these results suggested that the novel electrolysis system could achieve comparable disinfecting effects as conventional systems, with possible lower installation costs and definitely lower operation costs.

This novel RuO_2 electrolytic and TiO_2 photocatalytic technology may also be useful for safe and cost-effective disinfection in potable water tanks, ornamental pools, air-con cooling towers, wastewater treatment, etc. The results obtained the pilot-scale experiment also provide reference for optimal operating conditions in different treatment demand.

The pilot-scale system was installed, monitored and assessed at Harbour Place, Hung Hom. The technology for water treatment was tested on-site in order to demonstrate its outstanding treatment performances in residential estates. A SHK condominium estate (namely The Harbour Place) in the Hung Hom district has been selected for subsequent on-site testing of the system. The effectiveness of electrolytic disinfection mechanism and process has been optimized.

6.2. Recommendations

The RuO_2 electrolytic and TiO_2 photocatalytic water disinfection system could be further scaled-up and developed as final version for comprehensive site applications. This will involve a 15-20 times scale up to a full-scale system. The process engineering design and system optimization should be further studied in detail. The system should be put on on-site testing for long term performance, reliability and stability. The system could also be developed for comprehensive treatment of water, which will include features to remove suspended solids and other pollutants in addition to pathogenic disinfection.

References

Akira Fujishima, Tata N. Rao, Donald A. Tryk. Titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, Volume 1, Pages 1–21, 2000.

Bahnemann, D. Photocatalytic. Water treatment: solar energy applications. *Solar Energy* Volume 77, Pages 445–459, 2004.

Bi, J. and Liu, B. Water pollution and its control in the Tai Lake Basin, *Jiangsu Statistics Yearbook*, 2004.

Bradley, B.R., Daigger, G.T., Rubin, R. and Tchobanoglous, G. Evaluation of onsite wastewater treatment technologies using sustainable development criteria. *Clean Technologies and Environmental Policy*, Volume 4, Issues 2, Pages 87-99, 2002.

Byrne J.A., Eggins B.R., Brown N., McKinney B. and Rouse M. Immobilisation of TiO_2 powder for the treatment of polluted water. *Applied Catalysis B: Environmental*, Volume 17, Issue 1, Pages 25-36, 1998.

Byrne J.A., A. Davidson, P.S.M. Dunlop, B.R. Eggins. Water treatment using nano-crystalline TiO2 electrodes. *Journal of Photochemistry and Photobiology A: Chemistry*, Volume 148, Pages 365–374, 2002.

Cao S. and Zhu Y. Hierarchically Nanostructured α-Fe. *The Journal of Physical Chemistry C*, Volume 112, Issue 16, Pages 6253-6257, 2008.

Cassano, A.E. and Alfano, O.M. Reaction engineering of suspended solid heterogeneous photocatalytic reactors. *Catalysis Today*, Volume 58, Issues 2, Pages 167-197, 2000.

Chan, A.H., Chan, C.K., Barford, J.P. and Porter, J.F. Solar photocatalytic thin film cascade reactor for treatment of benzoic acid containing wastewater. *Water Research*, Volume 37, Issues 5, Pages 1125-1135, 2003.

Chen J., Liu M. and Zhang L. Application of nano TiO_2 towards polluted water treatment combined with electro-photochemical method. *Water Research*, Volume 37, Issue 16, Pages 3815-3820, 2003.

Chin, S.S., Lim, T.M., Chiang, K. and Fane, A.G. Hybrid low-pressure submerged membrane photoreactor for the removal of bisphenol A. *Desalination*, Volume 202, Issues 1, Pages 253-261, 2007.

Choi, B.J., Jeong, D.S., Kim, S.K., Rohde, C., Choi, S., Oh, J.H., Kim, H.J., Hwang, C.S., Szot, K. and Waser, R. Resistive switching mechanism of TiO_2 thin films grown by atomic-layer deposition. *Journal of Applied Physics*, Volume 98, Issues 3, Pages 33715, 2005.

Choi, H., Stathatos, E. and Dionysiou, D.D. Photocatalytic TiO2 films and membranes for the development of efficient wastewater treatment and reuse systems. *Desalination*, Volume 202, Issues 1, Pages 199-206, 2007.

Chong, M.N., Jin, B., Chow, C.W. and Saint, C. Recent developments in photocatalytic water treatment technology: a review. *Water Research*, Volume 44, Issues 10, Pages 2997-3027, 2010.

