Water treatment using one-dimensional manganese oxide based materials

Zhang, Tong

2013

Zhang, T. (2013). Water treatment using one-dimensional manganese oxide based materials. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/55055>

<https://doi.org/10.32657/10356/55055>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**WATER TREATMENT USING
ONE-DIMENSIONAL MANGANESE OXIDE
BASED MATERIALS**

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

2013

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MANGANESE OXIDE BASED MATERIALS**

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A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2013

ACKNOWLEDGEMENTS

First of all, I would like to thank my supervisor, Prof. Darren Delai Sun, for his continuous guidance and advice during the past years. Thank you for providing me the research opportunity to explore the new scientific areas in your research group.

Besides my supervisor, I would like to thank the rest of my thesis committee: Dr. Zhang Xiwang, Dr. Pan Jiahong, Dr Wang qin, Alan, Yajuan, Karina, Weijiong, Yinjie, Shiping, Jiawei, Hongwei, Shushu, Zhai Bing, Dr Liu Jincheng, Dr Liu Zhaoyang, Dr Yan Xiaoli, Pei Fung, Liu Lei, Xiaoxiao, Minghang, Yilei, Ayu, Gao Peng, Siew Xiang, Qin Detao, Desmond, Benny, Yixuan, Jeremy, Jermyn, Chengli and Fujie for their encouragement, insightful comments and resourceful questions.

I thank my fellow lab technicians in the Environment Laboratory: Mrs Phang-Tay Beng Choo, Mr Tan Han Khiang, Mr Yong, Mr Ong, Mrs Lai Sim, Mrs Lim-Tay Chew Wang, Pearlyn, Maria, Swee Ying, Mei Ling and Aidil for providing assistances during my years of study.

Last but not least, I am eternally grateful to my family for their endless love and understanding. I would like to thank them for supporting me spiritually throughout my life.

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SUMMARY

In recent years, there has been a growing trend in the usage of nanomaterials to enhance water purification efficiency. One-dimensional (1D) nanostructured manganese oxides and their derivatives have attracted considerable research interest due to their large surface area, adjustable transport properties and chemical specificities. However, separation and recovery of these nanosized materials in heterogeneous systems continue to remain a steep challenge. To overcome the engineering issue, various separation techniques such as free settling, centrifugation, magnetic separation and membrane filtration, have been proposed over the years.

This research topic mainly focused on the synthesis and environmental application of 1D nanostructured manganese oxide based materials in the easily separable forms including MnO_2 nanowires, magnetic manganese oxide nanocomposites, micro-/nano-structured MnO_2 spheres, and manganese oxide nanofibrous membrane. The synthesized materials were characterized and successfully applied in several water treatment processes. Furthermore, the nanomaterials were recycled from the treated water by using different routes, and the related separation mechanisms were also discussed in this dissertation.

As a basic material in this research, 1D cryptomelane-type manganese oxide (K-OMS-2) nanowires were synthesized via a hydrothermal method. The nanowires can be used as an adsorbent or oxidant for water treatment. After coupling with Fe_3O_4 nanoparticles, the synthesized K-OMS-2/ Fe_3O_4 nanocomposites became a multifunctional material with adsorption, oxidation and magnetic properties. Batch tests were conducted to evaluate the performance of the synthesized materials under different conditions. Due to the increased specific surface area, the synthesized K-OMS-2/ Fe_3O_4 nanocomposites exhibited higher oxidation and adsorption capacities for the removal of arsenic as compared to the K-OMS-2 nanowires.

To further enhance the oxidation capacity of the material, 1D MnO₂ nanowires were synthesized using a similar hydrothermal method based on the synthesis of K-OMS-2 nanowires. Moreover, a novel hybrid process combining the 1D MnO₂ nanowires oxidation and microfiltration was adopted to remove bisphenol A (BPA). The effects of pH, humic acid (HA) and coexisting metal ions on the removal rate of BPA were investigated, and membrane fouling mechanism caused by the MnO₂ nanowires was also discussed.

To further enhance the specific surface area of manganese oxides, a catalytic oxidation route was conducted to synthesize 3D MnO₂ spheres, which was assembled by 1D manganese oxide nanowires on the surface. Experimental results indicated that the adsorption and oxidation abilities of the MnO₂ sphere were increased as compared to the 1D K-OMS-2 nanowires, and a dead-end microfiltration setup was also used to investigate the separability of the material.

Finally, a novel free-standing nanofibrous microfiltration membrane was successfully assembled using hierarchical TiO₂/K-OMS-2 nanocomposites, which was synthesized based on the 1D K-OMS-2 nanowires. The synthesized membrane possesses self-cleaning property, and organic pollutants in water can be efficient removed via a concurrent microfiltration, adsorption, and photocatalytic oxidation (PCO) process. Fabrication of membranes using nanomaterials can solve the separation problems of the materials after water treatment.

Although 1D manganese oxide based materials have great potential in water purification process, the reductive dissolution of manganese oxides during the oxidation process may lead to secondary pollution. In addition, the regeneration of manganese oxide based material is also an important part of recycling. These problems should be considered in our future study.

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LIST OF ABBREVIATIONS, ACRONYMS AND NOTATIONS

0D: zero-dimensional

1D: one-dimensional

2D: two-dimensional

3D: three-dimensional

AO7: acid orange 7

BPA: bisphenol A

BET: Brunaur-Emmett-Teller

DOC: dissolved organic carbon

EDX: energy-dispersive x-ray spectroscopy

FESEM: field emission scanning electron microscopy

FTIR: Fourier transform infrared spectroscopy

HA: humic acid

HS: humic substances

HPLC: high-performance liquid chromatography

HPLC-ICP-MS: high-performance liquid chromatography inductively coupled
plasma mass spectrometer

ICP: inductively coupled plasma emission spectroscopy

K-OMS-2: cryptomelane-type manganese oxide

MB: methylene blue

MBR: membrane bioreactor

NOMs: natural organic matters

OMS: octahedral molecular sieve

OL: octahedral layer

PCO: photocatalytic oxidation

PEG: polyethylene glycol

PL: photoluminescence

PS: polystyrene

PVP: poly(vinyl pyrrolidone)

SAED: selected-area electron diffraction

TEM: transmission electron microscopy

TMP: transmembrane pressure

TOC: total organic carbon

UHV: ultrahigh vacuum

VSM: vibrating sample magnetometer

XPS: X-ray photoelectron spectroscopy

XRD: X-ray diffraction

C : concentration at time t

C_0 : initial concentration

C_e : solution concentration at equilibrium

J : water flux

k : a constant for a given adsorbate and adsorbent at a particular temperature

k_{eq} : equilibrium constant of adsorption

n : a constant for a given adsorbate and adsorbent at a particular temperature

q_e : the amount of substance absorbed by unit mass of adsorbent

q_{max} : maximum adsorption capacity

R : retention rate

R^2 : correlation coefficient

R_t : total resistance

R_m : intrinsic membrane resistance

R_c : cake layer resistance

R_p : pore blocking resistance

t : reaction time

T_C : Curie temperature

μ : dynamic viscosity

ΔP : transmembrane pressure

Chapter 1 INTRODUCTION

1.1. BACKGROUND

As a major source for life forms on this planet, water has received appreciable attention in view of the lack of clean water and sanitation. Nowadays, more than 1.1 billion people do not have access to improved drinking water supplies, and 2.6 billion people have little sanitation (Montgomery and Elimelech 2007). In both developing and developed countries, the demand for water as a precious resource has increased tremendously in terms of quantity and quality. The scarcity of such a precious source in Singapore has led the recycling and the reuse of biologically treated wastewater to an efficient alternative solution for the conservation and recovery of potable water. Owing to the development of industry, many contaminants are entering water supplies, such as heavy metals, arsenic and organic pollutants. These contaminants can be transmitted through unsafe water and become to a major threat to public health. For example, as a very toxic and carcinogenic pollutant, arsenic is widely existed in the ground water of many regions around the world, such as Argentina, Bangladesh, India, Mongolia, Thailand and Taiwan where people have substantial exposure risks to it (Ferguson and Gavis 1972; Roberts et al. 2004). Other pollutants, like waterborne bacteria and endocrine disrupters, can also lead to severe diseases or have adverse effects on the genetic systems of human being (Ferguson and Gavis 1972; Calafat et al. 2008).

In recent years, a growing number of technologies have been proposed and applied for water purification, such as biological, physical and chemical methods. The biological treatments of water mainly refer to the degradation of organic pollutants by bio-aided technology, for example, activated sludge system. Organic pollutants can be degraded by microorganism in the sludge, and subsequently, separating the solid and liquid fractions through a sedimentation tank. Physical methods for water purification include mixing, heat treatment, ultra-violet light, electric currents and

filtration processes. While chemical methods include biocides, oxidizing chemicals and catalysts. Current progress shows that the combination of biological, physical and chemical methods is an effective way for water treatment. For example, membrane bioreactor (MBR) is considered as a promising technology for water treatment (Daigger et al. 2005; Yang et al. 2006), which combines suspended biomass with a membrane process that replace gravity sedimentation to clarify the wastewater effluent (Shannon et al. 2008). MBR process requires small footprint, flexible design and automated operation properties, however, membrane fouling remains as a major obstacle for its applications. Polymers are widely employed for membrane fabrication by virtue of its good chemical and mechanical stability (Shannon et al. 2008). Nevertheless, some polymer membranes and organic pollutants are hydrophobic in nature, which aggravates the membrane fouling problem. To address this problem, many methods such as a coating process of hydrophilic layer on the original membrane and modification of the surface of polymers have been proposed (Ulbricht and Belfort 1996; Hester and Mayes 2002). As a result, many researchers are devoted to fabricating suitable inorganic membranes as substitutes which are chemically, thermally and mechanically resistant coupled with thermal regeneration abilities (Sholl and Johnson 2006).

Recently, nanomaterials have attracted considerable research interest in water treatment in view of their excellent catalytic, oxidation and adsorption properties (Luo et al. 2008; Pan et al. 2008; Zhang et al. 2009). Nanotechnology refers to the using of materials and structures with nanosized dimension ranging from 1 to 100 nm (Klevenz 2004). Essentially, new physical and chemical properties will emerge when reducing the size of materials to nanoscale. Chen and Mao (Chen and Mao 2007) reported that morphology of nanomaterials can also affect their properties and performance in specific applications. Nowadays, researchers have put in many efforts to develop new functional materials using nanotechnology in order to provide the need of water treatment for the removal of pollutants (Yuan et al. 2004; Yuan et al. 2008; Zhang et al. 2009). For instance, nanostructured manganese oxides can be used as oxidants for the detoxification of organic and inorganic pollutants, and they can also be applied as adsorbents or catalysts in

different processes. To further enhance their performance, manganese oxides with various morphologies can be synthesized via different methods(Shen et al. 2005; Li et al. 2006; Chen and He 2008; Zhang et al. 2008; Le et al. 2011; Liu et al. 2011; Qiu et al. 2011; Athar et al. 2012; Mohamed Ahmed et al. 2012; Rohani Bastami and Entezari 2012), such as zero dimensional (0D), one dimensional (1D), two dimensional (2D) and three dimensional (3D) nanostructured manganese oxides. Among them, 1D nanostructures including nanotubes, nanorods, nanobelts and nanowires/nanofibers, have become the focus of intensive research in view of their fascinating applications in mesoscopic physics and construction of nanoscale devices(Wang 2000). Recent progress indicates that 1D nanostructured nanomaterials play an important role in investigating the dependence of electrical and thermal transport or mechanical properties on dimensionality and size reduction(Devan et al. 2012). Furthermore, 1D nanostructured materials have demonstrated to be highly effective in environmental applications with enhanced performance in catalysis, oxidation and adsorption due to their large surface area, adjustable transport properties and chemical specificities(Dong et al. 2009; Zhang et al. 2009).

Although nanostructured materials possess high efficiency in water treatment process, separation and recovery of the nanosized materials in heterogeneous systems still remain a steep challenge, which leads to potential risks, such as the production of new toxic materials and related environmental hazards(Donaldson et al. 2004). To overcome this engineering issue, various separation techniques such as free settling, centrifugation, magnetic separation and membrane filtration, have been proposed over the years(Li et al. 2003; Pan et al. 2008).

The combination of nanomaterials with membrane filtration is an effective way for the materials recovery. In a typical process, pollutants in water are firstly degraded or adsorbed by nanomaterials, and subsequently, a membrane filtration process can be conducted to separate and recover the nanomaterials from the treated water(Molinari et al. 2002). However, the filtration process of nanomaterials always causes severe membrane fouling due to the fine sizes of the materials, resulting pore

blocking and thus largely decreasing membrane flux. One possible way to relieve this problem is to control the morphology of the synthesized nanomaterials. In comparison with nanoparticles, 1D nanowires/nanofibers are easier to be separated due to their high aspect ratios(Zhang et al. 2009).

Magnetic assisted process, which has been adapted from ore mining industries to anti-scale treatment of pipe lines to seeding magnetic flocculent, is another method for the separation of nanomaterials(Ambashta and Sillanpää 2010). Currently, nanosized Fe_3O_4 and its composites with other nanomaterials are most studied in water treatment process. Studies indicate that magnetic materials can be easily separated under a low-intensity magnetic field(Berkowitz et al. 1980). It has been proven that Fe_3O_4 nanoparticles possess large adsorption capacity for the arsenic removal(Yavuz et al. 2006), which can be directly used for water purification. Furthermore, other magnetic nanocomposites such as $\text{Fe}/\text{Fe}_3\text{O}_4$, $\text{CNTs}/\text{Fe}_3\text{O}_4$ and $\text{TiO}_2/\text{Fe}_3\text{O}_4$, have also been applied for water treatment due to their multifunctional properties(Dos Santos Coelho et al. 2008).

In addition, fabrication of nanofibrous membranes can also be a good candidate to eliminate the separation problem. Research progress today has enabled 1D nanostructures, such as nanowires and nanotubes, to be assembled into nanofibrous membranes that are free-standing, flexible and mechanically stable(Yuan et al. 2004; Dong et al. 2006; Yuan et al. 2008; Zhang et al. 2008; Zhang et al. 2009; Liang et al. 2010). In the previous work(Zhang et al. 2008; Zhang et al. 2009), our research group has successfully developed a robust and free-standing multifunctional TiO_2 nanofibrous membrane to overcome the fouling problem that arose from conventional polymeric membranes. The pore sizes of these TiO_2 nanofibrous membranes can be controlled by adjusting the diameter of TiO_2 nanowires, as well as the thickness of the membrane by fixing the dosage of the materials. Essentially, other 1D nanomaterials (e.g. MnO_2 , Si) can also be fabricated into nanofibrous membranes via a similar process. Compared with conventional polymeric membranes, the inorganic nanofibrous membranes are energy efficient and cost effective in water treatment process due to their excellent reusability after burning.

Since the nanomaterials would not be detached from the membrane during a filtration process, there is no need for further separation of the nanomaterials from aqueous solution after water treatment.

1.2. RESEARCH OBJECTIVES AND SIGNIFICANCE

This study mainly focused on the synthesis and environmental application of multifunctional 1D manganese oxide based materials. The synthesized materials possess high activity and can be easily recovered from the solution system as compared to the traditional nanosized materials. Moreover, the separation processes and mechanisms of the synthesized nanomaterials were also studied in this work. The specific aims of this research are as follows:

- a) To synthesize and characterize new functional 1D manganese oxide based nanomaterials, such as 1D MnO₂ nanowires, 1D manganese oxide based micro-/nano-structured spheres and 1D manganese oxide based nanocomposites.
- b) To study the properties of the synthesized materials, such as oxidation, adsorption and magnetism. According to the specific advantages of the synthesized materials, different water treatment applications were applied using the synthesized materials.
- c) To evaluate the performance of the synthesized materials for the removal of organic or inorganic pollutants, such as arsenic species (As(III) & As(V)), bisphenol A (BPA) and acid orange 7 (AO7). The removal rates and mechanisms of organic and inorganic pollutants by using the synthesized 1D manganese oxide based materials were studied under different conditions.
- d) To investigate the separation processes and mechanisms of the synthesized materials by using different methods, such as magnetic separation and microfiltration.

- e) To fabricate and characterize a novel type of 1D manganese oxide based nanofibrous membrane for water treatment. The synthesized membrane was characterized, and its performance was also evaluated.

Significance and benefits of this research are as follows:

The fundamental studies of water treatment using new functional 1D manganese oxide based materials indicate that the synthesized material can have potential in applications of environmental remediation. In particular, the detoxification and degradation mechanisms of pollutants on the surface of the synthesized materials were also investigated. These informations provide insights that can be employed to help in developing novel materials for water purification. The discussions on the separation methods such as microfiltration and magnetic separation, will herald pathways towards the recovery of nanomaterials. Moreover, the fabrication of a novel nanofibrous membrane using 1D manganese oxide as building blocks can finally eliminate the separation problem of nanomaterials.

1.3. THESIS OVERVIEW

This thesis is divided into eight chapters:

Chapter 1 provides a brief introduction, and Chapter 2 presents the literature review on the structure, property and environmental application of manganese oxides with different dimensions. A brief review on the separation of nanomaterials are discussed as well, and some separation methods are introduced.

In Chapter 3, the materials and methodology used in this research work are presented, such as the common chemicals and materials, synthesis methods and materials characterization techniques. The detailed experimental procedures for adsorption, oxidation, microfiltration and photocatalytic oxidation (PCO) are also elaborated in this chapter.

In Chapter 4, 1D octahedral molecular sieve (OMS) manganese oxide based magnetic nanocomposites are synthesized for arsenic removal. Morphology, structure and property of the synthesized material are investigated, and the arsenic removal process by the synthesized material is also studied. In addition, we evaluate the magnetic separation ability of the material under low magnetic field.

In Chapter 5, to further enhance the oxidation ability of manganese oxide, 1D MnO₂ nanowires are synthesized based on the hydrothermal method of Chapter 3. A novel hybrid process combining MnO₂ nanowires oxidation and microfiltration is adopted to remove BPA. Moreover, the membrane fouling mechanism caused by the MnO₂ nanowires is also discussed.

In Chapter 6, to further enhance the specific surface area of manganese oxide nanowires, 1D manganese oxide nanowire based 3D micro-/nano-structured spheres are synthesized and applied for the removal of arsenic species. Spectra studies are conducted to evaluate the As(III) oxidation and As(V) adsorption reactions with the synthesized 3D MnO₂ spheres. Moreover, a dead-end membrane filtration apparatus is employed to recycle the synthesized material.

In Chapter 7, based on the 1D manganese oxide nanowires, a novel nanofibrous membrane is fabricated and applied for concurrent filtration, adsorption and PCO in water treatment process. The synthesis, characterization and performance of the synthesized membrane are studied in this chapter.

Chapter 8 is a summary of the research project, and some recommendations for the future investigations are also incorporated.

Data and information presented in this thesis may have been published or in the preparation for publication as listed in the section “List of Publications”. Other publications during the candidature are also presented in this section.

Chapter 2 LITERATURE REVIEW

2.1. INTRODUCTION

Manganese, an abundant transition metal which can be found in the earth's crust, exists in various minerals such as carbonates, sulfides and oxides. The dominant oxidation states of manganese are +2, +3 and +4, which are some of the strongest oxidants naturally distributed in the environment. Manganese oxides and their derivatives are a series of important compounds which can be used in batteries, molecular sieves, catalysts, and adsorbents (Luo et al. 2008; Hosono et al. 2009). Manganese oxides include MnO , Mn_3O_4 , Mn_2O_3 , MnO_2 and Mn_2O_7 , while their derivatives may include much more compounds, such as $\text{K}_{2-x}\text{Mn}_8\text{O}_{16}$, KMnO_4 , NaMn_2O_4 and so on.

2.1.1. Porous materials

Recently, the synthesis and application of porous materials have attracted substantial research interests due to their unique physical and chemical properties. Compared with nonporous materials, porous materials exhibit more excellent properties in catalysis, adsorption, sensing, ion-exchange and separation (Cooper 2003; Melde and Johnson 2010; Sun and Zou 2010; Nguyen et al. 2011). Porous materials are solids containing pores with different diameters, and the porosity of the materials is generally ranging from 0.2 to 0.95 (Ishizaki et al. 1998). Based on the different pore sizes, porous materials can be further divided into microporous materials, mesoporous materials, and macroporous materials. According to the International Union of Pure and Applied Chemistry (Rouquerol et al. 1994), microporous materials have pore diameters of less than 2 nm; macroporous materials have pore diameters of greater than 50 nm; while the mesoporous materials have pore diameters between 2 nm and 50 nm. The classification of porous materials based on pore size is shown in Figure 2-1. The porosity of materials is very important to increase the surface area, and thus increase the

adsorption and catalysis properties. However, the increase of porosity will also decrease the mechanical strength of the materials. Therefore, it is necessary to synthesize suitable porous materials with different pore size for different applications. In addition, distribution of pore size can determine the properties of materials. For example, porous materials with narrow pore size distribution are suitable for gas separation because of their excellent selectivity(Ishizaki et al. 1998).

Figure 2-1. The classification of porous materials(Rouquerol et al. 1994).

2.1.2. Porous manganese oxides

Manganese oxides and related materials are of considerable importance in view of their wide applications in catalysts, oxidation and batteries(Shen et al. 1993). Among the manganese oxides and their derivatives, MnO_2 is a typical material and has been well studied by researchers(Wang et al. 2003; Robinson et al. 2010). There are several different structures of MnO_2 , such as α -, β -, γ -, δ -, and ϵ -type, which are made of MnO_6 octahedra with different connectivity(Gao et al. 2008). As shown in Figure 2-2, α - MnO_2 type materials are built from double chains of edge-sharing MnO_6 octahedra with $(2 \times 2) + (1 \times 1)$ tunnel structures(Gao et al. 2008). In addition, K^+ , Na^+ and Ba^{2+} ions can situate in the large (2×2) tunnels, which is less stable than the small (1×1) . These materials can be expressed as $\text{M}_x\text{Mn}_8\text{O}_{16}$ (M denotes the cations in the (2×2) tunnels; $0 \leq x \leq 2$)(Sato et al. 1999). Owing to the existence of tunnel ions, valences of manganese in MnO_2 changed, and the manganese oxides become mixed-valent materials(DeGuzman et al. 1994). Mixed valence is useful in electron and energy transfer, redox catalysis, and in battery materials(Tian et al. 1997; D'Alessandro and Keene 2006; Bibes and Barthélmy 2007). Previous study revealed that materials with multiple oxidation states especially those with one electron jumping such as $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{V}^{4+}/\text{V}^{5+}$ lead to

good conductivity(Suib 2008). Thus, mixed-valent porous manganese oxides have attracted a great deal of attention due to their great semiconducting ability, outstanding adsorptive property, and excellent activity in numerous catalytic reactions(Tian et al. 1997; Luo et al. 2008). Among the porous mixed-valent manganese oxides, OMS and octahedral layer (OL) materials are the typical compounds which possess great semiconductivity and porosity(Suib 2008). The mixed valence of OMS and OL materials results from the reduction of some Mn^{4+} ions to Mn^{3+} and Mn^{2+} , which are also based on octahedral MnO_6^{x-} ions. Current progress shows that OMS materials have great potential in environmental applications(Tian et al. 1997; Son et al. 2001; Yuan et al. 2008). Son and co-workers(Son et al. 2001) reported that alcohols can be selectively catalyzed to aldehydes and ketones with inexpensive OMS type manganese oxides, which are easily regenerable and environmentally friendly catalysts. Shen and co-workers(Shen et al. 2005) discovered that OMS materials possess different pore sizes and tunnel structure, which facilitate the transport for ion exchange in the materials(Giraldo et al. 2000). While suib(Suib 2008) reports that physical properties of porous manganese oxide materials are related with structures of the materials. Therefore, the performance of the materials can be further enhanced by designing specific structures.

