Nano-structured titanium dioxide microsphere for humic acid removal in water

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Nano-structured Titanium Dioxide Microsphere for Humic Acid Removal in Water

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SUMMARY

Natural organic matter (NOM) is always a key issue in water treatment. It does not only cause colour, odor and taste problems but also forms halogenated by-products such as trihalomethanes (THMs) during chlorine disinfection process. Adsorption is often used as an individual separation process to minimize the presence of NOM, particularly humic acid (HA), a subclass of NOM in water. Various adsorbents such as activated carbon and metal oxides have been reported to adsorb HA in water. The adsorption process in removing HA from water by TiO_2 has gained attention due to its high adsorption capacity, self regeneration, non-toxicity, high oxidation strength, high chemical stability and inexpensiveness. However the use of commercial TiO_2 in a suspension water treatment system has many limitations: physically unstable in aqueous phase and, difficulty in separation and recovery.

A novel nano-structured TiO_2 microsphere was developed in this study to overcome the above mentioned limitations. It was formed by embedding the size-selected anatase crystallite in the core (commercial TiO_2 , Degussa P25) via sol-gel spray coating technique. A titanium coating sol was prepared to bind the commercial TiO_2 P25 and eventually transform into anatase crystallite which embedded within the TiO_2 microsphere. The results showed that the anatase crystallite size of titanium coating sol was substantially affected by the mole ratio of ethanol to titanium alkoxide and also the calcination temperature. The anatase crystallite size of 10 nm was obtained at mole ratio of EtOH to alkoxide : 50 to 1 and calcinated temperature of 450°C . The resulting nano-structured TiO_2 microsphere displayed a spherical shape with particle size ranged between 10 to $50\ \mu\text{m}$ with BET surface area of $42\ \text{m}^2/\text{g}$. The photocatalytic activity of nano-structured TiO_2 microsphere had been improved. It was due to the nano-sized anatase crystallite which had been

incorporated into the nano-structured TiO₂ microsphere.

In the second phase of study, the nano-structured TiO₂ microsphere was used to remove HA from water. It was found that the adsorption extent and kinetic were significantly enhanced at low pH condition and with the presence of Ca²⁺ in solution. A second order polynomial equation was developed to explain the relationship between the adsorption extent and the variables (pH and Ca²⁺ concentration) within a pre-determined studied region. The adsorption extent could reach saturation with high Ca²⁺ concentration (50ppm) in acidic condition (pH 3). It was found that the adsorption behavior of HA on nano-structured TiO₂ microsphere was condition dependent and well fitted by Langmuir-Freundlich model. The adsorption kinetic of HA on nano-structured TiO₂ microsphere followed a 2-stage processes: diffusion-controlled process and attachment-controlled process.

Adsorption mechanism of HA on TiO₂ microsphere was proposed. It was revealed that electrostatic interaction was dominating the adsorption of HA onto TiO₂ microsphere surface. X-ray photoelectron spectrometer (XPS) revealed that the adsorption occurred through the formation of R-C(O)O-Ti bond between the oxygen atom of carboxylic group of HA and the surface Ti⁴⁺ cations. In addition to this, it was found that Ca²⁺ could bind with oxygen in carboxylic group of HA, partially neutralize them, form the Ca-C(O)O-R complex and finally attach on the surface of nano-structured TiO₂ microsphere.

It was shown in this study that strong adsorption of HA on nano-structured TiO₂ microsphere did not actually enhance the PCO process. The HA was successfully degraded through PCO process regardless of operating conditions (pH and cation strength). It was revealed that HA was merely adsorbed on nano-structured TiO₂ but not fully degraded at pH 3 at the end of the PCO degradation process. The

inhibition of PCO efficiency for well-adsorbed HA might be due to two possibilities: the blockage of active sites for PCO process on the TiO_2 microsphere surface and the surface recombination of photogenerated holes and electrons via adsorbed HA.

In summary, the novel nano-structured TiO_2 microsphere possessed as a potential adsorbent to remove HA in water. The unique property of this nano-structured TiO_2 would solve the engineering problem by promoting better separation and recovery in engineering application.

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2. Lee, P.F., Sun, D.D. and Leckie, J.O. (2007) "Adsorption and Photo degradation of Humic Acids by Nano-structured TiO₂ for Water Treatment" Journal of Advanced Oxidation Technologies, Vol. 10, No.1, 72-78.
3. Lee, P.F., Sun, D.D., Du, J.H. and Leckie, J.O. (2007) "Nano-structured TiO₂ Microsphere – A New Approach in Removing Natural Organic Matter", Water Science and Technology, Singapore, under review.
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6. Lee, P.F., Sun, D.D. and Leckie, J.O. "Adsorption behavior of humic acid onto nano-structured TiO₂ microsphere", in preparation.

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
SUMMARY	ii
LIST OF PUBLICATIONS	v
TABLE OF CONTENTS	vii
LIST OF FIGURES	xii
LIST OF TABLES	xvi
CHAPTER 1 INTRODUCTION	1
1.1 Background of Study	2
1.2 Objectives of Study	6
1.3 Scope of Work	6
1.4 Organization of Thesis	7
CHAPTER 2 LITERATURE REVIEW	9
2.1 Introduction	10
2.2 Photochemical Oxidation Technologies in Water Treatment	11
2.3 Heterogeneous Photocatalysis	12
2.4 Introduction of TiO ₂ Photocatalyst	14
2.4.1 The Crystalline Phase of TiO ₂	14
2.4.2 The Energy Bandgap and Band-Edge Positions of TiO ₂	16
2.4.3 Mechanism of TiO ₂ Photocatalysis	17
2.4.3.1 Primary Reactions and Characteristic Times	17
2.4.3.2 Secondary Reactions and Formation of Reactive Oxygen Species	18
2.4.4 Langmuir-Hinshelwood Kinetics	20
2.4.5 Quantum Yield of TiO ₂	22
2.5 Quantum Size Effect	24

2.6	Limitation of TiO ₂ Application	27
2.7	Synthesis of Immobilized TiO ₂ Photocatalyst	28
2.8	Synthesis of TiO ₂ Microsphere Photocatalyst	29
2.9	Synthesis of Nano-structured TiO ₂ Microsphere	31
2.10	Sol-gel Method	32
2.11	Parameters Involved in Sol-gel Processing	34
2.11.1	Choice of Precursors	35
2.11.2	Type of Solvent and Its Mole Ratio to Precursors	36
2.11.3	Calcination Temperature	37
2.11.4	pH	39
2.12	Humic Substances	40
2.13	Humic Acids in Water Treatment	43
2.14	Removal of Humic Acids in Water	44
2.14.1	Coagulation Process	44
2.14.2	Membrane Filtration	45
2.14.3	Advanced Oxidation Process-TiO ₂ Photocatalysis	45
2.14.4	Adsorption of Humic Acid on TiO ₂	48
2.15	Role of Adsorption in Photocatalytic Oxidation Process	50
2.16	Summary	51
CHAPTER 3	MATERIALS AND METHODOLOGIES	53
3.1	Introduction	54
3.2	Synthesis and Characterization of Nano-structured TiO ₂ Microsphere	55
3.2.1	Materials	55
3.2.2	Titanium Coating Sol Preparation	55
3.2.3	Spray-coating Process	56
3.2.4	Characterization Method	57
3.3	Preparation and Characterization of Humic Acid	60

3.3.1	Materials	60
3.3.2	Preparation of Humic Acid Stock Solution	61
3.3.3	Characterization of Humic Acid	61
3.3.3.1	Elemental Analysis of C,N,S,H and O	62
3.3.3.2	Functional Groups of Humic Acid	63
3.3.3.3	High Performance Size Exclusion Chromatography	67
3.4	Batch Adsorption Study	70
3.5	Photocatalytic Oxidation Study	71
3.6	Analytical Test	72
3.6.1	Chemical Analysis of Phenol	72
3.6.2	Colour Analysis	72
3.6.3	Total Organic Carbon (TOC) Analysis	74
CHAPTER 4	SYNTHESIS AND CHARACTERIZATION OF NANO-STRUCTURED TITANIUM DIOXIDE MICROSPHERE	75
4.1	Introduction	76
4.2	Characterization of Titanium Coating Sol	78
4.2.1	Effect of Mole Ratio of Ethanol to Ti alkoxide	78
4.2.2	Effect of Calcination Temperature	84
4.3	Characterization of Nano-structured TiO ₂ Microsphere	90
4.3.1	Particle Size and Surface Morphology	90
4.3.2	BET Surface Area and Pore Structure	91
4.3.3	Adsorption Isotherm	93
4.3.4	XRD Analysis	94
4.4	Photocatalytic Activity of Nano-structured TiO ₂ Microsphere	95
4.5	Conclusion	101
CHAPTER 5	ADSORPTION STUDY OF HUMIC ACID ON NANO-STRUCTURED TITANIUM DIOXIDE MICROSPHERE	102

5.1	Introduction	103
5.2	Adsorption of HA on Nano-structured TiO ₂ Microsphere	105
5.2.1	Binary System: HA and Nano-structured TiO ₂ Microsphere	105
5.2.2	Ternary System: HA, Nano-structured TiO ₂ Microsphere and Ca ²⁺	107
5.3	Regression Analysis	110
5.4	Adsorption Isotherms	114
5.5	Equilibrium-based Adsorption Model	116
5.5.1	Langmuir Model	116
5.5.2	Freundlich Model	119
5.5.3	Langmuir-Freundlich (L-F) Model	124
5.6	Adsorption Kinetics of Humic Acid on Nano-structured TiO ₂ Microsphere	128
5.6.1	Diffusion-Controlled Adsorption Kinetics	129
5.6.2	Attachment-Controlled Adsorption Kinetics	131
5.7	Molecular Size Analysis of HA Molecules	133
5.8	Conclusion	135
CHAPTER 6	ADSORPTION MECHANISM OF HUMIC ACID ON NANO-STRUCTURED TITANIUM DIOXIDE MICROSPHERE	136
6.1	Introduction	137
6.2	Adsorption Capacity of Mesoporous Phase	140
6.3	Zeta Potential Analysis	141
6.3.1	Binary System	141
6.3.2	Ternary System	144
6.4	Surface Analysis by X-ray Photoelectron Spectroscopy (XPS)	149
6.4.1	XPS Analysis on Nano-structured TiO ₂ Microsphere	149
6.4.2	XPS Analysis on Adsorbed Nano-structured TiO ₂ Microsphere	152
6.5	Conclusion	161

CHAPTER 7	PHOTOCATALYTIC DEGRADATION OF HUMIC ACID BY NANO-STRUCTURED TITANIUM DIOXIDE MICROSPHERE	163
7.1	Introduction	164
7.2	Kinetics of photocatalytic degradation of humic acid by nano-structured TiO ₂ microsphere	165
7.2.1	Effect of initial concentration	167
7.2.2	Effect of pH	171
7.2.3	Effect of Ca ²⁺	172
7.3	Role of Pre-adsorption of HA in Photocatalytic Oxidation Degradation Process	175
7.3.1	Effect of pH	176
7.3.2	Effect of Ca ²⁺ ion	179
7.3.3	Discussion	180
7.4	Extent of Mineralization	184
7.5	Recycling of Nano-structured TiO ₂ Microsphere	185
7.6	Conclusion	186
CHAPTER 8	CONCLUSION AND RECOMMENDATION	187
8.1	Conclusion	188
8.2	Recommendation	191
REFERENCE		193
APPENDICES		
Appendix A		
Appendix B		
Appendix C		

LIST OF FIGURES

Figure 2.1	Crystal structures of rutile and anatase	15
Figure 2.2	Energy for various semiconductors in aqueous electrolytes at pH = 1	17
Figure 2.3	Mechanism of TiO ₂ photocatalysis	20
Figure 2.4	MO model for particle growth for N monomeric units	25
Figure 2.5	Model structure of humic acid	42
Figure 2.6	Model structure of fulvic acid	43
Figure 3.1	Schematic diagram of spraying coating process	57
Figure 3.2	FTIR spectra of humic acid	63
Figure 3.3	Molecular weight distribution of humic acid at pH 3, 7 and 9	68
Figure 3.4	Molecular weight distribution of humic acid at different pH conditions (with the presence of Ca ²⁺)	69
Figure 3.5	PCO reactor setup	71
Figure 4.1	XRD patterns of dried gels at different mole ratio of EtOH to alkoxide and calcinated at 450°C for 3 hrs	79
Figure 4.2	FESEM images of crystallites prepared at a) R = 4 and b) R = 25	82
Figure 4.3	FESEM images of crystallites prepared at a) R = 50 and b) R = 100	83
Figure 4.4	TG analysis of dried gel R50 at heating rate of 10°C/min	84
Figure 4.5	XRD patterns of dried gels at R50 calcinated at elevated temperature	85
Figure 4.6a	Effect of calcination temperature on the growth of anatase TiO ₂ crystallites for dried gel R50 at elevated temperature	86
Figure 4.6b	Effect of calcination time on the growth of anatase TiO ₂ crystallite size for dried gel R50 at increased calcination duration	86
Figure 4.7	BJH pore size distribution of dried gel R50 at elevated calcination temperature	87
Figure 4.8	SEM micrograph of nano-structured TiO ₂ microsphere	90
Figure 4.9a	SEM surface morphology of nano-structured TiO ₂ microsphere	91
Figure 4.9b	SEM surface morphology of P25 TiO ₂	91

Figure 4.10	BJH pore size distribution of P25 TiO ₂ and TiO ₂ microsphere	92
Figure 4.11	Adsorption and desorption isotherms for P25 TiO ₂ and nano-structured TiO ₂ microsphere	93
Figure 4.12	α_s plot for nano-structured TiO ₂ microsphere using P25 TiO ₂ as the reference material	94
Figure 4.13	XRD of P25 TiO ₂ , dried gel of R50 and nano-structured TiO ₂ microsphere	95
Figure 4.14	Photocatalytic degradation of phenol as a function of irradiation time (phenol concentration: 100 mg/L; photocatalyst mass concentration: 1g/L)	96
Figure 4.15	UV-reflectometry of TiO ₂ specimens	100
Figure 5.1	Effect of pH on adsorption of HA onto nano-structured TiO ₂ microsphere	105
Figure 5.2	Normal probability plots of residuals	107
Figure 5.3	Effect of Ca ²⁺ concentration on adsorption of HA on nano-structured TiO ₂ microsphere at different pH condition	108
Figure 5.4	Normal probability plots of residuals	110
Figure 5.5	Response surface plot for the adsorption extent versus pH and Ca ²⁺ concentration	113
Figure 5.6	Adsorption isotherms of humic acid on nano-structured TiO ₂ microsphere at pH 3, 7 and 9	115
Figure 5.7	Adsorption isotherms of humic acid on nano-structured TiO ₂ microsphere at pH 3, 7 and 9 in the presence of Ca ²⁺	116
Figure 5.8	The corresponding Langmuir plot of humic acid on nano-structured TiO ₂ microsphere at pH 3, 7 and 9	117
Figure 5.9	Freundlich model fitted to experimental results at different pH values	120
Figure 5.10	Freundlich model fitted to experimental results at different pH values in the presence of Ca ²⁺	120
Figure 5.11	Freundlich model fitted to experimental results at different pH values with increasing Ca ²⁺ in solutions (0, 20 and 50 ppm)	123
Figure 5.12	Fitted L-F isotherms at different pH solutions (3, 7 and 9)	125
Figure 5.13	Fitted L-F isotherms at different pH solution (3, 7 and 9) in the presence of Ca ²⁺	125
Figure 5.14	Adsorption kinetics of HA on nano-structured TiO ₂ microsphere at pH 3, 7 and 9	130
Figure 5.15	Adsorption kinetics of HA at pH 7 in different Ca ²⁺ concentration	131

Figure 5.16	Adsorption kinetics of HA on nano-structured TiO ₂ microsphere at pH 3, 7 and 9	132
Figure 5.17	Adsorption kinetics of HA at pH 7 in different Ca ²⁺ concentration	132
Figure 6.1	Zeta potentials of humic acid, TiO ₂ microsphere in ultrapure water and TiO ₂ microsphere in HA solution	141
Figure 6.2	Zeta potentials of nano-structured TiO ₂ microsphere in the absence and in the presence of Ca ²⁺ in ultrapure water	145
Figure 6.3	Zeta potentials of humic acid at a concentration of 20mg/L in the presence of Ca ²⁺	146
Figure 6.4	Zeta potentials of post-adsorption of nano-structured TiO ₂ microsphere in HA solution	147
Figure 6.5	Ti 2p XPS spectra of nano-structured TiO ₂ microsphere	149
Figure 6.6	XPS spectra of the O 1s peak of nano-structured TiO ₂ microsphere	150
Figure 6.7	XPS spectra for C 1s of nano-structured TiO ₂ microsphere	152
Figure 6.8a	XPS spectra of Ti 2p for the adsorbed nano-structured TiO ₂ microsphere at pH 7	153
Figure 6.8b	XPS spectra of Ti 2p for the adsorbed nano-structured TiO ₂ microsphere at pH 3	153
Figure 6.8c	XPS spectra of Ti 2p for the adsorbed nano-structured TiO ₂ microsphere at pH 7 associated with Ca ²⁺	153
Figure 6.9a	Decomposition of O1s spectrum for adsorbed nano-structured TiO ₂ microsphere at pH 7	156
Figure 6.9b	Decomposition of O1s spectrum for adsorbed nano-structured TiO ₂ microsphere at pH 3	156
Figure 6.9c	Decomposition of O1s spectrum for adsorbed nano-structured TiO ₂ microsphere at pH 7 with Ca ²⁺	156
Figure 6.10a	Decomposition of C 1s spectrum for adsorbed nano-structured TiO ₂ microsphere at pH 7	158
Figure 6.10b	Decomposition of C 1s spectrum for adsorbed nano-structured TiO ₂ microsphere at pH 3	158
Figure 6.10c	Decomposition of C 1s spectrum for adsorbed nano-structured TiO ₂ microsphere at pH 7 with Ca ²⁺	158
Figure 6.11	High resolution Ca 2p spectrum of adsorbed nano-structured TiO ₂ microsphere in the presence of Ca ²⁺ at pH 7	160
Figure 7.1	Effect of initial humic acid concentration on PCO degradation after attaining adsorption equilibrium	168
Figure 7.2	Effect of pH on photocatalytic degradation of HA after reaching adsorption equilibrium.	171
Figure 7.3	Effect of the presence of Ca ²⁺ on photocatalytic degradation of HA after reaching adsorption equilibrium at pH 7	173

Figure 7.4	Adsorption of HA in the dark for 2 hrs before PCO process	176
Figure 7.5	Adsorption of HA in dark for 2 hrs before PCO process at pH 7	179
Figure 7.6a	Schematic diagram showing the PCO degradation of HA by nano-structured TiO ₂ micropshere: Poorly adsorbed HA on TiO ₂ microsphere at pH 7 or without the presence of Ca ²⁺	181
Figure 7.6b	Schematic diagram showing the PCO degradation of HA by nano-structured TiO ₂ micropshere: Highly adsorbed HA on TiO ₂ microsphere at pH 3 or associated with the presence of Ca ²⁺ in solution	181
Figure 7.7	Removal of TOC vs irradiation time during PCO process	184
Figure 7.8	Recycling of nano-structured TiO ₂ microsphere in PCO degradation of HA	185

LIST OF TABLES

Table 3.1	Elemental analysis of humic acid	62
Table 3.2	General assignments of the FTIR spectra of humic acid	64
Table 3.3	Total acidity, carboxylic acidity and phenolic acidity of humic acid	67
Table 3.4	Summary of extinction coefficients for wavelength 254nm and 436nm at different pH conditions	73
Table 4.1	Crystallite size of anatase of dried gel calcinated at 450°C for 3hrs	80
Table 4.2	Total pore volume of dried gel R50 calcinated at different temperatures	88
Table 4.3	Summary of BET surface area and pore volume of TiO ₂ samples	92
Table 4.4	Pseudo-first-order kinetic parameters	97
Table 4.5	L-H kinetic parameters	98
Table 4.6	Comparison of photocatalytic activities of TiO ₂ specimens	98
Table 5.1	ANOVA analysis for effect of pH on HA adsorption	106
Table 5.2	ANOVA analysis for effect of pH and Ca ²⁺ concentration on HA adsorption	109
Table 5.3	ANOVA for the fitted second-order polynomial model	112
Table 5.4	Estimated parameters and their significance	112
Table 5.5	Langmuir adsorption model parameters for the adsorption of HA on nano-structured TiO ₂ microsphere	118
Table 5.6	Freundlich adsorption model parameters for the adsorption of HA on nano-structured TiO ₂	122
Table 5.7	Freundlich adsorption model parameters for the adsorption of HA on nano-structured TiO ₂ microsphere	123
Table 5.8	L-F fitting parameters for humic acid adsorption on nano-structured TiO ₂ microsphere	126
Table 5.9	Percentage of molecular weight of HA at different pH values	133
Table 5.10	Percentage of molecular weight of HA at different pH values (with the presence of Ca ²⁺)	134
Table 6.1	Reduction of BET surface area and total pore volume of nano-structured TiO ₂ microsphere after adsorption	140
Table 6.2	Comparison of the assignment of the peaks for OH and bulk O ²⁻ with literature values	151

Table 6.3	Comparison of the assignment of the peaks for Ti and bulk O^{2-} with literature values	151
Table 6.4	Binding energies, assignments and quantitative data for chemical peaks under the C 1s envelopes for HA adsorbed on nano-structured TiO_2 microsphere	159
Table 7.1	Effect of initial HA concentration on the Pseudo-first-order kinetic parameters	168
Table 7.2	Effect of initial concentration on the L-H kinetic parameters	168
Table 7.3	Calculated half-life values from Pseudo first order kinetic model, L-H kinetic model and observed half life values from experimental data at different initial HA concentration.	170
Table 7.4	Effect of pH on the L-H kinetic parameters	171
Table 7.5	Effect of presence of Ca^{2+} on the L-H kinetic parameters (at pH 7)	173
Table 7.6	Effect of pH on the L-H kinetic parameters after recalibration	178
Table 7.7	Effect of Ca^{2+} on the L-H kinetic parameters after recalibration	180

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Currently, many countries face mounting technical obstacles in removing natural organic matters (NOMs) from water, as they strive to meet ever tightening regulations on the drinking water quality. This pattern is going to continue in both the medium and long-term future. There is an increasing NOMs accumulation in surface water from degradation of lignin, carbohydrate and protein; and then through upland run-off. The most important group contributes to NOMs is humic acid (HA) as it accounts for a significant fraction (40-90%) of the dissolved NOMs found in nearly all water supplies (Kilduff et al., 1996). The presence of NOMs affects water quality adversely in several ways. They produce undesirable colour and taste; serve as a substrate for bacterial growth. They can complex heavy metals and trace organic contaminants such as pesticides, insecticides, herbicides and hormone etc. to yield high concentration of these substances and enhance their transportation in water. HA has been shown to be especially reactive with a variety of oxidants and disinfectants that are used for the purification of drinking water, particularly chlorine. These substances react with chlorine to produce trihalomethanes (THMs), haloacetic acids (HAAs), and a host of other halogenated disinfection by-products (DBPs), a number of which have been shown to cause cancers in laboratory animals. The US Environmental Protection Agency (USEPA) has established maximum contaminant levels for the sum of four THMs and five HAAs at 80 and 60 $\mu\text{g/L}$, respectively (USEPA, 1998). The health hazard is not only chlorination by-products, it was reported that an intake of a huge amount of HA might be one of the etiological factors for the Blackfoot disease. Hence the minimization of the HA presence in drinking water and other process water is of great importance.