Chong, M.N., Jin, B., Zhu, H.Y., Chow, C.W. and Saint, C. Application of H-titanate nanofibers for degradation of Congo Red in an annular slurry photoreactor. *Chemical Engineering Journal*, Volume 150, Issues 1, Pages 49-54, 2009.

Chong, M.N., Vimonses, V., Lei, S., Jin, B., Chow, C. and Saint, C. Synthesis and characterisation of novel titania impregnated kaolinite nano-photocatalyst. *Microporous and Mesoporous Materials*, Volume 117, Issues 1, Pages 233-242, 2009.

Sichel C., Blanco J., Malato S. and Fernández-Ibáñez P. Effects of experimental conditions on E. coli survival during solar photocatalytic water disinfection. *Journal of Photochemistry and Photobiology A: Chemistry*, Volume 189, Issue 2-3, Pages 239-246, 2007.

Drees K P, Abbaszadegan M, Maier R M. Comparative electrochemical inactivation of bacteria and bacteriophage. *Water research*, Volume 37, Issues 10, Pages 2291-2300, 2003.

Dunlop P.S.M., J.A. Byrne, N. Manga, B.R. Eggins. The photocatalytic removal of bacterial pollutants from drinking water. *Journal of Photochemistry and Photobiology A: Chemistry*, Volume 148, Pages 355–363, 2002.

Esplugas, S., Gimenez, J., Contreras, S., Pascual, E. and Rodríguez, M. Comparison of different advanced oxidation processes for phenol degradation. *Water Research*, Volume 36, Issues 4, Pages 1034-1042, 2002.

Fan, L., Ni, J., Wu, Y. and Zhang, Y. Treatment of bromoamine acid wastewater using combined process of micro-electrolysis and biological aerobic filter. *Journal of Hazardous Materials*, Volume 162, Issues 2, Pages 1204-1210, 2009.

Fernández-Ibáñez, P., Blanco, J., Malato, S. and De Las Nieves, F.J. Application of the colloidal stability of TiO_2 particles for recovery and reuse in solar photocatalysis. *Water Research*, Volume 37, Issues 13, Pages 3180-3188, 2003.

Fu, J., Ji, M., Wang, Z., Jin, L. and An, D. A new submerged membrane photocatalysis reactor (SMPR) for fulvic acid removal using a nano-structured photocatalyst. *Journal of Hazardous Materials*, Volume 131, Issues 1, Pages 238-242, 2006.

Fujishima A. and Honda K. Photolysis-decomposition of water at the surface of an irradiated semiconductor. *Nature*, Volume 238, Issue 5385, Pages 37-38, 1972.

Gryta, M., Karakulski, K. and Morawski, A.W. Purification of oily wastewater by hybrid UF/MD. *Water Research*, Volume 35, Issues 15, Pages 3665-3669, 2001.

Gyürék, L.L. and Finch, G.R. Modeling water treatment chemical disinfection kinetics. *Journal of Environmental Engineering*, Volume 124, Issues 9, Pages 783-793, 1998.

Gómez-López, V.M., Gobet, J., Selma, M.V., Gil, M.I. and Allende, A. Operating conditions for the electrolytic disinfection of process wash water from the fresh-cut industry contaminated with E. coli o157:H7. *Food Control*, Volume 29, Issues 1, Pages 42-48, 2013.

Han C., Pelaez M. and Likodimos V. Innovative visible light-activated sulfur doped TiO2 films for water treatment. *Applied Catalysis B: Environmental*, Volume 107, Issue 1-2, Pages 77-87, 2011.

Harper J C, Christensen P A, Egerton T A, et al. Effect of catalyst type on the kinetics of the photoelectrochemical disinfection of water inoculated with E. coli. *Journal of Applied Electrochemistry*, Volume 31, Issue 6, Pages 623-628, 2001.

Hosono, E., Fujihara, S. and Kimura, T. Synthesis, structure and photoelectrochemical performance of micro/nano-textured ZnO/eosin Y electrodes. *Electrochimica Acta*, Volume 49, Issues 14, Pages 2287-2293, 2004.

Huang, X., Meng, Y., Liang, P. and Qian, Y. Operational conditions of a membrane filtration reactor coupled with photocatalytic oxidation. *Separation and Purification Technology*, Volume 55, Issues 2, Pages 165-172, 2007.