Figure 2-2. Crystal structure of $\alpha\text{-MnO}_2$ type materials(Gao et al. 2008).

2.1.3. Preparation of porous manganese oxides

As excellent adsorbents and catalysts, porous manganese oxide materials exist as manganese nodules in nature, which can be dredged from the ocean floors(Suib 2008). Currently, many techniques have been devoted to prepare porous manganese oxides (OMS and OL) with high surface, well-defined building blocks and controllable morphologies, such as precipitation, hydrothermal and sol-gel routes(Brock et al. 1998).

Precipitation is a very common method for the synthesis of porous manganese oxides, which usually involves the oxidation-reduction reactions of Mn^{7+} and Mn^{2+} . Manganese oxides with medium valences of Mn can be formed in this process, such as Mn_3O_4 , MnO_2 (Li et al. 2011; Xing et al. 2011). Ozkaya and co-workers(Ozkaya et al. 2008) prepared various manganese oxide powders via this method at room temperature. They found that the crystal structure, particle size and morphology of the synthesized materials can be significantly influenced by adding H_2O_2 . Further studies showed that the formation of porous manganese oxides can be significantly influenced by oxidation-reduction reaction velocity, which can be adjusted by the addition of polyethylene glycol (PEG) with different molecular weights(Hao et al. 2011). With the increase of PEG molecular weights in the reaction system, the crystallization of the produced materials decreased. In addition, the reaction velocity can be simply controlled by adjusting temperature.

Hydrothermal process is normally conducted in autoclaves reacting with aqueous solutions under controlled temperatures(Chen and Mao 2007). The internal pressure of the autoclave can be controlled by adjusting the temperature and the volume of solution added into the teflon cup. This method is also widely applied for the synthesis of porous manganese oxides(Shen et al. 2005; Yan et al. 2009). Owing to the high temperature and high pressure, Mn^{2+} precursors can be easily oxidized to manganese oxides with higher Mn valences in the autoclave. Shen and co-workers (Shen et al. 2005) prepared porous manganese oxides with different tunnel structures via this method. They found that temperatures and pH values are the key

factors for the synthesis. In addition, morphologies of porous manganese oxides can also be controlled in a hydrothermal process by using different oxidants (Subramanian et al. 2005; Yuan et al. 2005; Li et al. 2006). Suib's research group (Yuan et al. 2005; Chen et al. 2008) found that a mild and slow reaction facilitates the nucleation and growth of nanomaterials. They also reported that net redox potentials can affect reaction rates of the synthesis processes (Chen et al. 2008). For example, redox potential of $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ (1.33 V) is slightly larger than $\text{Mn}^{4+}/\text{Mn}^{2+}$ (1.23 V), hence, the redox reaction between $\text{Cr}_2\text{O}_7^{2-}$ and Mn^{2+} is mild and slow. As a result, this reaction determines the formation of 3D manganese oxide nanostructures (Yuan et al. 2005). Similarly, uniform Co_3O_4 can be synthesized via a redox reaction between $\text{S}_2\text{O}_8^{2-}$ and $\text{Co}^{2+}/\text{Co}^{3+}$. The redox potentials of $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ are 2.01 V and 1.808 V respectively (Chen et al. 2008), and the small net redox potential leads to the reducing of reaction and nucleation rate.

Reduction of KMnO_4 with organic reducing agents is an alternative way for the synthesis of porous manganese oxides which involves in the preparation of sol and gel. Sol-gel method is a wet-chemical technique commonly applied for the fabrication of materials. In a typical process, a sol is formed from the hydrolysis and polymerization reactions of the precursors such as metal alkoxides and metal chlorides. The wet gel is casted into a mold which will be converted to a dense ceramic after further drying or calcination process (Chen and Mao 2007). Ching and co-workers (Ching et al. 1997; Ching et al. 1997) have fabricated the cryptomelane-type manganese oxide (K-OMS-2) and birnessite-type manganese oxides using this method. In a typical process, glucose can be considered as a reducing agent as well as a controlling factor. By adjusting the glucose dosage, different types of manganese oxides can be formed. Long and co-workers (Long et al. 2003) also used this method to prepare mesoporous manganese oxide with high porosity. Most importantly, sol-gel processes introduce flexibility into the processability of porous manganese oxide materials. Moreover, the morphology of the synthesized materials are more particulate as compared to the manganese oxides synthesized through other routes (Brock et al. 1998).

2.2. NANOSTRUCTURED MANGANESE OXIDE

Unique physical and chemical properties of the material often emerge when the size of a material becomes nanometre scale. Due to this, the material may possess with better performance as compared to a conventional bulk material(Granqvist et al. 2007). Thus, there is a growing need for the synthesis and application of nanomaterials(Granqvist et al. 2007; Mauter and Elimelech 2008; Hochbaum and Yang 2010). Nanomaterials are associated with materials that have dimensions of roughly 1 to 100 nm. Beside that, they involve nanotechnology equipments that are capable of imaging, measuring, modeling, and manipulation of materials at a nanoscale(Mao et al. 2007). Nanomaterials usually possess with high ratio between surface and volume, which forms the new properties of the material. In addition, the material properties vary with the shape of the nanomaterials. As a consequences, many studies have been carried out to focus on the morphology control for the nanomaterials. For example, nanoparticles, nanorods, nanowires and nanotubes were successfully synthesized and characterized in the previous works, and these materials exhibited excellent electronic, optical, thermal, mechanical, magnetic, chemical, and other physical properties(Hu et al. 1999; Baughman et al. 2002; Patzke et al. 2002; Xia et al. 2003). Therefore, it is necessary to fabricate nanostructured porous manganese oxides and their derivatives to further enhance their performances in various applications(Yuan et al. 2004; Yuan et al. 2005).

Recently, nanostructured porous manganese oxides and their derivatives with different dimensions have already been successfully synthesized, such as 0D, 1D, 2D, and 3D nanostructures(Yang et al. 2004; Yuan et al. 2004; Li et al. 2005; Zheng et al. 2005; Baek et al. 2009). 0D nanostructures are materials wherein all the dimensions are measured within nanoscale, and the most common representation of 0D nanomaterials are nanoparticles. 1D nanostructures have a single dominant aspect, such as nanowires, nanorods, nanobelts and nanotubes. 2D nanostructures are materials in which two of the dimensions are not confined to the nanoscale, such as nanofilms, nanolayers, and nanocoatings. 3D nanostructures are bulk

nanomaterials with three dimensions or aspects, such as dispersions of nanopartilces, bundles of nanowires and nanotubes, and multinanolayers(Ashby et al. 2009).

In comparison to other nanostructured materials, 1D nanostructured materials such as nanowires, nanorods, nanobelts and nanotubes have become more popular due to their unique applications in physics, electrochemistry and environment(Hu et al. 1999; Wang 2000). 1D manganese oxides have been proven to be highly effective in environmental application with enhanced performance in catalysis, oxidation and adsorption processes(Dong et al. 2009; Zhang et al. 2009). Their effectiveness is not only attributable to their large surface area, adjustable transport properties and chemical specificities, but also due to their excellent separability from aqueous solutions as compared to other nanostructured materials by virtue of their high aspect ratios(Zhang et al. 2011).

2.2.1. 1D nanostructured porous manganese oxides

2.2.1.1. Manganese oxide nanowires

Nanowire is a common nanostructure of manganese oxides. MnO₂ nanowires were successfully synthesized by Wang and Li in 2002 for the first time(Wang and Li 2002). As shown in Figure 2-3, single crystal nanowires of α -MnO₂ and β -MnO₂ can be synthesized via hydrothermal processes, respectively (Wang and Li 2002). In a typical synthesis process, precursor Mn²⁺ was oxidized by S₂O₈²⁻ without the existence of any catalysts or templates. At the same time, the type of MnO₂ synthesized was determined by the concentration of S₂O₈²⁻. Based on this method, various types of MnO₂ nanowires were further fabricated by other researchers(Wang and Li 2003; Gao et al. 2005; Cheng et al. 2006; Zhang and Mu 2007). Yuan and co-workers(Yuan et al. 2003) synthesized single-crystalline MnO₂ nanowires using a combination method of hydrothermal treatment and calcination process; while Xiong and co-workers(Xiong et al. 2003) reported a novel coordination-polymer-precursor route to synthesize this kind of materials.

Figure 2-3. (A) TEM pattern of α -MnO₂ nanowires, scale bar 20 nm; (B) TEM pattern of β -MnO₂ nanowires, scale bar 1 μ m(Wang and Li 2002).

Recent progress shows that mixed-valent manganese oxide nanowires present enhanced performance in environmental chemistry and heterogeneous catalysis(Luo et al. 2008; Yuan et al. 2008; Huang et al. 2010; Zhang et al. 2011). Luo et al.(Luo et al. 2008) studied the structure, composition, morphology and properties of various K-OMS-2 nanowires. Their results revealed that the hydrophobility, acidity and microporosity of the material can enhance the reversible evolution of lattice oxygen and thus endow the material with great oxidation properties. Huang et al.(Huang et al. 2010) prepared porous K-OMS-2 nanowires using a microwave assisted hydrothermal process. The material can be rapidly synthesized within 10 s with the assistance of microwave treatment, which largely reduced the reaction time as compared to the conventional hydrothermal route(Yuan et al. 2004). Further study indicates that the prepared K-OMS-2 material exhibits outstanding catalytic activity for cinnamyl alcohol oxidation. Yuan and co-workers(Yuan et al. 2004) prepared K-OMS-2 nanowires via a hydrothermal method under 250 °C. This type of nanowires possesses diameters of about 40-100 nm, and are over several hundreds of microns in length, as shown in Figure 2-4A. Furthermore, the nanowires form a dark-brown paper-like material with free-standing characteristics

after placing on a substrate followed by heating. The composition of the membrane is $\text{KMn}_{2.65}\text{O}_{5.40} \cdot 0.17\text{H}_2\text{O}$, and the thickness of the membrane can be varied by controlling the amount of the nanowires. As shown in Figure 2-4B, the cross-section of the membrane reveals that the membrane consists of multilayers of K-OMS-2 nanowires bundles. There are three levels of structures for the membrane: primary structure with a nanowire microporous structure; secondary structure with a layer; and tertiary structure with the network of multilayers. Based on this work, Yuan and co-workers(Yuan et al. 2008) further designed a free-standing nanowires membrane with controllable wetting behaviour ranging from superhydrophilic to superhydrophobic for water treatment. In a typical process, superwetting K-OMS-2 nanowires membrane was firstly synthesized via a conventional hydrothermal method. Subsequently, a silicone coating procedure was carried out using a vapour deposition technique, which endowed the membrane with hydrophobic surface property. In the study, the synthesized membrane exhibits very good adsorption capacity for various type of oils. More importantly, this membrane can be easily regenerated after each use via ultrasonic washing and autoclaving, which will be very useful to develop novel recyclable adsorbents for environmental applications.

Figure 2-4. (A) TEM image of K-OMS-2 nanowires; (B) FESEM image of cross-section of K-OMS-2 nanowires membrane(Yuan et al. 2004).

2.1.1.2. Manganese oxide nanorods

Standard aspect ratios (length divided by width) of nanorods are 3 to 5, which is lower than nanowires. Typical MnO_2 nanorods are shown in Figure 2-5(Gao et al. 2009). Manganese oxide nanorods exhibit higher activity than the corresponding nanoparticles due to the increased numbers of active sites and crystal plane effects(Liang et al. 2008). Recently, different types of manganese oxides were synthesized and used as catalysts for the removal of pollutants(Liang et al. 2008; Iyer et al. 2010; Yang et al. 2010). Liang and co-workers(Liang et al. 2008) synthesized α -, β -, γ -, and δ - MnO_2 nanorods via hydrothermal methods and their catalytic properties for CO oxidation were also evaluated. Their results show that the catalytic property of MnO_2 partly depends on the phase structures, and the catalytic activity of the different types of MnO_2 follows the order: $\alpha \approx \delta > \gamma > \beta$. In addition, β - MnO_2 nanorods can be prepared by calcining γ - MnOOH nanorods precursor, and the material shows high catalytic activity in the synthesis process of isoamyl acetate(Yang et al. 2010). Furthermore, researchers found that β - MnO_2 nanorods possess excellent electrode performance, and low-valent manganese oxide (MnO) is the most effective precursor for the production of β - MnO_2 nanorods(Kim et al. 2009).

Figure 2-5. SEM image of MnO_2 nanorods(Gao et al. 2009).

2.1.1.3. Manganese oxide nanotubes

Nanotubes are a type of nanometer-scale tube-like structure. Manganese oxide nanotubes have already been successfully fabricated via different hydrothermal methods (Ma et al. 2004; Wang and Li 2004; Wu et al. 2004; Zheng et al. 2005; Luo et al. 2008; Luo et al. 2010). Ma and co-workers (Ma et al. 2004) prepared manganese oxide nanotubes via transforming 2D nanosheets into 1D nanotubes using a simple ion intercalation/deintercalation procedure at room temperature; while Wang and Li (Wang and Li 2003) also reported layer-structured curling α - MnO_2 via an intercalation process. In addition, Wu and co-workers (Wu et al. 2004) designed an electrochemical deposition method to synthesize MnO_2 nanotubes with polycrystalline structures. Although these methods are successful for the synthesis of MnO_2 nanotubes, the fabrication processes are complicated and the products are low-yield. To overcome the difficulties, one-step methods to fabricate manganese oxides nanotubes were designed recently (Zheng et al. 2005; Luo et al. 2008). As shown in Figure 2-6, α - MnO_2 nanotubes can be fabricated via a hydrothermal treatment of KMnO_4 in the hydrochloric acid solution. The morphology evolution indicated that the nanotube structure is formed from nanorod structure via a chemical etching process (Luo et al. 2008). Furthermore, the MnO_2 nanotubes were successfully coated onto the surface of Si (111) substrate in order to obtain vertically aligned nanotubes. This fabrication method synthesized well-crystalline MnO_2 nanotubes that possessed with superb optical property. In addition, β - MnO_2 nanotubes can be fabricated using a similar hydrothermal method in the presence of poly(vinyl pyrrolidone) (PVP) (Zheng et al. 2005). The presence of PVP can affect the growth rates of various crystallographic surfaces and it acts as a structure-directing agent in the synthesis process of β - MnO_2 nanotubes (Zheng et al. 2005).

Figure 2-6. (A) Side-view SEM image of the α -MnO₂ nanotubes. (B) Top-view SEM image of the α -MnO₂ nanotubes(Luo et al. 2008).

2.2.2. Other nanostructured porous manganese oxides

2.2.2.1. Manganese oxides nanoparticles

Nanoparticles are sized between 1 and 100 nanometers. In the previous work of Sayle and co-workers(Sayle et al. 2005), MnO₂ nanoparticles have been generated using a simulated amorphization and recrystallization strategy. The diameter of the nanoparticles is around 8 nm, and the material has a structure of 2×1 octahedra(Sayle et al. 2005). In addition, MnO₂ nanoparticles with uniform sizes can also be fabricated in the system of poly(3,4-ethylenedioxythiophene) (PEDOT) and KMnO₄ solution(Liu et al. 2010). MnO₂ nanoparticles exhibit very high specific capacitance which is functional for supercapacitor electrode materials(Liu et al. 2010). Yin et al. (Yin and O'Brien 2003) reported an effective way to synthesize monodisperse nanoparticles of MnO with alkyl chain capping groups, as shown in Figure 2-7. Besides that, they also discovered that the synthesized MnO nanoparticles are superparamagnetic at room temperature(Yin and O'Brien 2003).

Figure 2-7. TEM image of MnO nanoparticles(Yin and O'Brien 2003).

2.2.2.2. Manganese oxides nanoplates

Nanoplates or nanosheets are 2D nanostructures which have a thickness on the order of nanometers or smaller. MnO_2 nanosheets can be prepared using layered manganese oxide $\text{H}_{0.13}\text{MnO}_2 \cdot 7\text{H}_2\text{O}$ under the treatment of intercalation, osmotic swelling, and delamination(Omomo et al. 2003). The synthesized MnO_2 nanosheets are only 0.77 nm in thickness and several hundred nanometers in lateral size, as shown in Figure 2-8(Omomo et al. 2003). In addition, MnO_2 nanosheets can also be synthesized via an electrostatic self-assemble technique that is capable of fabricating superior electrochemical activity materials(Wang et al. 2003).

Figure 2-8. TEM image of MnO₂ nanosheets(Omomo et al. 2003).

2.2.2.3. Micro-/nano-structured manganese oxides

Micro-/nano-structured materials can be considered as 3D materials with hierarchical structures. Manganese oxides with hierarchical micro-/nano-structures are promising candidates in the fields of energy and environment because they are able to compromise both nanometer-sized building blocks and micro- or submicrometer-sized assemblies(Guo et al. 2008). Li and co-workers(Li et al. 2005) prepared hierarchical α -MnO₂ with a core-shell structure with spherically aligned nanorods via a room-temperature solution-based catalytic route. They found that the core of the microsphere was constructed from tightly aggregate nanoparticles which occupied 60%-90% volume in a microsphere, and the nanorods with uniform diameters around 30-40 nm were densely fixed on the surfaces of the microspheres. 3D manganese oxides can also be synthesized via a hydrothermal method, which is a recommended option for achieving higher temperature and higher pressure reaction. Ding and co-workers(Ding et al. 2006) successfully synthesized 3D hierarchical ϵ -MnO₂ using this method without any catalysts or templates. The hierarchical ϵ -MnO₂ material exhibited different magnetism under different Curie

temperature (T_C). The material is ferromagnetic below 25 K and paramagnetic above 25 K which is effective in producing semiconductors and magnetic devices.

Manganese oxide materials can also form hierarchically mixed-valent OMS, which have porous structures, open tunnels, and high surface areas. Yuan and co-workers(Yuan et al. 2005) reported a novel micro-/nano-structured K-OMS-2 microsphere using a template-free low-temperature hydrothermal route, as shown in Figure 2-9. The size of the synthesized material is in micro-scale, but the material also possesses nanostructures on its surface. To obtain a uniform morphology, the nucleation and growth rate of the material was controlled by adjusting the reaction rate. The well organized morphologies can be explained by the mild and slow reactions lead to the formation of materials with well-organized morphologies(Suib et al. 2010). In addition, a 3D K-OMS-2 with urchin-like morphology has also been developed via a direct reaction between sodium dichromate and manganese sulfate without addition of any organic templates(Li et al. 2006). The authors demonstrated that the shapes, crystal forms, and tunnel sizes of the material can be tailored for selective applications.

Figure 2-9. (A) FESEM image of 3D OMS-2 microspheres. (B & C) Higher magnification FESEM images of a selected microsphere(Yuan et al. 2005).

2.3. ENVIRONMENTAL APPLICATION OF NANOSTRUCTURED MANGANESE OXIDES

Manganese oxide materials are of environmental interest because of their adsorptive, oxidative and catalytic capabilities. Manganese oxides can participate in a wide range of redox, adsorption and catalytic reactions with organic and inorganic chemical species and compounds, which affect the distributions and bioavailability of many toxic elements in environment (Tebo et al. 2004). Nanostructured manganese oxides have been intensively studied for environmental application due to their easy control, low cost, and energy efficiency.

2.3.1. Oxidation

2.3.1.1. Oxidation of As(III)

Arsenic, as a pervasive metalloid which can be found in surface and groundwater, can be effectively oxidized by manganese oxides (Scott and Morgan 1995). Arsenic is a significant concern to environment in many regions of the world due to its severe toxic effects on human health (Nordstrom 2002). There is convincing evidence that arsenic is a human carcinogen, and is also associated with harmful effects on the heart and the circulatory system (Hughes 2002). Owing to its seriously potential risk, the US Environmental Protection Agency has established the maximum allowable arsenic in drinking water at 10 $\mu\text{g/L}$, replacing the former limit of 50 $\mu\text{g/L}$ (United States Environmental Protection Agency 2001). Arsenic can exist in several different chemical forms and oxidation states (-3, 0, +3, +5) in soil, water and air, and its predominant forms in natural water are As(III) and As(V) (Nordstrom 2002). As(III) is more toxic and soluble, while its removal from drinking water is less effective as compared to As(V) (Driehaus et al. 1995). The oxidation of As(III) in the presence of air or pure oxygen is slow. Hence, oxidation is considered as a necessary pretreatment process for As(III) removal. Although the oxidation process can not remove arsenic directly, arsenic can be oxidized to higher oxidation state (V), which can lower its toxicity. Manganese oxides have been

extensively investigated for As(III) oxidation, and the oxidation process can be well expressed as the following pathway in previous studies (Scott and Morgan 1995; Manning et al. 2002).

The net stoichiometry of the reaction is shown in Formula [2-1]. Oxidation of As(III) by MnO₂ is coupled with the reductive dissolution of the MnO₂ surface.

Nesbitt and co-workers (Nesbitt et al. 1998) further studied the reduction of MnO₂ by H₃AsO₃ using XPS measurement, which revealed that MnOOH* is an intermediate reaction product in the reaction. Formula [2-2] shows the first step of Mn(IV) to Mn(III).

Subsequently, the MnOOH* is attacked by H₃AsO₃ then Mn²⁺ will be formed in the reaction, as shown in Formula [2-3]. Finally, Mn²⁺ will be released to solution as another hazardous material which also needs to be considered.

In addition, As(V) can be adsorbed onto MnO₂ surface after the oxidation reaction, which can be shown in Formula [2-4].

where Mn-OH is a reactive hydroxyl group on the MnO₂ surface and (MnO)₂AsOOH is an As(V) complex.