The traditional treatment processes including adsorption, coagulation/flocculation, ozonation, and membrane technologies have been investigated and practised in the water treatment process for the removal of HA (Thorsen, 1999). Among these treatment processes, coagulation/flocculation is widely used for the removal of HA. However the coagulation/flocculation incurs a high operational cost and generates extra volume of sludge which requires further treatment and disposal. In addition, aluminium exposure has been suspected to develop the onset of Alzheimer's diseases (WHO, 1998). Ozonation is effective in removing HA, but the high operating cost restricts the technology from being widely used for removing HA from water. In addition, HA has been considered to be a significant foulant of membrane filtration and thus limit its application in this field.

Adsorption process is often used as a pretreatment process before the membrane process or used as an individual separation unit process to minimize the presence of NOMs, particularly HA. Various adsorbents such as activated carbon and metal oxides have been reported to adsorb HA in water. The application of activated carbon is not always technically advantageous due to the high regeneration cost involved and the need for further disposal. The adsorption of HA on metal oxides particularly titanium dioxide (TiO_2) has gained attention due to its regenerative characteristic. TiO_2 is the most popular one and often used as a photocatalyst in photocatalytic oxidation process (PCO) due to its non-toxicity, high oxidation strength, high chemical stability and inexpensiveness. The spent TiO_2 could be regenerated by UV light irradiation via PCO process. In view of this, TiO_2 possesses a potential to be an excellent adsorbent for the removal of HA in water treatment. However, there are some issues regarding the application of TiO_2 in current practice that need to be overcome.

Firstly, commercial TiO_2 , Degussa P25, with particle size of 25 to 30 nm, is not easily separated from treated water for reuse. Moreover, it easily agglomerates and loses photocatalytic activity in water. In order to overcome these disadvantages of the commercial TiO_2 fine powder, research was conducted by coating TiO_2 on support materials such as glass beads, glass fiber, sand, activated carbon, silica gel, reactor walls etc. using different coating technologies. However, PCO efficiency was decreased tremendously by limited adsorption mass transfer and light scattering/shielding. Therefore, separation of TiO_2 photocatalyst from water, prevention of TiO_2 agglomeration in water while maintaining or increasing TiO_2 adsorption mass transfer efficiency become the objective of this study. In addition, the photocatalytic activity of TiO_2 is also an issue that should not be overlooked. It was known that the photocatalytic activity of TiO_2 was always related to the crystallite phase and size. The photocatalysts would experience the quantum size effect if the crystallite size was ranged from 1 to 10 nm (Hoffmann et al., 1995). Hence it is important to control the crystallite size of TiO_2 in order to enhance its photocatalytic activity during the synthesis process.

Secondly, the adsorption behavior of HA onto metal oxides was not clearly defined by many researchers due to the nature of the adsorbent surface and adsorbate, and the solution condition. In addition, the roles played by various mechanisms which have been proposed to explain the interaction between HA and metal oxides such as electrostatic interaction, ligand exchange, hydrophobic interaction, cation bridging, entropic effect, hydrogen bonding, were less well understood. Different metal oxides and experimental conditions used by the individuals could attribute to the heterogeneity and complexity of HA and adsorbent surfaces. Because of these, different association mechanisms may be operative simultaneously and to varying degrees. In addition, for macromolecule like HA, solution chemistry such as pH and cation strength could also affect the conformation and hydration of the molecules,

and therefore will have an impact on the adsorption process. Hence the characterization of HA under different solution chemistry is indeed important in helping to understand the adsorption behavior of HA onto TiO_2 .

Although the removal of HA using TiO_2 PCO process had been studied extensively by many researchers, the photodegradation rate of HA under several operational parameters was merely investigated. Most of the researchers agreed that degradation efficiency of NOMs was higher in acidic condition and in the presence of cation, which are actually the favorable conditions for the adsorption of HA on TiO_2 surface. This phenomenon showed that there was, to a certain extent, dependency between the adsorption characteristics and the photodegradation rate. Hence, it is of interest to elucidate the role of adsorption of HA on TiO_2 prior to PCO process.

Hence it was indeed challenging to develop a novel nano-structured TiO_2 photocatalyst that has a large particle size (for separation and recovery purpose), with porous structure (for high adsorption ability) and small crystallite size for high photocatalytic activity in this study.

1.2 Objectives of Study

This study is aiming at developing a spherical TiO_2 photocatalyst in submicron size with high adsorption ability and photocatalytic activity for HA removal in water treatment process. The objectives of this study are:

- to synthesize and characterize a novel nano-structured TiO_2 microsphere with well defined crystallite size via sol-gel spray-coating method;
- to study the adsorption extent and rate of HA on nano-structured TiO_2 microsphere under various pH conditions and cation strengths, and further propose the interaction mechanisms between HA and TiO_2 ; and
- to study the photocatalytic activity of nano-structured TiO_2 microsphere in HA removal and the role of adsorption of HA in enhancing PCO process.

1.3 Scope of Work

- The first part of the study focused on the fabrication of TiO_2 microsphere via sol-gel method. The mole ratio of solvent to titanium alkoxide and calcination temperature were investigated to obtain the optimum fabrication method. The properties of resulting products were characterized using x-ray diffraction analysis, micropore analysis, thermogravimetric analysis, surface morphology analysis and UV-vis spectrophotometer.
- Synthetic HA prepared from commercially available HA powder and homemade TiO_2 microsphere were used for the adsorption and PCO process in this study. The HA adsorption using TiO_2 microsphere was investigated using

batch adsorption study. The influences of pH and calcium concentration on the adsorption process were examined. X-ray photoelectron spectroscopy and zetasizer were further used to investigate the interaction of HA and TiO₂ microsphere. The photocatalytic activity of TiO₂ microsphere for HA removal was assessed using PCO reactor. The influence of initial HA concentration, pH and calcium concentration on the PCO process were studied.

1.4 Organization of Thesis

The thesis was divided into 8 Chapters. Chapter 1 provided a general introduction on the impact of NOM in water treatment process and some issues regarding the application of TiO₂. Following which, will be the objectives of the research.

Literature review was presented in Chapter 2. Advanced oxidation processes (AOPs) were discussed particularly heterogeneous photocatalysis using TiO₂ photocatalyst, highlighting the principles, kinetics and current development of synthesis method of nano-sized TiO₂. A brief review on humic substances and treatment method were also discussed in detail.

The experiment methodology, procedure in synthesizing nano-structured TiO₂ microsphere, and characterization methods were presented in Chapter 3. It was followed by the experimental setup for adsorption and photodegradation of HA by nano-structured TiO₂ microsphere. Characterization results of HA used in this study was also included in this chapter.

Chapter 4 presented the results for the characterization study of the nano-structured TiO₂ microsphere. The effects of mole ratio of solvent to alkoxide and calcination

temperature on the growth of crystallite size were revealed in this chapter. The photocatalytic activity of nano-structured TiO₂ microsphere was evaluated as well.

Chapter 5 discussed the adsorption of HA onto nano-structured TiO₂ microsphere. The effect of solution chemistry on the adsorption extent and rate was presented. The interaction mechanism between HA and nano-structured TiO₂ microsphere was then proposed in next chapter.

The photocatalytic activity of nano-structured TiO₂ microsphere for the removal of HA and also the role of adsorption in enhancing PCO process were presented in Chapter 7. Conclusions were presented in Chapter 8 together with recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The literature review was divided into two parts. The first section gave a brief introduction of TiO_2 photocatalysis application for water treatment. The mechanism and kinetics of TiO_2 photocatalysis was reviewed. It was followed by the review on the quantum size effect which occurred for nano-sized TiO_2 . The nano-sized characteristic exhibited a unique property that was different from the bulk phase that projected to improve the photoactivity of TiO_2 and the quantum yield. However there were some limitations in the application of nano-sized TiO_2 that must be overcome. In view of this, various efforts had been done by other researchers to resolve the problems were reviewed extensively. A brief introduction on sol-gel method was given and the effect of several parameters including pH, type of precursors, choice of solvent, molar ratio of precursors to solvent, calcination temperature, were reviewed in this section too. The second part of the review discussed the role of humic substances particularly humic acid in water treatment process. The current removal strategies for humic acid were discussed, mainly photocatalytic oxidation process using TiO_2 .

2.2 Photochemical Oxidation Technologies in Water Treatment

There is an increasingly need for new and effective methods for detoxification, possibly complete mineralization of a wide range of organic compounds in water treatment. The traditional technologies typically include ultrafiltration, extraction, air stripping, carbon adsorption and others (Serpone and Khairutdinov, 1996). These technologies are non-destructive since the pollutant is merely transferred from aqueous phase to atmosphere or to solid phase. Photochemical processes provide alternative routes to water purification. UV irradiation in combination with other processes such as ozonation and peroxidation can remove dissolved organics and bacteria from solution. These photochemical oxidation reactions comprise Advanced Oxidation Technologies (AOTs) which employ a high energy source to induce chemical redox reactivity in a range of pollutants (Bahnemann et al., 1994). Both high energy-electron beam irradiation and ultraviolet (UV) light photoexcitation have been suggested as possible energy sources to initiate chemical reactions that attack and ultimately destroy undesirable components in water. UV light can be used in several ways:

- Direct photolysis of contaminants;
- homogeneous photocatalysis; and
- By heterogeneous photocatalysis.

In direct photolysis, the contaminants must absorb the incident light and subsequently degrade in its photochemically excited state. This process depends strongly on the sunlight absorptivity of the pollutants and in fact most of the contaminant is not highly active photochemically, thus this process is difficult to achieve under typical practical conditions. In UV-ozone or UV-H₂O₂ processes, the oxidative degradation occurs through the chemical generation of highly reactive hydroxyl radicals which is known to attack most organic compounds. Hydroxyl

radical ($\bullet\text{OH}$) will be formed during the UV photolysis contains ozone or hydrogen peroxide. However the efficiency of these processes depends on several factors: reactivity of the sensitizer, light absorbed by the solution or the additive, and quantity of the added oxidant. Heterogeneous photocatalysis appears to be a more attractive method for environmental detoxification. In this process, dispersed solid particles would absorb larger fractions of the UV spectrum efficiently and generate the chemical oxidant in situ from dissolved oxygen or water. These advantages make heterogeneous photocatalysis more attractive than the other two methods mentioned.

2.3 Heterogeneous Photocatalysis

Initial interest in heterogeneous photocatalysis was prompted by Fujishima and Honda's (1972) discovery that water could be splitted (simultaneously oxidized and reduced) upon illuminating a TiO_2 single crystal electrode to which a small electrochemical bias had been applied (Fox and Dulay, 1993). It soon became apparent that novel redox reactions of organic and other inorganic substrates could also be induced by band-gap irradiation of a variety of semiconductor particles. Heterogeneous photocatalysis describes a process whereby illumination of a semiconductor particle (TiO_2 and others) with UV/visible light of energy greater than or equal to the bandgap energy (E_{BG}) of the particular semiconductor device generates conduction band electrons (e^-_{CB}) and valence band holes (h^+_{VB}) (Bahnemann et al., 1994). This photogenerated electron-hole pair can then be captured by the surface of the solid photocatalyst. For example, the hole can be filled by electron transfer either from an adsorbed pollutant molecule or from an adsorbed water molecule. In the latter case, the hydroxyl radical will be formed. Alternatively, the photogenerated electron can be captured by oxygen adsorbed on the surface of the particle, completing the first step in the formation of superoxide

radical anion, hydroperoxide radical, hydrogen peroxide, or a hydroxyl radical. Subsequent chemical reactions by any of these species can induce oxidative degradation.

Most frequently, TiO_2 or ZnO have been used as the photocatalyst, since both efficiently absorb long wavelength UV light and are chemically stable to the reaction conditions. ZnO is not a desirable photocatalyst as compared to TiO_2 because it will be photocorroded by self-oxidization. It is unstable in the incongruous dissolution and may yield Zn(OH)_2 on the ZnO particle surfaces, leading to catalyst inactivation over time (Hoffmann et al., 1995). Other semiconductor particles such as CdS or GaP , can absorb larger fractions of the solar spectrum and form chemically activated surface bound intermediates, but unfortunately these photocatalysts will degrade during the repeated catalytic cycles involved in heterogeneous photocatalysis. The use of CdS has been limited since it will release environmentally harmful Cd^{2+} (Li and Wang, 1996).

Photocatalytic oxidation (PCO) with a primary focus on TiO_2 as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to water and air purification. The mineralization of several classes of compounds including chlorinated aromatics, surfactants, pesticides and herbicides has been studied (Chen and Ray, 1998; Chen et al., 1999; Chen and Ray, 1999; Topalov et al., 2000; Lewandowski and Ollis, 2003). It has also been shown to be useful for the destruction of microorganisms such as bacteria (Kühn et al., 2003; Sun et al., 2003) and viruses (Lee et al., 1997). In particular, for the removal of NOM mainly humic acids, several studies have also been conducted and reviewed (Bekbölet and Özköşemen, 1996; Eggins et al., 1997; Tay et al., 2001; Qiao et al., 2002; Wiszniowski et al., 2002). Moreover, TiO_2 is inexpensive, commercially available, non-toxic, non-polluting (the organic pollutants will completely

mineralized to carbon dioxide), stable under illumination, resistant to strong acid or base and display high catalysis activity. Hence interest for research on TiO_2 is increasing.

2.4 Introduction of TiO_2 Photocatalyst

Titanium dioxide (TiO_2) is an n-type semiconductor. It is widely used in heterogeneous catalysis, as a photocatalyst, in solar cells for the production of hydrogen and electric energy, as gas sensor, as white pigment (e.g. in paints and cosmetics products), as a corrosion-protective coating, as an optical coating, in ceramics, and in electric devices such as varistors. Its application in environmental field such as water purification, wastewater treatment, hazardous water control, air purification and water disinfection is well established and published elsewhere.

2.4.1 The Crystalline Phase of TiO_2

TiO_2 crystallizes in 3 major different structures: rutile, anatase and brookite. However, only rutile and anatase play the role in the application of TiO_2 . The tetragonal bulk unit cell of rutile has the dimensions, $a=b=4.587 \text{ \AA}$, $c=2.953 \text{ \AA}$, and that of anatase $a=b=3.782 \text{ \AA}$, $c=9.502 \text{ \AA}$. In both structures, the basic building block consists of a titanium atom surrounded by 6 oxygen atoms in a more or less distorted octahedral configuration. In each structure, the two bonds between the titanium and the oxygen atoms at the apices of the octahedron are slightly longer. A sizable deviation from a 90° bond angle is observed in anatase. In rutile, neighboring octahedron share one corner along (110) – type directions, and are stacked with their long axis alternating by 90° . In anatase, the corner-sharing octahedron forms (001) planes. They are connected with their edges with the plane of octahedral below. The stacking of the octahedral plane results in threefold

coordinated oxygen atoms. The two crystal structures differ by the distortion of each octahedron and by the assembly pattern on the octahedra chains. Figure 2.1 shows the unit cell structures of the rutile and anatase crystals.

Figure 2.1 Crystal structures of rutile and anatase. The bond lengths and angles of the octahedrally coordinated Ti atoms are indicated and the stacking of the octahedra in both structures is shown on the right side. (Diebold, 2003).

Anatase phase, the stable phase of TiO_2 at low temperature, has gained importance for photodecomposition and solar energy conversion because of its high photoactivity (Linsebigler et al., 1995; Reddy et al., 2001). Rutile is a stable phase of TiO_2 at high temperature. Anatase has been found in most of the cases that is more photoreactivity than rutile (Tsai and Cheng, 1997; Ding et al., 2000; Yu et al.,

2000; Jing et al., 2003). The poor photocatalytic activity of rutile was due to its lower band-gaps that leading to higher electron-hole recombination rate (Tsai and Cheng, 1997). There is much interest to synthesize single phase nano-crystalline anatase (Iwasaki et al., 1998; Zhang et al., 2001; Reddy, 2001).

2.4.2 The Energy Bandgap and Band-Edge Positions of TiO₂

A semiconductor is commonly characterized by the energy gap between its electronically populated valence band and its largely vacant conduction band. Irradiation of semiconductor particles with light energy greater than or equal to the bandgap of the semiconductor will promote an electron from the valence band to the conduction band. The energy levels and bandgap energies of several semiconductors are shown in Figure 2.2. The bandgap energy of TiO₂ is approximately 3.2 eV which is sufficient for promoting or catalyzing a wide range of chemical reactions.

Beside this, the band-edge position of TiO₂ is also important in photocatalysis. The ability of a semiconductor to behave as a photocatalyst for a redox reaction is governed by the position of its conduction and valence bands (band-edge positions). Figure 2.2 shows that TiO₂ has a valence band potential of +3.1 V and a conduction band potential of -0.1 V, relative to a normal hydrogen electrode (NHE). The positions are derived from the flat band potentials in a contact solution of aqueous electrolyte at pH = 1. The pH of the electrolyte solution influences the band-edge positions of the various semiconductors compared to the redox potentials for the adsorbate (Linsebigler et.al., 1995). Many organic compounds have a potential above that of the TiO₂ valence band and therefore can be oxidized.

Figure 2.2 Energy for various semiconductors in aqueous electrolytes at pH=1 (Linsebigler et al., 1995)

2.4.3 Mechanism of TiO₂ Photocatalysis

2.4.3.1 Primary Reactions and Characteristic Times

Hoffmann et al. (1995) has proposed the following general mechanism for heterogeneous photocatalysis on TiO₂. The characteristic times for the various steps are also provided.

Primary Process	Characteristic Times	
Charge-carrier generation		
$TiO_2 + h\nu \rightarrow h_{vb}^{+} + e_{cb}^{-}$	(femto s)	(2.1)
Charge-carrier trapping		
$h_{vb}^{+} + >Ti^{IV}OH \rightarrow \{>Ti^{IV}OH\}^{+}$	fast (10 nano s)	(2.2)
$e_{cb}^{-} + >Ti^{IV}OH \leftrightarrow \{>Ti^{III}OH\}$	shallow trap (100 piko s)	(2.3a)
	(dynamic equilibrium)

Charge-carrier recombination

Interfacial charge transfer

Where $>TiOH$ represents the primary hydrated surface functionality of TiO_2 , e_{cb}^- is a conduction band electron, e_{tr}^- is a trapped conduction band electron, h_{vb}^+ is a valence band hole, Red is an electron donor (reductant), O_X is an electron acceptor (oxidant), $\{>Ti^{IV}OH\}^+$ is the surface trapped valence band hole (surface bound hydroxyl radical) and $\{>Ti^{III}OH\}$ is the surface trapped conduction band electron. The dynamic equilibrium of equation 2.3a represents a reversible trapping of a conduction band electron in a shallow trap below the conduction band edge such that there is a finite probability that e_{tr}^- can be transferred back into the conduction band at room temperature.

2.4.3.2 Secondary Reactions and Formation of Reactive Oxygen Species

In most experiments and applications, oxygen is present as the primary electron acceptor. H_2O_2 is formed via the following mechanism as a consequence of two-electron reduction of oxygen. Hydroxyl radicals are also formed on the surface of TiO_2 by the reaction of h_{vb}^+ , with adsorbed H_2O , hydroxide, or surface titanol groups ($>TiOH$). H_2O_2 may contribute to the degradation of organic and inorganic electron donors by acting as a direct electron acceptor or as a direct source of

hydroxyl radicals. H_2O_2 can theoretically be formed via two different pathways as follows:

It is clear that the main mechanism of the PCO process is the photogeneration of electron-hole pairs. It is assumed that the substrate does not undergo direct hole transfer and that oxidative electron transfer occurs exclusively through a surface bound hydroxyl radical, $\{>TiOH\bullet\}^+$ or equivalent trapped hole species. Hence, oxidation may occur by either indirect oxidation via the surface bound hydroxyl radical (trapped hole at the particle surface) or directly via the valence-band hole before it is trapped either within the particle or at the particle surface. For the indirect oxidation, the radicals formed will react with substrates in solution to yield oxidized products. While for direct oxidation, the substrate is first adsorbed onto the catalyst surface and then reacts with valence band hole to produce the final products (Hoffmann et al., 1995). Generally, the mechanisms of TiO_2 photocatalysis as referred to Figure 2.3 can be summarized as follows:

- (1) Formation of charge carriers by a photon;
- (2) Charge carrier recombination to liberate heat;
- (3) Initiation of an oxidative pathway by a valence-band hole;
- (4) Initiation of an reductive pathway by a conduction-band electron;
- (5) Further thermal (hydrolysis or reaction with active oxygen species) and photocatalytic reactions to yield mineralization products;
- (6) Trapping of a conduction-band electron to yield $Ti(III)$; and
- (7) Trapping of a valence-band hole at a surface titanol group.