Issa-Zacharia A, Kamitani Y, Tiisekwa A, Morita K, Iwasaki K.In vitro inactivation of Escherichia coli, Staphylococcus aureus and Salmonella spp. using slightly acidic electrolyzed water. J Biosci Bioeng. 2010

Ilisz I., Dombi A., Mogyorósi K. and Dékány I. Photocatalytic water treatment with different TiO_2 nanoparticles and hydrophilic/hydrophobic layer silicate adsorbents. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Volume 230, Issue 1-3, Pages 89-97, 2003.

Jin-quan, L.P.W. and Yong-wen, T.X.M. Study on Hydrolytic Acidification-Catalytic Oxidation Process Treatment of Waste Water of Pulp and Paper Making from Waste Paper and the Microbes. *Paper and Paper Making*, VolumeIssues, Pages S1, 2007.

Joo, J., Kwon, S.G., Yu, T., Cho, M., Lee, J., Yoon, J. and Hyeon, T. Large-Scale Synthesis of TiO2 Nanorods via Nonhydrolytic Sol-Gel Ester Elimination Reaction and Their Application to Photocatalytic Inactivation of E. c oli. *The Journal of Physical Chemistry B*, Volume 109, Issues 32, Pages 15297-15302, 2005.

Kun, R., Mogyorósi, K. and Dékány, I. Synthesis and structural and photocatalytic properties of TiO_2/montmorillonite nanocomposites. *Applied Clay Science*, Volume 32, Issues 1, Pages 99-110, 2006.

Lazar M., Varghese S. and Nair S. Photocatalytic Water Treatment by Titanium Dioxide: Recent Updates. *Catalysts*, Volume 2, Issue 4, Pages 572-601, 2012.

Lee, H.S., Im, S.J., Kim, J.H., Kim, H.J., Kim, J.P. and Min, B.R. Polyamide thin-film nanofiltration membranes containing TiO_2 nanoparticles. *Desalination*, Volume 219, Issues 1, Pages 48-56, 2008.

Lee, N., Amy, G., Croue, J. and Buisson, H. Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water Research*, Volume 38, Issues 20, Pages 4511-4523, 2004.

Lee, S., Choo, K., Lee, C., Lee, H., Hyeon, T., Choi, W. and Kwon, H. Use of ultrafiltration membranes for the separation of TiO2 photocatalysts in drinking water treatment. *Industrial & Engineering Chemistry Research*, Volume 40, Issues 7, Pages 1712-1719, 2001.

Li, P., Zhao, G., Zhao, K., Gao, J. and Wu, T. An efficient and energy saving approach to photocatalytic degradation of opaque high-chroma methylene blue wastewater by electrocatalytic pre-oxidation. *Dyes and Pigments*, Volume 92, Issues 3, Pages 923-928, 2012.

Li, X., Kohama, A., Kim, J., Chiba, N., Nishimura, O. and Sudo, R. Grazing characteristic of nitrifying bacteria by Testacealobosia Arcella vulgaris and its effect on nitrification. *Journal of Japan Society on Water Environment*, Volume 23, Issues 11, Pages 661-667, 2000.

Li, X.N., Kohama, A., Kim, J.H., Chiba, N., Nishimura, O. and Sudo, R.G. Testacealobosia Arcella vulgaris as an Indicator in Nitrification Process. *Environmental Engineering Research*, Volume 37, Issues, Pages 41-49, 2000.

Liu Y., Zhou L. and Hu Y. Magnetic-field induced formation of 1D Fe_3O_4/C/CdS coaxial nanochains as highly efficient and reusable photocatalysts for water treatment. *Journal of Materials Chemistry*, Volume 21, Issue 45, Pages 18359, 2011.

Ma, H., Zhang, X., Ma, Q. and Wang, B. Electrochemical catalytic treatment of phenol wastewater. *Journal of Hazardous Materials*, Volume 165, Issues 1, Pages 475-480, 2009.

Malato, S., Fernández-Ibáñez, P., Maldonado, M.I., Blanco, J. and Gernjak, W. Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. *Catalysis Today*, Volume 147, Issues 1, Pages 1-59, 2009.

Matsunaga, T., Tomoda, R., Nakajima, T. and Wake, H. Photoelectrochemical sterilization of microbial cells by semiconductor powders. *Fems Microbiology Letters*, Volume 29, Issues 1, Pages 211-214, 1985.