Although many researchers have already used MnO_2 and its derivatives for As(III) detoxification, the limited reaction sites of normal manganese oxides materials restricted their applications. Nanostructured manganese oxide materials have stronger oxidation ability because of their higher surface areas and more reactive sites (Robinson et al. 2010; Zhao et al. 2010). Thus, nanostructured manganese oxides can be a good candidate to improve the oxidation efficiency of As(III).

2.3.1.2. Oxidation of organic pollutants

Manganese oxides and their derivatives also demonstrate high reactivity with many different organic contaminants. For example, phenol and aniline compounds are susceptible to oxidation by manganese oxides, and they can form intermediate radicals that may subsequently trigger a series of radical reactions in this process. A wide range of anthropogenic organic pollutants including phenols, anilines and other antibiotics and hormones have been reported for being effectively degraded by manganese oxides (Li et al. 2003; Zhang and Huang 2005; Zhang and Huang 2005; Lin et al. 2009). Lin and co-workers (Lin et al. 2009) used $\delta\text{-MnO}_2$ to degrade BPA, which is an ubiquitous environmental contaminant with endocrine disruption potential. Their studies revealed that the synthesized $\delta\text{-MnO}_2$ possessed good oxidative capacity. Furthermore, the mechanisms of BPA removal by $\delta\text{-MnO}_2$ were also discussed. In the oxidation process, several intermediates were identified and BPA molecule was degraded into smaller molecules, which can be attributed to a series of reactions of radical coupling, fragmentation, substitution, elimination and so on. Although most of the formed intermediates were still identified as phenolic compounds and thus may still have estrogenic potencies, MnO_2 is a promising material to remove phenolic compounds. Another example is the degradation of antibacterial agents triclosan and chlorophene by manganese oxides (Zhang and Huang 2003). The oxidation ability of manganese oxides is enhanced at a pH of less than 7, which can be attributed to the increased redox potential of the manganese oxide under acidic condition. Although manganese oxide materials showed excellent oxidation ability to remove some inorganic and organic pollutants, release

of Mn(II) to the environment during the oxidation process is a major issue because Mn(II) is also a contaminant for the environment.

2.3.2. Adsorption

Compared with the oxidation ability, adsorption property of manganese oxides is more commonly used in environment for the removal of organic and inorganic pollutants(Addis Lockwood and Chen 1973; Thanabalasingam and Pickering 1985; Yao and Millero 1996; Zhao et al. 2010). The points of zero charge of manganese oxides are ranging from 1.5 to 4.6. Thus, the surface charge of manganese oxides is usually negative under neutral pH conditions, which will facilitate the adsorption of heavy metals onto the materials. Manganese oxides are one kind of surface acidic oxides, which can provide efficient scavenging pathways for heavy metals in toxic system. Current research shows that trace metals and radionuclides, such as Co, Ni, Cu, Pb, can strongly interact with manganese oxides due to their large surface area and high affinity for metal ions(Han et al. 2006). Although manganese oxides are thought to have limited capacity to adsorb anions because of their negative surface charge at neutral pH, the surface charge on manganese oxides could be reversed by exchange of H^+ on the surface(Murray 1975). In addition, researchers also reported that phosphate can be strongly adsorbed by manganese oxide between pH 6 and 9 in the presence of divalent cations(Kawashima et al. 1986). Yao et al.(Yao and Millero 1996) studied the adsorption of phosphate onto MnO_2 in seawater, revealing that the adsorption reaction can be affected by pH, temperature, and salinity. The presence of Ca^{2+} and Mg^{2+} in seawater is the key factor for the adsorption process. To further enhance the adsorption property of manganese oxides, a lot of nanostructured manganese oxides with higher surface area have been synthesized and applied for the adsorption of contaminants in water treatment processes(Chen and He 2008; Pakarinen et al. 2010). Chen and co-workers(Chen and He 2008) prepared a novel kind of monodisperse manganese oxide nanostructures for methylene blue(MB) adsorption. The study indicated that hydrogen bonding and electrostatic attraction are also important factors influencing the adsorption capability of manganese oxides. In addition, the coupling of manganese oxides with other materials, such as

carbon nanotubes and graphene, can further enhance the adsorption ability for pollutants removal(Thanabalasingam and Pickering 1985; Wang et al. 2007).

2.3.3. Catalysis

Manganese oxides with a rather complex oxide system, forming several phased such as MnO , MnO_2 , Mn_2O_3 and Mn_3O_4 , are of considerable alternatives in environmental catalysis(Chen and Suib 2012). Mn_2O_3 is known to be an active catalyst for removing carbon monoxide and nitrogen oxide from waste gas, while MnO_2 and Mn_3O_4 can be used as catalysts for the oxidation of methane and carbon monoxide or the selective reduction of nitrobenzene(Baldi et al. 1998; Dimesso et al. 1999; Gu et al. 2005). K-OMS-2 type manganese oxide was recently used as a catalyst for the oxidation of volatile organic compounds and carbon monoxide, and related studies indicated that the synthesized K-OMS-2 possesses high porosity, hydrophobicity, strong affinity toward organic compounds and easy reversible evolution of lattice oxygen, which facilitate the catalytic oxidation of the organic pollutants in water(Luo et al. 2008). In addition, manganese oxides can also be applied in catalytic ozonation and wet oxidation(Andreozzi et al. 1996). Andreozzi et al.(Andreozzi et al. 1992) studied the role of manganese(II) in the ozonation process, revealing that manganese(II) ions can be profitably exploited for promoting the oxalic acid oxidation by ozone. The reduction of Mn(IV) to Mn(III) is a key step for the catalytic process(Andreozzi et al. 1992). Oxidizing and reducing properties respectively of ozone and of organic substrates make exploitable Mn catalysis in the ozonation system(Andreozzi et al. 1996).

2.4. SEPARATION AND RECOVERY OF NANOSTRUCTURED MATERIALS

Although various nanomaterials have been proposed as alternatives for water treatment, most of them are facing difficulties to be separated from treated water and thus restricting their applications in industry. In addition, many nanoparticles used in industry contain heavy metals, which may contribute to environmental issues due to their toxicity and bioaccumulation(Bystrzejewska-Piotrowska et al.

2009). Liu and co-workers(Liu 2006) reported that nanoparticles are capable of accumulating in prokaryotic and eukaryotic cells, which may portray potential toxic effect on organisms in natural environments. Recently, many researchers have been involved in the research concerning the interaction of nanoparticles with cells(Dunford et al. 1997; Kashiwada 2006; Zhu et al. 2006; McAuliffe and Perry 2007). According to the research of McAuliffe and Perry(McAuliffe and Perry 2007), nanomaterials can enter human bodies through inhalation or dermal contact, and secondarily by injection or ingestion. For example, nanosized TiO_2 can be widely used in water treatment as efficient photocatalysts, and they have been considered as a safe physical sunscreen because it is able to reflect and scatter UV light. However, Dunford and co-workers(Dunford et al. 1997) demonstrated that TiO_2 nanomaterials can also catalyze DNA damage in both vitro and human cells. The uptake of nanomaterials by cells has been observed by many studies(Kashiwada 2006; Zhu et al. 2006). Another example is that fishes can accumulate Latex nanoparticles in gills and intestine which affect its survivability(Kashiwada 2006). Other nanosized materials such as SiO_2 , ZnO and Ag , also have a toxic effect on cells which can be agitated by the presence of light(Adams et al. 2006). Therefore, it is necessary to separate nanomaterials from aqueous solution after water treatment process. Ultimately, seperation process can eliminate secondary pollutants induced by nanomaterials. Furthermore, the cost for the synthesis of materials can be reduced as nanomaterials can be recycled via regeneration process. Hence, technologies and mechanisms for the separation of nanomaterials from aqueous solution such as free settling, magnetic separation and membrane filtration have been widely studied. It is important to note that energy cost is a key factor in the separation process.

2.4.1. Centrifugation and free settling

Centrifugation is a separation process that uses centrifugal force to separate the materials from aqueous solution. This is a most common method used to separate nanomaterials in laboratory scale. Nanomaterials can increase effective gravitational force in the centrifugation process and precipitate at the bottom of the

centrifugal tube. The separation rate by centrifugation can be adjusted via controlling shapes and sizes of materials. Generally, smaller particles need a higher centrifugal speed or longer centrifugation time in the separation process.

Free settling is a process that particles can settle to the bottom of the solution, relying on the gravity of the materials. The settling speed is dependent on the density, shape and size of materials. Owing to the small particle size, nanoparticles need a longer time to be separated via a free settling process. To address this problem, various nanomaterials with different sizes or shapes have been developed by researchers. Effectively, some of these results exhibited excellent separation abilities through free settling processes(Li et al. 2003; Dong et al. 2009; Zhang et al. 2009). Li and co-workers(Li et al. 2003) revealed that TiO₂ materials with different sizes possess different settling velocity, as shown in Table 2-1. The average settling velocity of TiO₂ decreases with the decrease of the particle size. Dong et al.(Dong et al. 2009) reported that 1D nanostructured materials can be easily sedimentated in aqueous solution due to their large 1D size and high aspect ratios. In other words, materials with microstructure can be considered as easily separable materials that are capable to be applied in water purification process. In addition, nanomaterials can be coated onto various substrates, such as active carbon, glass beads and zeolites, which will enlarge the overall particle size and thus enhance the separability of the materials(Kuwahara et al. 2010). Hence, fabrication of new structured materials or composites is a possible way to solve the separation issues.

Table 2-1. Setting velocity of Different TiO₂ Catalysts(Li et al. 2003).

Sample	Particle Size	Average settling velocity
TiO ₂ powder	10-22 nm	3.3 mm•min ⁻¹
TiO ₂ powder	12-25 nm	3.8 mm•min ⁻¹
TiO ₂ microspheres	30-160 μm	150 - 900 mm•min ⁻¹

2.4.2. Magnetic separation

Magnetic separation is a process that uses magnetic force to separate materials from aqueous solutions. Magnetism is a unique physical property which is very useful in water purification, and its combination with other technologies is able to enhance the water treatment technology (Ambashta and Sillanpää 2010). Recently, magnetic nanomaterials were synthesized and widely applied in water treatment process, such as Fe_3O_4 nanoparticles, MnFe_2O_4 nanoparticles, and magnetic nanocomposites (Sun et al. 2004; Chin et al. 2006; Yavuz et al. 2006; Álvarez et al. 2010; Zhao et al. 2010). These magnetic nanomaterials can be used as adsorbents, oxidants and catalysts in water treatment process. More importantly, they can be recycled from treated water to relieve the secondary pollution caused by the nanomaterials, as well as lowering the cost for the synthesis process. Ultimately, magnetic separation is a promising technology with low-cost and high-efficient properties.

Fe_3O_4 is a very common magnetic material used in water treatment. Bulk Fe_3O_4 is ferromagnetic at room temperature, however, it becomes superparamagnetic when its size reduce to 34 ± 5 nm. Since superparamagnetic materials can be easily accumulated under a low magnetic field, Fe_3O_4 nanoparticles can be easily separated and reused after water treatment process. As shown in Figure 2-10, Park and co-workers (Park et al. 2004) successfully synthesized monodisperse Fe_3O_4 nanocrystals in large-scale using inexpensive and non-toxic metal salts at 320°C , and the particle size can be controlled simply by varying the experimental conditions. With the increase of oleic acid in the synthesis process, the size of the synthesized Fe_3O_4 nanoparticles became fine. This phenomenon can be attributed to the change of the boiling point of the solvent. Yavuz et al. (Yavuz et al. 2006) reported that monodisperse Fe_3O_4 nanoparticles can be directly used as an excellent adsorbent for arsenic removal, and the adsorption capacity of the synthesized Fe_3O_4 nanoparticles was largely determined by the particle size. In addition, Fe_3O_4 nanoparticles also exhibit high adsorption capacity for heavy metals removal (Wang et al. 2003), indicating the Fe_3O_4 is a multi-purpose material for water purification.

Although Fe_3O_4 nanoparticles possess outstanding adsorption and magnetic properties, they are chemically weak. In order to rectify this weakness, a protection shell is required to ensure their stability (Yang et al. 2005). Recently, Zhou and co-workers (Zhou et al. 2009) successfully synthesized Fe_3O_4 /Chitosan core-shell nanocomposites, which displayed high adsorption capacity for Cu^{2+} removal from aqueous solution. XRD and FTIR indicated that the synthesized material possessed high stability and no release of iron oxides was observed in the regeneration experiments. $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core-shell nanocomposites which are considered as good adsorbents for heavy metal removal, have also been further investigated by researchers (Deng et al. 2009; Hu et al. 2010; Wang et al. 2010). Compared with organic coating materials, SiO_2 is considered as an ideal shell material for Fe_3O_4 nanoparticles because of its strong stability under acidic conditions and resistance to redox reactions (Wang et al. 2010). Thus, the synthesized material can be easily regenerated by acid treatment. Other magnetic nanomaterials, including ZnFe_2O_4 , MnFe_2O_4 and CoFe_2O_4 , have also been synthesized and characterized (Sun et al. 2004; Laokul et al. 2011). Sun and co-workers (Sun et al. 2004) prepared monodisperse MFe_2O_4 ($\text{M} = \text{Fe}, \text{Co}, \text{Mn}$) nanoparticles using a high-temperature solution phase reaction, and the monodisperse nanoparticles exhibited better magnetic property than Fe_3O_4 . Importantly, the nanoparticles and their dispersions in various media have great potential in magnetic nanodevice and biomagnetic applications (Sun et al. 2004). Owing to the superparamagnetic property of magnetic nanomaterials, separation process can be easily conducted by magnetic field interactions. Thus, fabrication of magnetic nanocomposites can act as an alternative for the separation of nanomaterials in water.

Figure 2-10. TEM image of 12 nm magnetite nanocrystals. Inset is a photograph showing a Petri dish containing the monodisperse magnetite nanocrystals, and a US one-cent coin for comparison(Park et al. 2004).

2.4.3. Membrane filtration

Membrane filtration process is a physicochemical separation technique that uses the variation in permeability of water constituents as a separation mechanism. The separation process of nanomaterials using a membrane filtration occurs when a solution is forced through a membrane where nanomaterials are been separated. Sopajaree et al.(Sopajaree et al. 1999) designed a reactor for heterogeneous photocatalysis applications. This setup combines a batch-recirculated photoreactor with a hollow fibrous membrane ultrafiltration unit. In the study, TiO_2 nanoparticles (Degussa P-25) were mainly used for the degradation of MB. In addition, investigations on other parameters including cross-flow velocity, transmembrane pressure, and TiO_2 dose on the permeate flux through the membrane were also performed. The results showed that TiO_2 nanoparticles can be completely separated by the ultrafiltration membrane after the photocatalytic reaction, and it also indicates that membrane filtration is an effective way for the separation of nanomaterials from aqueous solutions. However, membrane fouling

problem occurs due to the formation of cake layer on the membrane surface and the pore blocking of membrane(Lee et al. 2001).

Membrane fouling is considered as the most significant issue which can affect the design and operation of membrane filtration facilities, severe flux decline, and influence the quality of water produced. Cake layer can retain additional smaller materials as well as generating flow hydraulic resistance. However, this cake layer can be easily removed by back washing method. Pore blocking occurs when the particles blocked the membrane pores, resulting the decreasing of effluent efficiency. Although both of them result in the decrease of flux or increase of transmembrane pressure and thus increase the energy cost, pore blocking is more important for the separation of nanomaterials due to its dominating effect on the total fouling resistance in the membrane filtration process.

Morphology of nanomaterials can be controlled to address this problem. 1D nanomaterials, including nanowires, nanofibers, nanorods and nanotubes allowed easy separation and recycling from aqueous solutions than the nanoparticles by virtue of their high aspect ratios. Nanoparticles can enter the membrane pores and cause serious pore blocking. As 1D nanomaterials are longer than the diameter of membrane pore size, they have lower probabilities to enter membrane pores. Zhang and co-workers(Zhang et al. 2009) described the separation of TiO_2 nanoparticles and TiO_2 nanowires via a membrane filtration process. As shown in Figure 2-11(Zhang et al. 2009), TiO_2 nanowires cause more porous cake layer and less pore blocking as compared to TiO_2 nanoparticles. Pan and co-workers(Pan et al. 2008) synthesized a novel kind of hierarchically mesoporous F- TiO_2 hollow microspherical photocatalyst, which exhibited higher photocatalytic activity for the degradation of MB and total organic carbon (TOC) than the TiO_2 nanoparticles. The filtration result of cross-flow membrane shows that the hollow sphere caused less membrane fouling than the nanoparticles, as shown in Figure 2-12(Pan et al. 2008).

Figure 2-11. Schematic diagram of membrane fouling caused by TiO₂ nanoparticles, and two types of TiO₂ nanowires with different diameters(Zhang et al. 2009).

Figure 2-12. (A) MB, TOC removal, and (B) membrane flux over mesoporous F-TiO₂ hollow microspheres and P25. Inset of panel b: Schematic diagram of membrane fouling caused by TiO₂ hollow spheres and TiO₂ nanoparticles(Pan et al. 2008).

2.4.4. Fabrication of inorganic membranes with nanomaterials

Membranes have been widely used in water treatment due to their outstanding performance on pollutants removal, relatively low energy cost, well arranged process conduction, and no addition of chemicals (Mulder 1991; Molinari et al. 2002; Sholl and Johnson 2006). Generally, synthetic membrane can be further divided into organic and inorganic membranes. Although organic membranes are commonly used in water treatment processes, the applications of these membranes are restricted by fouling processes, low chemical resistance and low thermal stability (Maier et al. 1993; Sholl and Johnson 2006). To address these defects, inorganic membranes have been widely studied due to their chemical resistance, thermal resistance and mechanical resistance. Owing to their thermal resistance, these membranes can be regenerated thermally (Ke et al. 2007; Shannon et al. 2008). Current progress shows that inorganic membranes can be fabricated by materials with nanowire structure. Similar to glass fibres, the nanowires can be fabricated into a free-standing membrane that possesses with mechanical stiffness and certain degree of flexibility (Yuan et al. 2004; Dong et al. 2006). Moreover, this kind of membranes was successfully used in water treatment process, and they can be efficiently applied for the treatment of organic pollutants (Yuan et al. 2008; Zhang et al. 2008; Zhang et al. 2009).

Recently, TiO_2 membranes have been becoming increasingly attractive in environmental application due to their photocatalytic activity, excellent chemical resistance and thermal stability (Ding et al. 2006a; Ding et al. 2006b; Jing et al. 2009). In the previous works carried out by our group (Zhang et al. 2008; Zhang et al. 2009), microfiltration and ultrafiltration TiO_2 nanowire membranes were respectively synthesized and applied for water treatment process, as shown in Figure 2-13. The synthesized membranes are robust, flexible and possess multifunctions. These membranes are capable to overcome the polymeric membrane problems such as membrane fouling and high-temperature applications. As shown in Figure 2-14 (Zhang et al. 2008), the TiO_2 nanowire membrane exhibits excellent anti-fouling property with the assistance of UV light, which facilitate the

regeneration of the membrane and thus lower the cost for membrane cleaning. The fabrication of nanofibrous membrane provide another pathway for nanomaterials involved in water purification process and there is no need for further separation of nanomaterials from aqueous solution after treating the water.

Figure 2-13. Digital photos of TiO₂ nanowire membranes(Zhang et al. 2008; Zhang et al. 2009).

Figure 2-14. TMP change of TiO₂ nanowire membrane during filtration: (a) with UV irradiation and (b) without UV irradiation(Zhang et al. 2008).

2.5. SUMMARY

This chapter focuses on the review of nanostructured manganese oxides including the synthesis, morphologies, properties and environmental applications. Among them, 1D nanostructured manganese oxides were reviewed as the most effective type. The objective of this study is to develop multifunctional 1D nanostructured manganese oxide based materials for water treatment, and the synthesized nanomaterials should be easily separated from aqueous solutions. Thus, recent developments of the separation methods for nanomaterials such as magnetic separation, microfiltration and fabrication of nanofibrous membrane, were also reviewed and discussed.

Chapter 3 MATERIALS & METHODOLOGY

3.1. MATERIALS

Potassium sulfate (K_2SO_4 , 99%), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, 99%), manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 99%), sodium hydroxide (NaOH , 99%), ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, 99%), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99%), concentrated hydrochloric acid (HCl , 36.5%), concentrated sulfuric acid (H_2SO_4 , 98%), ammonia persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, 99%), manganese(II) acetate tetrahydrate ($\text{C}_4\text{H}_6\text{O}_4\text{Mn} \cdot 4\text{H}_2\text{O}$, 99%), oxone monopersulfate compound, silver nitrate (AgNO_3 , 99%), titanous sulfate (TiOSO_4 , 99%), sodium chloride (NaCl , 99%), acid orange 7 (AO7, 99%), potassium hydroxide (KOH , $\geq 85\%$, pellets), potassium bromide (KBr , 99%), humic acid (HA, 99%), bisphenol A (BPA, 99%), calcium chloride (CaCl_2 , 99%), magnesium chloride (MgCl_2 , 99%), manganese chloride (MnCl_2 , 99%), monosodium phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 99%), sodium carbonate (Na_2CO_3 , 99%), sodium sulfate (Na_2SO_3 , 99%), sodium arsenite (NaAsO_2 , 99%) and sodium arsenate ($\text{NaHAsO}_4 \cdot 7\text{H}_2\text{O}$, 99%) were purchased from Aldrich. Commercial TiO_2 P25 was purchased from Evonik Degussa. All solvents were purchased from Merck, including acetonitrile (99.99%) methanol (99.99%) and ethanol (99%). Standard polystyrene (PS) microspheres of diameters 0.05, 0.1, 0.2, 0.5, 1, and 2 μm , were purchased from Alfa Aesar. The deionized water (18.3 $\text{M}\Omega\text{-cm}$ resistivity) was produced from Millipore Milli-Q water purification system.

3.2. SYNTHESIS

3.2.1. Synthesis of K-OMS-2 nanowires

(For Chapter 4 & 7)

To synthesize K-OMS-2 nanowires, a modified hydrothermal method was carried out according to a previous report (Yuan et al. 2004). In a typical procedure, 12

mmol of K_2SO_4 , 12 mmol of $\text{K}_2\text{S}_2\text{O}_8$, and 8 mmol of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were dissolved in 70 ml of deionized water. The solution was then transferred to a 125 ml Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated in an oven at 250 °C for 4 days. The resulting black precipitate was suspended in 1000 ml deionized water, and stirred vigorously for 12 hours. After thorough washing with deionized water to remove remaining ions present in the product, the samples were dried at 105 °C for 24 hours.