Figure 2.3 Mechanism of TiO₂ photocatalysis (Hoffmann et al., 1995)

2.4.4 Langmuir-Hinshelwood Kinetics

In most of the studies, Langmuir-Hinshelwood model has been used to describe the degradation rate expression in terms of the disappearance of compounds or the formation of CO₂ (Bahnemann et al., 1994; Hoffmann et al., 1995; Chen and Ray, 1999; Li et al., 2004). The kinetics of TiO₂ PCO degradation process can be expressed in terms of Langmuir-Hinshelwood equation in the following form:

$$r = -\frac{dC}{dt} = k_{LH} KC / (1 + KC) \quad (2.10)$$

where r is the reaction rate, k_{LH} is an apparent reaction rate constant, K is the adsorption equilibrium constant of the reactant on the surface of the catalyst, C is the concentration of reactant. By integration of the above equation, the half-life is expressed as:

$$t_{1/2} = \frac{0.693}{k_{LH}K} + \frac{0.5C_o}{k_{LH}} \quad (2.11)$$

where C_o is the initial concentration of the solute.

It is clear that equation 2.11 will change to the Pseudo first order kinetics form when KC is much less than one (low concentration),

$$r = -\frac{dC}{dt} = kC \quad (2.12)$$

k is a pseudo first order rate constant. The corresponding half-life value is expressed as follows:

$$t_{1/2} = \frac{0.693}{k} \quad (2.13)$$

In the Langmuir-Hinselwood equation, the K value obtained is a PCO “kinetic –related” adsorption-desorption equilibrium constant. K is denoted by K^* to distinguish it from the K_{ads} values obtained directly from adsorption measurements (K_{ads} is adsorption equilibrium constant). It is important to understand the pre-equilibrium adsorption and the rate-determining reactions events within an adsorbed monolayer at the TiO_2 aqueous solution interface. It was suggested that the preliminary adsorption of substrate on the catalyst surface was a prerequisite for a more efficient oxidation (Matthews, 1988; Xu and Langford, 2001). Direct oxidation of substrates by a valence band hole occurs as the main mechanism throughout the process. In view of this, much effort had been addressed to the effect of adsorption (Cunningham et al., 1994; Zhang et al., 1998; Wu et al., 1999). In all these studies, the removal rate of the substrate was determined from the decreased concentration of the substrate in the aqueous phase. However for a target substrate that has high adsorption on the TiO_2 or supported TiO_2 catalyst, L-H type photodegradation might not represent the real removal rate. The total amount of the substrate degraded after irradiation might not exactly equal to the amount of the substrate lost in the aqueous phase. Hence the role of adsorption in relation to TiO_2 photocatalyzed degradation of targeted compound will be investigated in this study.

2.4.5 Quantum Yield of TiO₂

The efficiency of the photocatalytic process is measured as a quantum yield: the number of events occurring per photon absorbed. To be more specific, quantum yield can be defined as the ratio of electron-hole pairs involved in redox reactions at the surface of TiO₂ particles to total electron-hole pairs generated. The photon generated electrons and holes will migrate to the surface and serve as redox sources that react with adsorbed reactants, leading to the destruction of pollutants. Normally, it is very difficult to measure the actual absorbed light in heterogeneous systems due to the scattering of light by the semiconductor surface. It is usually assumed that all the light is absorbed and the efficiency is quoted as apparent quantum yield. If several products are formed from the photocatalytic reaction then the efficiency is sometimes measured as the yield of a particular product. The quantum yield for an ideal system, ϕ , is given by the simple relationship (Linsebigler et.al., 1995) :

$$\phi \propto \frac{k_{CT}}{k_{CT} + k_R} \quad (2.14)$$

ϕ is proportional to the rate of the charge transfer processes (k_{CT}) and inversely proportional to the sum of the charge transfer rate (k_{CT}) and the electron-hole recombination rate (k_R) (bulk and surface). It is assumed that diffusion of the products into the solution occurs quickly without the reverse reaction of electrons recombining with donors, and holes recombining with acceptors. Without recombination, the quantum yield will take on the ideal value of 1 for the photocatalytic process. However, in a real system recombination does occur and the concentration of electrons and holes at the surface is not equal.

Therefore, the overall quantum efficiency for interfacial charge transfer is determined by two critical processes: the competition between charge carrier recombination and trapping (picoseconds to nanoseconds), and followed by the competition between trapped carrier recombination and interfacial charge transfer (microseconds to milliseconds). It is believed that the increase in either the recombination lifetime of charge carriers or the interfacial electron-transfer rate constant will result in higher photoreactivity of TiO_2 . The different recombination lifetimes and interfacial electron transfer rate constant may be due to the different preparation methods of the samples that result in different crystal defect structures and surface morphologies (Linsebigler et al., 1995).

In order to enhance interfacial charge-transfer reactions of TiO_2 , the properties of the particles have been modified by selective surface treatments such as addition of metals, dopants, or combination with other semiconductors. Surface modifications are beneficial in decreasing the electron and hole recombination rate and thereby increasing the quantum yield of the photocatalytic process. These methods were extensively discussed in several reviews (Hoffmann et al., 1995; Agrios and Pichat, 2005; Ni et al., 2007). Alternatively the synthesis of TiO_2 in nano scale might improve the photoactivity of TiO_2 and subsequently the quantum yield.

Nano-particles represent a state of matter in the transition region between bulk solids and molecular structures. Their physical and chemical properties gradually change from solid state behavior to molecular with decreasing particle size. The sizes of the individual particles are normally in the range of 1 – 100 nm in diameter (Siegel, 1993; Kurihara, 2000). A unique property of nano-particles is their extremely high surface area. They have many more sites for achieving property enhancements, making them ideal for a wide variety of applications. The nano-sized

properties are believed to trigger the quantum size effect for semiconductor particles.

2.5 Quantum Size Effect

Quantum size effect (QSE) is a phenomenon occurs for semiconductor particles on the order of 1-10 nm in size. The anomalies arise when the size of the semiconductor particles become comparable to the de Broglie wavelength of the charge carriers in the semiconductor. The electron and hole produced are confined in a potential well of small geometrical dimensions, and do not experience the electronic delocalization present in the bulk semiconductor possessing a conduction band and a valence band. Instead, the confinement produces a quantization of discrete electronic states and increases the effective band gap of the semiconductor (Linsebigler et al., 1995). Such effects can change the spectra properties of the material (due to the altered optical absorption maxima) and the photocatalytic properties. The band edges would also shift to yield larger redox potentials. For example, the band gap increases and the band edges shift to yield larger redox potentials as shown in figure 2.4 by Hoffman et al. (1995). Thus Q-sized TiO_2 particles may result in increased photoefficiencies for systems in which the rate limiting step is charge transfer.

Figure 2.4 MO model for particle growth for N monomeric units. (Hoffmann et al., 1995.)

LUMO: lowest unoccupied molecular orbital

HOMO: highest occupied molecular orbital

The band gap is determined from the threshold of the absorption edge of these microcrystallites. For a semiconductor particle displaying size quantization, the increase in band gap energy ΔE_g can be approximated using Equation (2.15) (Serpone et al., 1995):

$$\Delta E_g = \frac{h^2 \pi^2}{2R^2} \left\{ \frac{1}{m_e} + \frac{1}{m_h} \right\} - 1.786 e^2 / \epsilon R (0.248 E_{RY}) \quad (2.15)$$

where h is the reduced Planck's constant taken as 1.0545×10^{-34} ; R , is the radius of the particle; E_{RY} , is the effective Rydberg energy calculated to be 4.3×10^{-39} J; ϵ is the dielectric constant of anatase $\text{TiO}_2 = 86$; m_e and m_h are the electron and hole masses, respectively. From this relation, ΔE_g for an average particle size of 5-10 nm is calculated to be around 0.1-0.2 eV. This provides an estimate for the bandgap E_g for the synthesized TiO_2 to be about 3.3-3.4 eV and for the commercial sample it is about 3.2 eV with a crystallite size of 39 nm (Reddy et al., 2002). Hence, this model

predicts an increase in the bandgap with decrease in particle size. The size dependent shift in the bandgap is found to be 0.1-0.2 eV. Photocatalytic activity of TiO_2 will increase with increasing of magnitude of the blue shift in the bandgap (Serpone et al., 1995).

Anpo et al. (1987) first revealed that the photocatalytic efficiency of semiconductor particle was dependent on particle size. The photocatalytic activity increased as diameter of TiO_2 particle became smaller (<10 nm). The photocatalytic activity of the TiO_2 was strongly influenced by crystal size (Maira et al., 2000; Almquist and Biswas, 2002). As the size of TiO_2 diminished, the surface structure of the atom ensembles can deviate from that of a bulk crystal. This could result in a significant difference in the number and types of catalytic sites present in nanocrystals and that of a larger crystal. It had been shown that the adsorption of organics onto surfaces of nano-crystalline TiO_2 was size dependent and that particle size was a crucial factor in decomposition of substrates (Zhang et al., 1999). The smaller crystals had a larger surface area for the adsorption of reactants. This would make a positive contribution to the catalyst reactivity. Xu et al. (1999) also suggested that the absorption rate and adsorbility of Methylene Blue on TiO_2 particle increased as the particle size decreased, especially when the particle size is less than 30 nm. It was found that most of the nano-sized TiO_2 experience QSE that could subsequently lead to high photocatalytic activity.

However, Wang et al. (1997) reported that the photocatalytic efficiency did not monotonically increase with decreasing particle size, and there existed an optimal particle size of about 10 nm for pure nano-crystalline TiO_2 photocatalyst in the aqueous-phase decomposition of chloroform. The opposing effect of large surface area was higher rate of electron-hole recombination at the particle surface, due to the enhanced proximity of the charges. On the other hand, a model developed by

Gerischer (1995) was able to predict a significant increase in quantum yield as particle size decreases from 1000 to 10 nm. A higher fraction of the electron-hole pairs was partaking in redox reactions at the surface when fewer electron-holes were generated within the particle. Grela and Colussi (1996) developed a numerical stochastic model that predicted an increase in quantum yield as particle size increased from 3 to 21 nm.

From the above literature review, it was found that the nano-sized particles possessed a unique characteristic that was different from the bulk phase. Only an optimum range of nano particle size could actually increase the band gap of TiO_2 and subsequently increase quantum yield, resulting in higher photocatalytic activity. Therefore the control of particle size during the synthesis process was indeed crucial to attain the quantum size effect.

2.6 Limitation of TiO_2 Application

The most commonly used commercial TiO_2 photocatalyst is Degussa P25 with an anatase to rutile ratio of 70:30 (Mills and Le Hunte, 1997). It has a surface area of $50 \pm 15 \text{ m}^2/\text{g}$ and an average particle diameter by number count of 21 nm. It is a high surface area powder which is not thermally stable and loses surface area readily (Hanprasopwattana et al., 1996; Zhang et al., 2003). These TiO_2 photocatalyst particles usually do not present individually in aqueous system, but rather as physically unstable complex primary aggregates ranging from 25 nm to $0.1 \text{ }\mu\text{m}$ (Mills and Le Hunte, 1997). These physically unstable complex aggregates would reduce the surface area and create problems for separation and recovery in engineering application (Jing et al., 2003; Fang, 2003; Xie and Yuan, 2003). Even though TiO_2 is harmless to environment, the photocatalyst particles must be filtered prior to the discharge of the treated water. On the other hand, photocatalytic activity

of TiO_2 is also an important aspect that should not be overlooked. It was suggested that the photocatalytic activity is strongly dependent on its morphological and crystallographical properties (Yu et al., 2002).

2.7 Synthesis of Immobilized TiO_2 Photocatalyst

In general, the photocatalyst has been used in two forms: suspended in aqueous solutions in the form of slurry and immobilized onto rigid inert supports. In the former case, a high ratio of illuminated surface of photocatalyst to the effective reactor volume can be achieved for small well-designed photocatalytic reactors and almost no mass transfer limitation exists since the maximum diffusional distance is very small resulting from the use of ultra-fine (<30 nm) particles (Chen et al., 2001).

To resolve the separation problem, many supported photocatalysts of TiO_2 were prepared by immobilizing or coating a thin film of photocatalysts on the surfaces of many carriers such as glass, fiber or stainless steel (Byrne et al., 1998; Yu et al., 2000; Sonawane et al., 2002; Jing et al., 2003). However, the immobilization of TiO_2 on supports also created some problems. There are at least two problems arising from this arrangement: the accessibility of the catalytic surface to the photons and the reactants, and significant influence of external mass transfer particularly at low fluid flow rate, due to increasing diffusional length of reactant from bulk solution to the catalyst surface (Chen et al., 2001; Rachel et al., 2002; Shephard et al., 2002; Li et al., 2003). Hence the overall photocatalyzed degradation rate is lower as compared with the suspended system (Zhang et al., 2003). Rachel and his groups (2002) claimed that the efficiency of photoactivity using the immobilized photocatalysts could be drastically declined to only 1/200 of that using TiO_2 slurry. On the other hand, TiO_2 particles might fall off easily from the carriers

after a long period of usage. In addition, the presence of foreign cations from the support used inhibited the crystallization of TiO_2 which subsequent led to a drastic decrease in photocatalytic activity of these TiO_2 films (Guillard et al., 2002).

Therefore, a possibly practical alternative would be maintaining the supported catalyst in a suspension form. Efforts have been devoted in recent years to coating TiO_2 on supports or free carriers such as polystyrene bead (Fabiya and Skelton, 2000; Yin et al., 2003), carbon (Ding et al., 2001; Nagaoka et al., 2002), silica (Hanprasopwattana et al., 1996; Holgado et al., 2000; Haraguchi et al., 2004), hematite (Qiao et al., 2002; Sun et al., 2004), γ -alumina (Ding et al., 2001). However, the advantage of good contact with a light source was kept to some degree. It was found that the attachment of TiO_2 powder on those free carriers was not strong enough for a long period of operation from an engineering point of view (Li et al., 2003). Hence, this study aimed at developing a new submicron size TiO_2 that could be easily separated from treated water, with high photocatalytic activity and also sufficient mechanical strength for a long term operation.

2.8 Synthesis of TiO_2 Microsphere Photocatalyst

Some researchers reported the synthesis of submicron TiO_2 microsphere which would possess an effective separation (Rubio et al., 1997; Li et al., 2003; Ren et al., 2003; Zhang et al., 2003; Eiden-Assmann et al., 2004). The TiO_2 microsphere in suspension can be easily fluidized by air bubbling and simply settled by gravity after reaction. Another advantage of these spherical photocatalysts is the high adsorption ability due to their porous structure. A porous structure usually coupled with large surface area and big pore volume which favor the adsorption of organic compound onto the photocatalyst. High adsorption of organic compounds on the surface of the photocatalyst will enhance the direct oxidation by valence-band hole.

Most of the synthesis involved the use of both organic and inorganic modifiers to create the porous structure by adding to the sol-gel precursor solution. The resulting products would have a well-defined pore structure after decomposition of modifiers during calcination. Polyethylene glycol (PEG) is a common used organic modifier in the sol preparation (Kato and Niihara, 1997; Nagaoka et al., 2002; Trung et al., 2003). It was found that PEG would affect the crystallization by remaining in the coating at temperature as high as 400°C and decomposing to carbon dioxide at the temperature just before the crystallization of the coating. The sols with added PEG tend to precipitate, hence the coating sol prepared cannot be stored for a long period (Balasubramanian et al., 2003).

Some of the latest methods used for the production of porous TiO₂ structures involve sol-gel processes and templating procedures of polymers (Zhang et al., 2005), metals (Yang et al., 2005) or ceramics (Caruso et al., 1998; Zhao et al., 2005). Templating is an approach which able to tailor the inner structural arrangements, such as pore size and overall porosity, followed by the outer shape and the size of the sample (Shchukin and Caruso, 2004). The polymer template is an entity that can be modified in shape and size by the use of different surfactants, different surfactant to water ratios, different monomers and different combinations of monomer and surfactant. Therefore, the final TiO₂ network could be produced to tailor-fit numerous systems. The polymer gel template is conveniently removed during the calcinations process. A nano-crystal grain TiO₂ porous microsphere was prepared by reversed suspension polymerization and sol-gel method using monomer droplet (Zhang et al., 2003). Shchukin and Caruso (2004) used porous polymeric beads as templates for the fabrication of porous metal oxide spheres. Wang et al. (2000b) reported the synthesis of mesoporous TiO₂ spheres with the particle sizes ranging from submicrometer to micrometer by using neutral surfactant dodecylamine. Ren et al. (2003) also reported the synthesis of TiO₂ microsphere

with the assistance of nonionic poly(alkylene oxide) surfactant. In this method, the final porous monolithic or film structures could not be dispersed in solution without structural modification to break the samples into smaller pieces. Hence the templating of “individual entities” required extreme care to allow infiltration and coating while preventing aggregation of the material. There was also the possibility that the templates cannot be removed completely during the calcinations process. In this case, this would affect the degree of crystallinity of the TiO_2 . Different templates would have different decomposition temperature. Hence they might not compromise with the optimum calcination temperature for phase transformation of TiO_2 especially if the low temperature to form anatase phase was preferred.

2.9 Synthesis of Nano-structured TiO_2 Microsphere

Nano-structured material is a term used to describe any material produced or composed in which the scale of the main microstructural features is ultra-fine, usually in the range 1 to 100 nm (Siegel, 1993; Kumzerov, 2000; Kurihara, 2000). Hence the nano-structured material might come into view at the size of submicron. It has a feature of high fraction of atoms that reside at grain boundaries or interfaces in the material (Kear and Mayo, 2000). The basic idea of nano-structured materials is to generate a new class of solids (differing structurally and property wise from crystals and glasses) by incorporating defects or grain boundaries into an initially perfect crystal that these defects become comparable to the fraction of atoms in the residual crystals (Gleiter, 1993). Depending on the type of defects incorporated, different kinds of nano-structured materials will be resulted. However, all of these materials have the microstructural feature in common.

In this study, a novel nano-structured TiO_2 microsphere was synthesized by embedding the size-selected anatase nano-particles in a porous matrix or core via

chemical coating. The coating that enters the inner surfaces of the pores in different porous matrices will create new types of nano-structures. Hence the nano-structured photocatalyst is always related to high porous structure and high surface area. The high surface area allows maximum contact between the network and reaction media. It will promote the continuity of the network by preventing traps or dead spots. The nano-structured TiO_2 microsphere is formed via sol-gel spray-coating process without using PEG or polymer templates. P25 will be used as a core/nuclei site for the synthesis of submicron TiO_2 microsphere, which will be bounded using titanium coating sol that would eventually transform into anatase crystallite. The resulting product will be a submicron microsphere which comprised of nano-sized anatase crystallite. The control of several parameters such as mole ratio of solvent to alkoxides and calcination temperature are hypothetical that will play the key role in synthesis.

2.10 Sol-gel Method

There has been a growing interest in using chemical routes for the synthesis because of the many advantages as compared to the other technologies. The advantages of chemical routes include the ability to control the chemical composition, the particle size distribution, agglomerate size distribution, particle morphology, porosity, low temperature processing, bulk quantity production and cost effectiveness. Examples of chemical routes used for preparing nano-structured coatings are sol-gel processing, electroplating, electroless plating, electrophoretic deposition and electrolytic anodization.

Sol-gel processing which is based on inorganic polymerization reactions, can loosely be defined as the preparation of inorganic oxides such as glasses and

ceramics by wet chemical methods (Brinker and Scherer, 1990). The sol-gel technique has been extensively used for the synthesizing of nano-sized material.

Sol-gel processing can control the structure of a material on a nanometer scale from the earliest stages of processing. This approach to material synthesis begins with reaction of organometallic precursors and solvents to obtain the gels. The gels may form by the network growth from an array of discrete particles or by formation of an interconnected 3-D network by the simultaneous hydrolysis and polycondensation of organometallic precursors. The size of the sol particles and the cross-linking between the particles depend on factors such as pH, solution composition, and temperature etc. Thus by controlling the experimental conditions, one can obtain the nano-structured target materials in the form of powder or thin film. Based on different kinds of precursors, the sol-gel processing is roughly divided into three branches: silica sol-gel processing, metal alkoxide processing and Pechini-type processing.

Metal alkoxides as precursors in the sol-gel process will undergo hydrolysis which is the main step in the transformation of alkoxides to oxides. All metals are capable of forming an alkoxide in which an alkyl group is bonded to the metal by means of oxygen atom. The number of alkyls bonded depends on the valence of the metal. Metal alkoxides have the general formula $\text{Me}(\text{OR})_x$ in which Me is a metal with valence x and O is oxygen that is used to bond the alkyl group, R, to the metal at each valence site.