Meng, Y., Huang, X., Yang, Q., Qian, Y., Kubota, N. and Fukunaga, S. Treatment of polluted river water with a photocatalytic slurry reactor using low-pressure mercury lamps coupled with a membrane. *Desalination*, Volume 181, Issues 1, Pages 121-133, 2005.

M. F. J. Dijkstra, H. Buwalda, A. W. F. de Jong, A. Michorius, J. G. M. Winkelman, A. A. C. M. Beenackers. Experimental comparison of three reactor designs for photocatalytic water purification. *Chemical Engineering Science,* Volume 56, Pages 547-555, 2001.

Molinari, R., Pirillo, F., Falco, M., Loddo, V. and Palmisano, L. Photocatalytic degradation of dyes by using a membrane reactor. *Chemical Engineering and Processing: Process Intensification,* Volume 43, Issues 9, Pages 1103-1114, 2004.

Molinari, R., Borgese, M., Drioli, E., Palmisano, L. and Schiavello, M. Hybrid processes coupling photocatalysis and membranes for degradation of organic pollutants in water. *Catalysis Today*, Volume 75, Issues 1, Pages 77-85, 2002.

Molinari, R., Grande, C., Drioli, E., Palmisano, L. and Schiavello, M. Photocatalytic membrane reactors for degradation of organic pollutants in water. *Catalysis Today*, Volume 67, Issues 1, Pages 273-279, 2001.

Nagaveni, K., Hegde, M.S., Ravishankar, N., Subbanna, G.N. and Madras, G. Synthesis and structure of nanocrystalline TiO2 with lower band gap showing high photocatalytic activity. *Langmuir*, Volume 20, Issues 7, Pages 2900-2907, 2004.

Nagaveni, K., Sivalingam, G., Hegde, M.S. and Madras, G. Photocatalytic degradation of organic compounds over combustion-synthesized nano-TiO_2. *Environmental Science & Technology*, Volume 38, Issues 5, Pages 1600-1604, 2004.

Nickels P., Zhou H., Basahel S.N., Obaid A.Y., Ali T.T., Al-Ghamdi A.A., El-Mossalamy E.H., Alyoubi A.O. and Lynch S.A.. Laboratory scale water circuit including a photocatalytic reactor and a portable in-stream sensor to monitor pollutant degradation. *Industrial & Engineering Chemistry Research*, Volume 51, Issue 8, Pages 3301-3308, 2012

Ochiai T., Nakata K., Murakami T., Fujishima A., Yao Y., Tryk D.A. and Kubota Y. Development of solar-driven electrochemical and photocatalytic water treatment system using a boron-doped diamond electrode and TiO_2 photocatalyst. *Water Research*, Volume 44, Issue 3, Pages 904-910, 2010.

Ochuma, I.J., Fishwick, R.P., Wood, J. and Winterbottom, J.M. Photocatalytic oxidation of 2, 4, 6-trichlorophenol in water using a cocurrent downflow contactor reactor (CDCR). *Journal of Hazardous Materials*, Volume 144, Issues 3, Pages 627-633, 2007.

Orhon, D., Babuna, F.G. and Karahan, O. Industrial wastewater treatment by activated sludge, *IWA Publishing*, 2009.

Patermarakis G and Fountoukidis E. Disinfection of water by electrochemical treatment. *Water Research*, Volume 24, Issues 12, Pages 1491-1496, 1990.

Pera-Titus, M., García-Molina, V., Baños, M.A., Giménez, J. and Esplugas, S. Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Applied Catalysis B: Environmental*, Volume 47, Issues 4, Pages 219-256, 2004.

Preety S. Mukherjee and Ajay K. Ray. Major Challenges in the Design of a Large-Scale Photocatalytic Reactor for Water Treatment. *Chemical Engineer Technology*. Volume 22, Pages 253-260, 1999.

Rahmawati, F., Kusumaningsih, T. and Hastuti, A. Photo- and electro-catalysis for solar disinfection of. *Toxicological & Environmental Chemistry*, Volume 93, Issues 8, Pages 1602-1612, 2011.

Richardson, A.W. Municipal water use policies. Water Quality and Quantity Issues for Turfgrasses in Urban Landscapes. *CAST Special Publication*, Volume 27, Issues, Pages 53-63, 2008.