3.2.2. Synthesis of magnetic K-OMS-2/ Fe_3O_4 nanocomposites

(For Chapter 4)

To fabricate the magnetic manganese oxide nanocomposites, nanoparticles of Fe_3O_4 were deposited onto the synthesized K-OMS-2 nanowires using a chemical co-precipitation method. 10 ml of 0.02 mol/L ferric sulfate and 10 ml of 0.02 mol/L ferrous sulfate were vigorously stirred in a beaker at room temperature. 5 mol/L KOH was then added dropwise into the solution. When pH of the solution was raised to 10, 0.5 g of the synthesized K-OMS-2 nanowires were added into the system and continuously stirred for 5 mins. After that, pH value of the solution was adjusted to 12 and stirred for another 20 mins. In order to remove all soluble ions in the solution, the product was washed several times before being separated using a magnet.

3.2.3. Synthesis of 1D MnO_2 nanowires

(For Chapter 5)

To synthesize 1D MnO_2 nanowires, a modified hydrothermal process was conducted (Wang and Li 2002). In a typical procedure, 0.02 mol of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and an equal amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were dissolved in 80 ml of deionized water by stirring for 5 min. The mixture was then loaded into a 125 ml Teflon-lined stainless-steel autoclave, which was sealed and heated in an oven at 120 °C for 12 h.

Finally, the resulting black precipitate was obtained by centrifugation and washed with deionized water for five times to remove any ions possibly remaining in the product, followed by drying at 105 °C for 24 hours.

3.2.4. Synthesis of 3D micro-/nano-structured MnO₂ spheres

(For Chapter 6)

Based on a catalytic oxidation route, 3D micro-/nano-structured MnO₂ spheres were successfully synthesized in large scale. 2 g of analytical grade manganese(II) acetate tetrahydrate, 15 g of oxone monopersulfate compound and 5 ml of AgNO₃ solution (0.06 mol/L) were mixed together in 200 ml of distilled water under room temperature. The AgNO₃ solution acted as a catalyst, which would catalyze the redox reaction between Mn²⁺ and S₂O₈²⁻ under room temperature. Then, 10 ml concentrated sulfuric acid was added into the solution for pH control. After the homogenous solution stood for 36 hours, the resulting black precipitate was washed with deionized water for five times to remove any ions possibly remaining in the product, the sample was dried at 105 °C for 24 hours.

3.2.5. Synthesis of hierarchical TiO₂/K-OMS-2 heterojunctions

(For Chapter 7)

50 mg of the synthesized K-OMS-2 nanowires, 400 mg titanous sulfate, and 0.4 ml concentrated H₂SO₄ (98%) were dissolved in 70 ml deionized water. After homogenization by an ultrasonic homogenizer (Sonics and Materials, CT, USA) for 10 min, the solution was transferred to the 125 ml teflon-lined autoclave again and heated at 105 °C for 20 h. In order to remove all soluble ions in the solution, the product was washed several times before being separated using a centrifuge. Then, the resulting product was dried in vacuum for 48 h.

3.2.6. Assembly of TiO₂/K-OMS-2 nanofibrous membrane

(For Chapter 7)

To synthesize the TiO₂/K-OMS-2 nanofibrous membrane, suspension of the synthesized hierarchical TiO₂/K-OMS-2 heterojunctions were vigorously stirred for 10 min. Then, the suspension was filtered using a vacuum-filtration setup with a glass filter (ADVANTEC, GC-50, 0.45 μm), and the hierarchical heterojunctions would form a compact cake layer on the glass filter. After drying at 105 °C for 1 day, a free-standing membrane was formed after removal of the glass filter. The membrane was further pressurized under 5 bar at 120 °C on a customized hot press for 2 mins. Finally, the membrane was calcined at 550 °C for 1 h.

3.2.7. Synthesis of TiO₂

(For Chapter 7)

Pure TiO₂ was also synthesized via a hydrothermal process identical to that of aforementioned hierarchical TiO₂/K-OMS-2 heterojunctions, except without the addition of K-OMS-2 nanowires.

3.3. MATERIAL CHARACTERIZATION

The X-Ray Diffraction (XRD) data was collected on a Bruker D8 Advance X-ray diffractometer (Cu Kα λ=1.5406 Å). Morphology of the synthesized materials were studied using a field-emission scanning electron microscope (FESEM) Jeol JSM-6340F (Japan) operated at 5 kV, and transmission electron microscopy (TEM) was carried out on a Jeol JEM-2100F (Japan) operated at 200 kV. Element compositions of photocatalyst were detected by an Oxford energy dispersive X-ray spectrometer (EDX) attached to the SEM (Jeol JSM-6360). Brunaur-Emmett-Teller (BET) surface areas of the synthesized materials were measured by N₂ sorption using a Quantachrome Autosorb-1 instrument (USA). X-ray photoelectron spectroscopy (XPS) analyses were carried out in an ultrahigh vacuum (UHV)

chamber with a base pressure below 2.66×10^{-7} Pa at room temperature. Fourier Transform Infrared Spectroscopy (FTIR) results were recorded on a Perkin Elmer GX FTIR system using compressed KBr disc technique. Vibrating sample magnetometer (VSM) was used to determine the magnetism of the materials. Zeta potential data was collected with a Zetasizer instrument (nano-zs, Malvern) and the concentration of the material for zeta potential measurement was 0.2 g/L. The room temperature photoluminescence (PL) spectra were recorded on a Fluorolog-3 spectrofluorometer (Horiba Scientific, New Jersey, USA) at an excitation wavelength of 300 nm.

3.4. AS(III) OXIDATION AND AS(V) ADSORPTION EXPERIMENTS

(For Chapter 4 & 6)

As(III) oxidation experiments were carried out by contacting As(III) solutions (Chapter 4: 0.06 mM; Chapter 6: 0.1 mM) with the synthesized manganese oxides suspensions (Chapter 4: 1.8 g/L; Chapter 6: 0.25 g/L) in batch reactors at pH 5 and 20 ± 1 °C, with an ionic strength of 0.01 M NaCl. A teflon-coated magnetic stirrer was used to homogenize the suspension at 500 rpm. Then, samples of 4 ml were withdrawn from the reactor periodically (5 min, 10 min, 15 min, 20 min, 30 min, 45 min, 60 min, 75 min, 90 min and 120 min), and the samples were immediately filtered using glass syringe filters (0.2 μ m) to remove the manganese oxides for subsequent analysis.

The adsorption kinetics study was initiated by the addition of adsorbents (K-OMS-2, K-OMS-2/Fe₃O₄ or MnO₂ spheres) to As(V) solution, and samples of 4 ml were taken from the reactor at the following intervals: 0 min, 5 min, 15 min, 30 min, 45 min, 1 h, 2 h, 4 h, 6 h, 8 h and 24 h. Adsorption isotherms were determined at different concentrations of As(V), which ranged from 0.025 mM to 8 mM. In order to study the effect of ionic strength and pH on adsorption reactions (for Chapter 6), 3 series of samples were prepared using 0.1 M, 0.01 M and 0.001 M of NaCl solutions under pH values of 2, 3, 4, 5, 6, 7, 8, 9 and 10. The effects of anions (for

Chapter 6) on the removal of As(V) was also examined, including the addition of SO_4^{2-} , CO_3^{2-} and PO_4^{3-} in different amounts. All the samples were equilibrated by shaking for a further 48 h. Then, the samples were filtered using 0.2 μm glass syringe filter to remove the adsorbents. An inductively coupled plasma emission spectroscopy (ICP, Perkin Elmer Optima 2000DV) was used to determine the concentrations of As(V) in the adsorption tests. As (III) and As (V) species were quantified by high-performance liquid chromatography inductively coupled plasma mass spectrometer (HPLC-ICP-MS, Perkin Elmer Elan DRC-e). All samples were analyzed within 24 h of collection.

3.5. BPA DEGRADATION EXPERIMENTS

(For Chapter 5)

A stock solution containing 1 g/L BPA was prepared by dissolving 0.1 g of BPA in 100 mL of methanol. Oxidation experiments were conducted in 250 ml glass bottles at room temperature (20 ± 1 °C). In a typical process, 0.174 g 1D MnO_2 nanowires and 100 ml of water/methanol 50/50 (V/V) solution were added into the reactor. A teflon-coated magnetic stirrer was used to homogenize the suspension at 600 rpm, and 0.01 mol/L HCl and 0.01 mol/L NaOH were applied for pH adjustor when required. After 1 h of homogenization, the batch reaction was initiated by the addition of 1 ml of BPA stock solution to the suspension, making an initial BPA concentration of 10 mg/L. Samples of 3 ml were withdrawn from the reactor periodically. The samples were immediately filtered using glass syringe filter (0.45 μm) to remove the nanowires for subsequent analysis. Degradation of BPA over time in the reaction system was determined by a reverse-phase high-performance liquid chromatography (HPLC, PerkinElmer Series 200) coupled with a UV-vis detector (PerkinElmer 785A) with absorbance detection at 220 nm. A Thermol Scientific Hypersil GOLD HPLC column (4.6 $\times$ 150 mm, 5 μm) was employed for the separation. The mobile phase consisted of 60% pure water and 40% acetonitrile solution. The flow rate and injection volume were 1.5 mL/min and

25 μL , respectively. Under these conditions, the typical retention time for BPA in the HPLC system was 4.3 min.

3.6. MEMBRANE PORE SIZE MEASUREMENT

(For Chapter 7)

The pore size of the synthesized $\text{TiO}_2/\text{K-OMS-2}$ nanofibrous membrane was measured using PS microspheres (Nakao 1994). The concentration of PS microspheres solution was prepared to 0.033 wt.%, and a lab-scale dead-end filtration setup was used for filtration. The concentration of microspheres in the feed and filtrate were determined by a Shimadzu TOC-VCSH TOC analyzer. The retention rate (R) of the microspheres by the membrane were determined using the formula below:

$$R = \left(1 - \frac{\text{TOC}_{\text{filtrate}}}{\text{TOC}_{\text{feed}}}\right) \times 100\% \quad [3-1]$$

3.7. KINETICS OF AO7 ADSORPTION ON THE SYNTHESIZED MATERIALS

(For Chapter 7)

Kinetic experiments were carried out in 250 ml glass bottles at room temperature (20 ± 1 °C). 0.1 g of the synthesized TiO_2 , K-OMS-2 and $\text{TiO}_2/\text{K-OMS-2}$ were added into 100 ml of 20 mg/L AO7 solutions to obtain a 1 g/L suspension, respectively. The suspensions were mixed using a magnetic stirrer, and the pH was maintained at 5 with controlled addition of 0.01 mol/L HCl and 0.01 mol/L NaOH. Samples of 3 ml were withdrawn from glass bottle periodically. The samples were immediately filtered using glass syringe filter (0.45 μm) to separate the material for subsequent analysis. Concentration of AO7 was determined by a UV-visible spectrophotometer (Thermo Scientific Evolution 300) at a fixed wavelength of 484 nm.

3.8. PHOTOCATALYTIC EXPERIMENTS

Photocatalytic activities of the synthesized materials were evaluated by measuring the degradation rate of AO7 aqueous solution in a 150 ml cylindrical quartz vessel under UV light ($\lambda=254$ nm) irradiation. Before commencement of irradiation, the reaction suspension containing AO7 solution (100 ml, 100 mg/L) and synthesized nanocomposites (50 mg) was stirred in the dark for 30 min to achieve equilibrium. The pH was maintained at 5 with controlled addition of 0.01 mol/L HCl and 0.01 mol/L NaOH solutions. The PCO process started once the lamp was lighted. 2 ml of the solution was taken from the cylindrical quartz vessel at fixed time interval (5 min, 10 min, 15 min, 20 min, 25 min and 30 min). The samples were centrifuged at 10,000 rpm for 3 min for subsequent UV-vis spectroscopic analysis. TOC content was measured using a TOC analyzer (TOC-V CSH Shimadzu).

3.9. CONCURRENT FILTRATION, ADSORPTION AND PCO EXPERIMENTS

(For Chapter 7)

The concurrent filtration, adsorption and PCO process using the synthesized $\text{TiO}_2/\text{K-OMS-2}$ membrane was conducted in a dead-end filtration equipment as shown in Figure 3-1. AO7 was chosen as a model organic pollutant, and a UVP lamp (Upland 3SC9, 254 nm) was employed as the UV light source. In a typical procedure, 500 ml of 20 mg/L AO7 solution was filtered in continuous mode over the synthesized membrane under UV irradiation. The AO7 and TOC concentrations of the permeate were measured. Membrane flux was maintained at 30, 40, 50, 60, 70, 80 $\text{L/m}^2\cdot\text{h}$, respectively. The membrane filtration without UV irradiation was also carried out as control.

Figure 3-1. The setup of concurrent filtration, adsorption and photocatalytic oxidation.

3.10. MICROFILTRATION OF THE SYNTHESIZED 1D MnO₂ NANOWIRES

(For Chapter 5)

The experiments were carried out on a laboratory-scale crossflow membrane filtration apparatus, Model C10-T (Nitto Denko Co., Japan). The suspension of 1D MnO₂ nanowires after the oxidation experiment was pumped through a membrane cell for the filtration to take place. The cell was designed in a rectangular form (46 mm × 180 mm) with a 60 cm² effective membrane surface, and 0.2 μm membranes (Sartorius AG, thickness: average 120 μm) were used in the experiments. Transmembrane pressure (TMP) and cross flow flux were kept constant at 0.1 Mpa and 20 mL/min, respectively.

3.11. MICROFILTRATION OF THE SYNTHESIZED MICRO-/NANO-STRUCTURED MnO₂ SPHERES

(For Chapter 6)

The separation of 3D MnO₂ spheres was evaluated using a dead-end microfiltration apparatus. The suspension of 3D MnO₂ spheres after the oxidation experiment was filtered through a membrane cell. A microfiltration membrane (ADVANTEC MFS Inc., pore size: 0.2 µm, diameter: 47 mm) was used and TMP was kept constant at 0.2 Mpa in the experiments.

3.12. ANALYSIS OF THE FILTRATION RESULTS

(For Chapter 5 & 6)

The turbidity values of the solutions before and after membrane filtration were measured by a turbidimeter (Hach 2100N) in evaluating the rejection rate of the synthesized materials during the filtration process. The membrane flux was monitored to evaluate the fouling mechanism, and it can be expressed as follows according to the resistance-in-series model(Belfort et al. 1994):

$$J = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu(R_m + R_c + R_p)} \quad [3-2]$$

Where J is the water flux of the membrane (L/m²·h); ΔP is the TMP (Pa); μ is the dynamic viscosity (Pa·s); R_t is the total resistance (m⁻¹); R_m is the intrinsic membrane resistance (m⁻¹); R_c is the cake layer resistance (m⁻¹); R_p is the pore blocking resistance (m⁻¹). Individual resistance value in the equation can be quantified by selecting operating conditions in which the individual forms of fouling can be isolated. Firstly, R_m was determined from flux measurement of

deionized water. Then, R_t was calculated from the final flux data of BPA solution (or As(III) solution) filtration with and without the synthesized materials. Thereafter, cake layer on the membrane surface was removed after the second step, and the flux of deionized water was measured again to obtain the combined resistance value of $R_m + R_p$. Finally, R_p and R_c were determined respectively.

Chapter 4 1D MANGANESE OXIDE BASED MAGNETIC NANOCOMPOSITES FOR ARSENIC DETOXIFICATION AND REMOVAL

4.1. INTRODUCTION

Arsenic species that are present in water can be effectively removed by manganese oxides(Manning et al. 2002; Zhang et al. 2007). The toxicity and mobility of arsenic are mainly determined by its speciation. It was reported that As(III) is around 60 times more lethal than As(V) and more difficult to be removed from water due to its neutral, uncharged molecular state under the pH of around 8(Tamaki and Frankenberger Jr 1992; Petrick et al. 2000). As an arsenic detoxification pathway, the oxidation process of As(III) to As(V) is very important before the removal of arsenic from water.

Recently, nanostructured manganese oxides and their derivatives have received considerable research interest due to their vast applicabilities in environmental remediation(Luo et al. 2008). 1D nanowires are of great interest due to their excellent physical and chemical properties(Zhang et al. 2008; Zhang et al. 2009), leading to high efficiency in the above mentioned applications(Wang and Li 2002; Yuan et al. 2004; Yuan et al. 2008). In view of their unique physical and chemical properties, substantial research focus has been devoted to the environmental applications of manganese oxides in leveraging their catalytic activity, oxidative ability and adsorption capability(Villalobos et al. 2005; Luo et al. 2008). However, separation or recovery of these nano-dimensional materials in heterogeneous systems still remains a steep challenge. Being an efficient and economical method, magnetic separation would be an ideal alternative since the removal of in-situ nanomaterials via magnetic induction has been reported to be more selective and efficient than centrifugation or free settling method(Yavuz et al. 2006).

The objective of this work is to synthesize a novel kind of multifunctional manganese oxide nanocomposites with magnetic property for the removal of

arsenic species. In this work, K-OMS-2 nanowires were synthesized via a hydrothermal method, which was used as a substrate. Subsequently, magnetic Fe_3O_4 nanoparticles were grafted onto the K-OMS-2 nanowires via a co-precipitation method. The synthesized 1D manganese oxide based magnetic nanocomposites can be used directly to oxidize As(III) and adsorb As(V) in water, and the K-OMS-2 nanowires were also used for comparison. Furthermore, the separation of the materials was investigated by using a simple magnetic separation method, and the magnetic property of the synthesized nanocomposites was also illustrated.

4.2. RESULTS & DISCUSSION

4.2.1. Characterization of materials

Figure 4-1. (A) FESEM image of K-OMS-2 nanowires (B) FESEM image of magnetic K-OMS-2/ Fe_3O_4 nanocomposites.

Figure 4-2. TEM image of the synthesized K-OMS-2/Fe₃O₄ nanocomposites, electron diffraction pattern of Fe₃O₄ (upper left inset) and electron diffraction pattern of K-OMS-2 (lower left inset).

FESEM image of the synthesized K-OMS-2 nanowires is shown in Figure 4-1A. These K-OMS-2 nanowires have diameters of about 40 nm and are over several hundreds of microns in length. Several nanowires readily combine to form larger bundles of nanowires with diameters over 100 nm. Figure 4-1B shows that Fe₃O₄ nanoparticles were evenly grafted on the surfaces of the K-OMS-2 nanowires after a co-precipitation process. In this synthetic strategy, pH is a key factor in controlling the morphology of K-OMS-2 nanowires and the formation of Fe₃O₄ nanoparticles. KOH solution was added dropwise into the initial solution, which contains equal amounts of Fe²⁺ and Fe³⁺. In the process, Fe(OH)₃ was mostly precipitated at acidic conditions of pH 3.7, whereas Fe(OH)₂ was precipitated at pH 9.6(Clark and Bonicamp 1998). K-OMS-2 nanowires can only be added into the solution when the pH of solution is above 9.6 so that the mixed valences (III/IV) of manganese in K-OMS-2 will not be destroyed by Fe²⁺ present in the solution. KOH was continuously added until the pH reached 12, and Fe₃O₄ nanoparticles were gradually deposited onto the K-OMS-2 nanowires.

TEM image of the synthesized K-OMS-2/Fe₃O₄ nanocomposites is shown in Figure 4-2. It illustrates that the diameter of the Fe₃O₄ nanoparticles ranges from 5 nm to 10 nm and the surface of K-OMS-2 nanowires is partially covered by Fe₃O₄ nanoparticles. The synthesized Fe₃O₄ nanoparticles should be superparamagnetic due to their size which is smaller than 34 nm (Berkowitz et al. 1980). The extent of Fe₃O₄ nanoparticles on K-OMS-2 nanowires is controllable by the dosage of Fe₃O₄ and it is interesting to note that a small quantity of Fe₃O₄ grafted on K-OMS-2 is suffice in inducing magnetic separation of the K-OMS-2/Fe₃O₄ nanowires. Moreover, the partially-covered surfaces of K-OMS-2 nanowires ensures availability of surface reactive sites without compromising on application efficiencies. Electron diffraction patterns are shown in the inset of Figure 4-2. The selected-area electron diffraction (SAED) rings (upper left inset of Figure 4-2) can be assigned to superposition of the diffraction patterns of polycrystalline Fe₃O₄. Furthermore, another SAED patterns can be indexed in accordance with the [100] zone axis of a K-OMS-2 crystal (lower left inset of Figure 4-2), indicating that the nanowire is monocrystalline (Yuan et al. 2008).

Figure 4-3. XRD patterns of the synthesized K-OMS-2 nanowires and magnetic K-OMS-2/Fe₃O₄ nanocomposites.

Figure 4-4 Energy-dispersive X-ray spectroscopy graphs of the synthesized K-OMS-2/Fe₃O₄.

The crystal structures of the products were examined using powder XRD. All diffraction peaks of the upper curve in Figure 4-3 can be perfectly indexed to the K-OMS-2 crystalline phase (JCPDS 44-1386). After Fe₃O₄ grafting, the diffraction peaks of K-OMS-2 nanowires showed slight changes while no marked Fe₃O₄ diffraction peaks were observed since there was only a minimal amount of nanosized Fe₃O₄ present in the sample. The BET surface areas of the synthesized Fe₃O₄, K-OMS-2/Fe₃O₄ and K-OMS-2 are 48.9 m²/g, 30.8 m²/g and 18.9 m²/g, respectively. SEM-EDX analysis in Figure 4-4 further confirmed that the external surface of the as-synthesized sample contains Mn, Fe and O.

4.2.2. XPS analysis of the synthesized materials

Figure 4-5. XPS survey spectra (A), high-resolution XPS spectra of the Fe 2p (B) and Mn 2p region (C) taken on the synthesized K-OMS-2/Fe₃O₄.

Figure 4-6. (A) XPS survey spectrum of the K-OMS-2 nanowires; (B) high-resolution XPS spectrum of the Mn 2p taken on the K-OMS-2 nanowires.

XPS was carried out to identify the surface elemental composition of the as-synthesized K-OMS-2/Fe₃O₄ nanocomposites and the survey spectra in Figure 4-5A indicates that the sample contains Mn, Fe, O and K. Figure 4-5B shows the high-resolution XPS spectra of Fe 2p. The respective binding energies of 710 eV and 724 eV indexed to Fe 2p_{3/2} and Fe 2p_{1/2}, are consistent with the reported values of Fe₃O₄(Yamashita and Hayes 2008). It indicates the presence of Fe₃O₄ on the surface of the sample. The high-resolution XPS spectra of Mn 2p is shown in Figure 4-5C and Gaussian curve fitting of Mn 2p_{3/2} was performed to describe the oxidation states of Mn more specifically. The Mn 2p_{3/2} binding energies are centered at 641.7 eV and 643.0 eV, representing Mn³⁺ and Mn⁴⁺ respectively(Zou et al. 2010). In addition, the XPS spectra of K-OMS-2 nanowires are also shown in Figure 4-6. The high-resolution XPS spectra of Mn 2p in K-OMS-2 nanowires

(Figure 4-6B) reveals that the mixed valences of Mn have already formed after the hydrothermal process, and the grafting process did not destroy the oxidation states of Mn in the K-OMS-2. It is important to note that the presence of mixed valences of Mn can endow the synthesized K-OMS-2/Fe₃O₄ nanocomposites with semiconductor catalytic properties(Tian et al. 1997). Similarly, the result of Figure 4-7 indicates that the presence of K-OMS-2 nanowires in the synthesis process did not affect the valences of Fe₃O₄ nanoparticles.