Sol-gel processing involves 2 major reactions: hydrolysis and condensation. Equations 2.16 to 2.18 briefly described the reactions (Brinker and Scherer, 1990):

The precursors of metal alkoxides will be hydrolyzed upon addition of water or react with alcohols:

where if m is up to x , then the reaction is total hydrolysis, followed by either a water condensation,

or an alcohol condensation,

Where R is typically alkyl group, Me is the required metallic cations and x is the valence of cations.

2.11 Parameters Involved in Sol-gel Processing

There was no standard procedure stated in sol-gel method. But it was well established from the studies done by many researchers that the sol-gel processing can be controlled by several process parameters such as mole ratio of solvent to precursor, pH conditions, acid or basic catalyst, type of solvent, calcination temperature etc. Once process parameters have been found, the crystallite size of resulting products can be easily tailored.

2.11.1 Choice of Precursors

In sol-gel process, the metal alkoxides Ti(OR)_4 are generally used as precursors. Further hydrolysis creates clusters containing many oxides molecules and subsequent polymerization causes the formation of a three-dimensional network with octahedral TiO_6 coordination. The fundamental chemical process is based on hydrolysis and condensation reactions, which lead to the formation of macromolecular networks. If hydrolysis proceeded slowly, the resultant films were very thin, relatively smooth and non light absorbing. On the other hand, very high hydrolysis rates were also unfavourable since they led to the formation of large aggregates. There have been several reports about the formation of sol-gel TiO_2 thin films and it was well established that the choice of the precursor strongly influences the final film properties (Falaras and Xagas, 2002; Ting and Chen, 2001; Babonneau et al., 1988).

Generally alkoxides with large alkyl groups hydrolyzed slowly and diffused slowly. Since polymerization required partial hydrolysis and diffusion, larger alkoxides tended to produce smaller polymeric condensations; as a consequence the oxide component of their molecules was smaller. Therefore the use of the larger alkyl groups of alkoxides would be helpful for achieving nano-structured products (Yan et al., 2003). This was in agreement with research conducted by Falaras and Xagas (2002). They used two different titanium (IV) alkoxides : titanium isopropoxide and titanium butoxide as the precursors in preparing the TiO_2 films. The titanium isopropoxide presented higher hydrolysis rates leading to more rough and complex characteristics whereas titanium butoxide films showed a relatively smoother surface. The mechanism of the polymerization followed SN_2 type, including a nucleophilic attack of titanium metal center and steric hindrance by the presence of the alkyl groups. Thus the bulkier butoxide ligand was expected to impede the access to the titanium atom, inhibiting the propagation of hydrolysis as compared to

less bulky isopropoxide. This was in concurrence with Ting and Chen (2001) who claimed that the chemical reactivity of the ligand and groups initially coordinated on the titanium precursor plays a decisive role in the structure development of sol-gel TiO₂ films.

2.11.2 Type of Solvent and Its Mole Ratio to Precursors

Most sol-gel processes are preferably accomplished in a common solvent. Alcohol is the substance usually chosen as the common solvent. The choice of alcohol should be made by availability, toxicity, solubility of the possible salts used in the selected alcohol and properties such as boiling point. The host medium of the condensation of process also affects the diffusion rates. The hydrolytic condensation of alkoxides carried out in lower alcohol yields material with a higher equivalent oxide content, reflecting a greater degree of polymerization as well as the ester exchange of heavier alkyls with lighter alkyls. Type of solvent used in the synthesis step would affect the structure and catalytic behavior of the resulting products (Capel-Sanchez et al., 2003). In their work on the synthesis of amorphous Ti/SiO₂ catalyst, it was found that the amount of titanium incorporated to the silica depends strongly on the solvent used in the hydrolysis/anchorage step of the Ti precursor.

Evaporation rate of the solvent was indeed a critical component of depositing thin films on the substrates (Haas and Quijada, 2000). A faster evaporation resulted in thicker final film thickness, while slower evaporation leaves more time for fluid out-flow and gives a thinner final coating. Hence the choice of the solvent is important in sol preparation. At the same time, the mole ratio of solvent to precursor is also important in preparing the coating sol. The mole ratio of solvent to precursor must exceed a critical value (value corresponds to the maximum specific surface

area), the hydrolysis is more complete and more alkoxides convert to the corresponding metal hydrates (Yu and Wang, 2000). Ito et al. (1999) revealed that the volume ratio of H₂O to EtOH was the key for crystallinity of the particles.

2.11.3 Calcination Temperature

During calcination, pore reduction occurs due to a process of particle bonding by thermal energy. The driving force is a reduction in surface area and therefore is a reduction in surface energy of the system. Usually calcination is conducted in oxygen-rich atmospheres to ensure a clean burnout of organics and also to enhance the formation of the target crystal phase at lower temperature. The amorphous particles resulting from thermal decomposition process could form well crystallized products. If gels are heat-treated by elevating temperature at a certain heating rate, thermal decomposition of gels and crystallization of oxides take place in sequence. The crystallite size is increasing as the calcination temperature increases. Longer calcinations time is believed to produce more crystallized samples. So contradiction is arising on optimum calcination temperature to obtain a desired particle size with better crystallinity. Many research have been carried out on the effect of calcination temperature in improving the photoactivity of TiO₂. However, the optimum calcination temperature during the preparation of catalyst was not usually established, and different studies were insufficiently defined to allow ready comparison.

Calcination is a common phase-change treatment used to increase photocatalytic activity, although it is unclear how it affected the physicochemical parameters either by controlling the crystallite size to enhance the QSE or improving the crystallinity of the catalysts (Zhang et al., 2000). In general, increasing the calcination temperature could also improve the adhesion of the TiO₂ film onto the substrates

(Jing et al., 2003). The activities were found to depend on the calcination temperature of the catalysts (Tsai and Cheng, 1997).

It was known that the anatase phase played a vital role in photocatalytic activity of TiO_2 . Hence the transformation from amorphous phase to anatase phase was promoted by the calcination. An opposing effect was observed with increasing calcination temperature, the increase of anatase crystallinity and associated with the decrease of specific surface area (Hague and Mayo, 1993; Ito, et al., 1999; Negishi and Takeuchi, 1999). The pore diameter of the thin films increased and pore volume decreased with increasing calcinations temperature. They reported that the nano-pores lost at higher calcination temperature. Kim et al. (2002) and Ahn et al. (2003) found that the TiO_2 thin films calcined at 400-900°C were anatase and the anatase to rutile phase transformation occurred at 1000°C. Authors claimed that the phase transformation temperature turned out to rely upon the concentration of catalyst HCl during the preparation.

Porter et al. (1999) studied the effect of calcination on the microstructural characteristics and photoreactivity of a commercial photocatalyst Degussa P25. They claimed that the sample calcined at 650°C for 3 hours obtained the highest photoreactivity, which could be ascribed to an improvement in crystallinity on calcination. Zhang et al. (2000) showed that the improved crystallinity by calcination at 400°C increased the photoactivity of catalyst. But after calcination at 600°C, the photoactivity decreased significantly as semiconductors of larger size resulted in the recombination of electrons and holes at higher rate. This was dissimilar to Jing et al. (2003) who claimed that 600°C was the appropriate calcining temperature during the preparation process of nanoparticle TiO_2/Ti film photocatalyst.

Besides improving the crystallinity of the catalyst, calcination would also affect the crystallite size of the primary particle. Kim et al. (2002) showed that the crystallite size of anatase phase increased about 3.9 times from 9.6 to 38.2 nm with increasing temperature from 400°C to 1000°C, respectively. The crystallite size was about 30 to 40 nm in size at 700°C and increased markedly by a factor of 10 at 1000°C.

In conclusion, most research agreed that changes in the morphology of the TiO₂ thin films are related to the calcination temperature. However, the effect of calcination duration was seldom mentioned in those reviews. Hence the optimum calcination temperature and also the calcination duration will be studied in order to obtain the high specific surface area, and desired crystallinity with optimum crystallite size, and also a good adhesion onto the substrate.

2.11.4 pH

Acidic or basic hydrolyzing agents can affect the pore structure of the gel (Brinker and Scherer, 1990). In basic conditions, both partially and totally hydrolyzed monomers would create more densely, highly branched, crosslinked polymers. A densely crosslinked structure would result in a larger pore size upon gelation. On the other hand, acidic conditions tended to produce partially hydrolyzed monomers which subsequently condensed into a more linear, lightly crosslinked network (Brinker and Scherer, 1990). Correspondingly, the particulate granular morphology could be accomplished via hydrolytic polycondensation of alkoxides under acidic conditions, whereas the honeycomb morphologies of the material were usually formed under basic condition with ammonia. The catalysts dramatically influenced the resultant morphologies.

The pH value of the sol-gel system for the preparation of uniform nano particles of anatase titania from condensed TiO_2 gel was a key factor for controlling the final particle size and shape of the product (Ahn et al., 2003; Kim et al., 2002; Sugimoto and Zhou, 2002; Chen et al., 2003). From Ahn's group, the crystallite size of the films was increased with increasing catalyst concentration and calcination temperature. The TiO_2 thin films prepared also showed high transparency in the visible range of 400-900nm. A uniform particle distribution was obtained at low pH values (Chen et al., 2003).

2.12 Humic Substances

Humic substances are ubiquitous in the aquatic environment. They are composed of degradation product of lignin, carbohydrate and protein, etc. (Yoon et al., 1998). Humic substances are primarily composed of carbon, oxygen, hydrogen, nitrogen, and sulfur in complex carbon chains (aliphatic components that make up approximately 40% - 50% of the total) C-C-C-C and 4, 5, and 6 member carbon rings (aromatic components that make up 35% - 60% of the total) with C-C, C-N, and C=O groupings. They have been shown to contain a wide variety of molecular components. Some typical components are: polysaccharides; fatty acids; polypeptides; lignins; esters; phenols; ethers; carbonyls; quinones; lipids; peroxides; various combinations of benzene, acetal, ketal, and lactol, and furan ringed compounds; and aliphatic (carbon chains) compounds. The oxidative degradation of some humic substances produces aliphatic, phenolic, and benzene carboxylic acids in addition to n-alkanes and n-fatty acids. The major phenolic acids released contain approximately 3 hydroxyl (-OH) groups and between 1 and 5 carboxyl (-COOH) groups (Pettit, 1998).

Humic substances can be subdivided into three major fractions (1) humin, (2) humic acids (HAs), and (3) fulvic acids (FAs). These fractions are arbitrarily based on the solubility of each fraction in water adjusted to different acid - alkaline (pH levels) conditions.

HUMINS - Humins are that fraction of humic substances which are not soluble in water at any pH. Humin complexes are considered macro-organic (very large) substances because their molecular weights (MW) range from approximately 100,000 to 10,000,000. In comparison the molecular weights of carbohydrates (complex sugars) range from approximately 500 to 100,000.

HUMIC ACIDS - HAs comprise a mixture of weak aliphatic (carbon chains) and aromatic (carbon rings) organic acids which are not soluble in water under acid conditions but are soluble in water under alkaline conditions. HAs consist of that fraction of humic substances that are precipitated from aqueous solution when the pH is decreased below 2. Figure 2.5 shows the model structure of humic acid.

HAs are termed as polydisperse because of their variable chemical features. From a three dimensional aspect, they are coiled, long chain molecules which may be slightly crosslinked (Yoon, 1998). On average 35% of the HA molecules are aromatic (carbon rings), while the remaining compounds are in the form of aliphatic (carbon chains) molecules. The molecular size of HAs ranges from approximately 10,000 to 100,000. HA polymers readily bind clay minerals to form stable organic-clay complexes.

Figure 2.5 Model structure of humic acid
(<http://www.ar.wroc.pl/~weber/kwasy2.htm> on 24/11/03)

FULVIC ACIDS - FAs are a mixture of weak aliphatic and aromatic organic acids which are soluble in water at all pH conditions (acidic, neutral and alkaline). Their composition and shape is quite variable. The size of FAs is smaller than HAs, with molecular weights which range from approximately 1,000 to 10,000. Figure 2.6 shows the model structure of fulvic acid. FAs have an oxygen content twice that of HAs. They have many carboxyl (-COOH) and hydroxyl (-COH) groups, thus FAs are much more chemically reactive. The exchange capacity of FAs is more than double that of HAs. This high exchange capacity is due to the total number of carboxyl (-COOH) groups present. The number of carboxyl groups present in FAs ranges from 520 to 1120 cmol (H⁺)/kg. FAs collected from many different sources and analyzed, show no evidence of methoxy (-CH₃) groups. They are low in phenols, and are less aromatic compared to HAs from the same sources.

Figure 2.6 Model structure of fulvic acid
(<http://www.ar.wroc.pl/~weber/kwasy2.htm> on 24/11/03)

2.13 Humic Acids in Water Treatment

Humic substances comprise most of the natural organic matter (NOM) in surface waters. Their removal is gaining importance and the most important groups are humic acids (HAs). HAs account for a significant portion (40-90%) of the dissolved organic matter found in nearly all water supplies (Kilduff et al., 1996). They produce undesirable colour and taste; serve as a food for bacterial growth (Palmer et al., 2002; Lorenc-Grabowska and Gryglewicz, 2005). They can complex heavy metals and organic pollutants such as pesticides, insecticides and herbicides to yield high concentration of these substances and enhance their transportation in water (Bekbölet et al., 1998). They also react with chlorine during disinfection of water to give organochloride compounds which are well known to be carcinogenic products (Singer, 1999; Wang et al., 2001). HAs have been shown to be especially reactive with a variety of oxidants and disinfectants that are used for the purification of drinking water, particularly chlorine. These substances react with chlorine to produce trihalomethanes (THMs), haloacetic acids (HAAs), and a host of other halogenated disinfection by-products (DBPs), a number of which have been shown to cause cancers in laboratory animals (Singer, 1999). Additionally, the consumption of chlorinated drinking water has been linked, through epidemiological studies, to cancers of the urinary and digestive tracts and to a

variety of adverse reproductive outcomes. The US Environmental Protection Agency has established maximum contaminant levels for the sum of four THMs and five HAAs at 80 and 60 µg/l, respectively, in US drinking waters (USEPA, 1998). The health hazard is not only chlorination products. It was reported that an intake of a huge amount of HAs might be one of the etiological factors for the Blackfoot disease (Hseu and Yang, 2002). Hence the minimization of the HAs presence in drinking water and other process waters is of great importance.

2.14 Removal of Humic Acids in Water

2.14.1 Coagulation Process

The conventional treatment methods for the removal and degradation of HAs, such as adsorption, coagulation, ion-exchange, and biological degradation, have their own limitations. In many countries, the HA is eliminated from water before chlorination by coagulation with aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$) or ferric chloride (FeCl_3) and filtration. HA rapidly chelated with aluminium or iron salts used for coagulation to the extent that the concentration and character of the HA present controlled the dosage requirements for coagulation with conventional inorganic coagulants. Enhanced coagulation at the very first step in the water treatment process has been reported from a number of workers with varying results. The HA removal can be optimized through the careful management of the pH of coagulation and optimization of alum dose. However, it is difficult to achieve more than 60% of NOM removal in conventional treatment process, particularly the lower molecular weight fraction (Bursill, 2001). Furthermore the coagulation process brings two main disadvantages: (1) production of residual sludge with high aluminium/iron concentration; (2) treated water needs high quality monitoring of dissolved aluminium/iron concentration. The water contains more than 0.2g/L of Al is not recommended for drinking (WHO, 1993). It is suspected that aluminium exposure

aids in the development or acceleration of the onset of Alzheimer's disease (WHO, 1998). Moreover, it was only 10-50% of the TOC were being eliminated during this conventional treatment process (Wang et al., 2000).

2.14.2 Membrane Filtration

Membrane filtration exhibits the promising technology in water and wastewater purification. Membrane filtration in removing humic substances is becoming widely increase (Thorsen, 1999). However the effectiveness of membrane process will be noticeably reduced by the fouling phenomenon which usually occurs on the membrane surface. HAs have been considered to be a significant foulant (Nystrom et.al., 1996; Sun et al., 2004). It is known that the inorganic ions, di- and trivalent cations found in water system can coagulate the HA to form the new complex precipitated compounds such as aggregate. The increased concentration of HA and these ions will arise on the membrane surface and promote membrane fouling tendency. The fouling by HA not only results in a rapid decline of the permeation flux, but also is irreversible (Yuan and Zydney, 2000; Deng and Bai, 2004). Irreversible fouling results a long term flux decline that cannot be fully recovered by hydraulically membrane cleaning. Membrane fouling caused by organic matter has been generally experienced in surface water filtration plants for the production of drinking water. Hence prefiltration of HA significantly reduced the rate and extent of fouling by removing the large HA aggregates or precipitated compound from solution.

2.14.3 Advanced Oxidation Process – TiO₂ Photocatalysis

Advanced oxidation processes (AOPs) are applied for the removal of HAs (Bekbölet and Özköşemen, 1996), to produce hydroxyl radicals for oxidation of

organic and inorganic water impurities. The end products of these AOPs processes are reported as lower molecular fractions of better biodegradability from the parent high molecular weight molecules. AOPs which are available for water treatment to treat NOM, including ozone alone, ozone with hydrogen peroxide (H_2O_2) addition, ozone with ultraviolet (UV) light, UV light with hydrogen peroxide and titanium dioxide (TiO_2)-catalyzed UV irradiation.

Above all, PCO using TiO_2 has gained attention in water treatment (Bahnemann et al., 1994). Water purification by TiO_2 photocatalysis has been attracting an immense research interests, especially in the removal of toxic organic pollutants (Matthews, 1987, 1988; Ollis et al., 1991; Mills and Morris, 1993; Inel and Okte, 1996; Chen and Ray, 1998, 1999) and bacteria (Sun et al., 2003). However not many studies were done on removal of HAs by TiO_2 photocatalysis due to its complexity. A preliminary investigation on the photocatalytic degradation of HAs using TiO_2 was pioneered by Bekbölet and Özkösem (1996). From the study, with the optimum TiO_2 concentration of 1.0 g/L and acidic medium, removal for 50 mg/L HAs could be attained. The evaluation of the THMs of treated solutions revealed that the destructive removal of humic acid was sufficient to keep the THMs levels below the limit of 80 $\mu\text{g/L}$. Eggins et al. (1997) also investigated TiO_2 photocatalysis as an alternative for the degradation of aquatic humic substances. It took approximately 12 min to reduce the HAs concentration by half and 60 min to achieve about 50% complete mineralization for initial 100 mg/L HAs concentration. Al-Rasheed and Cardin (2003a and b) explored the effectiveness of PCO of HAs in the saline water.

Bekbölet et al. (1996) further investigated the relative changes in the HAs and its biodegradability. The BOD_5/COD ratio increased with irradiation time and more biodegradable substances were formed. The same phenomenon was also observed

by Wiszniowski et al. (2002). It was suggested that PCO could be used as pretreatment process as the increased of biodegradability would promote the biodegradation in subsequent treatment steps. Photocatalysis process could break long organic molecules into smaller biodegradable compounds and can make their biological treatment eligible.

In order to accelerate the reaction rate, addition of H_2O_2 as an electron scavenger and bicarbonate as a hole scavenger on the degradation of HAs had been investigated (Bekbölet and Balcioglu, 1996). It was found that bicarbonate ion slowed down the degradation rate by scavenging the hydroxyl radicals when its concentration was high. The change in the rate of photocatalytic degradation was also not very significant in the presence of H_2O_2 . However, another study done by Wang et al. (2000a; 2001a) showed that the presence of H_2O_2 was found to promote the photodegradation efficiency of HA. The low concentration of H_2O_2 (less than 0.016M) would accelerate the reaction rate greatly, while over dosage made this positive effect declined (Tay et al., 2001). Hence, excessive dosage did not further improve the degradation of HA.

Cho and Choi (2002) investigated the degradation and sensitization behaviors of HA on TiO_2 under visible light irradiation. However, the visible light-induced reactions of HA in the TiO_2 suspension did not lead to a decrease in dissolved organic matter concentration. From the review, it is found that the use of PCO with TiO_2 in removing HA still has not reached the steady stage. In most of the cases, PCO is suggested to be used as a pretreatment process for HA removal. There are still some parts in this research area such as the chemical reactivity between HA and TiO_2 remained poorly understood. The influence of the size of novel nano-structured TiO_2 microsphere in removing HA, such as adsorption coefficients and chemical reactivity will be of interest.

2.14.4 Adsorption of Humic Acid on TiO_2

Adsorption process is often used as a pretreatment process before the membrane process or used as an individual separation unit process to minimize the presence of HAs in water. Various adsorbents, including activated carbon (Starek et al., 1994; Li et al., 2002; Han et al., 2003; Tomaszewska et al., 2004; Lorenc-Grabowska et al., 2005), metal oxides (Vermeer et al., 1998; Avena and Koopal., 1999; Illés and Tombácz, 2004; Uyguner and Bekbölet, 2004), polypyrrole-coated granules (Bai and Zhang, 2001), vermiculite (Abate and Masini, 2003) have been reported to adsorb HAs from water.

Activated carbon is a widely used adsorbent for HAs removal from water. However the application of activated carbon is not always technically advantageous due to the high regeneration cost and further safe disposal of waste activated carbon. Beside activated carbon, the use of mineral or metal oxides for HAs removal are also widely studied, for example iron oxides, vermiculite, aluminium oxide, titanium dioxide. Among these metal oxides, TiO_2 appears to have a higher potential as an adsorbent, as the spent TiO_2 could be regenerated by UV light irradiation via PCO process.