Sopajaree, K., Qasim, S.A., Basak, S. and Rajeshwar, K. An integrated flow reactor-membrane filtration system for heterogeneous photocatalysis. Part II: Experiments on the ultrafiltration unit and combined operation. *Journal of Applied Electrochemistry*, Volume 29, Issues 9, Pages 1111-1118, 1999.

Sopajaree, K. Photocatalytic oxidation of methylene blue by titanium dioxide in a photoreactor, *Proceedings of the 6th Intrnetional Conference on Environmental Science and Technology*, Pages 2-8, 1999.

Suárez, S., Carballa, M., Omil, F. and Lema, J.M. How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters? *Reviews in Environmental Science and Bio/Technology*, Volume 7, Issues 2, Pages 125-138, 2008.

Sun, Z., Chen, Y., Ke, Q., Yang, Y. and Yuan, J. Photocatalytic degradation of a cationic azo dye by TiO_2/bentonite nanocomposite. *Journal of Photochemistry and Photobiology A: Chemistry*, Volume 149, Issues 1, Pages 169-174, 2002.

Tan, T.T.Y., Yip, C.K., Beydoun, D. and Amal, R. Effects of nano-Ag particles loading on TiO_2 photocatalytic reduction of selenate ions. *Chemical Engineering Journal*, Volume 95, Issues 1, Pages 179-186, 2003.

Viessman, C. Hammer. Water Supply & Pollution Control, *Harper and Row*, New York, U.S.A, 1998.

Wang, Y. and Hong, C. Effect of hydrogen peroxide, periodate and persulfate on photocatalysis of 2-chlorobiphenyl in aqueous TiO_2 suspensions. *Water Research*, Volume 33, Issues 9, Pages 2031-2036, 1999.

Wang W., Serp P., Kalck P., Silva C.G. and Faria J.L. Preparation and characterization of nanostructured MWCNT-TiO2 composite materials for photocatalytic water treatment applications. Materials Research Bulletin, Volume 43, Issue 4, Pages 958-967, 2008

Wintgens, T., Salehi, F., Hochstrat, R. and Melin, T. Emerging contaminants and treatment options in water recycling for indirect potable use. *Water Science and Technology*, Volume 57, Issues 1, Pages 99-107, 2008.

Xi, W. and Geissen, S. Separation of titanium dioxide from photocatalytically treated water by cross-flow microfiltration. *Water Research*, Volume 35, Issues 5, Pages 1256-1262, 2001.

Xie, Z.M., Chen, Z. and Dai, Y.Z. Preparation of TiO_2/sepiolite photocatalyst and its application to printing and dyeing wastewater treatment. *Environmental Science & Technology*, Volume 32, Issues, Pages 123-127, 2009.

X .Z. Li and H. Liu. Photocatalytic oxidation using a new catalysts TiO_2 microspheresfor water and wastewater treatment. *Environmental Science & Technology*, Volume 37, Pages 3989-3994, 2003.

Yang, H. and Cheng, H. Controlling nitrite level in drinking water by chlorination and chloramination. *Separation and Purification Technology*, Volume 56, Issues 3, Pages 392-396, 2007.

Yang, Y. and Wang, P. Preparation and characterizations of a new PS/TiO_2 hybrid membranes by sol–gel process. *Polymer*, Volume 47, Issues 8, Pages 2683-2688, 2006.

Zhang D, Guisheng Li and Jimmy C. Yu. Inorganic materials for photocatalytic water disinfection. *Journal of Materials Chemistry*, Volume 20, Pages 4529–4536, 2010.

Zhang G., Ji S., Gao X. and Liu Z. Adsorptive fouling of extracellular polymeric substances with polymeric ultrafiltration membranes. *Journal of Membrane Science*, Volume 309, Issue 1, Pages 28-35, 2008.

Zhang, X., Zhang, T., Ng, J. and Sun, D.D. High‐Performance Multifunctional TiO_2 Nanowire Ultrafiltration Membrane with a Hierarchical Layer Structure for Water Treatment. *Advanced Functional Materials*, Volume 19, Issues 23, Pages 3731-3736, 2009.

Zhao, Y., Zhong, J., Li, H., Xu, N. and Shi, J. Fouling and regeneration of ceramic microfiltration membranes in processing acid wastewater containing fine TiO_2 particles. *Journal of Membrane Science*, Volume 208, Issues 1, Pages 331-341, 2002.