Figure 4-7. (A) XPS survey spectrum of Fe₃O₄ nanoparticles; (B) high-resolution XPS spectrum of the Fe 2p taken on the Fe₃O₄ nanoparticles.

4.2.3. Magnetization of the synthesized materials

Figure 4-8. Magnetization curve of Fe_3O_4 nanoparticles (A), K-OMS-2 nanowires (B), and the synthesized K-OMS-2/ Fe_3O_4 (C), photographs of a vial containing the synthesized K-OMS-2/ Fe_3O_4 nanocomposites in pure water (i) before and (ii) after magnetic separation for 20 s.

The magnetic properties of Fe_3O_4 nanoparticles, K-OMS-2 nanowires, and K-OMS-2/ Fe_3O_4 nanocomposites were measured using a vibrating sample magnetometer (VSM) at room temperature with an applied field of $-10 \text{ KOe} < H < 10 \text{ KOe}$, as shown in Figure 4-8. The results show that the K-OMS-2/ Fe_3O_4 nanocomposites have saturation magnetization of 11.32 emu/g (Figure 4-8C) which is lower than 53.89 emu/g of Fe_3O_4 nanoparticles (Figure 4-8A). The results obtained can be explained by the existence of K-OMS-2 nanowires. To further investigate the sample effectiveness, a magnetic separability test was carried out which the sample exhibited remarkable magnetic separability. The sample took less than 20 seconds to accumulate and attract all the suspended particulates at the

region where a commercial magnet was held (inset of Figure 4-8C). As a result, the sample can be easily recycled after its application in water treatment.

A possible interpretation for the coupling of K-OMS-2 nanowires and Fe_3O_4 nanoparticles was attributed to electrostatic interaction between the two materials. To further examine the stability of the synthesized nanocomposites, a turbidimeter was used to determine the turbidity values of the solution after magnetic separation process. However, we discovered that the adhesions between Fe_3O_4 nanoparticles and K-OMS-2 nanowires remained strong (turbidity ≈ 0) under high pH condition ($\text{pH} > 14$, both surfaces of Fe_3O_4 and K-OMS-2 are negatively charged). This outcome shows that the affinity of the two substances may be ascribed to other reasons. Figure 4-8B reveals that the saturation magnetization of the synthesized K-OMS-2 nanowires is 0.389 emu/g, and is thus rendered as a paramagnetic substance (Suib and Iton 1994). It suggests that the coupling of K-OMS-2 nanowires and Fe_3O_4 nanoparticles may be a result of magnetic dipole-dipole interactions, which is similar to the interaction mechanism of monodisperse Fe_3O_4 nanocrystals (Butter et al. 2003; Yavuz et al. 2006). When the superparamagnetic Fe_3O_4 nanoparticles are dragged by an external magnetic field, each individual Fe_3O_4 nanoparticle will contribute a portion of its traction on moving the K-OMS-2 nanowires. Moreover, the nanostructures of K-OMS-2 and Fe_3O_4 can provide high surface area of contact for the Fe_3O_4 nanoparticles in transferring mechanical forces to the K-OMS-2 nanowires. It is observed from our experimental work that the synthesized K-OMS-2/ Fe_3O_4 nanocomposites are very stable as no Fe_3O_4 nanoparticles collapsed from the K-OMS-2 nanowires after water treatment process.

4.2.4. Oxidation of As(III) on the synthesized materials

Figure 4-9. Variation in concentration of As species during the oxidation process of As(III) with K-OMS-2 nanowires as a function of time. Initial As(III): 0.06 mM; Initial oxidants: 1.8 g/L.

Figure 4-10. Variation in concentration of As species during the oxidation process of As(III) with K-OMS-2/Fe₃O₄ nanocomposites as a function of time. Initial As(III): 0.06 mM; Initial oxidants: 1.8 g/L.

The oxidation reactions of As(III) to As(V) by the synthesized materials were conducted at pH 5 and 20 ± 1 °C. Figure 4-9 and Figure 4-10 show the variation of As species in the presence of K-OMS-2 nanowires and K-OMS-2/Fe₃O₄ nanocomposites, respectively. Results revealed that both the synthesized K-OMS-2 nanowires and K-OMS-2/Fe₃O₄ nanocomposites exhibited effective oxidation capabilities, confirming the stability of the K-OMS-2 nanowires during the coating process. A small quantity of Fe₃O₄ can only occupy limited oxidation reaction sites on the surface of the K-OMS-2 nanowires, which would not significantly weaken the oxidation ability of the material. As shown in Figure 4-10, concentration of As(III) species gradually abated with the lapse of the reaction time and most of the As(III) species was removed after 90 min. Previous study (Zhang et al. 2007) reported that materials with tiny particle size was more favourable for the diffusion of As(III) and thus the synthesized K-OMS-2/Fe₃O₄ nanocomposites possess good oxidation capability due to the nanowire structure of the K-OMS-2. The oxidation of As(III) to As(V) is a detoxification process, which can also lower the mobility of arsenic species and thus facilitate the removal of arsenic in the subsequent treatment (Zhu et al. 2009).

In addition, the adsorption reactions cannot be negligible. Total arsenic concentrations (As(III+V)) decreased with the increment of time which can be explained by the concurrent adsorption effect of the synthesized materials. As shown in the figures, the K-OMS-2/Fe₃O₄ nanocomposites have a higher adsorption capacity as compared to the K-OMS-2 nanowires. These results are shown in Figure 4-10 and Figure 4-9 respectively where the test using K-OMS-2/Fe₃O₄ nanocomposites provide a lower final arsenic concentration (As(III+V)).

4.2.5. Adsorption of As(V) on the synthesized materials

Figure 4-11. Adsorption Kinetics study of As(V) on the synthesized K-OMS-2/Fe₃O₄ nanocomposites. Initial As(V): 0.2 mM; Initial adsorbents: 2.5 g/L.

Figure 4-12. Adsorption Kinetics study of As(V) on the synthesized K-OMS-2 nanowires and. Initial As(V): 0.05 mM; Initial adsorbents: 0.5 g/L.

Adsorption kinetics studies were carried out to evaluate the removal rates of As(V) by the synthesized K-OMS-2/Fe₃O₄ nanocomposites and K-OMS-2 nanowires, as shown in Figure 4-11 and Figure 4-12 respectively. The adsorption process can be explained in two stages(Zhang et al. 2009). Firstly, a rapid adsorption reaction occurs at the beginning. Subsequently, the adsorption process slows down due to the reduction in the available active sites. As shown in Figure 4-11, more than 80% of As(V) was removed by the K-OMS-2/Fe₃O₄ nanocomposites within 4 hours. Then, the adsorption reaction became low and the concentration of As(V) decreased with time increment. Over 93% of the As(V) species was adsorbed onto the K-OMS-2/Fe₃O₄ nanocomposites after 48 h where most of the adsorption sites were occupied by As(V). This phenomenon indicated that the adsorption equilibrium with an equilibrium time of 48 h was achieved. Thus, this reaction time will be applied to the subsequent experiments. Similarly, the equilibrium time for the adsorption of As(V) onto the K-OMS-2 can also be determined (24 h) according to the Figure 4-12.

Figure 4-13. Adsorption isotherms of As(V) on the synthesized K-OMS-2/Fe₃O₄ nanocomposites. Initial adsorbents: 0.5 g/L.

Figure 4-14. Adsorption isotherms of As(V) on the synthesized K-OMS-2 nanowires. Initial adsorbents: 0.5 g/L.

The adsorption capacity of the synthesized K-OMS-2/Fe₃O₄ nanocomposites for As(V) was investigated using the isotherms presented in Figure 4-13. The synthesized K-OMS-2 nanowires were also used for comparison, as shown in Figure 4-14. The adsorption processes were described by using the Langmuir and Freundlich equations, respectively expressed as below:

Langmuir isotherm equation:

$$q_e = \frac{q_{\max} k_{eq} C_e}{1 + k_{eq} C_e} \quad [6-1]$$

Where q_e is the amount of As(V) adsorbed by the adsorbent (mg/g); k_{eq} is equilibrium constant of adsorption; $q_{\max}$ is maximum adsorption capacity (mg/g); C_e is the As(V) concentration at equilibrium.

Freundlich isotherm equation:

$$q_e = kC_e^{1/n} \quad [6-2]$$

Where k and $1/n$ are constants for a given adsorbate and adsorbent at a particular temperature.

The Langmuir model assumes the adsorbent surface to be homogenous and the sorption energies for each sorption site to be equivalent; while the Freundlich model gives an empirical expression which describes the data for heterogeneous adsorbents (Elass et al. 2010). The constants from Langmuir and Freundlich isotherms were calculated and shown in Table 4-1. According to the correlation coefficients (R^2), it was found that Langmuir model was more suitable for describing the adsorption behaviour of As(V) on the synthesized adsorbents. As shown in Table 4-1, the maximum adsorption capacity of K-OMS-2/Fe₃O₄ nanocomposites (20.83 mg/g) is higher than that of K-OMS-2 nanowires (9.43 mg/g) due to the presence of Fe₃O₄ nanoparticles. Although there is only a small dosage of Fe₃O₄, Fe₃O₄ nanoparticles possess outstanding adsorption capability for the removal of arsenic species according to the previous report (Yavuz et al. 2006). Thus, the grafting of Fe₃O₄ nanoparticles not only endowed the material with magnetic property, but also enhanced the adsorption capability of the material.

Table 4-1. Langmuir and Freundlich parameters for As(V) adsorption on K-OMS-2 nanowires and K-OMS-2/Fe₃O₄ nanocomposites.

	Langmuir			Freundlich		
	$q_{\max}(\text{mg/g})$	k_{eq}	R^2	k	n	R^2
K-OMS-2	9.43	0.126	0.959	2.62	3.73	0.937
K-OMS-2/Fe₃O₄	20.83	0.042	0.967	1.87	2.04	0.932

4.3. CONCLUSIONS

In this work, K-OMS-2/Fe₃O₄ nanocomposites were successfully synthesized and applied for water treatment. The material was synthesized via a combination of hydrothermal and chemical co-precipitation methods. The synthesized K-OMS-2/Fe₃O₄ nanocomposite is a supermagnetic material, which can be easily accumulated under a low magnetic field and thus facilitate the separation of the nanocomposites from aqueous phase. This work heralds a pathway towards the low-field magnetic separation of weak magnetic substances.

In addition, the synthesized nanocomposites possessed good oxidation and adsorption properties. Experimental results indicated that 0.06 mM As(III) can be effectively oxidized to As(V) in a short time by the synthesized materials. Based on the Langmuir model, the maximum adsorption capacity of K-OMS-2/Fe₃O₄ nanocomposites for As(V) is 20.83 mg/g, which is higher than that of the K-OMS-2 nanowires. Thus, the synthesized K-OMS-2 is a multifunctional material, which possessed oxidation, adsorption and magnetic properties.

Chapter 5 1D MnO₂ NANOWIRES FOR BISPHENOL A REMOVAL

5.1. INTRODUCTION

Based on the study in chapter 4, K-OMS-2 nanowires have been proven to be very effective in the As(III) oxidation process. However, some organic pollutants such as phenols, dyes, natural organic matters, cannot be efficiently degraded by the synthesized K-OMS-2 nanowires due to the presence of low state Mn in the material. To further enhance the oxidation ability of the material, it is necessary to improve the oxidation states of Mn in the material. MnO₂ have been considered as a promising material for the removal of organic contaminants owing to its high reactivity, environmental compatibility and cost effectiveness. It has been demonstrated that a wide range of anthropogenic organic pollutants including phenols(Stone 1987; Lin et al. 2009), anilines(Klausen et al. 1997; Li et al. 2003) and other antibiotics and hormones(Xu et al. 2008; Chen et al. 2010) are prone to effective degradation by MnO₂ via a series of radical reactions(Zhang and Huang 2003; Zhang and Huang 2005; Zhang et al. 2008).

Nanostructured MnO₂ possesses many advantages due to their superior properties relative to conventional bulk materials(Yuan et al. 2008). As we discussed in chapter 2, 1D nanostructured materials such as nanowires, nanofibers, nanotubes and nanorods have good performance in environmental application in catalysis, oxidation and adsorption(Dong et al. 2009; Zhang et al. 2009). However, 1D nanostructured materials are susceptible to breakage during operation process such as mixing, and their brittleness is a significant drawback hindering the practical application. For example, nanowires may break into pieces with shorter length, leading to membrane pore blockage in the separation process. To achieve high recovery and reuse efficiency, 1D nanostructured materials with good toughness are more attractive.

Bisphenol A (BPA) can be used as a model organic pollutant. As a pervasive chemical intermediate primarily from the production of polycarbonate plastics and epoxy resin, it has become a global concern to the environment due to its estrogenic effects(Kang et al. 2007). There is convincing evidence that BPA can cause severe adverse effects on the genetic systems and brain functions of human being, especially on fetuses, infants and young children(Kang et al. 2006; Braun and Hauser 2011; Wolstenholme et al. 2011). In the European Union and Canada, the application of BPA is banned for the fabrication of baby bottles. However, BPA is still widely produced and used in containers, metal products coating and water supply lines. In addition, BPA also exists in effluents of industrial sewage treatment plants, which may pose substantial exposure risk to human beings(Lee and Peart 2000; Welshons et al. 2006; Calafat et al. 2008). Over the past few years, considerable effort has been devoted to the development of effective treatment technologies for the removal of BPA, such as Fenton's reagent, ultrasonic cavitation(Torres et al. 2007), photocatalysis(Tsai et al. 2009), and ozonation(Deborde et al. 2008). However, each of these techniques suffers from certain drawbacks, such as production of $\text{Fe}(\text{OH})_3$ precipitation, energy consumption and so on.

In this work, 1D MnO_2 nanowires were synthesized via a facile one-step hydrothermal method, and a novel hybrid process combining MnO_2 nanowires oxidation and microfiltration was adopted to remove BPA. Careful characterizations were performed to elucidate the physical properties influencing the reactivity. Laboratory-scale batch experiments were conducted to investigate the degradation of BPA under different conditions such as MnO_2 dosage, pH values, and various aqueous matrix species (e.g. humic acid (HA), CaCl_2 , MgCl_2 , MnCl_2). Moreover, feasibility study on the separation of MnO_2 nanowires was also evaluated via a cross-flow membrane filtration process.

5.2. RESULTS & DISCUSSION

5.2.1. Characterization of Materials

Figure 5-1. (A) FESEM image of the synthesized MnO₂ nanowires; (B) TEM image of the synthesized MnO₂ nanowires.

Figure 5-2. XRD pattern of the synthesized MnO₂ nanowires.

FESEM and TEM images of the as-prepared MnO₂ nanowires are shown in Figure 5-1. From Figure 5-1A, it can be found that the synthesized nanowires are several

microns in length. The diameters of the nanowires are ranging from 30-60 nm as shown in Figure 5-1B. As shown in Figure 5-2, the crystal structure of the product was examined by XRD analysis. All diffraction peaks of the curve in Figure 5-2 can be perfectly indexed to the β -MnO₂ crystalline phase (JCPDS 24-0735). BET surface area of the β -MnO₂ nanowires was recorded to be 68.85 m²/g, which is much higher as compared to the bulk MnO₂ with BET surface area of 32.0 m²/g(Manning et al. 2002). The as-prepared high surface area β -MnO₂ nanowires could facilitate contaminant removal in water since the oxidation process is primarily driven by electron transfer reactions at the surface of oxides(Zhang and Huang 2005; Zhang et al. 2008).

5.2.2. Efficacy of BPA removal by the synthesized MnO₂ nanowires

In the presence of the synthesized MnO₂ nanowires, concentration of BPA gradually abated with the lapse of the reaction time and BPA was completely removed after 90 min, as shown in Figure 5-3. On the contrary, in the absence of MnO₂ nanowires, no BPA degradation was observed under all conditions throughout the experimental duration. It suggests that the synthesized MnO₂ nanowires play a crucial role in the process of BPA removal. The oxidation mechanism has been investigated by Lin et al. on bulk MnO₂ powder(Lin et al. 2009). Their data indicated that BPA radicals were generated via electron transfers to MnO₂. These BPA radicals triggered a suite of reactions of radical coupling, fragmentation, substitution, and elimination, which eventually resulted in the degradation of BPA. This mechanism is plausible on the synthesized MnO₂ nanowires as well. As shown in Figure 5-3, several peaks appear at short retention times and can be assigned to the production of intermediates and products, of which the majority were reported as small molecular weight compounds(Lin et al. 2009).

Figure 5-3. HPLC chromatograms of BPA as a function of oxidation time.

Figure 5-4 shows that Mn^{2+} was formed and its concentration increased during BPA degradation on the solid MnO_2 nanowires. This transformation may be due to the partially reductive dissolution of the solid MnO_2 nanowires. The formation of Mn^{2+} indicates that electron transfer between the manganese oxides and BPA took place and further confirms the above oxidation mechanism. Nevertheless, some of the released Mn^{2+} could be adsorbed onto the surface of MnO_2 nanowires, which may occupy the adsorption and reaction sites, thus inhibiting BPA degradation (Morgan and Stumm 1964). Some other reports have also observed similar inhibitory effect on pollutant removal from the reductive dissolution of manganese dioxides and increased leaching of Mn^{2+} ions into the system. Liu and co-workers (Liu et al. 2008) reported that mineralization of dissolved organic carbon (DOC) was inhibited in heterogeneous systems, which can be ascribed to the adverse effect of high dissolved Mn^{2+} concentration that can capture oxidative species.

Figure 5-4. The degradation of 10 mg/L BPA at pH 5 and the released Mn²⁺ concentration in the solution. Initial MnO₂: 1.74 g/L.

5.2.3. Effect of the synthesized MnO₂ dosage

The effect of varying the dosage of MnO₂ nanowires was studied in a series of experiments as shown in Figure 5-5. Generally, BPA removal rates increased with the increased dosage of MnO₂ nanowires. For example, with 0.87 g/L, 1.74 g/L, and 3.48 g/L dosage of MnO₂ nanowires, BPA removal rates at 20 min were 64.0%, 81.9%, and 99.5%, respectively. This phenomenon is related with the increase in the number of the reaction sites on the surface of oxides. The oxidation process of pollutant mainly proceeds on the surface of the material, and greater amount of material can provide larger surface area and thus more reaction sites. Therefore, more BPA molecules are able to contact with the increased reaction sites, resulting in the improvement of oxidation efficiency. Moreover, higher loading of MnO₂ nanowires will maintain the relative proportions of different valence states of manganese ions within the system, which can enhance the oxidizing power of manganese oxide (Stone 1987).

Figure 5-5. Effect of MnO₂ nanowires dosage on the removal of 10 mg/L BPA at pH 5 and 20 ± 1 °C.

5.2.4. Effect of pH

The influence of pH on the interaction of BPA molecules and the surface of the MnO₂ nanowires was investigated in a series of experiments with pH values ranging from 3 to 11, and the initial concentrations of BPA and MnO₂ nanowires were 10 mg/L and 1.74 g/L respectively (Figure 5-6). Previous studies(Zhang and Huang 2005; Zhang et al. 2007; Zhang et al. 2008; Allard et al. 2009) found that oxidation process of pollutants using MnO₂ was evidently dependent on pH. Our experimental results also showed that BPA removal rates varied significantly under different pH conditions (pH 3 > pH 5 > pH 11 > pH 9 > pH 7). These results indicate that both acidic and basic conditions have promoted BPA degradation to certain extents, whereas the neutral pH condition led to a diminished efficiency. The increase in BPA removal rate at decreased pH can be partly explained by the increase in redox potential of MnO₂ at acidic conditions(stumm and Morgan 1996). In addition, the decrease of pH can result in an increase of total reactive surface sites, which could also enhance BPA oxidation process(Zhang and Huang 2005).

Moreover, H^+ ions participate in the oxidation reaction (eq 5-1), which will promote the forward reaction.

[5-1]

Interestingly, BPA removal rates are also noted to increase under basic conditions, and this could be attributed to the change of BPA constituents in the solution. According to an ideal solution model, the respective dissociation constants of the first and second proton of BPA are $pK_1 = 9.59$ and $pK_2 = 10.2$ (Kosky et al. 1991). Figure 5-7 shows the distribution of BPA at different pH values (Kosky et al. 1991; Lin et al. 2009). It reveals that the total concentration of mono- and di-anions BPA increase with the alkalinity of solution, and these unprotonated species become the main species of BPA when pH is around 10. Although electrostatic forces may inhibit interactions between the synthesized MnO_2 and BPA under basic conditions, the unprotonated species of BPA under higher pH condition are more active than the protonated ones, thus enhancing the oxidation process (Stone 1987). According to the experimental results, we postulate that the species of BPA is the predominant factor for the oxidation rate of BPA. Hence, the removal of BPA can be facilitated under basic condition.

Figure 5-6. Degradation of BPA by the synthesized MnO_2 nanowires treatment under different pH values. Initial MnO_2 : 1.74 g/L; Initial BPA: 10 mg/L.

Figure 5-7. Distribution of BPA at different pH values.

5.2.5. Effect of HA

Humic substances (HS), a major component of natural organic matters (NOMs), are present throughout the ecosystem and most often in surface and ground water (Stevenson 1994). As a major organic constitute of HS, HA may affect the oxidative ability of manganese oxides under different conditions (Stone and Morgan 1984; Xu et al. 2008). It is widely approved that HA exhibits inhibitory effect on the removal of pollutants by MnO_2 due to its direct competition for reactive sites, as well as reductive dissolution of MnO_2 by HA (Stone and Morgan 1984; Zhang and Huang 2003). However, Xu and co-workers recently found that the presence of HA greatly enhanced oxidative removal of estrogens by MnO_2 via formation of Mn(II) -HA complexation (Xu et al. 2008). In addition, Zhang and co-workers reported that HA has little effect on the removal of arsenic by manganese oxide composites (Zhang et al. 2007). Hence, it can be noted that HA exhibits differing effects on oxidation of different pollutants over MnO_2 (Zhang and Huang 2003; Xu

et al. 2008). To evaluate influence of HA on the removal of BPA by the synthesized MnO_2 nanowires, a series of experiments were carried out at pH 5 and $20 \pm 1^\circ\text{C}$ by varying the concentration of HA, as shown in Figure 5-8. The initial concentrations of BPA and MnO_2 nanowires were kept at 10 mg/L and 1.74 g/L respectively. In the oxidation process, it was observed that HA induced an inhibitory effect on removal of BPA and the removal rate decreased with an increase in HA concentration. This phenomenon can be attributed to two major factors. Firstly, HA can be efficiently adsorbed by manganese oxide (Bernard et al. 1997), which would compete with BPA molecules in terms of surface adsorption on the MnO_2 nanowires. Secondly, the existence of HA can cause the reductive dissolution of the MnO_2 nanowires, leading to the leaching of Mn^{2+} ions into the aqueous matrix (Godtfredsen and Stone 1994; Klausen et al. 1997). Mn^{2+} ions can be adsorbed onto the surface of the MnO_2 nanowires, and result in the blockage of reactive Mn(IV) surface sites and consequently inhibit the BPA degradation (Klausen et al. 1997).