In general the adsorption of HAs onto metal oxides was affected by solution chemistry (Gu et al., 1994; Vermeer et al., 1998; Avena and Koopal, 1999). Firstly, the solution chemistry (pH and cation strength) would greatly affect the character of HAs. At neutral to high pH, HAs are more negatively charged due to the ionization of carboxylic COOH and phenolic OH groups. At low pH values, these functional groups are mostly protonated which makes HAs less negatively charged and reduces intramolecular electrical repulsion. Metal ions such as calcium can bind to the negatively charged carboxylic groups, resulting in charge reduction and coiling of the molecule. It was reported that HAs molecules can change from a large,

flexible and linear shape at high pH, low ionic strength and low humic concentration, to a small, rigid and spherical shape at low pH, high ionic strength and high humic concentration. (Jucker and Clark, 1994; Yoon et al., 1998; Wang et al., 2001b; Li et al., 2002; Fang, 2003).

TiO₂ was found to be an amphoteric material which the surface charge would change at different pH conditions. The surface of TiO₂ became charged when particles were dispersed in aqueous system (Illés and Tombácz, 2004). According to Henrich and Cox (1994) reported that the surface of TiO₂ powders that have been exposed to air are always hydroxylated (covered with a monolayer of OH⁻) unless they have been heated to at least 775 K in vacuum. A model was proposed for the adsorption sites of the OH⁻ on the (110) surface. It was postulated that H₂O dissociated into OH⁻ ions that adsorbed via their O end on top of five-fold coordinated surface Ti ions, with the other H⁺ ion bonding to a lattice O ion to form a second type of adsorbed OH⁻ species. Sparks (1995) supports this statement by claiming that the surface of metal oxide is unhydrated and has metal ions that are Lewis acid and that have a reduced coordination number. The oxide anions are Lewis base. The surface metal ions coordinate to H₂O molecules forming a Lewis acid site, and then a dissociative chemisorption (chemical bonding to the surface) leads to a hydroxylated surface with surface -OH groups. The water molecule was unstable and could be exchanged for an inorganic or organic anion (Lewis base or ligand) which then bonds to the metal cation. Upon hydration, surface hydroxyl groups (TiOH) are formed on TiO₂. These surface hydroxyl groups can undergo proton association or dissociation reactions, thereby bringing about surface charge which is pH-dependent:

where TiOH^{2+} , TiOH , TiO are positive, neutral and negative surface hydroxyl groups, respectively.

The adsorption behavior of HAs onto metal oxides was not clearly defined by many researchers due to the nature of the adsorbent surface and adsorbate, and the solution condition. Furthermore, the roles played by various mechanisms which have been proposed to explain the interaction between HA and metal oxides such as electrostatic interaction (Vermeer et al., 1998), ligand exchange (Gu et al., 1994), hydrophobic interaction (Chi and Amy, 2004), cation bridging (Engebretson and Wandruszka, 1998), entropic effect, hydrogen bonding etc. were less well understood and yet to be proven. Different metal oxides and experimental conditions used by the individuals could attribute to the heterogeneity and complexity of HAs and adsorbent surfaces. Because of these, different mechanisms may be operative simultaneously and to varying degrees. Therefore the interaction mechanisms between HAs and nano-structured TiO_2 microsphere surface will be elucidated and proposed in this study.

2.15 Role of Adsorption in Photocatalytic Oxidation Process

In the PCO process, the sorption of organic substrates onto the surface of TiO_2 catalysts is an important factor that affects the photocatalytic degradation rate (Wiszniewski et al., 2002). This is because the photocatalytic oxidation mainly occurs at the surface of the catalysts and not in the bulk solution (Yu et al., 2000). Lee et al. (2003) suggested that better adsorption of organic substances onto a surface were important for enhanced photocatalysis. The photocatalysis rates were strongly dependent on pH due to pH-dependent adsorption of HAs on TiO_2 with the maximum rate observed at pH 3 (Cho and Choi, 2002). Most of the researchers agreed that the degradation efficiency of HAs was better in acidic medium due to

strong adsorption of substances on the surface of TiO₂ catalysts (Eggins et al, 1997; Chen and Jenq, 1998; Qiao et al., 2002).

Beside pH condition, some studies have reported the influence of ionic strength in TiO₂ PCO process. Dionasiou et al. (2000) reported that ionic strength influenced the adsorption capacity and adsorption mechanism but did not affect the rates of the photocatalytic oxidation reaction significantly. Chen et al. (1999) reported that manganese ions increased the photooxidation of 2-chlorophenol. They have found that manganese ions enhanced the oxidation rate by surface reaction, increasing photo-generated electrons and holes, and inhibiting electron/hole recombination. It has been reported that HAs adsorption caused by calcium ion bridging between HA in solution would increase with increasing pH (Nefedov et al., 1998; Yoon et al., 1998). Recently, Li et al. (2002) found that the degradation of HAs could be significantly enhanced either at low pH (below 4) or by adding calcium and magnesium ions. The increase of cation strength in aqueous solution could provide favorable condition for the adsorption of HAs onto TiO₂ surface. These results provide an alternative for improving the photooxidation rate in TiO₂-based photooxidation processes without adjusting pH. The impact of inorganic anions commonly found in natural waters, were also studied for the removal rate of colour of HAs by PCO (Bekbölet et al., 1998). The presence of the common anions such as chloride, nitrate, sulfate and phosphate ions inhibited the rate of colour removal. The most pronounced effect was observed in the presence of phosphate ions at around 90%.

2.16 Summary

This chapter identifies the pertinent literature in relation to the scope of the thesis. The review on the current development and application of TiO₂ inspires the author

in developing a submicron TiO_2 microsphere with embedded selected-size of anatase crystallite, providing an alternative to overcome the limitation of TiO_2 application. Fundamentals of sol-gel process provide the stage where a nano-structured TiO_2 microsphere will be fabricated. The review on the parameters involved in sol-gel process was substantially important in identifying the scope of study. Adsorption and PCO mechanisms discussed in the literature provides the basis of experimental work in relation to the adsorption and photodegradation of humic acid by nano-structured TiO_2 microsphere. Two parameters of solution chemistry: pH and cation strength were identified as the crucial factors that have to be studied in relation to the HAs adsorption study on TiO_2 microsphere and further to the photocatalytic efficiency of TiO_2 microsphere.

CHAPTER 3

MATERIALS AND METHODOLOGIES

3.1 Introduction

The objectives of this study were to synthesize a novel nano-structured TiO_2 microsphere with well defined crystallite size. Based on the literature review, it was clear that the concentration of solvent and calcination temperature will affect the crystallite size of TiO_2 . In view of this, it is of interest to investigate the optimum mole ratio of solvent to alkoxide and calcination temperature for the preparation of titanium coating sol which would be used to synthesize the nano-structured TiO_2 microsphere. This chapter will briefly introduce the methods in producing the nano-structured TiO_2 microsphere and also the characterization methods that were used for the characterization of the nano-structured TiO_2 microsphere. The synthesized TiO_2 was characterized using x-ray diffraction analysis, micropore analysis, thermogravimetric analysis, surface morphology analysis and UV-vis spectrophotometer. The resulting TiO_2 was subsequently be used to remove HA via adsorption and subsequent photocatalytic process. The adsorption procedure and PCO process will be described in detail in this chapter.

In addition, the preparation and characterization of HA used in this study was also included in this chapter. The characterization methods used include elemental analysis, qualification and quantification of HA's functional group and molecular weight distribution analysis. These characterization results are useful in understanding the interaction of HA between TiO_2 microsphere.

3.2 Synthesis and Characterization of Nano-structured TiO₂ Microsphere

3.2.1 Materials

- **Tetra-n-butylorthotitanate [Ti(OC₄H₉)₄] (TB)**

Contains $\geq 98\%$ Ti(OC₄H₉)₄, obtained from MERCK, Germany, was used as the starting material for preparation of the coating sol solution.

- **P25 TiO₂**

Containing 70% anatase and 30% rutile with an average particle size of 30 nm, surface area = 50 m²/g, was obtained from Degussa Corp., Japan.

- **Ethanol (CH₃CH₂OH)**

Ethanol absolute (analytical grade), obtained from Fluka, Switzerland, was used as the solvent for the preparation of coating sol solution.

- **Deionized Ultrapure water**

ELGA ultra pure water machine, model UHQ, was used to produce ultra pure water for this study.

- **Hydrochloric acid (HCl)**

Analytical grade HCl, obtained from APS AJAX Finechem, Australia, was used as the catalyst to increase the hydrolysis rate for sol-gel process.

3.2.2 Titanium Coating Sol Preparation

TB was added dropwise to absolute ethanol (EtOH) in order to avoid the formation of large agglomerate in the EtOH and stirred continuously at room temperature. Hydrochloric acid was then added until the pH of solution reached 3. After 15 min

of vigorous stirring, the sol was then aged for 24 hrs. The mole ratio of EtOH to Ti alkoxide was varied (4, 10, 25, 50 and 100). For the sol analysis, the sol was dried at room temperature for 24 hrs in order to vaporize water into gels and was then ground into fine powders. The dried gel samples at different mole ratio were calcined at 450°C in air for 3 hrs for the study of crystallite size and phase composition. The effect of calcination temperature was further investigated by calcining the dried gel sample at elevated temperatures: 300°C, 450°C, 550°C, 650°C, 750°C, 900°C.

3.2.3 Spray-coating Process

The commercial P25 TiO₂ particles were first dispersed in the particles to sol ratio at 1 to 5 (w/w) under vigorous magnetic stirring and subsequently put into a sprayer. The mixture was aggregated to form the semisolid microspheres. The nozzle of the sprayer performed two functions: regulating the flow of mixture and atomizing the mixture into droplets during spraying process. The schematic diagram of spraying coating process is shown in Figure 3.1. During the spraying process, the solvent was evaporated while the droplets transformed into solid microsphere. In general, the microsphere of approximately 10 - 50 microns could be produced from this method. The microspheres were collected and dried overnight at 103°C. The microspheres were then calcined at 450°C for 3 hours to convert the amorphous TiO₂ into anatase phase.

Figure 3.1 Schematic diagram of spraying coating process

3.2.4 Characterization Method

- **Thermogravimetric Analysis**

Thermogravimetric analysis TGA 7 was used to determine the temperature of the decomposition and phase change of titania coating sol. The heating rate of 10°C/min from 30°C to 800°C was employed.

- **X-Ray Diffraction Analysis**

Brukers D8 advanced powder x-ray diffraction (XRD) was employed for studies of phase composition and crystallite size of resulting TiO₂. The crystallite size of TiO₂ was determined by using the TOPAS refinement software obtained from Brukers. The crystallite size from this study was referred as the primary particle size of the TiO₂.

- **Micropore Analysis**

The Micropore system Autosorb-1 by Quantachrome, Italy was used to measure the BET (Brunauer, Emmett and Teller) surface area, adsorption

and desorption isotherms, pore size distributions and total pore volume of the samples.

- **Surface morphology Analysis**

The physical shape of resulting TiO₂ microsphere was observed by scanning electron microscope (SEM) on a Leica stereoscan 420 at low magnification. The surface morphologies of all the samples were observed by field emission scanning electron microscope (FESEM) on a JEOL JSM 6340F model, Japan at high magnification. The samples were first dried in the oven at 103°C and subsequent coated with gold and platinum for SEM and FESEM analysis, respectively.

- **UV-Vis Spectrophotometer**

UV-Vis Spectrophotometer Jasco-V550 from Japan was used to study the photoactivity of nano-structured TiO₂ microsphere. An integrating sphere attachment (ISV-469) was used for powder measurement. The integrating sphere attachment was used to probe the band structure or molecular energy levels in the materials since UV or visible light excitation would create photo-generated electrons and holes.

- **Zeta potential measurement**

Zeta potential of particles in the solution was measured by a Zetasizer Model 3000, which was manufactured by Malvern Instruments Co., Ltd. Laser Doppler velocimetry was applied to measure the movement of particles in an electric field to determine the zeta potential.

- **X-Ray Photoelectron Spectroscopy Measurement (XPS)**

The XPS measurement for clean nano-structured TiO₂ before and after the

adsorption tests were performed in the ultrahigh vacuum chamber of a Kratos Ultra XPS system (Kratos Analytical, Surface Analysis Product Group, Manchester, England). The XPS spectra were obtained by applying the energy source of monochromatic Al K_{α} radiation (1486.71 eV) operated at 15kV and 10 mA. The survey scans were conducted to from 0 to 1200 eV with a pass energy of 160 eV. The elements to be analyzed were scanned over different energy with the pass energy of 40 eV. For calibration purposes, the binding energy of the spectra was standardized with the Cls peak at 285 eV. When comparing the results with the reference, peaks were identified as the same id the difference of the peak position is within 0.5 eV. The XPS spectra peaks were decomposed into subcomponents by fixing the 0% Lorentzian–Gaussian curve-fitting program with a linear background to the spectra through an XPS peak 4.1 software package.

3.3 Preparation and Characterization of Humic Acid

3.3.1 Materials

- **Humic Acid**

Commercially available HA powder was obtained from Aldrich Chemicals with a reported purity > 97% for the study. The powder was derived from decomposition organic material of mining excavation in Germany.

- **Ultrapure water**

ELGA ultra pure water machine, model UHQ, was used to produce ultra pure water during the experiment. Ultrapure water was used to prepare all the solutions throughout the experiments.

- **Hydrochloric acid (HCl)**

Analytical grade HCl, obtained from APS AJAX Finechem, Australia, was used for adjusting pH of the solutions.

- **Sodium hydroxide (NaOH)**

Analytical grade NaOH pellets, obtained from MERCK, Germany, were used for adjusting pH of the solutions.

- **Calcium chloride solution (CaCl₂)**

Analytical grade CaCl₂ was obtained from Ajax laboratory chemicals. 1000 mg/L of CaCl₂ stock solution was prepared and used to provide the ionic strength of the solutions.

3.3.2 Preparation of Humic Acid Stock Solution

HA powder was not readily soluble in water, with most of it floating on the surface of water. Thus NaOH was used to improve dissolution in water. At pH > 12, a good solution was obtained and could be preserved for a long time. 1 g HA was added and stirred to 100 ml of 0.1N NaOH solution and kept overnight. After the HA was dissolved, it was diluted to 1000 ml with ultrapure water. The dissolved HA solution was filtered by using 1.22 μm glass fibre filter paper provided by Advantec and then filtered by using 0.45 μm cellulose acetate filter paper provided by Whatman Limited. The HA was not totally dissolved in the NaOH solution. The residue HA on filter papers was dried at 103°C and weighted to calculate the final HA concentration. The final concentration of HA solution was calculated as following:

$$\begin{aligned}\text{HA concentration (mg/L)} &= (\text{HA}_{\text{initial}} - \text{HA}_{\text{residue}}) \text{ mg} / 1 \text{ L} \\ &= (1000 - 217.9) / 1 \\ &= \mathbf{782.1 \text{ mg/L}}\end{aligned}$$

The stock solution was stored in the dark refrigerator at 4°C for further use. pH of the stock solution was about 11.

3.3.3 Characterization of Humic Acid

It was essential to characterize the HA used in this study to determine their impact in the adsorption process and subsequently photocatalytic process. This section presented the method and results of the elemental analysis of HA to acquire the distribution of major constituent element in HA. A titration method was used for quantifying functional groups particularly phenolic and carboxyl groups present in HA. The apparent molecular weight distribution of HA was analyzed by high performance size exclusion chromatography (HPSEC).

3.3.3.1 Elemental Analysis of C, N, S, H and O

HA used in this study was analyzed by CHNS/O elemental analyzer, Perkin Elmer 2400 Series II. The CHNS/O analyzer was used for rapid, simultaneous determination of carbon, hydrogen, nitrogen and sulphur content in HA. Ultimate analysis provides information on the distribution of the major constituent elements in HA. As shown in Table 3.1, the predominant elements were carbon and oxygen. The carbon content of HA was 42.66% which was lower than the data reported by Stevenson (1994) and Schitezer and Khan (1972). This was accompanied by an increase of in the oxygen content. The hydrogen, nitrogen and sulfur content were approximately within the range as reported. The O/C atomic ratio for Aldrich HA was 1.18 which might reflect higher amounts of carboxylic acid (COOH) and/or carbohydrates in the HA (Stevenson, 1994).

Table 3.1 Elemental analysis of humic acid

	HA range (Stevenson, 1994)	Lake sediment HA (Schnitzer and Khan, 1972)	Aldrich HA (In this study)
Carbon	53.8 – 58.7	53.7	42.66
Hydrogen	3.2 – 6.2	5.8	5.07
Nitrogen	0.8 – 4.3	5.4	1.23
Sulfur	0.1 – 1.5	N/A	1.35
Oxygen*	32.8 – 38.3	35.1	50.31

*Oxygen content is calculated from the difference $O = 100 - (C + H + N + S)$

3.3.3.2 Functional Groups of Humic Acid

3.3.3.2.1 Qualification by Fourier Transform Infrared Spectroscopic (FTIR)

The FTIR instrument (Perkin Elmer) with a detector in a wave number range of $500\text{--}4000\text{ cm}^{-1}$, was used for qualitative description of functional groups. The major oxygen-containing functional groups in humic substances are carboxyls, phenolic and alcoholic hydroxyls, carbonyls and methoxyls (Schnitzer and Khan, 1972). The FTIR spectra obtained in Figure 3.2 was similar to the results obtained by Lin et al. (2000). The functional groups corresponding to the respective wave numbers are shown in Table 3.2. Generally the major functional groups found in HA were carboxylic and phenolic groups. The absorption with a maximum at 3400 and 1640 cm^{-1} was due to the presence of oxygen-containing functional groups (hydroxyl, carboxyl, carbonyl). The bands of 2920 , 2850 and 1450 cm^{-1} were attributed to aliphatic groups in HA. However the band centered at 1640 cm^{-1} which is, in part, attributed to $\text{C}=\text{C}$ in aromatic structured showed lower intensity, this might reveal that the HA was aliphatic character (Lorenc-Grabowska and Gryglewicz, 2005).

Figure 3.2 FTIR spectra of humic acid

Table 3.2 General assignments of the FTIR spectra of humic acid

Wavenumber (cm ⁻¹)	Assignment
3600-3000	Hydrogen-bonded OH groups, free OH, intermolecular-bonded OH
3077-3030	Aromatic C-H stretching
2950-2850	Aliphatic C-H, C-H ₂ , C-H ₃ stretching
2850-2500	Carboxylate ion
1725-1640	C=O stretching of carboxylic acids
1640-1585	C=O stretching vibration of double bonds in cyclic and acyclic compounds, ketones and quinones
1515	C=C stretching vibration of benzene, pyridines
1470-1420	Aliphatic C-H deformation
1400-1390	OH deformation and C-O stretching of phenolic OH, C-H deformation of CH ₃ groups
1390-1332	Salts of carboxylic acids
1280-1137	C-O stretching of esters, ethers and phenols
1090-1040	C-O stretching of alcoholic compounds
880-750	Hydrogen-bonded OH stretching vibration of carboxylic groups
650-510	Deformation of COOH

3.3.3.2.2 Quantification by Titration Method

A titration method was used for quantifying functional groups (Stevenson, 1994). Barium hydroxide method (Baryta absorption) and Ca-acetate method was used to determine the total acidity and carboxylic groups in HA, respectively. The phenolic acidity was then calculated as the difference between the total acidity and carboxyl acidity.

a) Barium Hydroxide (Baryta Absorption) Method

The Barium hydroxide [Ba(OH)₂] approach is an indirect potentiometric method in that it is based on release of H⁺ from acidic groups that ionization up to the pH of the reaction solution. Due to its simplicity, this has been the most popular method for determining total acidity of humic substances. Briefly, the sample is allowed to react with excess Ba(OH)₂, following which the unused reagent is titrated with

standard acid. The overall reaction is

Where R is the macromolecule and H is the proton of a COOH or acidic OH group.

Procedure of this method is as follows:

Analytic grade Ba(OH)₂ was obtained from Sigma-Adrich. A volume of 20mL of 0.2 N Ba(OH)₂ was added into a 50mL flask containing 10mL sample, agitated for 24 hr, filtered and the filtrate titrated with 0.5 N HCl to pH 8.4. The total acidity is calculated as:

$$\text{Total acidity (meq/g TOC)} = \frac{(V_b - V_s)N(10^6)}{VC} \quad (3.2)$$

Where V_b is the HCl volume for the blank test (mL), V_s is the HCl volume for sample (mL), V is the sample volume and C is the sample TOC concentration (mg/L).

b) The Ca-acetate Method

The Ca-acetate method is based on ion exchange and can be regarded as an indirect potentiometric titration approach. Extensive use has been made of the method for determining COOH groups. The reaction is

The acetic acid (CH₃COOH) liberated during the reaction is titrated with a standardized NaOH solution.

The procedure is as follows:

Analytic grade $\text{Ba}(\text{OH})_2$ was obtained from Sigma-Adrich. A volume of 10mL of 1 N $\text{Ca}(\text{CH}_3\text{COO})_2$ and 40mL of CO_2 free distilled water were added into a 100mL flask containing 10mL of sample, agitated for 24 hr, filtered and the filtrate titrated with 0.1 N NaOH to pH 9.8. The content of COOH groups is obtained by the equation:

$$\text{COOH (meq/g TOC)} = \frac{(V_s - V_b)N(10^6)}{VC} \quad (3.4)$$

Where V_b is the NaOH volume for the blank test (mL), V_s is the NaOH volume for sample (mL), and C is the sample TOC concentration (mg/L). The phenolic acidity is then calculated as the difference between the total acidity and carboxyl acidity.

Table 3.3 shows the total acidity in the HA was about 9.6 meq/g which was lower than 15 meq/g or 14.5 meq/g, value reported by Lin et al. (2000) and Davis et al. (1999), respectively. However this value was higher than the range as suggested by Stevenson (1994) which obtained from soils of widely different climatic zones. The carboxylic group determined from the HA (5.8 meq/g) was within the value (4-13 meq/g) as reported by others (Reckhow et al., 1990; Karanfil et al., 1996; Lin et al., 2000). This value was still slightly higher than the range as reported by Stevenson. While the magnitude of phenolic acidity (3.8 meq/g) was within the reported values of about 1 – 5.7 meq/g. It could be then inferred that total acidity in terms of carboxylic acidity for aquatic HA was higher than soil HA. However it has to be noted that the comparison of these values was with knowledge that the titration methods used by these investigators could be different.

The results obtained were interpreted with caution. The acidities of the various

groups might overlap due to the complex nature of humic substances. On the other hand, substituted phenols are often more strongly dissociated than the unsubstituted compound. Some groups may be unreactive because of H-bonding or through steric hindrance. Other problems in the quantitative determination of functional groups include insolubility of humic acid in water, oxidation and reduction and interactions with reagents used for forming derivatives and the nonstoichiometric nature of the reactions (Stevenson, 1994).

Table 3.3 Total acidity, carboxylic acidity and phenolic acidity of humic acid

	Stevenson (1994)	Lin et al. (2000)	In this study
Total acidity (meq/g)	5.6 - 8.9	15.0	9.6
Carboxylic acidity (meq/g)	1.5 – 5.7	9.1	5.8
Phenolic acidity (meq/g)	2.1 – 5.7	5.9	3.8

3.3.3.3 High Performance Size Exclusion Chromatography (HPSEC)

The relative molecular weight distribution of HA was determined using a HPSEC with a RI detector/ UV detector which were manufactured by Waters. Ultrahydrogel column types 120, 250 and 500 from Waters and a Shodex standard P-82 standard were used for HPSEC analysis. Prior to HPSEC measurement, HA water samples were filtered by a 0.45 μ m microfiltration membrane to remove large particles and colloids.

Molecular weight (MW) is one of the fundamental properties that need to be measured in order to understand the physical and chemical characteristics and chemical reactivity of HA. Lower MW molecules have smaller radii, permitting nanopore adsorption, tend to be more hydrophilic resulting in greater bioavailability and increased mobility through porous media and display rapid diffusion allowing

for rapid adsorption to mineral surfaces. On the other hand, higher MW molecules tend to be more aromatic resulting in enhanced hydrophobic organic carbon partitioning, have higher electrostatic potential and more ligands per molecule, hence greater metal binding capacity, and tend to have increased adsorption affinities resulting in decreased mobility through the water column (Kerc et al., 2004). pH and cation strength were found to have crucial effect on structure of HA in aqueous solution. The results of MW distribution of HA were presented in Figure 3.3 and 3.4. It was found that the MW of HA molecules decreased with decreasing pH value (Figure 3.3) and in the presence of cation in solution (Figure 3.4). The interpretation of the results will be discussed in Chapter 5.7 to provide better understanding on the effect of solution chemistry on adsorption extent and rate of HA onto nano-structured TiO_2 microsphere.

Figure 3.3 Molecular weight distribution of humic acid at pH 3, 7 and 9.

Figure 3.4 Molecular weight distribution of humic acid at different pH conditions (with the presence of Ca²⁺).

3.4 Batch Adsorption Study

The dark adsorption study was carried out in 250 mL beakers wrapped with aluminium foil. For determination of the adsorption isotherm, the concentrations of HA solution were varied from 5 to 50 mg/L at a fixed dosage of TiO_2 at 1g/L. Nano-structured TiO_2 microsphere was placed into the HA solution and stirred at 120 rpm for 24 hours to attain adsorption equilibrium. For the adsorption kinetics study, two sets of tests were conducted to investigate the kinetics of HA adsorption affected by different pH and Ca^{2+} concentration respectively. The concentration of HA solution and the dosage of TiO_2 was fixed at 20 mg/L and 1g/L, respectively. HA concentration was fixed at 20 mg/L to simulate the real natural water body. The first set of tests was conducted in 3 different initial pH value (3, 7, and 9) with absence of Ca^{2+} ion. The second set of tests was carried out at pH 7 with 4 different concentration of Ca^{2+} concentration (0, 20, 50 and 80 mg/L). The pH of the suspension was adjusted by using HCl or NaOH. Samples were collected periodically and evaluated both in terms of Colour_{436} and UV_{254} values for HA concentration. All adsorption processes were carried out at 25°C.

3.5 Photocatalytic Oxidation Study

PCO degradation study was carried out in a PCO reactor. The PCO reactor consisted of an outer cylindrical acrylic casing fitted with an air diffuser at the bottom as shown in Figure 3.5. The UV lamp used was an 18.4 watts low pressure mercury UV lamp (NEC). The major emission of the UV lamp is 253.7 nm. An air pump was used to supply oxygen and create air bubbles for suspensions. TiO_2 microsphere was suspended in 1000 mL solution in dark for 2 hrs to attain adsorption equilibrium before the PCO study set off. Samples were taken at different time intervals after UV light was turned on. All samples were filtered through 0.45 μm cellulose acetate membrane filters prior to analysis.

Figure 3.5 PCO reactor setup. (C_0 = Initial concentration of solution; C_t = Concentration of solution at t time)

3.6 Analytical Test

3.6.1 Chemical Analysis of Phenol

Phenol was used as the targeted compound in this preliminary study to elucidate the photocatalytic activity of nano-structured TiO_2 microsphere. The phenol concentration was analyzed by high performance liquid chromatography (HPLC PerkinElmer, Series 200). The HPLC column used was C-18 (PerkinElmer, Brownlee Columns) with mobile phase of a mixture of 40% methanol and 60% of 1%-acetic acid solution. Standard curve was prepared by diluting phenol (analytical grade) at different concentration. The detection wavelength was set at 280 nm for phenol analysis. The retention time for phenol peak under these conditions was recorded at 1.9 min.

3.6.2 Colour Analysis

Absorption at UV_{254} and Colour_{436} was measured using UV-Vis 2401 PC double-beam spectrophotometer (Shimadzu Corporation, MD). This spectrometer covers the wavelength range between 190 and 1100 nm and thus ranges from the near UV region (400-190 nm) to the near IR region (1100-750 nm).

The dark colour of neutral, acidic or alkaline aqueous solutions of humic substances has stimulated chemists to use colour as a criterion for the analysis of these materials. Absorption in the visible region is useful for quantitative analysis. Absorption in the UV (200-400 nm) and visible (400-800 nm) regions is caused by atomic and electrometric vibrations, and involves elevation of electrons in σ -, π -, η -orbitals from the ground state to higher energy levels. Absorption in the UV region is due to the presence of multiple bonds and to unshared pairs in organic molecules. These linkages or groups confer colour on organic substances and are called

chromophores. Typical chromophores known to occur in humic substances are C=C and C=O. UV-Visible spectrophotometer had been used as a tool for analytical investigations of humic substances in this study. The relationship between absorption and concentration is given by the Beer-Lambert law:

$$\text{Absorbance} = \text{Log}_{10} \frac{I_0}{I} = kcl \quad (3.5)$$

where I_0 is the intensity of the incident light, I is the intensity of the transmitted light, k is the extinction coefficient, c is the concentration of the substance under investigation and l is the path length or thickness of the cell that contains the solution. k is numerically equal to optical density if c is 1 mole per liter and l is 1cm. Thus, k is a measure of the intensity of absorption at a given wavelength. The extinction coefficient of humic compounds has been observed to increase with: a) and increase in molecular weight, b) C percentage, c) degree of condensation, and d) ratio of C aromatic rings to C in aliphatic structures.

In this study, the graphs plotted to obtain the extinction coefficient for HA at different pH was shown in Appendix A. Table 3.4 summarizes the extinction coefficients and the concentration of humic acid could be calculated based on the extinction coefficient obtained. The extinction coefficient decreased as the pH values decreased.

Table 3.4 Summary of extinction coefficients for wavelength 254nm and 436nm at different pH conditions

pH	UV ₂₅₄	Colour ₄₃₆
3	0.0308	0.0046
7	0.0321	0.0053
9	0.0336	0.0067

3.6.3 Total Organic Carbon (TOC) Analysis

A TOC analyzer, TOC-5000, SHIMADZU was used in the study. Total carbon (TC) is measured by injecting the diluted samples into a heated reaction chamber packed with an oxidative catalyst. The water will vaporize and the organic carbon will oxidize to CO_2 and H_2O . The CO_2 from the oxidation of organic and inorganic carbon is transported in the carrier-gas streams and is measured by means of a nondispersive infrared analyzer. Inorganic carbon (IC) is measured by injecting the sample into a separate reaction chamber packed with phosphoric acid-coated quartz beads. Under the acidic conditions, all inorganic carbon is converted to CO_2 , which will be measured. Under these conditions organic carbon will not be oxidized and only IC is measured. TOC is obtained by calculating the difference between TC and IC. A series of standard solutions in the range of 10 to 20 ppm for TC and 5 to 10 ppm for IC was prepared for calibration before the samples analysis.

CHAPTER 4

SYNTHESIS AND CHARACTERIZATION OF NANO-STRUCTURED TITANIUM DIOXIDE MICROSPHERE

4.1 Introduction

Chapter 2 revealed that much efforts have been done by other researchers such as immobilizing or coating a thin film of photocatalysts on the surfaces of various substrates such as glass, fiber or stainless steel and also free carriers such as polystyrene, carbon, silica. However TiO_2 particles might fall off easily from the carriers after a long period of usage. In addition, the presence of foreign cations from the support used inhibited the crystallization of TiO_2 which subsequent led to a drastic decrease in photocatalytic activity of this TiO_2 film. Some researchers reported the synthesis of submicron TiO_2 microsphere which would possess an effective separation. These synthesis works involved the use of templates or polymer gels to create the porous structure. Nevertheless these additives had some drawbacks during the synthesis: the resulting products was not consistent, the templates was not removed completely during the calcination process.

To attain the same objective, this study was aimed at developing a TiO_2 microsphere without using polyethylene glycol (PEG) or polymer templates. A novel nano-structured TiO_2 microsphere was synthesized by embedding the size-selected anatase nano-particles in a porous matrix or core via sol-gel spray coating process. The coating that entered the inner surfaces of the pores in different porous matrices would create new types of nano-structures. P25 TiO_2 was used as the core/nuclei site for the synthesis of submicron TiO_2 microsphere which was bounded using titanium coating sol that would eventually transform into anatase crystallite. The critical factors that affecting the crystallite size were elucidated. In this study, the effect of mole ratio of solvent to titanium alkoxide, and calcination temperature in attaining optimum anatase crystallite size were reported.

Principally this chapter consisted of three parts: (1) characterization of titanium coating sol, (2) characterization of nano-structured TiO_2 microsphere and, (3)

photocatalytic activity of nano-structured TiO_2 microsphere. In the first section, the effects of mole ratio of solvent to alkoxide and calcination temperature on the growth of anatase crystallite size were investigated by TGA and XRD. The optimum condition for the synthesis process was summarized based on the characterization results in this section. Secondly, the properties of nano-structured TiO_2 microsphere were studied using XRD, SEM, FESEM and micropore analysis. The photocatalytic activity was measured in the photodegradation of phenol. Detailed experimental procedures were given in Chapter 3.

4.2 Characterization of Titania Coating Sol

The preparation of titania coating sol is important in synthesizing the nano-structured TiO_2 microsphere. Firstly, the titania coating sol acted as the binder to bind the P25 TiO_2 during the spray-coating process in forming the microsphere. After calcination, the titania coating sol was crystallized into nano-sized anatase which provides the photocatalytic activity of TiO_2 microsphere. Hence the optimum condition in preparing the titania coating sol was elucidated to obtain the desirable anatase crystallite size. The effects of mole ratio of ethanol to Ti alkoxide and calcination temperature on the growth of anatase crystallite size were reported and discussed.

4.2.1 Effect of Mole Ratio of Ethanol to Ti alkoxide

Yu and Wang (2000) claimed that the mole ratio of solvent to alkoxide was the major factor that could govern the characteristics of gel-derived oxides. The crystallite size and crystallinity were greatly influenced by the mole ratio of solvent in the sol-gel process (Hu et al., 1992; Ito et al., 1999; Yu et al., 2002). It was important to study the critical value for the mole ratio of solvent to alkoxide used in the process to prepare the required oxides with optimum crystallite size. In this study, the concentration of titania coating sol was varied. The mole concentration of Ti alkoxide was fixed at 1 while the mole concentration of ethanol (EtOH) was varied from 4 to 100 (R was the mole concentration of EtOH). Figure 4.1 displays the XRD pattern of dried gel at different mole ratio of EtOH to alkoxide calcinated at 450°C for 3 hrs. The intensity and crystallinity of anatase phase was reduced as the concentration of solvent increased. Apparently, the quantity of residual unhydrolyzed alkyls in the precursors decreased with increasing amount of solvent, resulting in reduction of steric hindrance by the residual alkyls that could prevent crystallization to crystalline anatase (Terabe et al., 1994).

Figure 4.1 XRD patterns of dried gels at different mole ratio of EtOH to alkoxide and calcinated at 450°C for 3 hrs.

In addition, variations in the mole ratio of EtOH to alkoxide showed a significant effect on the size of anatase crystallite. The crystallite size decreased as the mole ratio of EtOH to Alkoxide increased. The crystallite size decreased in the factor of two from 17.208 ± 0.602 nm to 8.257 ± 1.916 nm as the mole concentration of ethanol increased from 4 to 100 respectively (Table 4.1). The crystallite size of 10 nm and below could be obtained when the mole of ethanol was 50 and above. The photocatalytic activity increased as crystallite size of TiO_2 became smaller (<10 nm) due to quantum size effect (Anpo, 1987). Therefore EtOH to alkoxide: 50 to 1 was determined as the optimal mole ratio for the titania coating sol preparation. This result confirmed that the increment of alcohol would produce a smaller crystallite size. This finding was agreeable with Legrand-buscema and co-workers (2002). It was probably due to the fact that EtOH solvent suppressed the hydrolysis of titanium alkoxide and rapid crystallization of the TiO_2 by adsorbing on the surfaces of TiO_2 particles (Ito et al., 1999; Yu et al., 2002).

Table 4.1 Crystallite size of anatase of dried gel calcinated at 450°C for 3hrs.

Sample Code	Crystallite size, nm	Phase Composition
R4	17.208 ±0.602	Anatase
R10	17.010 ±0.655	Anatase
R25	15.750 ±0.575	Anatase
R50	10.675 ±2.001	Anatase
R100	8.257 ±1.916	Anatase

In general, metal alkoxides (M-OR) are very reactive due to the presence of highly electronegative -OR groups that stabilize M- in its highest oxidation state and render M- very susceptible to nucleophilic attack. For coordinatively saturated metals, hydrolysis and condensation both occur by nucleophilic substitution (S_N) mechanisms involving nucleophilic addition (A_N). The transfer of proton from the attacking molecule to an alkoxide or hydroxo-ligands within the transition state and removal of the protonated species as either alcohol (alcoxolation) or water (oxolation) (Brinker and Scherer, 1990).

Hydrolysis:

Alcoxolation:

Oxolation:

In this study, water was not used as solvent since titanium alkoxide (titanium butoxide, $Ti(OBu^t)_4$) was very reactive towards water, the H^+ from water would attack Ti precursor to form the precipitate $Ti-OH$. A homogenous gel was preferred rather than precipitates. A stable and homogenous sol was obtained by using EtOH as the solvent. EtOH would retard the hydrolysis and condensation reaction rates in order to control the condensation pathway. However, the quantity of EtOH added must be sufficient to facilitate these pathways. Firstly, x mole of EtOH was involved in the alcohol exchange process. S_N reaction occurred between the nucleophilic reagent (EtOH) and the titanium alkoxide:

Exchange was facilitated since EtOH was sterically less bulky than Bu^tOH . It was known that alcohol exchange rates decreased as methanol ($MeOH$) > ethanol ($EtOH$) > isopropanol (Pr^iOH) > butanol (Bu^tOH). During this reaction, Bu^tOH was removed while a stable sol was obtained with titanium ethoxide, $Ti(OEt)_4$. Secondly, a sufficient amount of EtOH (x' mole) was needed to enhance the alcoxolation process. Alcoxolation was the favoured condensation reaction between partially hydrolyzed and coordinatively saturated titanate precursors:

At the end of the reaction, the mole of EtOH required, $R(x + x')$ was expected to be greater than the stoichiometric requirement for the hydrolysis reaction and condensation process as agreed by Hanprasopwattana et al. (1996), and Yu and Wang (2000). It was agreed that the structure of the condensed products was depended on the relative rates of hydrolysis and alcoxolation or oxolation.

When R was less than the required stoichiometric mole ($R < 4$), the hydrolysis reaction was incomplete and uncontrolled, thus leading to rapid gelation and crystallization. The sol was instable with a shorter shelf life.

As R increased from 4 to 25, the required stoichiometric mole, the hydrolysis was rapid and the condensation reaction occurred between the monomers of $\text{Ti}(\text{O}^t\text{Bu})_{4-x}(\text{OEt})_x$, where $x \leq 4$, to form chain-like structures. Continuous proceeding of the condensation reaction caused these chain-like structures to have a fast interaction between unreacted $-\text{OR}$ groups and subsequently form the interchain bonding, which increased the strength of gel structure. However heat treatment would collapse the structures of the resultant cross-linked gels, resulting in the formation of large crystallites with irregular shape as shown in Figure 4.2.

Figure 4.2 FESEM images of crystallites prepared at a) $R = 4$ and b) $R = 25$.

Increasing R to 50 would increase the hydrolysis rate and promote the condensation via alcoxolation. Therefore more alkoxyl groups in the alkoxide would be substituted by hydroxyl groups of solvent. The monomers, $\text{Ti}(\text{OEt})_{4-x'}(\text{OH})_{x'}$, where $x' \leq 4$, would interact with each other to establish a three dimensional network structure during condensation process. The solids with textures like fragments of monolith would be formed. A more stable crystallite was obtained after the heat

treatment as shown in Figure 4.3a.

Figure 4.3 FESEM images of crystallites prepared at a) $R = 50$ and b) $R = 100$.

However when R exceeded the critical value (the value corresponds to the optimum crystallite size), the hydrolysis was more complete and more alkoxides converted to the corresponding metal hydrates, Ti(OH)_z , where $z > R$. The monomers of Ti(OH)_z then reacted with each other to form particle-like polymers as shown in Figure 4.3b. The amount of residual alkyls preventing crystallization to anatase was small (Yu et al., 2003).

Although increasing solvent content could produce smaller anatase crystallites, the crystallinity was reduced. It was found that the mole ratio of solvent/alkoxide played an important role in governing the characteristics of gel-derived oxides. $R = 50$ (R_{50}) was proposed as the critical value in preparing the required oxides with optimum anatase crystallite size of about 10 nm, which could trigger the quantum size effect of the photocatalyst.

4.2.2 Effect of Calcination Temperature

Figure 4.4 shows the results of TGA of the titanium coating sol R50 without heat treatment. The as-prepared sol had about 23% weight loss. A weight loss on the TG curve at 100°C due to evaporation of water was first observed. It followed by the weight loss at around 180°C, which was due to the dehydration of the hydrous TiO_2 sol. The weight loss between 200 and 500°C was due to the decomposition of residual organic species such as butoxy groups (OC_4H_9) as agreed by Rubio and groups (1997). The main inflection point was observed at 400°C, which was probably related to the condensation of Ti-OH groups with the subsequent release of water and the phase transformation from amorphous to anatase. This result suggested that the calcination temperature applied to attain the crystallinity for the titanium coating sol at R50 must be more than 400°C. XRD analysis was further carried out to determine the pertinent calcination temperature.

Figure 4.4 TG analysis of dried gel R50 at heating rate 10°C/min.

The dried gel of R50 was calcined at 300°C, 450°C, 550°C, 650°C, 750°C and 900°C for 3 hrs for phase transformation behavior study. Figure 4.5 displays the

XRD patterns of the dried gel R50 calcined at elevated temperature. It was observed that amorphous TiO_2 was transformed into TiO_2 anatase form at between 300 and 550°C. The anatase-rutile transformation started at 550°C and subsequently completed at 900°C. This result was agreeable with Hu et al. (2003).

Figure 4.5 XRD patterns of dried gels at R50 calcined at elevated temperature.

The crystallite size of anatase increased as the calcination temperature increased. Figure 4.6a reveals that TiO_2 anatase crystallite size increased exponentially from 5 to 40 nm with increasing calcination temperature from 300°C to 900°C, respectively with $R^2 = 0.9824$. The growth of anatase crystallite could actually be described in two distinct stages: amorphous - anatase and anatase - rutile. The inflection point was observed at about 550°C where the anatase crystallite size was about 15 nm. The phase transformation from anatase to rutile was initiated when the size of anatase crystallite attained the critical size which was 15 nm in this study. This result was in agreement with that reported by Hu et al. (2003). It was obvious that the beginning of the phase transformation was dependent upon the critical size of anatase particles. The rutile crystallite started to grow during the anatase-rutile transformation. The anatase-rutile transformation was a nucleation growth process,

the rutile crystallite was nucleated on the surface and then spread into the anatase crystallite (Ting and Chen, 2001). Because of this, the crystallite size of rutile grew tremendously from 20 nm to 60 nm as calcination temperature increased from 550°C to 750°C, respectively. The rate of transformation increased as the reacting anatase was very finely crystalline and possessed the critical size to supply more number of potential nucleation sites. In view of this, the calcination temperature was determined at 450°C in order to attain the crystallite size of about 10 nm or below in anatase phase.

Figure 4.6 a) Effect of calcination temperature on the growth of anatase TiO₂ crystallite size for dried gel R50 at elevated temperature; b) Effect of calcination time on the growth of anatase TiO₂ crystallite size for dried gel R50 at increased calcination duration.