Figure 5-8. Degradation of BPA by the synthesized MnO_2 nanowires treatment under different concentrations of HA. Initial MnO_2 : 1.74 g/L; Initial BPA: 10 mg/L.

5.2.6. Effect of metal ions

Three kinds of metal ions with different concentrations were employed to assess the effects of co-existing cations on BPA removal at pH 5 and 20 ± 1 °C. Figure 5-9 shows that addition of metal ions considerably decreased degradation rate of BPA over the synthesized MnO_2 nanowires and the inhibitory effect increased with an increase in metal ion concentration. It can be ascribed to the competitive binding effect of metal ions, which occupy the reactive surface sites of the material (Barrett and McBride 2005). As shown in Figure 5-10, the isoelectric point of the synthesized MnO_2 nanowires is located at around pH 4.5, which suggests that they are negatively charged under pH 5 and would hence promote metal ion binding due to electrostatic charge attraction between the material and cations. Henceforth, the reduction of reactive sites would also result in an abatement of BPA removal rate. Furthermore, it should be noted that the inhibitory effects of metal ions vary with different types of cationic species. As the most frequent divalent cations in drinking water, Ca^{2+} and Mg^{2+} ions did not show a pronounced inhibition of BPA removal from our experimental work. Moreover, Liu et al (Liu et al. 2009) found that Ca^{2+} can enhance the adsorption of pollutants on MnO_2 and promote aggregation of MnO_2 in the aqueous phase, which accentuates the potential application of the MnO_2 nanowires in treatment of drinking water. It is important to highlight that different metal ions exhibit different effects on the surface characteristics of the synthesized MnO_2 nanowires. Figure 5-9 reveals that Mn^{2+} ions resulted in a significant suppression of BPA oxidation even at low concentrations, which can be attributed to the higher adsorption capacity of Mn^{2+} on MnO_2 , thus leading to severe reduction of surface sites by the Mn^{2+} ions (Liu et al. 2008). Although the existence of metal ions can increase ionic strength which enhances adsorption of pollutant molecules on MnO_2 , its effect was inconsequential as the competition for adsorption sites between metal ions and BPA molecules, induced stronger detrimental effects on BPA removal. Besides that, based on the results shown in Figure 5-9, these reactions were also considered as the predominant governing factor (Du et al. 1997; Chang et al. 2009).

Figure 5-9. Degradation of BPA by the synthesized MnO₂ nanowires treatment under different metal ions. Initial MnO₂: 1.74 g/L; Initial BPA: 10 mg/L.

Figure 5-10. Zeta potential of the synthesized MnO₂ nanowires.

5.2.7. Membrane filtration for recycling of the MnO₂ nanowires

Figure 5-11. Membrane fluxes over 10 mg/L BPA solution without the MnO₂ nanowires, the solution after treatment by 1.74 g/L MnO₂ nanowires for 90 mins and 1.74 g/L MnO₂ nanowires suspension without BPA.

After the oxidation process, the MnO₂ nanowires suspension was filtered by a microfiltration membrane in a crossflow setup. The turbidity of effluent after filtration was nearly zero, indicating that the used MnO₂ nanowires could be easily and entirely separated via the membrane filtration process. This may be attributed to the fact that the used MnO₂ nanowires were unbroken and remained in the size of several microns, which is larger than the membrane pore size of 0.2 μ m. In order to quantify membrane fouling caused by the suspension of MnO₂ nanowires, changes in membrane flux during the crossflow microfiltration process were recorded and shown in Figure 5-11. BPA solution without addition of MnO₂ nanowires and MnO₂ nanowires suspension without BPA were also filtered by the crossflow filtration process for flux comparison. All fluxes of the three solutions were markedly reduced during membrane filtration, indicating that membrane fouling inevitably occurred during the filtration process. To further identify the membrane fouling mechanisms involved, the respective resistances were quantified and listed

in Table 5-1. R_m is dependent on the physical and chemical characteristics of the membrane, and it can be assumed to be constant across the entire filtration process. Two resistances are mainly accountable for the membrane fouling, namely, cake layer resistance (R_c), and pore blocking resistance (R_p). For the solution without dosage of MnO_2 nanowires, BPA in the solution can engender formation of cake layer and give rise to pore blocking of the membrane resulting in the decrease of flux under a constant pressure. When MnO_2 nanowires are added into the solution, R_c was noted to increase significantly as compared to the former, resulting in the increase of total resistance (R_t) and decline in membrane flux. According to analysis of the data in Table 5-1, we could postulate that it is less probable for nanowires to enter into the membrane pores to cause pore blocking, so the cake layer formed by nanowires became the prevailing membrane fouling mechanism. It was further confirmed by direct FESEM observation on the cross-section of filtered membrane. As shown in Figure 4-12, the used MnO_2 nanowires were successfully rejected on the membrane, and retained the original 1D structure with lengths of several microns after reaction, exhibiting their excellent mechanical stability. There are no MnO_2 nanowires found in the cross-sectional FESEM image after filtration process. This result indicates that the nanowires have little chance of contributing to pore blocking resistance. Additionally, it is noteworthy that the magnitude of R_p has declined from $0.45 \times 10^{11} \text{ m}^{-1}$ (R_{p1}) to $0.22 \times 10^{11} \text{ m}^{-1}$ (R_{p2}) after treatment by the MnO_2 nanowires, indicating that the oxidation process was able to mitigate pore blocking of the membrane. We believe that this phenomenon is due to production of smaller molecules during BPA degradation as discussed in section 5.2.2. Moreover, during the filtration of the suspended MnO_2 nanowires suspension with the absence of BPA, both R_p and R_c decreased as compared to the BPA solution after reacting with MnO_2 nanowires. This can be attributed to the absence of oxidative intermediates in the process, and MnO_2 is the only factor accountable for membrane fouling. The reduced R_p indicates that BPA, oxidative intermediates and Mn^{2+} could be adsorbed on the membrane. It is worthy to note that the value of R_{c3} ($23.84 \times 10^{11} \text{ m}^{-1}$) is very close to R_{c2} of the BPA solution after treatment by MnO_2 nanowires ($24.78 \times 10^{11} \text{ m}^{-1}$), therefore corroborates our previous two statements: 1) the 1D structure of MnO_2 nanowires have little chance to contribute to pore

blocking resistance and, 2) the nanowires possess good mechanical strength in retaining their original 1D structure after reaction. The findings suggest that membrane filtration can be employed in an integrated water treatment system as a post-separation procedure after the oxidation reaction, to recover the MnO_2 nanowires from the treated effluent, so that they can be reused for multiple cycles. It is also noteworthy that since predominant cake layer fouling is reversible and can be regenerated conveniently by a low-energy intensive forward flushing procedure, effectiveness and lifespan of the microfiltration membrane will also be enhanced.

Table 5-1. Summary of resistances for the membrane filtration

Resistance	Values ($\times 10^{11} \text{ m}^{-1}$)	Percentage (%)
(1) 10 mg/L BPA solution without $\beta\text{-MnO}_2$ nanowires		
R_{m1}	5	48.3
R_{p1}	0.45	4.3
R_{c1}	4.89	47.3
R_{t1}	10.34	100
(2) 10 mg/L BPA solution after treated by 1.74 g/L $\beta\text{-MnO}_2$ nanowires		
R_{m2}	5	16.7
R_{p2}	0.22	0.7
R_{c2}	24.78	82.6
R_{t2}	30	100
(3) 1.74 g/L $\beta\text{-MnO}_2$ nanowires solution without BPA		
R_{m3}	5	17.3
R_{p3}	0.08	0.3
R_{c3}	23.84	82.4

Figure 5-12. Upper-surface of the membrane (A) before and (B) after filtration of the MnO₂ nanowires solution; Cross-section of the membrane (C) before and (D) after filtration of the MnO₂ nanowires solution.

5.3. CONCLUSION

1D MnO₂ nanowires synthesized via a facile hydrothermal method were characterized by XRD, TEM, FESEM, and N₂ sorption. Furthermore, an oxidation process of BPA using the synthesized material was investigated under different conditions. It was demonstrated that the synthesized MnO₂ nanowires can degrade BPA effectively. Investigation on operation parameters indicated that oxidation of BPA using the synthesized MnO₂ nanowires was evidently dependent on pH, while HA and coexisting metal ions such as Ca²⁺, Mg²⁺, and Mn²⁺ induced suppressive

effects. After oxidation, a crossflow microfiltration process was conducted to recover the MnO_2 nanowires from treated water. Results indicated that the synthesized MnO_2 nanowires have good mechanical stability and can be effectively recovered for reuse by a conventional crossflow microfiltration process with minimal membrane pore blocking, owing to its 1D nanostructure in the form of nanowires and the efficient degradation of BPA molecules. Although the MnO_2 nanowires tend to form a thin cake layer on the membrane surface, it is widely accepted that cake layer fouling is reversible and more easily rectified than pore blocking. Hence, we believe that the synthesized MnO_2 nanowires, when combined with membrane filtration, can provide a promising pathway for BPA degradation in water treatment process.

Chapter 6 3D MICRO-/NANO-STRUCTURED MnO₂ FOR ARSENIC DETOXIFICATION AND REMOVAL

6.1. INTRODUCTION

As building blocks, 1D manganese oxide nanowires can also be used to assemble active and integrated multidimensional nanosystems, such as 2D and 3D nanomaterials. Here we present a facile and economical one-step strategy to synthesize 3D micro-/nano-structured MnO₂ spheres at room temperature. In comparison to other nanostructures, 3D nanostructures have their outstanding advantages in environmental applications. On the one hand, the specific surface areas of 3D materials significantly increased due to their nanostructures, and thus enhance their adsorption and oxidation abilities on the removal of pollutants. On the other hand, 3D nanomaterials can be easily separated from liquid phase as compared to other nanosized materials by virtue of their microstructures(Pan et al. 2008).

It is important to keep nanomaterials out of storage and distribution systems as releasing them to the environment could pose considerable environmental consequences. With the development of commercial membrane technology, membrane filtration can be employed for the separation of nanomaterials(Wiesner 2006); nevertheless, fouling of the membranes poses a new set of challenge to this engineering process(Lee et al. 2001; Fu et al. 2006). To address this issue, different nanostructures (such as 1D structures and 3D structures) have been fabricated to relieve the membrane fouling problem(Pan et al. 2008; Zhang et al. 2009).

In this study, the synthesized material is suitable to be applied for water treatment, since the material can be easily produced at a large scale. Furthermore, the synthesized material exhibited good oxidation, adsorption and separation abilities in the removal process of As(III) and As(V). The objectives of this study include (1)

the synthesis and characterization of 3D micro-/nano-structured MnO_2 spheres; (2) the evaluation of the oxidation and adsorption properties of the material on the removal of arsenic; (3) the spectroscopic studies of the arsenic removal mechanism on the surface of the synthesized material; and (4) the mechanism study on the separation of MnO_2 spheres using a microfiltration process.

6.2. RESULTS AND DISCUSSION

6.2.1. Characterization of 3D micro-/nano-structured MnO_2 spheres

Figure 6-1. XRD pattern of the synthesized MnO_2 .

Figure 6-2. (A)-(C) FESEM images of the synthesized MnO_2 at different magnifications; (D)-(F) TEM images of the synthesized MnO_2 at different magnifications.

The crystal structure of the product was examined using XRD, as shown in Figure 6-1. All diffraction peaks can be indexed to the $\alpha\text{-MnO}_2$ crystalline phase (JCPDS 44-1386) with lattice parameters $a = 9.78 \text{ \AA}$ and $c = 2.86 \text{ \AA}$ (Li et al. 2005). The morphology of the synthesized material was characterized using FESEM and TEM. Some representative images in Figure 6-2 indicate that the hierarchically assembled MnO_2 sphere is a multi-scale organized nanoarchitecture, which is a combination of micro- and nano-structure. As shown in Figure 6-2B, the diameters of the MnO_2 spheres range from $1 \mu\text{m}$ to $3 \mu\text{m}$, indicating the microstructure of the synthesized material. The high-resolution FESEM image in Figure 6-2C shows that the prepared MnO_2 sphere possesses dense nanostructures on its surface, constructing a hierarchical dandelion-like structure. Although it is difficult to identify an individual nanostructure from the FESEM image, it can be found that the synthesized MnO_2 nanostructures were uniformly aligned on the surface of the spheres. As shown in Figure 6-2E, TEM image identified the nanostructures on the surface of the MnO_2 sphere, and they have diameter of about 5 nm with a length of more than 100 nm . Furthermore, the high resolution TEM image in Figure 6-2F shows that the nanowires are crystalline with clear lattice fringes. The width of 0.24 nm from the inter-plane distance of individual nanowire corresponds to (211) planes of $\alpha\text{-MnO}_2$, which conforms with to the XRD result.

Figure 6-3 N₂ adsorption/desorption isotherm curve of the synthesized MnO₂, and inset is the pore size distribution of the synthesized MnO₂.

The N₂ adsorption/desorption isotherm is shown in Figure 6-3. This result identified BET surface area of the synthesized MnO₂ spheres to be 162.54 m²/g, which is much higher than the bulk MnO₂ with a BET surface area of 32.0 m²/g (Manning et al. 2002). Moreover, the porosity of the synthesized MnO₂ spheres are well justified based on the inset of Figure 6-3, where pore size distribution curve indicates a sharp peak centred at the pore diameter of 65 nm, providing evidence that the sample contains a majority of macropores (pore size > 50 nm). The high specific surface area and porous structure of the synthesized MnO₂ spheres would enhance the oxidation and adsorption capacities of the synthesized material.

6.2.2. Oxidation of As(III) by the prepared MnO₂ spheres

Figure 6-4. Variation in concentration of As species during the oxidation process of 0.1 mM As(III) with 0.25 g/L MnO₂ as a function of time.

Figure 6-5. Linear regression analysis of normalized As(III) uptake by the synthesized MnO₂.

The oxidation of As(III) to As(V) by the synthesized MnO₂ spheres was conducted at pH 5, and the variation of As species in the reaction system is shown in Figure 6-4. In the presence of MnO₂ spheres, the concentration of As(III) gradually abated

over time, while the concentration of As(V) increased continuously throughout the reaction due to the oxidation of As(III). It can be seen that there was a rapid oxidation of As(III) and formation of As(V) in the initial stage and no As(III) can be detected after 60 min. These results validate the fact that the synthesized MnO₂ is a powerful oxidant for reduced arsenic species. The rapid oxidation performance can be attributed to the high surface area of the nanostructured MnO₂ since the oxidation process is largely driven by surface reactions on the oxides. It should be noted that the final concentration of As(III+V) also decreased in the oxidation process due to the adsorption effect of the MnO₂. These obtained results indicated that the synthesized MnO₂ spheres possess with both oxidation and adsorption abilities. According to previous studies(Zhang et al. 2007; Zhu et al. 2009), oxidation reaction is necessary to lower the mobility of As species and thus achieve a higher removal of As species in the adsorption reaction. Furthermore, the oxidation of As(III) on the surface of the synthesized MnO₂ can be described in terms of the pseudo-first order reaction as follows(Manning et al. 2002):

$$-\ln \frac{C}{C_0} = kt \quad [6-1]$$

where C is the As(III) concentration at time t , C_0 is the initial As(III) concentration and t is the reaction time. As shown in Figure 6-5, the rate of As(III) oxidation was first-order dependent on the concentration of As(III) in the initial reaction (0-45 min) since oxidation of As(III) on the surface of the synthesized MnO₂ was the major reaction during the initial period. However, adsorption reactions became predominant with increasing time, resulting in a poorly fitted regression line in the whole reaction time.

6.2.3. Adsorption of As(V) on the prepared MnO₂ spheres

Kinetic studies were conducted to investigate the rate of As(V) removal from solution with time. The initial concentrations of As(V) and MnO₂ were 0.2 mM and

2.5 g/L respectively, and the pH value was adjusted to 5 by HCl and NaOH solutions. As shown in Figure 6-6, there was an initial high removal rate resulting in more than 90% of As(V) removed by the MnO₂ spheres within a period of approximately 4 hours. Then, the rate of As(V) retention was followed by gradual sorption reactions, which clearly described the steady decrease of As(V) concentrations with reaction time. Our results showed that the As(V) adsorption equilibrium was slowly achieved at pH 5 (e.g. maximum adsorption occurred in more than 24 h), which may be attributed to the formation of bidentate nuclear As(V)-MnO₂ complexes in the adsorption process(Manning et al. 2002). Previous EXAFS results(Fendorf et al. 1997; Raven et al. 1998) indicate that the formation of bidentate complexes is slower than the predominantly monodentate reactions of As(V) on adsorbents such as Fe-oxides and clay minerals. Based on the result of adsorption kinetics, equilibrium time of 48 h was used in the other batch adsorption reactions of As(V).

Figure 6-6. Adsorption kinetics study of As(V) on the prepared MnO₂ spheres. Initial As(V): 0.2 mM; initial MnO₂ microspheres: 2.5 g/L.

Figure 6-7. Adsorption isotherms of As(V) on the prepared MnO₂ spheres. Initial As(V): 0.2 mM; Initial MnO₂ microspheres: 2.5 g/L.

The adsorption capacity of the synthesized MnO₂ spheres for As(V) was evaluated using the isotherms presented in Figure 6-7. The sorption of As(V) from aqueous solution onto the MnO₂ surface is found to be increased from 2.79 mg/g to 14.48 mg/g with the increment of As(V) concentrations. This increment can be attributed to the increase in the driving force of the concentration gradient(Naeem et al. 2007). The Langmuir and Freundlich equations were employed to describe the adsorption process, as shown in Figure 6-7. The important values of both the Langmuir and Freundlich parameters obtained from the linearized versions of the two isotherms are listed under Table 6-1. The values of both the correlation coefficients indicate the data are best fitted to Langmuir equation, and the isotherms can be characterized by a steep initial curve followed by a plateau. The computed maximum adsorption capacity is 14.5 mg/g, which is higher than the previous report of common MnO₂ (7.5 mg/g)(Lenoble et al. 2004). In addition, the adsorption capacity of the synthesized MnO₂ microspheres can be further increased when As(III) exists in the solution. This is because the oxidation of As(III) by MnO₂ may cause surface alteration of MnO₂, which can create fresh reaction sites for As(V) on the MnO₂ surfaces(Manning et al. 2002).

Table 6-1. Langmuir and Freundlich parameters for As(V) adsorption on 2.5 g/L MnO₂ microspheres

	$q_{\max}$ (mg/g)	n	k	R ²
Langmuir	14.5	-	0.036	0.966
Freundlich	-	3.66	2.69	0.711

6.2.4. Effect of pH and ionic strength on As(V) adsorption

Figure 6-8. Effects of ionic strength on the removal of As(V) under different pH conditions.

The influence of pH and ionic strength on the removal of As(V) was investigated in a series of experiments with pH values ranging from 2 to 10, and the initial concentrations of As(V) and MnO₂ were 0.2 mM and 2.5 g/L respectively (Figure 6-8). Previous studies found that adsorption processes of pollutants using MnO₂ was dependent on pH (Thanabalasingam and Pickering 1985; Power et al. 2005; Camacho et al. 2011). In this study, the adsorption capacity of MnO₂ decreased

with the increase of pH. These changes could be attributed to the electrostatic forces between the adsorbent and As(V) species. According to an ideal solution model, the equilibrium constants for the dissociation of arsenic are $pK_1 = 2.24$, $pK_2 = 6.94$ and $pK_3 = 11.5$ (Antelo et al. 2005). The dominant species of As(V) is $H_2AsO_4^-$ in the pH range from 2.24 to 6.94; while $HAsO_4^{2-}$ and AsO_4^{3-} would respectively become the dominant species in solution with increasing pH values. Although the negatively charged As(V) species are dominant in acidic and basic environments, lower pH will facilitate the protonation of MnO_2 and thus enhance the electrostatic attraction between positive surface sites on MnO_2 and $H_2AsO_4^-$ anions. Conversely, the surface of MnO_2 will be negatively charged under higher pH, which results in the repulsion effect between MnO_2 and As(V) species and thus inhibit the adsorption process. Moreover, ligand exchange phenomenon may also partly explain the higher removal rate of As(V) under higher pH values (Gupta et al. 2009). Previous reports demonstrated that As(V) can exist as an inner-sphere surface complex as follows (Arai et al. 2001; Gupta et al. 2009):

There would be more dinegative As(V) species and hydroxyl ions in basic solution, and the competition between them for sorption sites would eventually lower the As(V) removal rate.

With regards to the effects of ionic strength, it was apparent that an increase in the electrolyte concentration from 0.001 mM to 0.1 mM increased the adsorption of As(V) on the synthesized MnO_2 spheres (Figure 6-8). Previous studies on surface complexation mechanism revealed that the effects of ionic strength can be determined by the type of complexes (outer-sphere complexes and inner-sphere complexes) formed by the adsorbed ions with the adsorbent surface (Antelo et al. 2005). Ions that form outer-sphere complexes compete for adsorption sites with ions of the supporting electrolyte, and thus decrease the adsorption of the target ions with increasing ionic strength. On the other hand, ions that form inner-sphere complexes can coordinate to surface groups directly with less competition between

the electrolyte ions. This phenomenon explained that such ions are less dependent on ionic strength. Furthermore, inner-sphere complex formation may also cause an increase in adsorption with the increment in ionic strength, which can be attributed to the higher activity provided by the counter ions presence in the solution. These counter ions are capable of compensating the surface charge generated by specific ion adsorption (McBride 1997; Goldberg and Johnston 2001; Antelo et al. 2005). Thus, the result of this work suggested that As(V) displayed the mechanism of forming inner-sphere surface complexes on the synthesized MnO₂ microspheres, which is in agreement with a previous study (Nesbitt et al. 1998).

6.2.5. Effect of anions on As(V) adsorption

Figure 6-9. Effects of anions on the removal of As(V). Initial As(V): 0.2 mM; Initial MnO₂ microspheres: 2.5 g/L.