Figure 4.6b displays the effect of calcination duration on the growth of anatase crystallite size at fixed calcination temperature of 450°C. There was only a slight increase of crystallite size from 10 to 14 nm as the calcination time increased from 1 to 12 hours respectively. Hence calcination duration had a marginal effect on the growth of anatase crystallite size in this study. In conclusion, the resulting nano-structured TiO₂ microsphere needs to be calcined at 450°C to ensure that the titanium coating sol which had been embedded within the TiO₂ microsphere was transformed into anatase crystallite phase.

Figure 4.7 BJH pore size distribution of dried gel R50 at elevated calcination temperature.

Figures 4.7 (a–f) shows that the growth of anatase crystallite size at elevated temperature would affect the pore size distribution. The samples showed monomodal distribution consisting of intercrystalline pore in amorphous phase (Figure 4.7a) and calcinated at 300°C (Figure 4.7b). The pore size of dried gel lied in the microporous region with a single peak of 4 nm pore size in amorphous phase.

As the sample calcined at 300°C, the maximum pore size of 4 nm became more defined while the micropores were eliminated. The maximum pore shifted into larger pore as the calcination temperature increased. The pore size distribution displayed the bimodal distribution as sample was calcinated at 400°C and above. At 450°C, the 4 nm pore size peak was eliminated and replaced by a 10 nm pore size peak (Figure 4.7d). Eventually most of the pores were eliminated as calcination temperature approached 750°C. The pore size increased and eventually eliminated as the calcination temperature increased due to the growth of crystal.

Table 4.2 summarizes the pore volume of samples calcinated at elevated temperature. The optimum pore volume of 0.229 cm³/g was obtained at 450°C. The total pore volume decreased when the calcination temperature was beyond 450°C. The decrease of total pore volume reflected that most of the pores in the sample were eliminated during calcination process. Most of the pores was laid in the mesoporous region. The micropore was only detected when the dried gel was in amorphous phase.

Table 4.2 Total pore volume of dried gel R50 calcinated at different temperatures.

Sample	Pore Volume (< 2 nm), cm ³ /g	Pore Volume (2 -50 nm), cm ³ /g	Pore Volume (>50 nm), cm ³ /g	Total Pore Volume, cm ³ /g
Amorphous	0.047	0.1110	0.0320	0.1900
300°C	0.005	0.1500	0.0350	0.1900
400°C	N/A	0.1400	0.0300	0.1700
450°C	N/A	0.1900	0.0390	0.2290
500°C	N/A	0.1200	0.0380	0.1580
750°C	N/A	0.0350	0.0337	0.0687

According to Mayo (1996), pore shrinkage during calcination process could be explained in three stages. In the first stage, interparticle necks were formed by diffusion between adjacent, touching particles. The neck formation increased the mechanical strength of the compact but might lead to little actual densification. On the other hand, it was possible that the surface diffusion combined with applied or residual stress and allowed the small grains to slip past one another along their boundaries and rearrange in a more packing efficient manner. After extensive interparticle neck formation, the sample was analogous to that of hard sponge, containing a cast interpenetrating network of tubular pores which was opened to the external surface of the sample. At the second stage of pore shrinkage, the microstructure characteristic was dominating. In the ideal case, these open tubular pores would shrink in radius, though not in length, thereby leading to sample densification. The pores ultimately collapsed once they reached a certain small diameter/length ratio due to Rayleigh instabilities. The open tubular pores then formed closed spherical pores. The gradual shrinkage and elimination of these close pores then marked the final stage of pore shrinkage as the calcination temperature increase gradually.

The above findings led the author to propose the optimum sol-gel condition in preparing titanium coating sol which would eventually transform into the predetermined anatase crystallite embedded within the nano-structured TiO_2 microsphere in the next section. The titanium coating sol was prepared at EtOH/alkoxide ratio of 50/1 and calcination temperature at 450°C . These conditions will ensure that the titanium coating sol will transform into anatase crystallite phase with crystallites of about 10.675 ± 2.001 nm with total pore volume of $0.2290 \text{ cm}^3/\text{g}$.

4.3 Characterization of Nano-structured TiO₂ Microsphere

4.3.1 Particle Size and Surface Morphology

Nano-structured TiO₂ microsphere was first observed by SEM. Figure 4.8 shows a typical TiO₂ microsphere at about 30 μm . The particle size of TiO₂ microsphere was ranged between 10 and 50 μm from SEM analysis. The surface morphology of the TiO₂ microsphere was enlarged to a scale of 1:50 000 using FESEM (Figure 4.9a). The surface of TiO₂ microsphere was composed of well-dispersed nano-sized TiO₂ particles. The nano-sized crystallites of P25 TiO₂ had been bounded together to form larger unit, a microsphere, in this study. Figure 4.9b shows the FESEM micrograph of commercial P25 TiO₂. It could be seen that the original P25 TiO₂ was made of cubic particles with rounded edges which was similar with the result discovered by Mills and Le Hunte (1997). Clearly, most of the particles were aggregated and a non interagglomerate porous structure was formed. After forming the microsphere, the nano particles were distributed evenly on the surface of the microsphere.

Figure 4.8 SEM micrograph of nano-structured TiO₂ microsphere.

Figure 4.9 a) Surface morphology of nano-structured TiO_2 microsphere; b) Surface morphology of P25 TiO_2 .

4.3.2 BET Surface Area and Pore Structure

As expected two types of pores were present in the TiO_2 microsphere: intercrystalline pore (pore within nano-sized crystallites) and interaggregate pore (pore within microsphere). Figure 4.10 displays the BJH pore size distribution of P25 TiO_2 and TiO_2 microsphere. 2 peaks were observed for each TiO_2 sample. The first peak of 2-3 nm pore size was referred to intercrystalline porosity. It could be observed that intercrystalline pore was diminished for TiO_2 microsphere, indicating that the P25 TiO_2 particles within a microsphere were strongly bounded together by the nano-sized anatase crystallite which was transformed from the titania coating sol. The nano-sized anatase crystallite size was embedded within the TiO_2 microsphere. It was known that P25 TiO_2 would agglomerate to form aggregate ranging from 25 nm to 0.1 μm (Mills and Hunte, 1997). The micropore system was unable to detect the interagglomerate pore of P25 TiO_2 as it might approach the limits of detection range of machine resolution. Hence it was possible that pore size larger than 200 nm existed in the agglomerated P25 TiO_2 . The second peak of TiO_2 microsphere at 30 nm was rather termed as interaggregate porosity as the microsphere was actually a strongly bounded stable aggregate.

Figure 4.10 BJH pore size distribution of P25 TiO₂ and TiO₂ microsphere.Table 4.3 Summary of BET surface area and pore volume of TiO₂ samples.

Sample	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)
P25 TiO ₂	43.74 ± 5.02	0.952 ± 0.245
TiO ₂ microsphere	41.89 ± 3.98	0.472 ± 0.092

The BET surface area of P25 TiO₂ and TiO₂ microsphere was 43.74 ± 5.02 m²/g and 41.89 ± 3.98 m²/g, respectively (Table 4.3). Both surface area of TiO₂ samples were identical even though the particle size of TiO₂ microsphere had been restructured into micron range. It was due to the alteration of porosity. The pore system of TiO₂ microsphere constituted of voids between the primary particles within the secondary particle, together with those between a secondary particles. Both types of pores were well defined as compared to the pore system of P25 TiO₂. Hence the surface area of TiO₂ microsphere and P25 TiO₂ aggregates were almost identical. The total pore volume of P25 TiO₂ and TiO₂ microsphere was 0.952 ± 0.245 cm³/g and 0.472 ± 0.092 cm³/g, respectively (Table 4.3). The decrease of total pore volume might be due to the diminishing of intercrystalline porosity.

4.3.3 Adsorption Isotherm

Figure 4.11 exhibits the corresponding nitrogen adsorption-desorption isotherm of commercial P25 and nano-structured TiO_2 microsphere. The results show that the commercial P25 adsorption curve obtained was type II, representing an unrestricted monolayer-multilayer adsorption. The isotherm of nano-structured TiO_2 microsphere was recognized as type IV (hysteresis loop) according to IUPAC isotherm classifications (BS 7591: Part 2: 1992).

Figure 4.11 Adsorption and desorption isotherms for P25 TiO_2 and nano-structured TiO_2 microsphere.

The presence and type of porosity at the surface were determined by using the α_s plot (Gregg and Sing, 1982). Porosity of the nano-structured TiO₂ microsphere was assessed by plotting the adsorption isotherm for powder in a reduced form; the volume of adsorbed N₂ at a given relative pressure (P/P_0), V_{ads} was plotted against $V_s/V_{0.4}$ ($=\alpha_s$), where V_s was the volume adsorbed by the adsorbent at the same P/P_0 and $V_{0.4}$ was the volume adsorbed by the adsorbent at $P/P_0=0.4$ (Gregg and Sing, 1982). Commercial P25 was taken as the reference material for the construction of the α_s curve. The α_s -plot in Figure 4.12 demonstrates an upward deviation from the linearity commencing at the relative pressure indicating that the mesopores had been introduced into the commercial P25 TiO₂.

Figure 4.12 α_s plot for nano-structured TiO₂ microsphere using P25 TiO₂ as the reference material.

4.3.4 XRD Analysis

Figure 4.13 depicts the XRD diffractogram of TiO₂ microsphere, P25 TiO₂ and dried gel of R50. P25 TiO₂ consisted of mainly anatase with low percentage of rutile. The intensity of anatase phase was amplified for TiO₂ microsphere, but no

significant change was observed, indicating that the original TiO_2 had barely undergone a phase transformation during calcination process at 450°C .

Figure 4.13 XRD of P25 TiO_2 , dried gel of R50 and nano-structured TiO_2 microsphere.

It is clear that the resulting nano-structured TiO_2 microsphere was revealed as a submicron spherical photocatalyst with embedded nano-sized anatase crystallite. The submicron particle size of TiO_2 microsphere will possess a better potential in providing better separation and recovery in engineering application. At the same time the photocatalytic activity of TiO_2 microsphere could be preserved due to the embedded nano-sized anatase crystallite. The photocatalytic activity of nano-structured TiO_2 microsphere was verified in the next section.

4.4 Photocatalytic Activity of Nano-structured TiO_2 Microsphere

A preliminary test was carried out to elucidate the photocatalytic activity of nano-structured TiO_2 microsphere. Phenol (analytical grade) with an initial concentration of 100 ppm was chosen as the targeted compound in this preliminary study. The choice of this compound was motivated by the fact that phenol exhibited

weak adsorption on TiO_2 particles (Chhor et al., 2004). Figure 4.14 shows the degradation of phenol as a function of the irradiation time at pH 7. It was observed that the degradation of phenol followed an exponential decay form. Blank study (absence of photocatalyst) was carried out as a background check. About 40% of phenol was degraded after 60 min of UV light irradiation with the absence of the photocatalyst. The removal efficiency was greatly enhanced when the photocatalyst was added into the solutions. The removal efficiency after 60 min UV light irradiation was 60% and 70% for P25 TiO_2 and nano-structured TiO_2 microsphere, respectively. It was obvious that the nano-structured TiO_2 microsphere possessed a better photocatalytic activity than P25 TiO_2 .

Figure 4.14 Photocatalytic degradation of phenol as a function of irradiation time (phenol concentration: 100 mg/L; photocatalyst mass concentration: 1g/L).

The photodegradation kinetics of phenol in TiO_2 suspension was first assessed by first-order kinetic relationship and the coefficients obtained from the linear regression were given in Table 4.4. The pseudo first order reaction rate was 1.52 mg/L.min and 2.25 mg/L.min for P25 TiO_2 and nano-structured TiO_2 microsphere,

respectively. The half life values were calculated as 46 min for P25 TiO₂ and 31 min for nano-structured TiO₂ microsphere. The photocatalytic removal rates obtained according to the first-order kinetic model showed that nano-structured TiO₂ microsphere was more efficient than P25 TiO₂ in photodegradation of phenol.

Table 4.4 Pseudo-first-order kinetic parameters

Photocatalyst	Rate (mg/L.min)	k (min ⁻¹)	t _{1/2} (min)	R ²
P25 TiO ₂	1.52	0.0152	46	0.9883
Nano-structured TiO ₂	2.25	0.0225	31	0.9615

Langmuir-Hinselwood (L-H) equation was also used to explain the kinetics of the phenol photodegradation by P25 TiO₂ and nano-structured TiO₂ microsphere. The values of k_{L-H} and K_{ads} are used to explain the coefficients defining the rate determining reaction events and adsorption within an adsorbed monolayer at the oxide surface and the aqueous solution interface, respectively. Table 4.5 shows the L-H kinetic parameters from a linearization plot of $1/R$ vs $1/C$. The reactivity constant, k_{L-H} values were found as 1.041 mg/L.min and 2.868 mg/L.min for P25 TiO₂ and nano-structured TiO₂ microsphere, respectively. The tendency of phenol to be adsorbed by the two TiO₂ specimens was explained by the K_{ads} values obtained. P25 TiO₂ (K_{ads} = 0.0375 L/mg) showed a strong adsorption capacity as compared to nano-structured TiO₂ microsphere (K_{ads} = 0.0077 L/mg). The reduced adsorption capacity of TiO₂ microsphere might be due to the increased particle size of TiO₂ microsphere. Although the surface area of TiO₂ microsphere was identical to P25 TiO₂, the mass transfer was in fact slower. Nevertheless, the photocatalytic efficiency of nano-structured TiO₂ microsphere was better than P25 TiO₂.

Table 4.5 L-H kinetic parameters

Photocatalyst	Rate (mg/L.min)	k_{L-H} (min^{-1})	K_{ads} (L/mg)	$t_{1/2}$ (min)	R^2
P25 TiO ₂	1.041	1.319	0.0375	39	0.8267
Nano-structured TiO ₂	2.868	6.592	0.0077	21	0.9287

Table 4.6 Comparison of photocatalytic activities of TiO₂ specimens

Photocatalyst	Photocatalytic activity (mg/L.min)	Intrinsic photocatalytic activity (mg/L.min.m ²)	Specific photocatalytic activity (mg/L.min.g)
P25 TiO ₂	1.52	0.035	1.52
Nano-structured TiO ₂	2.25	0.054	2.25

It is also a common practice to compare photocatalyst activities based on catalyst surface area “intrinsic photocatalytic activity, mg/L.min.m²” and catalyst mass “specific photocatalytic activity, mg/L.min.g” (Bekbölet et al., 2002). In order to eliminate the BET surface area factor, and make the comparisons on a relative basis, intrinsic and specific photocatalytic activities for both TiO₂ species were also calculated (Table 4.6). BET surface area for P25 TiO₂ and nano-structured TiO₂ microsphere was 44 m²/g and 42 m²/g, respectively. The results in Table 4.6 showed that the actual photocatalytic rate did not necessarily depend on the BET surface area of the catalyst but rather on the availability of active sites for reactions. Therefore properties such as morphological and crystallographical might play important roles in the photocatalytic efficiencies.

It was clear that the increased photocatalytic efficiency of TiO_2 microsphere was due to its nano-sized anatase crystallite of about 10 nm which embedded within the TiO_2 microsphere. This was in agreement with Zhang et al. (1998), who reported that crystallite size of about 10 nm was an optimal crystallite size for TiO_2 to achieve the maximum photocatalytic efficiency. It was due to the fact that when the crystallite size fell below a critical size of approximately 10 nm, the semiconductors would exhibit chemical and optical properties different from those of the bulk material which was known as quantum size effect (Hoffmann et al., 1995).

In view of this, the photocatalytic activity of nano-structured TiO_2 microsphere was studied by UV-Vis spectrophotometer. The UV-Vis spectrophotometer with an integrating sphere attachment was used to probe the band structure or molecular energy levels in the materials since UV or visible light excitation would create photo-generated electrons and holes. Figure 4.15 shows the UV-Vis absorption spectra of P25 TiO_2 and nano-structured TiO_2 microsphere. Nano-structured TiO_2 microsphere showed a blue shift of about 3 nm at the absorption edge. The spectra of TiO_2 microsphere was shifted to higher energy which due to size quantization (Reddy et al., 2001). The blue shifts increased the effective band gap of TiO_2 microsphere, which in turn increased the redox potential (Hoffmann et al., 1995; Cao et al., 1999). Therefore it explained that the photocatalytic efficiency of nano-structured TiO_2 microsphere was better than P25 TiO_2 . In addition, the enhancement of crystallinity of anatase phase of nano-structured TiO_2 microsphere was also important in promoting the high photocatalytic efficiency as shown in Figure 4.14. This was in agreement with reports of Ding et al. (2000) and Yu et al. (2000), who claimed that anatase was much more photoactive than rutile.

Figure 4.15 UV-reflectometry of TiO₂ specimens.

Moreover, the morphological property of nano-structured TiO₂ microsphere was also crucial in enhancing its photocatalytic efficiency. It was known that aggregation of TiO₂ was difficult to avoid, particularly nano-sized TiO₂. The morphology and size of these aggregates can actually affect the light-scattering properties of the TiO₂, and subsequently the photon penetration (Maira et al., 2000). For TiO₂ microsphere, the secondary particle size of TiO₂ microsphere was well controlled between 10 to 50 μm , which formed from crystals of about 10 nm (from titanium coating sol) and 25 nm (P25 TiO₂). While the secondary particle size of P25 TiO₂ was uncontrolled, which formed from crystals of about 25 nm. The smaller crystals are generally poorer light scatterer than larger crystals as the scattering efficiency is proportional to r^4 in Rayleigh scattering (Maira et al., 2000). Hence the incident photons were scattered and lost mostly by reflection for P25 TiO₂ aggregation. As for TiO₂ microsphere, the nano-sized anatase crystallite was well distributed within the surface morphology as shown in Figure 4.7a, hence the surface active sites of TiO₂ microsphere was increased and allowed a greater number of scattered photons to penetrate into the microsphere. This suggested that

the increased photocatalytic efficiency of TiO_2 microsphere was due to better photo absorption and penetration.

4.5 Conclusion

Nano-structured TiO_2 microsphere was successfully synthesized via sol-gel spray coating technique without using any template. P25 TiO_2 , as the core and titania coating sol R50, as binder, were used to form nano-structured TiO_2 microsphere in this study. The titanium coating sol would transform into anatase crystallite with predetermined size. This method is very simple and easy to scale-up. The results of photodegradation of phenol showed that TiO_2 microsphere was more efficient than P25 TiO_2 , indicating that the actual photocatalytic rate did not necessarily require the dependency on the BET surface area of catalyst. Therefore the morphological such as secondary particle size and crystallographical properties such as crystallite size and crystallinity of TiO_2 played important roles in the photocatalytic efficiencies. This larger particle size of TiO_2 microsphere has a good potential in providing better separation and recovery in engineering application while the nano-sized anatase crystallite which embedded within the TiO_2 microsphere preserved its photocatalytic activity.

CHAPTER 5

ADSORPTION STUDY OF HUMIC ACID ON NANO-STRUCTURED TITANIUM DIOXIDE MICROSPHERE

5.1 Introduction

HA comprises one of the most widely investigated groups of natural organic matters. It will impart undesirable colour, complex with metal ions and act as a precursor for the formation of trihalomethanes. These naturally occurred organic matters are the culprits in drinking water supply which consequently lead to the deterioration of human health. Treatment processes include chemical coagulation/flocculation, adsorption, sand filtration, and membrane technologies have been incorporated in water treatment processes for the removal of HA (Thorsen, 1999; Bai and Zhang, 2001; Sun et al. 2004).

Adsorption process is often used as a pretreatment process before the membrane filtration or as an individual separation unit process to minimize the presence of HA in water. Various adsorbents, including activated carbon (Starek et al., 1994; Han et al., 2003; Tomaszewska et al., 2004; Lorenc-Grabowska and Gryglewicz, 2005), metal oxides (Gu et al., 1994; Vermeer et al., 1998; Illés and Tombácz 2004; Uyguner and Bekbolet, 2004), aminated polyacrylonitrile fibers (Deng and Bai, 2004) have been reported to adsorb HA from water. The application of activated carbon is not always technically advantageous due to the high regeneration cost involved and further disposal required. The adsorption of HA on metal oxides particularly TiO_2 has gained attention due to its regenerative characteristic. TiO_2 is the most popular and often used as a photocatalyst in photocatalytic oxidation process (PCO) due to its non-toxicity, high oxidation strength, high chemical stability and inexpensiveness. The spent TiO_2 could be regenerated by UV light irradiation via PCO process. However, commercial TiO_2 Degussa P25 is a fine powder (25-30 nm) and is not easily separated from treated water for reuse. Another drawback of commercial TiO_2 P25 is that it easily agglomerates and loses photocatalytic activity in water. A novel nano-structured TiO_2 microsphere was developed as described in Chapter 4 to overcome these problems.

However the adsorption behavior and kinetics of HA onto TiO_2 remained unclear. The adsorption of HA is a rather complex process which depends on the properties of HA and TiO_2 , and the solution condition. In addition, for macromolecule like HA, solution chemistry such as pH and cation strength could also affect the conformation and hydration of the molecules, and therefore will have an impact on the adsorption process (Vermeer et al., 1998; Avena and Koopal, 1999; Illés and Tombácz 2004). In general the adsorption of HA onto metal oxides is observed with decreasing pH and increasing cation strength.

This chapter discussed the adsorption of humic acid (HA) onto the nano-structured TiO_2 microsphere. The objective of this chapter was to understand the effects of solution chemistry on the extent and kinetics of adsorption of HA onto nano-structured TiO_2 microsphere. This chapter was divided into two sections. First section focused on the effect of pH and Ca^{2+} concentration on the adsorption extent of HA on nano-structured TiO_2 microsphere. The adsorption kinetics of HA on nano-structured TiO_2 microsphere was discussed in the second section.