Three kinds of oxyanions (SO₄²⁻, CO₃²⁻, PO₄³⁻) with different concentrations were employed to assess the effects of co-existing anions on As(V) adsorption. Figure 6-9 showed two major findings. Firstly, the increase in inhibitory effect with the increase in anions concentration. Secondly, the inhibitive effects of anions varied with different types of anionic species. This phenomenon can be ascribed to the

competitive binding effect by anions, which occupy the reactive surface sites on the synthesized MnO_2 microspheres (Gu et al. 2005). It should be noted that phosphate resulted in the greatest decrease in As(V) removal. Since orthophosphoric acid possesses very similar pK_a values with H_3AsO_4 (H_3PO_4 : $\text{pK}_{a1}=2.1$, $\text{pK}_{a2}=7.2$, $\text{pK}_{a3}=12.3$), the chemical properties of phosphate are very similar to arsenate. Furthermore, phosphate is also an inner-sphere complex-forming anion which can be adsorbed onto mineral surfaces in a similar process to As(V) . Thus, these properties of phosphate result in strong competitions with As(V) for binding sites in the adsorption process (McBride 1994; Su and Puls 2001).

6.2.6. Analysis of FTIR spectra

Figure 6-10. FTIR spectra of (i) MnO_2 , (ii) $\text{MnO}_2 + \text{As(III)}$, and (iii) $\text{MnO}_2 + \text{As(V)}$. Initial As(V) or As(III) : 2 mM, initial MnO_2 microspheres: 2.5 g/L, reaction time: 10 min.

The FTIR spectra in Figure 6-10 indicated that the bond near 1631 cm^{-1} can be assigned to the H-O-H stretching vibrations of water molecules (Szabó et al. 2005), indicating the presence of adsorbed water on the synthesized MnO_2 spheres. The weak band centred at 1048 cm^{-1} was related to vibrations of hydroxyl groups, and

the bands at 1416 cm^{-1} and 716 cm^{-1} resulted from the characteristic vibrations of the O-Mn-O bonding (Shi et al. 2010). For spectrum of iii, a new weak peak appeared at 886 cm^{-1} after the adsorption of As(V), indicating that As(V) binds weakly to Mn center (Zhang et al. 2007). It should be noted that the spectrum of sample ii was quite similar to that of sample iii (Figure 6-10), revealing the interfacial oxidation of As(III) to As(V) during As(III) adsorption onto the synthesized MnO_2 spheres. Furthermore, the As-O stretching vibration peak shifted from 886 cm^{-1} to 877 cm^{-1} as the material reacted with As(III). This phenomenon can be explained by the adsorption reaction between residual As(III) species and the synthesized MnO_2 spheres. As the As(III)-O and As(V)-O vibration peaks located at 795 cm^{-1} and 907 cm^{-1} respectively (Goldberg and Johnston 2001; Zhang et al. 2007), the peak would shift toward the position of As(III)-O.

6.2.7. Analysis of XPS spectra

Figure 6-11. (A) Mn_{2p} XPS spectra of MnO_2 , $\text{MnO}_2 + \text{As(III)}$, and $\text{MnO}_2 + \text{As(V)}$; (B) As_{3d} XPS spectra of the MnO_2 before and after reaction with As(III) and As(V)

respectively; (C) curve fitting of the As3d XPS spectrum after reaction with As(V); (D) curve fitting of the As3d XPS spectrum after reaction with As(III). Initial As(V) or As(III): 2 mM, initial MnO₂ microspheres: 2.5 g/L, reaction time: 10 min.

To further identify the interaction between As species and MnO₂ spheres, XPS measurement was carried out. As shown in Figure 6-11A, there is no significant modification in the binding energy of Mn2p before and after As(V) adsorption, indicating no specific interaction between As(V) and Mn atoms. However, the Mn2p spectrum taken after reaction with As(III) showed that the binding energy shifted from 642.4 eV down to 642.0 eV. Previous studies (Ioffe et al. 1997; Nesbitt et al. 1998) revealed that the binding energy of Mn(IV) ranges from 642.2 eV to 642.5 eV, and Mn in a lower oxidation state exhibited lower binding energy in a XPS spectrum. Thus, the depressed binding energy can be attributed to the increase in reduced Mn species, and the oxidation property of Mn(IV) was responsible for the conversion of As(III) to As(V) (Zhang et al. 2007). Figure 6-11B shows the XPS spectra of the As3d taken on the MnO₂ before and after reaction with As(III) and As(V) solutions. The two peaks centred at 49.50 eV and 44.46 eV relate to the Mn3p and As3d respectively, indicating the adsorption of As species by the synthesized MnO₂ spheres. Furthermore, Gaussian curve fitting of As3d was performed to further describe the oxidation states of As species more specifically, as shown in Figure 6-11C and 6-11D. The As3d taken on MnO₂ + As(V) (Figure 6-11C) was centred at 44.8 eV, representing As(V) species; while fit result of As3d taken on MnO₂ + As(III) (Figure 6-11D) displayed that the curve can be fitted with two peaks having binding energies around 44.3 eV and 45.2 eV, representing As(III) and As(V) species respectively (Ouvrard et al. 2005). These results indicated that both As(III) and As(V) species can be adsorbed onto the synthesized MnO₂ microspheres, which also played a crucial role in the conversion of As(III) to As(V).

6.2.8. Membrane filtration for recycling of the prepared MnO₂ spheres

A dead-end membrane filtration apparatus was employed to recycle the MnO₂ spheres after the As(III) oxidation process. The turbidity of the effluent after filtration was nearly zero, indicating that the used MnO₂ spheres could be effectively removed via the membrane filtration process. As the size of the synthesized MnO₂ spheres is larger than the membrane pore size of 0.2 μm , the material can be easily intercepted and form a stacked layer on the commercial membrane. The declining trend of the permeate flux (MnO₂ + As(III)) is shown in Figure 6-12A. An obvious flux decline occurred in the system during the microfiltration process, indicating that the existence of MnO₂ microspheres caused membrane fouling. In order to identify the dominant fouling mechanism involved, we conducted a resistance analysis and the values are listed in Table 6-2. As R_m can be assumed to be constant in this study, R_c and R_p are mainly accountable for the membrane fouling. The MnO₂ spheres can form a layer and block membrane pores leading to the decrease of flux under a constant pressure. As shown in Table 2, the calculated R_c accounted for 27.1 % in total resistance which was much higher than the 3.1 % of R_p , revealing that the dominant fouling resulted from the formation of stacked layer on the membrane. A schematic diagram (Figure 6-12B) was used to explain the proposed fouling mechanism. Owing to the microstructure of the synthesized MnO₂ spheres, they are less probable to enter into the membrane pores, where most of them are rejected and form a layer on the membrane. Thus, the layer formed by the MnO₂ spheres became the prevailing membrane fouling mechanism. More importantly, the dandelion-like structure of the material will enhance the porosity of the microsphere layers and maintains a higher flux in the filtration process. We speculate that the nanowire structures on the surface of MnO₂ microspheres formed various nanosized channels, which facilitated water to pass through the cake layer and thus relieved membrane fouling problem (Figure 6-12B). Furthermore, FESEM measurements were carried out on the top view and the cross section of the filter membrane. As shown in Figure 6-12C, the MnO₂ microspheres were successfully rejected by the membrane. The cross-section image (Figure 6-12D) revealed that the synthesized MnO₂ microspheres have little chance to cause

pore blocking resistance, which will extend the membrane life as well as lowering the energy consumption in the membrane cleaning process (e.g. forward flush).

Figure 6-12. (A) Membrane flux over distilled water and 0.1 mM As(III) solution after treatment by 0.25 g/L MnO₂ microspheres for 120 mins. (B) Scheme diagram of membrane fouling caused by the synthesized material. (C) Upper-surface of the membrane after filtration of MnO₂ spheres suspension. (D) Cross-section of the membrane after filtration of MnO₂ spheres suspension.

Table 6-2. Summary of resistances for the membrane filtration system (MnO₂ + As(III)).

Resistance	Values ($\times 10^{11} \text{ m}^{-1}$)	Percentage (%)
R_m	1.57	69.8
R_c	0.61	27.1
R_p	0.07	3.1
R_t	2.25	100

6.3. CONCLUSIONS

In conclusion, 1D manganese oxide based 3D micro-/nano-structured MnO₂ spheres were successfully prepared via a solution-based catalytic route, and the related characterization revealed that the synthesized material possesses multi-scale organized nanoarchitecture which is a combination of microstructure and nanostructure. 1D nanowire is the major structure on the surface of the synthesized material. Batch experiments showed that As(III) species can be effectively oxidized by the synthesized MnO₂ followed by the adsorption of As(V) species. Investigation on operation parameters revealed that removal of As(V) using the MnO₂ spheres was evidently dependent on pH and ionic strength, while co-existing anions such as CO₃²⁻, SO₄²⁻, and PO₄³⁻ induced suppressive effects. The synthesized material possesses good adsorption and oxidation properties for the removal of arsenic species under controlled conditions. FTIR along with XPS revealed the surface change of the synthesized MnO₂ microspheres after reaction with As(III) and As(V), indicating that As(III) and As(V) interacted differently with the synthesized MnO₂. The determination of oxidation states of As and Mn by XPS indicated the reductive dissolution of Mn in the conversion of As(III) to As(V). Moreover, the synthesized MnO₂ spheres can be effectively recovered for reuse by a microfiltration process with minimal membrane pore blocking owing to the microstructure of the material. Besides that, the material also formed a porous cake layer on the membrane which kept a relatively high flux. Thus, the synthesized MnO₂ spheres are multifunctional materials with good oxidation, adsorption, and separation properties, and the material may have potential for water purification.

Chapter 7 1D MANGANESE OXIDE BASED NANOFIBROUS MEMBRANE FOR WATER TREATMENT

7.1. INTRODUCTION

Inorganic membranes are of considerable importance in water treatment due to their chemical resistance, thermal resistance and mechanical resistance and ease of thermal regeneration (Maier et al. 1993; Sholl and Johnson 2006; Ke et al. 2007; Albu et al. 2008; Shannon et al. 2008). Recently, many inorganic nanofibrous membranes with different structures and properties have been successfully applied for water purification (Yuan et al. 2008; Zhang et al. 2009; Liang et al. 2011). Successful application of inorganic membranes will depend upon the ability to prepare membranes with desired pore sizes (Xu and Anderson 1991), which would affect the selectivity and permeability of the membrane. Previous studies have shown that various techniques such as self-assembly, electrospinning and selective etching of templates are capable of synthesizing inorganic nanofibrous membranes (Yuan et al. 2008; Jia et al. 2009; Zhang et al. 2009; Zhang et al. 2012). Unfortunately, these techniques suffer from poor selectivity and permeability, complicated technical requirements as well as high operational costs, which severely restrict their applications (Kohli et al. 2004; Yuan et al. 2008). Therefore, there is a growing need in developing a facile method to fabricate inorganic nanofibrous membranes with good selectivity and permeability.

Nowadays, research progress has enabled 1D nanostructures, such as nanofibers and nanotubes to be assembled into a free-standing, flexible and mechanically stable nanofibrous membranes (Srivastava et al. 2004; Yuan et al. 2004; Dong et al. 2006; Zhang et al. 2008; Liang et al. 2010). Recently, self-cleaning TiO_2 nanofibrous membranes are increasingly drawing attention in environmental research due to their concurrent filtration and PCO capabilities (Albu et al. 2007; Zhang et al. 2009). However, the separation ability of inorganic membranes is mainly dependant on the pore size (Keizer et al. 1988), and reports have shown that

smaller organic pollutants with low affinity towards TiO_2 nanowires are not efficiently rejected by these membranes (Kuwahara et al. 2010). To address this issue, an adsorption technique can be adopted in the filtration process. It is predictable that membranes with higher organic adsorption capacity would enhance rejection of organic molecules. Various strategies such as increasing specific surface area and ionic-doping of TiO_2 have been proposed to improve the materials' adsorption abilities (Balasubramanian et al. 2004; Ooka et al. 2004; Xu et al. 2010). Apart from being an efficient and economical method, loading of TiO_2 onto various supporting materials such as glass beads, silica gels and activated carbon (Kobayakawa et al. 1998; Balasubramanian et al. 2004; Maekawa et al. 2006; Kuwahara et al. 2010) can enhance their organic adsorption efficiency. This can be achieved by reconditioning its surrounding environment (Ikeue et al. 2001). Furthermore, the supporting material can act as a dispersing template in controlling the morphology of TiO_2 , downsizing its particulate size and increasing of specific surface area to volume ratio (Koodali and Zhao 2010; Suib et al. ; Xu et al. 2010). Hence, it is desirable to synthesize hybrid TiO_2 nanomaterials with efficient adsorption and PCO properties. Researchers have shown that 1D K-OMS-2 type manganese oxide nanowires can be considered as a good candidate to pair up with TiO_2 nanostructures (Luo et al. 2000; Yuan et al. 2004; Lahann 2008; Luo et al. 2008; Yuan et al. 2008; Hu et al. 2010). As compared with other supporting materials, 1D K-OMS-2 nanowires exhibit larger BET surface area which leads to more adsorption sites with increased BET surface area. Moreover, the hydrophobic property of K-OMS-2 plays a crucial role in the surface reactions of the synthesized materials. Effectively, materials equipped with hydrophobic surfaces are capable of performing photocatalytic degradation of organics in water efficiently (Maekawa et al. 2006; Kuwahara et al. 2010). Owing to its property, the synthesized material can be further developed into a free-standing and nanofibrous membrane that incorporates filtration, adsorption, and self-cleaning properties.

In this work, we reported the fabrication of a novel free-standing nanofibrous microfiltration membrane assembled using hierarchical TiO_2 /K-OMS-2 nanowires. Firstly, a hydrothermal method was employed to synthesize the K-OMS-2

nanowires which served as substrates to guide the growth of secondary TiO_2 nanostructures. Subsequently, another hydrothermal process was carried out to form TiO_2 nanostructures on the K-OMS-2 nanowires. Finally, TiO_2 /K-OMS-2 nanofibrous membrane was formed via a combination of vacuum-filtration, hot press and calcination techniques. The synthesized membrane was applied for filtration process, and organic pollutants can be rejected by the membrane via a combination effect of interception and adsorption. Furthermore, a PCO process can be carried out, making it possible to degrade organic pollutants and alleviate membrane fouling simultaneously. An illustration of the concurrent filtration, adsorption and PCO in water treatment process is shown in Figure 7-1. In a typical process, the organic contaminated water was filtrated through the membrane under an external pressure. Large organic particles would be intercepted directly by membrane pores; while the small ones would be adsorbed onto the nanowires via an adsorption process. This reaction was greatly enhanced by the hydrophobic nature of the supporting K-OMS-2 nanowires, as well as large surface area of the hierarchical nanowires. The organic pollutants attached on the photocatalytic membrane were simultaneously degraded by the PCO process under a UV light irradiation, alleviating membrane pore blocking by small organic molecules, thus maintaining a constant permeate flux. In addition, the PCO process helps to free up adsorption sites occupied by organic pollutants, contributing to regeneration of the membrane.

Figure 7-1. Scheme of the concurrent filtration, adsorption and PCO in water treatment process using the synthesized membrane.

7.2. RESULTS AND DISCUSSION

7.2.1. XRD analysis

Figure 7-2. XRD patterns of the synthesized K-OMS-2, TiO₂/K-OMS-2 before calcination and TiO₂/K-OMS-2 after calcination at 550 °C.

The XRD patterns of the synthesized nanostructured K-OMS-2 and TiO₂/K-OMS-2 are presented in Figure 7-2. All diffraction peaks of the upper curve in Figure 7-2 can be perfectly indexed to the K-OMS-2 crystalline phase (JCPDS 44-1386). Along side with the K-OMS-2, the XRD pattern of synthesized TiO₂/K-OMS-2 nanostructures after calcination shows much intense and sharper peaks as compared to the sample before calcination. The K-OMS-2 phase is also observed in the synthesized TiO₂/K-OMS-2 hierarchical heterojunctions, indicating that the crystal structure of the K-OMS-2 nanowires was not changed in the coating process of TiO₂ nanostructures. The result obtained shows that the TiO₂ grafted on the K-OMS-2 nanowires acquired both diffraction peaks of anatase and rutile phases TiO₂. The peaks existed at 25° and 63° revealed the presence of anatase phase of TiO₂ (JCPDS 21-1272) in the synthesized nanocomposites, while the peaks at 27°, 36° and 55° indicated the co-existence of rutile phase of TiO₂ (JCPDS 21-1276).

7.2.2. FESEM and TEM observation

FESEM image of the synthesized K-OMS-2 nanowires is shown in Figure 7-3A. As a primary substrate, the K-OMS-2 nanowires have diameters of about 40-80 nm and are over several hundreds of microns long. After a hydrothermal process, the secondary TiO₂ nanostructures were readily grafted onto the surfaces of the K-OMS-2 nanowires, constructing a hierarchical heterostructure (Figure 7-3C). Although it is difficult to determine an individual structure of TiO₂ from the FESEM image, it can be found that the K-OMS-2 nanowires were uniformly coated.

To further identify the surface morphology of the synthesized materials, TEM characterization was conducted. TEM images of K-OMS-2 nanowire and K-OMS-2/TiO₂ hierarchical heterojunctions are shown in Figure 7-3B and Figure 7-3D respectively. These results confirmed the matrix of the material where high density secondary TiO₂ hair-like structures was anchored onto the surface of the primary underlying K-OMS-2 nanowire. In the role of a scaffold, K-OMS-2

nanowires acted as a dispersing template to downsize the TiO_2 nanostructures and thus increasing reactive sites for degradation of pollutants(Xu et al. 2010). It can be seen from Figure 7-3D that the TiO_2 nanostructures are of lengths ranging from 20-40 nm and have diameters of about 3 nm. In the TiO_2 coating process, the hydrolysis of titanous sulfate proceeded very slowly, which reduced the reaction and nucleation rate and in turn facilitated the growth of TiO_2 nanostructures on the surface of K-OMS-2. Previous studies revealed that a mild and slow reaction would lead to the formation of materials with well-organized morphologies(Yuan et al. 2005; Fei and Wei 2011), which can explain the formation of evenly coated TiO_2 nanostructures on the surface of K-OMS-2 nanowires. As compared to other fabrication methods (e.g. sol-gel), the morphology of TiO_2 was controlled in this work. In this way, the effective specific surface area was increased and thus enhancing the material's environmental performance. To support the discussions above, Figure 7-3E and Figure 7-3F revealed that the calcination at 550 °C for 1 h did not change the apparent morphology of the synthesized material.

Figure 7-3. (A) FESEM image of the K-OMS-2 nanowires. (B) TEM image of the K-OMS-2 nanowire. (C) FESEM image of the hierarchical TiO₂/K-OMS-2 heterojunctions before calcination. (D) TEM image of the hierarchical TiO₂/K-OMS-2 heterojunctions before calcination. (E) FESEM image of the hierarchical TiO₂/K-OMS-2 heterojunctions after calcination at 550 °C for 1 h. (F) TEM image of the hierarchical TiO₂/K-OMS-2 heterojunctions after calcination at 550 °C for 1 h.

7.2.3. BET surface area and pore structure

Figure 7-4. N₂ adsorption/desorption isotherm curve of the hierarchical TiO₂/K-OMS-2 heterojunctions; Inset is the pore size distribution of the hierarchical TiO₂/K-OMS-2 heterojunctions.

To examine the surface area as well as the pore size distribution, nitrogen adsorption/desorption analysis was conducted on the synthesized materials. From figure 7-4, an IV-type nitrogen isotherm with a H3-type hysteresis loop indicated that the synthesized TiO₂/K-OMS-2 heterojunctions were of mesoporous nature. According to the IUPAC classification, mesoporous materials used to characterize the Type H3 loop are commonly observed with aggregates of plate-like particles, leading to formation of slit-shaped pores (Sing et al. 1985). This is in good agreement with the long slit pores possibly formed by the interweaving of long nanowires, while the plate particles may be induced by the mesh-like hierarchical structure of overlaying nanowires of the 2 hybrid compounds in K-OMS-2 and TiO₂. In addition, the mesoporosity of the K-OMS-2/TiO₂ heterojunctions is well-justified based on the inset of figure 7-4, where pore size distribution curve indicates a sharp peak centred at the pore diameter of 35 nm, providing evidence that the sample

contains a majority of mesopores ($2\text{ nm} < \text{pore size} < 50\text{ nm}$). The BET surface areas of the synthesized K-OMS-2, TiO_2 and $\text{TiO}_2/\text{K-OMS-2}$ (after calcination at $550\text{ }^\circ\text{C}$) are recorded at $25.08\text{ m}^2/\text{g}$, $72.74\text{ m}^2/\text{g}$ and $111.58\text{ m}^2/\text{g}$, respectively. The mesoporous structure and high BET surface area of $\text{TiO}_2/\text{K-OMS-2}$ are expected to enhance adsorption of organic compounds onto the membrane. It is noteworthy that the loading of TiO_2 nanostructures on the K-OMS-2 nanowires has greatly increased the specific area of the material. This phenomenon can be attributed to the presence of K-OMS-2 scaffold, which acts as a dispersing template to downsize the TiO_2 nanostructures during the synthesis process (Xu et al. 2010). Henceforth, adsorption capacity and photocatalytic activity of the synthesized membrane can be enhanced since adsorption and PCO processes are predominantly driven by surface reactions on the material. Moreover, it has been reported that K-OMS-2 doped TiO_2 materials possess good PCO efficiency due to the presence of OH bonded groups on the catalyst surface (Jothiramalingam and Wang 2007).

7.2.4. XPS analysis

Figure 7-5. High-resolution XPS spectra of Mn 2p (A) and Ti 2p region (B) taken on the $\text{TiO}_2/\text{K-OMS-2}$ heterojunctions.

The synthesized $\text{TiO}_2/\text{K-OMS-2}$ heterojunctions were investigated by XPS to identify the surface elemental compositions and binding energies. The result indicated that the sample contains K, Mn, O and Ti. The high-resolution XPS

spectra of Mn 2p taken on the surface of K-OMS-2/TiO₂ heterojunctions is shown in figure 7-5A and Gaussian curve fitting of Mn 2p_{3/2} was performed to describe the oxidation states of Mn more specifically. The peaks are centred at 641.7 eV and 643.0 eV, indicating the presence of Mn³⁺ and Mn⁴⁺ respectively(Zou et al. 2010). It is noteworthy that the mixed-valences of Mn are important in electron transfer, which lead to the conductivity of resultant material and thus enhance the photocatalytic activity of the synthesized material(Suib 2008). Figure 7-5B shows that the peaks for Ti 2p_{3/2} and Ti 2p_{1/2} are centered at 458.8 eV and 464.4 eV, representing the presence of a Ti⁴⁺ oxidation state in the sample(Thind et al. 2011). As a result, the presence of TiO₂ on the surface of K-OMS-2 nanowires was identified. These observations were crucial because the presence of TiO₂ can endow the synthesized material with self-cleaning property under UV or solar light irradiation.

7.2.5. Adsorption ability of the synthesized materials.

Figure 7-6. Adsorption kinetics of AO7 onto the prepared K-OMS-2, TiO₂ and TiO₂/K-OMS-2 at pH 5 and 20 °C.

To evaluate adsorption capacity of the hierarchical $\text{TiO}_2/\text{K-OMS-2}$ heterojunctions for organic pollutant removal, an adsorption kinetics study of AO7 was conducted. From the results (Figure 7-6), the synthesized $\text{TiO}_2/\text{K-OMS-2}$ exhibited much higher adsorption capacity than pristine TiO_2 which was prepared using an identical procedure as that of $\text{TiO}_2/\text{K-OMS-2}$. For example, using $\text{TiO}_2/\text{K-OMS-2}$ over pristine TiO_2 led to an increase in removal efficiency of AO7 from 8.8% to 36.5% in 360 min. The increased BET surface area of $\text{TiO}_2/\text{K-OMS-2}$ may partly explain the enhanced adsorption capacity. However, the adsorbed amount of AO7 on $\text{TiO}_2/\text{K-OMS-2}$ is around 4 times greater than that on pristine TiO_2 ; while the BET surface area of $\text{TiO}_2/\text{K-OMS-2}$ ($111.58 \text{ m}^2/\text{g}$) is only about 1.5 times larger than that of pristine TiO_2 ($72.74 \text{ m}^2/\text{g}$). K-OMS-2 has been found to possess excellent hydrophobicity and strong affinity towards organic compounds (Luo et al. 2008; Hu et al. 2010), which in turn affects the surrounding environment of the constructed TiO_2 nanostructures. Figure 7-6 shows that AO7 can be efficiently removed by K-OMS-2 nanowires, which indicates that the hydrophobic nature of K-OMS-2 nanowires may also account for the high adsorption capacity of the synthesized $\text{TiO}_2/\text{K-OMS-2}$.

7.2.6. Photocatalytic activity of the synthesized materials.

Figure 7-7. Changes of AO7 concentration and TOC during photolysis and photocatalytic degradation in the presence of the synthesized TiO_2 and the $\text{TiO}_2/\text{K-OMS-2}$.

Figure 7-8. Pseudo first-order photocatalytic degradation of AO7 over the synthesized TiO_2 and $\text{TiO}_2/\text{K-OMS-2}$.

The photocatalytic activity of the synthesized $\text{TiO}_2/\text{K-OMS-2}$ heterojunctions was evaluated by the degradation of AO7 under UV light irradiation, and the synthesized pure TiO_2 was also used for comparison. Figure 7-7 shows the concentration changes of AO7 and TOC as a function of time, indicating that the $\text{TiO}_2/\text{K-OMS-2}$ heterojunctions exhibit higher photodegradation ability than the pure TiO_2 under the same condition. As shown in Figure 7-7, the residue of AO7 in 30 min was decreased to 19.1 % by using the $\text{TiO}_2/\text{K-OMS-2}$ as a photocatalyst, which is more effective than the pure TiO_2 . Although the degradations of TOC follow the similar trends with AO7, the TOC removal rates are much slower due to the incompletely decomposition of AO7 at the beginning of the PCO process.

Photocatalytic degradations for organic pollutants are often described in terms of the Langmuir-Hinshelwood model, which can be simplified as pseudo-first order reaction as follows(Hoffmann et al. 1995):

$$r = -\frac{dC}{dt} = kC \quad [7-1]$$

Where k refers to the corresponding reaction rate kinetic constant (h^{-1}). Hence, the pseudo first-order reaction rate can be further applied:

$$-\ln \frac{C}{C_0} = kt \quad [7-2]$$

Where C (mg L^{-1}) is the AO7 concentration at time t , C_0 (mg L^{-1}) is the initial AO7 concentration measured after 30 min of dark adsorption and t (h) is the reaction time.

As shown in Figure 7-8, the reaction rate constants for the synthesized $\text{TiO}_2/\text{K-OMS-2}$ and pure TiO_2 are 3.216 h^{-1} and 1.921 h^{-1} , respectively. The photocatalytic degradations of AO7 follow pseudo first-order kinetics in the studied concentration range, and thus the corresponding k constants indicate a good evaluation of the overall photocatalytic reaction rates. As a result, the comparison of the reaction rate constants indicates a higher photocatalytic efficiency of the synthesized $\text{TiO}_2/\text{K-OMS-2}$. This could be explained by the following factors:

(1) The K-OMS-2 acts as a dispersing template to downsize the TiO_2 nanostructures during the synthesis process and thus increasing the specific surface area of the synthesized material. The larger surface area of the photocatalyst can directly enhance photocatalytic activity since PCO processes are predominantly driven by surface reactions on the material. Moreover, with the increase of specific surface area, there are more AO7 molecules adsorbed onto the synthesized $\text{TiO}_2/\text{K-OMS-2}$

nanocomposites than the pure TiO_2 (Figure 7-7). Previous report(Kuwahara et al. 2010) revealed that more efficient oxidation can occur in the very vicinity of photocatalyst, thus the photocatalyst with higher adsorption capacity would endow the material with higher photocatalytic efficiency. In addition, it has been reported that K-OMS-2 doped TiO_2 materials possess good PCO efficiency due to the presence of OH bonded groups on the catalyst surface(Jothiramalingam and Wang 2007).

(2) The recombination rate of electrons and holes on the surface of the photocatalyst can also affect photocatalytic efficiency(Zhang et al. 2010; Sun et al. 2011). As mixed valence in organic system leads to conductivity of the resultant materials, the $\text{Mn}^{3+}/\text{Mn}^{4+}$ in the synthesized $\text{TiO}_2/\text{K-OMS-2}$ nanocomposites play a crucial role in electron transfer and thus suppress the recombination of electron and hole pairs(Suib 2008; Bouazza et al. 2009). PL emission spectra are useful to study the efficiency of charge transfer behavior of photogenerated electrons and holes(Zhang et al. 2000). Figure 7-9 shows the PL spectra of pure TiO_2 and $\text{TiO}_2/\text{K-OMS-2}$, indicating that the PL intensity of pure TiO_2 was substantially quenched by the addition of K-OMS-2 nanowires. It is well known that the intensity of PL emission is strongly dependent on the recombination rate of photogenerated electrons and holes(Cong et al. 2007). In this study, K-OMS-2 nanowires act as trapping sites to capture photogenerated electrons from the TiO_2 conduction band, separating the photogenerated electron-hole pairs. Thus, the presence of K-OMS-2 nanowires can retard the photogenerated charge carrier recombination rate of the synthesized material, leading to the decline of PL spectrum intensity. A proposed mechanism to illustrate the processes of light activation, charge transfer and degradation of AO7 under UV light is shown in Figure 7-10. In a typical process, electrons are excited from the valence band to the conduction band under UV light absorption with energy equal to or greater than the band gap of the TiO_2 nanostructures in the synthesized material. K-OMS-2 can act as an electron reservoir, which helps to trap the photoinduced electrons emitted from the TiO_2 photocatalyst and thus retard the recombination of electron and hole pairs. Consequently, more holes (h^+) can migrate to the surface of the photocatalyst, where the holes react with adsorbed

water or hydroxyl anions to form hydroxyl radicals ($\bullet\text{OH}$) for the oxidation of AO7. In addition, owing to the electron transfer in the manganese oxide, excited oxygen species ($\bullet\text{O}_2^-$) can also be formed and involved in the oxidation of AO7. Therefore, the degradation of AO7 can be considered as a combination effect of h^+ and $\bullet\text{O}_2^-$.

Figure 7-9. PL spectra of the synthesized pure TiO_2 and $\text{TiO}_2/\text{K-OMS-2}$ heterojunctions.

Figure 7-10. Proposed cycle of photo oxidation of AO7 on the surface of $\text{TiO}_2/\text{K-OMS-2}$ heterojunctions under UV light irradiation.

7.2.7. Characterization of the synthesized $\text{TiO}_2/\text{K-OMS-2}$ nanofibrous membrane

Figure 7-11. (A) Digital photo of the $\text{TiO}_2/\text{K-OMS-2}$ membrane. (B) EDX spectrum of the synthesized $\text{TiO}_2/\text{K-OMS-2}$ nanofibrous membrane.

Figure 7-12. (A) Top view FESEM image of the TiO₂/K-OMS-2 membrane. (B) FESEM image of the cross-section. (C) High resolution top view FESEM image of the TiO₂/K-OMS-2 membrane. (D) High resolution FESEM image of the cross-section.

The digital photo of the synthesized free-standing membrane, fabricated by a combination of filtration, hot press and calcination processes, is shown in Figure 7-11A. The thickness and diameter of the membrane can be controlled by adjusting the dosage of the materials and monitoring the filtration apparatus. In this work, the thickness and diameter of the membrane is about 300 μm and 40 mm respectively. In addition, from the EDX result in Figure 7-11B, we can further confirm that the external surface of the synthesized TiO₂/K-OMS-2 heterojunctions contain K, Mn, Ti, and O.

Figure 7-12A shows the top view FESEM image of the membrane, which reveals a relatively flat topology with no observed cracks or pinholes. From the high-resolution FESEM image (Figure 7-12C), it can be deciphered that the open porous network was formed by overlapping and interweaving of the ultra long hierarchical TiO₂/K-OMS-2 nanowires. Owing to this structure, permeability of water during the filtration process was enhanced. Based on the FESEM image, pore size of the synthesized membrane approximately ranges from 0.05 to 0.3 μm which classify it under the microfiltration membrane category. To further determine membrane pore size, PS microspheres were used in a filtration process, and the rejection rate for 0.1 μm and 0.05 μm microspheres were 93.9% and 85.8% respectively, as shown in Table 7-1. Since pore size of a membrane can be defined as the diameter of latex microspheres which are 90% retained by the membrane (Nakao 1994), the pore size of the synthesized membrane can be characterized at 0.1 μm . In addition, cross-sectional images (Figure 6-12B and 6-12D) of the synthesized membrane further reveal that the membrane consists of nanowires assembled over multiple length scales, and the tightly interwoven nanowires can endow the membrane with a compact functional layer.

Table 7-1. Rejection rates of the synthesized membrane for PS microspheres with different diameters.

PS (μm)	Rejection rate (%)
0.05	85.8
0.1	93.9
0.2	97.3
0.5	97.9
1	98.1
2	98.3

7.2.8. Evaluation of the membrane performance

Figure 7-13. The upper-surface FESEM image of the $\text{TiO}_2/\text{K-OMS-2}$ membrane after the filtration of $0.5 \mu\text{m}$ PS microspheres solution: A) Low magnification image, B) High magnification image.

Figure 7-14. Effect of the permeate flux on the performance of the synthesized membrane on AO7 and TOC removal.

The performance of the synthesized membrane was evaluated using a dead-end filtration cell, as shown in Figure 3-1. The flux can be controlled by the computer setup and a UV lamp was also employed in the filtration process. Since the membrane pore size is around 0.1 μm , pollutants with large particle sizes can be rejected directly by the synthesized membrane. As shown in Figure 7-13A and 7-13B, PS microspheres with 0.5 μm can be retained and subsequently accumulated to form a cake layer on the surface of the synthesized membrane. In addition, Figure 7-13A indicates that the membrane after filtration process kept its original surface morphology, which facilitates its regeneration for further application.

To investigate membrane performance on degradation of smaller organic pollutants, aqueous AO7, which exhibits high solubility in water, was used as a model organic pollutant. As the synthesized $\text{TiO}_2/\text{K-OMS-2}$ nanocomposites have good adsorption capability on AO7, some of the AO7 molecules can be adsorbed onto the membrane during the filtration process. When flux was maintained at 30 $\text{L}/\text{m}^2\cdot\text{h}$, experimental results indicated that only 8.7 % of AO7 was removed using the only synthesized membrane. This phenomenon could be attributed to the sole adsorption capability

of the membrane. In this process, 500 ml of 20 mg/L AO7 solution was filtered and the TiO₂/K-OMS-2 nanocomposites for membrane fabrication were only 50 mg. By applying this method, the membrane would reach its maximum adsorption capacity when the adsorption sites were fully occupied during the filtration process. Thus, the continuous adsorption of AO7 is not feasible. However, when a UV lamp and the same flux were employed concurrently, the AO7 removal rate of 96.3 % was achieved, as shown in Figure 7-14. Owing to the PCO process, the AO7 adsorbed onto the membrane can be quickly degraded, which can free up the adsorption sites on the surface of the membrane. Thus, the membrane can be regenerated under photocatalysis. On the other hand, the high removal rate of AO7 can be attributed to the combination effect of adsorption and photocatalysis activities. However, removal rate of TOC was only 54.1 % (Figure 7-14) due to the incomplete photocatalytic mineralization of the AO7 molecules.

AO7 and TOC removal rates were also evaluated under different permeate flux, including 30 L/m²·h, 40 L/m²·h, 50 L/m²·h, 60 L/m²·h, 70 L/m²·h, 80 L/m²·h. As shown in Figure 7-12, the AO7 and TOC removal rates generally decreased with increase of permeate flux. Furthermore, they were relatively stable at a preset flux of not exceeding 60 L/m²·h. On the other hand, when the flux reached 70 L/m²·h, the removal rates of AO7 and TOC began to decrease significantly, which can be attributed to the limited retention time available for the pollutants on the membrane. The results indicated that a maximum flux of 60 L/m²·h was the critical point in establishing an optimal balance between photocatalytic degradation of AO7 and flux under the stated experimental conditions.

7.3. CONCLUSIONS

In conclusion, we have successfully synthesized a novel hierarchical TiO₂/K-OMS-2 heterojunctions based on the 1D K-OMS-2 nanowires. Furthermore, a free-standing, hybrid TiO₂/K-OMS-2 nanofibrous membrane was fabricated and characterized. The synthesized membrane has a layer-by-layer structure, and it can be classified under the microfiltration membrane category. To evaluate the

membrane performance, a concurrent microfiltration, adsorption, and photocatalytic oxidation module was developed to study the removal of organic pollutants by the membrane. The membrane exhibited good performance in the removal of organic pollutants because of its unique features as follows: 1) The K-OMS-2 nanowires can act as a dispersing template to control the morphology of TiO_2 and hence increase specific surface area, reaction sites and UV light adsorption efficiency of the membrane. 2) Since the synthesized material is mesoporous in nature, organic pollutants have higher affinity towards the hydrophobic K-OMS-2 nanowires, resulting in greater adsorption efficiency. 3) The doping of cryptomelane can enhance the photocatalytic activity of TiO_2 . We believe that the synthesized hierarchical TiO_2 /K-OMS-2 nanofibrous membrane will have potential in extensive applications of membrane filtration and water treatment technologies.

Chapter 8 CONCLUSIONS AND RECOMMENDATIONS

8.1. CONCLUSIONS

This research project aims to develop new functional 1D manganese oxide based materials for water treatment. The report investigates and discusses the fabrication, characterization and environmental applications of the synthesized materials. Basically, 1D K-OMS-2 nanowires were synthesized as a basic material. From which, nanostructures such as K-OMS-2/Fe₃O₄ nanocomposites, MnO₂ nanowires, MnO₂ spheres and TiO₂/K-OMS-2 heterojunctions were also successfully synthesized. After obtaining sufficient experimental information and results, a novel TiO₂/K-OMS-2 nanofibrous membrane was finally fabricated for concurrent filtration, adsorption and PCO process.

K-OMS-2 nanowires were firstly synthesized via a hydrothermal method. Subsequently, a novel nanocomposite was formed by grafting Fe₃O₄ nanoparticles onto the synthesized K-OMS-2 nanowires via a chemical co-precipitation process. During the fabrication process, the valence of Mn unchanged which detained the oxidation property of the synthesized K-OMS-2/Fe₃O₄. Experimental results indicated that As(III) can be effectively oxidized by the synthesized K-OMS-2/Fe₃O₄ nanocomposite within a short period of time. The results obtained displayed that the K-OMS-2/Fe₃O₄ achieved a higher maximum As(V) adsorption capacity of 20.83 mg/g as compared to K-OMS-2 nanowires (9.43 mg/g) for As(V) removal. This outcome can be explained by the presence of Fe₃O₄ nanoparticles. Moreover, the synthesized materials can be separated from the water easily by employing a low magnetic field. Concurrently, detachment of Fe₃O₄ nanoparticles from the K-OMS-2 nanowires was not found. These observations displayed the excellent magnetic property and stability of the material. Ultimately, an effective method for the separation of nanomaterials from water can be obtained from this study.

A follow up experiment was conducted to investigate the effectiveness of MnO₂ nanowires. Similarly, these nanowires were synthesized via a modified hydrothermal process. The precursor was prepared using (NH₄)₂S₂O₈, which enhance the formation of Mn⁴⁺ in the synthesized material. Owing to the high oxidation state of Mn, the synthesized MnO₂ nanowires possess stronger oxidation ability as compared to K-OMS-2 nanowires. According to the experimental results, BPA was completely degraded by the synthesized MnO₂ nanowires within 90 min under the designed reaction system. It is important to note that pH values can significantly affect the removal rate of BPA. Furthermore, both acidic and basic conditions are found to be important parameters to facilitate the degradation process. However, the presence of HA and metal ions would suppress the removal of BPA. Owing the high aspect ratios of the synthesized MnO₂ nanowires, the material can be easily recovered via a crossflow microfiltration process with slight membrane pore blocking. In this way, regeneration of the membrane and reduction in operating cost can be facilitated. Moreover, the material was found to possess with good mechanical strength where the morphology of the recycled MnO₂ nanowires remained the same as the original state. In this work, we developed a hybrid process combining oxidation on MnO₂ nanowires with microfiltration for BPA removal.

In order to further investigate the effectiveness of MnO₂, 1D manganese oxide nanowires were grown on the surface of the 3D MnO₂ spheres. For this part of the study, the materials had been synthesized and applied for the removal of arsenic species. MnO₂ spheres were synthesized via a catalytic oxidation route, and they possess higher specific surface area as compared to 1D manganese oxide nanowires. Due to the presence of the larger reactive sites, MnO₂ spheres were expected to portray a higher pollutants degradation rates in water purification. The micro-/nano-structures of the synthesized material endow the material with excellent adsorption, oxidation and easy separation properties. Compared with K-OMS-2 nanowires, the MnO₂ sphere showed higher activity for the As(III) oxidation and As(V) adsorption reactions. The adsorption of As(V) on the material was significantly affected by pH and ionic strength. Moreover, the presence of anions was found to be capable of inducing suppressive effects due to the

competitive binding outcome. Among these anions, PO_4^{3-} showed the greatest decrease in As(V) removal, which can be attributed to the similar chemical properties between phosphate and arsenate. According to the FTIR result, the peaks centred at 886 cm^{-1} and 877 cm^{-1} can be assigned to the coordination of arsenic with Mn. For the sample after reaction with As(III), XPS spectra indicated that the binding energy around 44.3 eV and 45.2 eV represented As(III) and As(V) species, respectively. The results revealed that As(III) species were firstly adsorbed onto the synthesized MnO_2 microspheres for subsequent reactions. Moreover, a dead-end membrane filtration system was conducted to evaluate the separability of the synthesized materials. It was found that the synthesized material caused minimal pore blocking, and the cake layer fouling could also be relieved due to the hierarchical structure of the material. As a result, the synthesized material has potential to be employed for water treatment processes.

To avoid the separation process after water treatment, nanomaterials were further fabricated into a membrane structure. Therefore, a novel free-standing nanofibrous microfiltration membrane was assembled using hierarchical $\text{TiO}_2/\text{K-OMS-2}$ nanocomposites for this part of the research. Due to the materials hydrophobicity, 1D K-OMS-2 nanowires were employed to enhance the adsorption ability supplementary to acting as a scaffold. Subsequently, TiO_2 nanostructures were successfully grafted onto the surface of the K-OMS-2 nanowires via a hydrothermal process. For this experiment, the morphology and structure of the synthesized hierarchical $\text{TiO}_2/\text{K-OMS-2}$ nanocomposites were characterized. Furthermore, adsorption and PCO activities of the material were also evaluated. The incorporation of TiO_2 nanostructures can endow the membrane with self-cleaning property, as a result, addressing the membrane fouling problem in filtration process. The synthesized membrane was classified under the microfiltration membrane category. Furthermore, a concurrent adsorption, filtration and PCO process was conducted for AO7 removal. The result showed that an AO7 removal rate of 96.3 % was obtained when flux was maintained at $30\text{ L/m}^2\cdot\text{h}$. This removal process can be explained by a combination effect of adsorption and PCO effect. However, the AO7 removal rate was found to decrease with the increment of flux. Further experiments

indicated that any flux below $60 \text{ L/m}^2\cdot\text{h}$ was the optimum condition to result in a stable AO7 removal rate. In this work, we first developed a 1D manganese oxide based nanofibrous membrane to remove organic pollutants in water via a concurrent adsorption, filtration and PCO process. Ultimately, we believe that the synthesized membrane can be used in wider environmental applications.

In summary, several 1D manganese oxide based materials had been synthesized for specific applications in this research. The adsorption and oxidation performances of manganese oxides in water treatment process can be enhanced by controlling the morphology and structure of the materials. In addition, it is important to note that the synthesized materials can be easily separated from aqueous solution via different methods, such as magnetic separation and membrane separation. With the effective separation methods, the fabrication of a novel nanofibrous membrane using nanomaterials can be considered as a most promising candidate for water treatment in future. The work carried out in this thesis aims to provide some pathways for 1D manganese oxides in the application of water treatment. This study could serve as a reference for further development of water purification using nanomaterials.

8.2. RECOMMENDATIONS FOR FUTURE WORK

This thesis work primarily involved the development of 1D manganese oxide based materials for water treatment. Future works to complement this thesis will include the following aspects:

1. Further study of magnetism, oxidation and adsorption properties of the synthesized K-OMS-2/ Fe_3O_4 with different Fe_3O_4 contents to find out the optimum Fe_3O_4 ratio to achieve the highest performance.
2. Stability studies of the recovered nanomaterials after water treatment process to be conducted. The morphology and activity of the materials should be investigated after repetitive applications.

3. Possible released ions such as Mn^{2+} and Fe^{3+} from the synthesized nanomaterials should be investigated to avoid the secondary pollutions in water.
4. The synthesized nanomaterials and separation system should be applied in a practical water treatment process.
5. The synthesized $\text{TiO}_2/\text{K-OMS-2}$ nanofibrous membrane should be applied with a complicated system such as multiple organics environment. Furthermore, the potential application of the membrane in actual water should also be further evaluated.

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