5.2 Adsorption of HA on Nano-structured TiO₂ Microsphere

5.2.1 Binary System: HA and Nano-structured TiO₂ Microsphere

The experimental procedure was described in chapter 3. In the binary system, there would be only nano-structured TiO₂ microsphere present in the HA solution. Thus the effect of solution pH on the adsorption of HA onto nano-structured TiO₂ microsphere was identified in the binary system. The investigated pH values were 3 (acidic), 7 (neutral) and 9 (basic) to replicate the 3 different conditions in solution. The effect of solution pH on the adsorption of HA is shown in Figure 5.1. Obviously, the extent of adsorption generally increased with a decrease of initial pH. About 5.1 mg/g of the HA was adsorbed at pH 9. There was a slight increase of adsorption extent of HA at pH 7 to 5.7 mg/g. As the pH solutions decreased to pH 3, the HA adsorption increased to about 16.7 mg/g which was about 80% removal from the solution.

Figure 5.1 Effect of pH on adsorption of HA onto nano-structured TiO₂ microsphere.

The analysis of variance (ANOVA) was used to evaluate the effect of pH on the adsorption extent of HA onto nano-structured TiO₂ microsphere. The information of

ANOVA on single-factor experiment for fixed effect model was disclosed in Appendix B. Hypothesis was made that different pH values did not affect the adsorption of HA onto nano-structured TiO₂ microsphere. The hypotheses were:

$$H_0 = \mu_1 = \mu_2 = \mu_3 = 0$$

$$H_1 = \mu_i \neq 0 \text{ for at least one } i.$$

Where μ_i = mean of the i^{th} treatment.

Confidence level, $\alpha = 0.05$ was used in the analysis. The AVONA was summarized in Table 5.1.

Table 5.1 ANOVA analysis for effect of pH on HA adsorption.

<i>Source of Variation</i>	<i>Sum of squares</i>	<i>Degrees of Freedom</i>	<i>Mean Square</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.8437	2	0.4218	151.989	1.16×10^{-7}	8.022
Within Groups	0.0250	9	0.0028			
Total	0.8686	11				

Since $F_{\text{critical}} = 8.022$, H_0 was rejected and it was concluded that pH conditions would significantly affect the mean adsorption extent of HA onto the nano-structured TiO₂ microsphere. It was found that the P-value for this test statistic was 1.16×10^{-7} . Since this P-value was considerably smaller than $\alpha = 0.05$, it was also evidenced to conclude that H_0 was not true.

ANOVA assumes that the observations are normally and independently distributed with the same variance for each factor level. These assumptions should be checked by examining the residuals (that is the difference between an observation and the corresponding observed treatment mean). Figure 5.2 shows the normal probability plot of residuals from the adsorption of HA on nano-structured TiO₂ microsphere. It

did not revealed any model inadequacy or unusual problem with the assumptions.

Figure 5.2 Normal probability plots of residuals.

5.2.2 Ternary System: HA, Nano-structured TiO₂ Microsphere and Ca²⁺

The experimental procedure was same as in binary system as described in chapter 3. The ternary system which comprised of Ca²⁺, HA and nano-structured TiO₂ microsphere was carried out to distinguish the effect of Ca²⁺ in the adsorption extent of HA onto nano-structured TiO₂ microsphere in aqueous solution. The Ca²⁺ concentration was fixed at 0 mg/L, 20 mg/L, 50 mg/L and 80 mg/L. The pH value of the solution was also fixed at 3 (acidic), 7 (neutral) and 9 (basic). Experimental results clearly indicated that the presence of Ca²⁺ in the solution greatly enhanced the adsorption capacity of HA. Figure 5.3 shows that the adsorption extent of HA was significantly increased with the presence of Ca²⁺ regardless the pH conditions. At 80 mg/L Ca²⁺ concentration, the adsorption extent was increased by 60% and 50% for pH 9 and pH 7, respectively. Apparently, the adsorption extent was gradually increased with increasing Ca²⁺ in solution. The adsorption extent almost reached saturation with increasing Ca²⁺ concentration to 80 mg/L.

Figure 5.3 Effect of Ca^{2+} concentration on adsorption of HA on nano-structured TiO_2 microsphere at different pH condition.

ANOVA was used to evaluate the effect of Ca^{2+} concentration on the adsorption of HA onto nano-structured TiO_2 microsphere and the interaction of Ca^{2+} and pH condition. The information of ANOVA on two-factor experiment for fixed effect model was disclosed in Appendix B. Hypothesis was made that the different Ca^{2+} concentration and pH values did not affect the adsorption of HA onto nano-structured TiO_2 microsphere. The tested hypotheses were as follows:

a) Effect of pH (factor A)

$$H_{0A} = \mu_{A1} = \mu_{A2} = \mu_{A3} = 0 \text{ (no main effect of factor A)}$$

$$H_{1A} = \mu_{Ai} \neq 0 \text{ for at least one } i.$$

b) Effect of Ca^{2+} concentration (factor B)

$$H_{0B} = \mu_{B1} = \mu_{B2} = \mu_{B3} = \mu_{B4} = 0 \text{ (no main effect of factor B)}$$

$$H_{1B} = \mu_{Bi} \neq 0 \text{ for at least one } i.$$

c) Interaction effect between pH and Ca^{2+} concentration

$$H_{0AB} = \mu_{A1}\mu_{B1} = \mu_{A1}\mu_{B2} = \mu_{A1}\mu_{B3} = \mu_{A1}\mu_{B4} = \mu_{A2}\mu_{B1} = \mu_{A2}\mu_{B2} = \mu_{A2}\mu_{B3} = \mu_{A2}\mu_{B4} \\ = \mu_{A3}\mu_{B1} = \mu_{A3}\mu_{B2} = \mu_{A3}\mu_{B3} = \mu_{A3}\mu_{B4} = 0 \text{ (no interaction)}$$

$$H_{1AB} = \text{at least one } (\mu_A\mu_B)_{ij} \neq 0$$

$\alpha = 0.05$ was used in the analysis. The AVONA was summarized in Table 5.2.

Table 5.2 ANOVA analysis for effect of pH and Ca^{2+} concentration on HA adsorption.

<i>Source of Variation</i>	<i>Sum of Squares</i>	<i>Degrees of Freedom</i>	<i>Mean Square</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Sample	0.2549	2	0.1275	139.936	4.83×10^{-9}	3.885
Columns	0.9392	3	0.3131	343.671	6.77×10^{-12}	3.490
Interaction	0.1879	6	0.0313	34.383	7.01×10^{-7}	2.996
Within	0.0109	12	0.0009			
Total	1.3929	23				

Since $139.936 > 3.885$, the null hypothesis H_{0A} was rejected at level 0.05, hence it could be concluded that different pH values did affect the adsorption extent which was agreed in the binary system analysis. The null hypothesis H_{0B} was also rejected since $343.671 > 3.490$; hence the Ca^{2+} concentration could affect the adsorption extent of HA onto nano-structured TiO_2 microsphere. The interaction effect between pH and Ca^{2+} concentration was significant since $34.38 > 2.996$ as shown in Table 5.2. In fact, it was found that the P-value for all the test statistics was considerably small to support the entire conclusion. Figure 5.4 shows the normal probability plot of residuals from the adsorption of HA onto nano-structured TiO_2 microsphere. It did not revealed any model inadequacy or unusual problem with the assumptions.

Figure 5.4 Normal probability plots of residuals.

5.3 Regression Analysis

Experimental results indicated that pH and Ca^{2+} could affect the adsorption extent of HA onto nano-structured TiO_2 microsphere. A model that could approximate the true response function within a studied region was determined. The amount HA adsorbed was the dependent output in this study. Regression analysis was performed on the data obtained. The following equations show that the response functions with first order and second order for pH and Ca^{2+} concentration, respectively:

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_{12} X_1 X_2 \quad (5.1)$$

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_{11} X_1^2 + b_{22} X_2^2 + b_{12} X_1 X_2 \quad (5.2)$$

Where Y is the predicated response, b_i , b_{ii} and b_{ij} are coefficients estimated by the model. The represent the first order, second order and interaction effects of X_1 (pH values) and X_2 (Ca^{2+} concentration) factors on the response, respectively. The fit quality of the model was determined by the coefficient of determination (R^2) and

the analysis of variance (ANOVA). The experimental results indicated an empirical relationship between the response and the input variables expressed by the following fitted regression model, a second order polynormal equation:

$$Y = 0.833 - 0.095X_1 + 0.234X_2 + 0.089X_1^2 - 0.188X_2^2 + 0.114X_1X_2 \quad (5.3)$$

$$(R^2 = 0.9147, p = 0.00027)$$

Analysis of variance (ANOVA) was conducted in order to determine the abovementioned second-order polynomial equation was a significant fit with the experimental result. The result of ANOVA is given in Table 5.3. The result revealed that Equation 5.3 was adequate to explain the relationship between the response and the variables. The coefficient of determination was 0.9147, indicating a high correlation between the experimental results and predicted values. In addition, a very low p-value of 0.000274 obtained from the F-test demonstrated a very high significance for this second order equation. In general, a p-value lower than 0.01 indicated the model was considered to be statistical significant.

Besides the linear effect of pH and Ca^{2+} concentration on the adsorption of HA onto nano-structured TiO_2 microsphere, Equation 5.3 also provided an understanding on the quadratic and interaction effect of the parameters. The significance of the estimated parameters was tested via p-values and t-value from t-test. t-test was used to determine the significance of the regression coefficients of the parameters. Conversely, the p-values were used to check the significance of each of the interactions among the variables. According to Myers and Montgomery (1995), a larger t-value and smaller p-values identify the effect that appears to be very important.

Experimental results showed that all the effects were highly significant except for second-order main effect of pH (X_1^2). The first-order main effect of Ca^{2+} concentration was the most significant effect with a smallest p-value. The magnitudes of X_2 and X_2^2 indicated a positive influence on HA adsorption extent, while X_1 and X_1^2 indicated a negative influence. In terms of interaction, the relation between pH and Ca^{2+} concentration (X_1X_2) was also significant with the p-value of 0.04.

Table 5.3 ANOVA for the fitted second-order polynomial model

Source of variation	Sum of squares	Degrees of freedom	Mean square	Fo	P-value	F crit
Regression	0.6665	5	0.1333	12.87	0.000274	0.9976
Error	0.0621	6	0.0104			
Total	0.7286	11				
R ² =	0.9147					

Table 5.4 Estimated parameters and their significance

Variable	Parameter		t for Ho	
	Estimate	Standard Error	Coefficient = 0	P-Value
Intercept	0.83	0.07	11.69	
x ₁	-0.09	0.04	-2.62	0.0307
x ₂	0.23	0.04	5.99	0.0003
x ₁ ²	0.09	0.07	1.25	0.2470
x ₂ ²	-0.19	0.07	-2.74	0.0256
x ₁ x ₂	0.11	0.05	2.44	0.0405

Figure 5.5 shows the response surface contour plot (Equation 5.3) depicting the adsorption extent of HA onto nano-structured TiO₂ microsphere over different pH and Ca^{2+} concentration. The adsorption extent could reach almost saturation at lower pH with increased Ca^{2+} concentration. This result was agreeable with most of the studies (Dionasiou et.al., 2000; Jones and O'Melia, 2000; Wang et al., 2001b; Li et al., 2002). Hence the second-order polynomial equation developed in this study

was a significant fit with the experimental result. In terms of individual effect, the effect of Ca^{2+} concentration was more prominent than pH condition although both effects were found significant in enhancing the adsorption extent of HA on TiO_2 microsphere. The interaction between pH and Ca^{2+} concentration was also significant. The study revealed that the adsorption extent could reach saturation with high Ca^{2+} concentration (50 mg/L) in acidic condition (pH 3).

Figure 5.5 Response surface plot for the adsorption extent versus pH and Ca^{2+} concentration.

5.4 Adsorption Isotherms

Adsorption isotherms describe the relation between the activity or equilibrium concentration of the adsorptive and the quantity of adsorbate on the surface at constant temperature. In general, adsorption isotherms have been classified into four types depending on their shapes as L-type, S-type, C-type and H-type (Sparks, 1995).

The equilibrium adsorption data of HA onto nano-structured TiO₂ microsphere at different pH value is shown in Figure 5.6. The isotherms observed were classified as L-shaped (Langmuir) isotherms. The slopes showed a decreasing trend as concentration increased as the vacant adsorption sites was decreased when the adsorbent became covered. The adsorption behavior of this type of isotherm could be explained by high affinity of the adsorbent for the adsorbate at low concentration, which then decreased as concentration increased. The results clearly indicated that the adsorption capacities increased as the initial HA concentration increased. The isotherm curve obtained at pH 3 was remarkably higher than those two isotherm curves obtained at pH 7 and pH 9. Thus it could be explained that the strong affinity between nano-structured TiO₂ microsphere and HA was due to the electrostatic attraction between them.

Figure 5.6 Adsorption isotherms of humic acid on nano-structured TiO_2 microsphere at pH 3, 7 and 9.

Figure 5.7 shows the adsorption isotherms of HA onto nano-structured TiO_2 microsphere at different pH value in the presence of Ca^{2+} . The isotherms displayed are classified as H-type (high affinity) isotherm, indicating the strong adsorbate-adsorbent interaction which is often not reversible. The high affinity between the adsorbate and adsorbent was enhanced by the ionic strength of Ca^{2+} in solutions. However the adsorption isotherms were purely descriptions of macroscopic data and did not definitely prove a reaction mechanism. Further discussion on the adsorption behavior between HA and nano-structured TiO_2 microsphere was conferred in next section.

Figure 5.7 Adsorption isotherms of humic acid on nano-structured TiO_2 microsphere at pH 3, 7 and 9 in the presence of Ca^{2+} .

5.5 Equilibrium-based Adsorption Model

Several equilibrium-based models were used to describe the adsorption of HA onto nano-structured TiO_2 microsphere including the Langmuir equation, widely used Freundlich equation and Langmuir-Freundlich equation in this section.

5.5.1 Langmuir Model

Langmuir equation is a commonly used adsorption model. It has been used in many fields to describe the sorption on colloidal surfaces. For most organic compound adsorption capacity on TiO_2 catalyst could be well described by Langmuir equation (Chen and Ray, 1999). However most of the assumptions made in the development of the equation are not valid for the heterogeneous surfaces such as TiO_2 . The Langmuir adsorption equation can be expressed as:

$$q_e = \frac{q_{\max} C_e}{1/K_a + C_e} \quad (5.4)$$

where q_e is the amount of humic acid adsorbed per unit weight of nano-structured TiO_2 microsphere at equilibrium concentration (mg/g), C_e is the final concentration in the solution (mg/L), $q_{\max}$ is the maximum adsorption at monolayer coverage (mg/g), and K_a is the adsorption equilibrium constant (L/mg). Rearranging to a linear form, Equation (5.4) becomes

$$\frac{1}{q_e} = \frac{1}{K_a q_{\max} C} + \frac{1}{q_{\max}} \tag{5.5}$$

Figure 5.8 The corresponding Langmuir plot of humic acid on nano-structured TiO_2 microsphere at pH 3, 7 and 9. (solid line: Langmuir plot; ■, ◇, ● : experimental results)

The data are plotted as $1/q$ versus $1/C$ and shown in Figure 5.8, indicating that the adsorption of HA onto nano-structured TiO_2 microsphere were well fitted by Langmuir model. The adsorption parameters was obtained from the slope and intercept of the plots and summarized in Table 5.5. The maximum adsorption, $q_{\max}$ was 33.557 mg/g in acidic medium and 7.758 mg/g in basic medium, respectively. In Langmuir isotherm, $q_{\max}$ were determined solely by the nature of the adsorbent

and were independent of the nature of the adsorbate. Hence the orientation of adsorbate molecules on the surface of adsorbent would affect the monolayer capacity as determined from the area occupied by the molecules (Faust and Aly, 1987). Apparently, pH condition had affected the orientation of HA on the surface of TiO₂ microsphere and therefore $q_{\max}$ value obtained in this study varied at different pH value. $q_{\max}$ was higher in acidic medium and vice versa. With the same surface area of adsorbent, high adsorption capacity of HA molecules onto TiO₂ microsphere in lower pH condition implied that the structure or shape of HA molecules was small. Indeed, HA molecules could change from a large, flexible and linear shape at high pH to a small, rigid and spherical shape at low pH (Wang et al., 2001b). This suggested that the HA molecules could adsorb in more compactly packing state at pH 3 than at pH 7 and 9.

Table 5.5 Langmuir adsorption model parameters for the adsorption of HA on nano-structured TiO₂ microsphere.

No	pH Value	Ionic strength	R ²	$q_{\max}$ (mg/g)	K _a
1	3	N/A	0.9728	33.557	0.613
2	7	N/A	0.9473	6.949	0.321
3	9	N/A	0.8940	7.758	0.117

The system became complex in the presence of Ca²⁺ in solution. Langmuir model was not able to fit the experimental data. Despite the limitation in this model, it was not sufficient to model the adsorption behavior of HA in an ionic solution. There was also another possibility that the adsorption system proceed beyond monomolecular layers, hence Langmuir model was not applicable for analytical description of this system. Experimental results suggested that the Langmuir model was sufficient to explain the adsorption behavior of HA onto nano-structured TiO₂ microsphere in a simple binary system which consisted only HA and TiO₂. In view of this, Freundlich model was applied to model the adsorption behavior of HA onto

nano-structured TiO₂ microsphere.

5.5.2 Freundlich Model

The Freundlich equation is an empirical adsorption model that has been widely used to describe gas phase adsorption and solute adsorption. This model encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. It can be expressed as

$$q = K_d C^{1/n} \quad (5.6)$$

where q is the amount of humic acid adsorbed per unit weight of nano-structured TiO₂ microsphere at equilibrium concentration (mg/g), C is the final concentration in the solution (mg/L), K_d is the distribution coefficient representing the adsorption capacity, and n is a correction factor depicting the adsorption intensity (dimensionless). The linear form of Equation 5.6 can be expressed as

$$\log q = \frac{1}{n} \log C + \log K_d \quad (5.7)$$

The Freundlich model was applied to explain the adsorption of HA onto nano-structured TiO₂ microsphere in this study. The adsorption of HA on TiO₂ was successfully interpreted by Freundlich model (Bekbölet et al., 2002). The plots of Log q versus Log C of experimental data associated with and without the presence of cation strength are presented in Figures 5.9 and 5.10 respectively. The Freundlich adsorption model constants (K_d and $1/n$) are shown in Table 5.6.

Figure 5.9 Freundlich model fitted to experimental results at different pH values. (solid line: Freundlich plot; ■, ◇, ● : experimental results)

Figure 5.10 Freundlich model fitted to experimental results at different pH values in the presence of Ca^{2+} . (solid line: Freundlich plot; ■, ◇, ● : experimental results)

The results revealed that K_d values was 13.152 for $\text{pH} = 3$ and 1.089 for $\text{pH} = 9$ indicating higher adsorption capacity of TiO_2 microsphere for HA under acidic condition with the absence of cation. By addition of cation in the solutions, the K_d

values increased by at least 2 fold to 27.040 at lower pH condition and 9.528 at higher pH condition. The adsorption capacity was greatly enhanced with the presence of cation in solution. Most of the $1/n$ values obtained were less than 1, implying that the adsorptive capacity was only slightly reduced at low equilibrium concentration. For $1/n$ close to 1, indicating a high adsorptive capacity at high equilibrium concentration that rapidly diminished at low equilibrium concentration. It was observed that the adsorption intensity values for isotherms at pH 7 and pH 9 with the presence of ionic strength were approaching to linearity. Hence equation (5.6) could be turned into a simpler form:

$$q = K_d C \quad (5.8)$$

K_d can be termed K_p , partition coefficient. Equation 5.8 suggests a linear adsorption isotherm. This type of isotherm suggests a reversible adsorption/desorption, with a small temperature effect on adsorption and non-competitive when other adsorbents are added. K_p provides the ratio of the amount of a material that is adsorbed to the amount that is in solution (Sparks, 1995).

Freundlich equation did not predict an adsorption maximum. Therefore the adsorption density τ was used to explain the amount of adsorbed solute per unit surface area of the adsorbent (Uyguner and Bekbölet, 2004):

$$\tau = \frac{C_s}{A} \quad (5.9)$$

where C_s is the amount of solute adsorbed (mg/g), A is the surface area of the adsorbent (m^2/g). The average BET surface area of nano-structured TiO_2 microsphere was about $42 m^2/g$ from chapter 4.3.2. The adsorption density was

calculated at the point where the curvature of the adsorption pattern changed. With the presence of cation strength in solution, the adsorption density of nano-structured TiO_2 microsphere at pH 3, 7 and 9 increased significantly by 4-6 times.

Table 5.6 Freundlich adsorption model parameters for the adsorption of HA on nano-structured TiO_2 .

No	pH value	Ionic strength	R^2	$1/n$	K_d	τ
1	3	N/A	0.8609	0.312	13.152	0.529
2	7	N/A	0.9894	0.332	2.286	0.143
3	9	N/A	0.9511	0.556	1.089	0.156
4	3	Ca^{2+}	0.8629	0.677	27.040	2.236
5	7	Ca^{2+}	0.9679	0.920	6.266	0.975
6	9	Ca^{2+}	0.8706	1.077	9.528	1.070

Figure 5.11 shows the experimental results fitted by Freundlich model with increasing Ca^{2+} in solution. The adsorption of HA in the ternary system (HA, TiO_2 microsphere and Ca^{2+}) was fitted well by Freundlich model. It was observed that the adsorption capacity increased with increasing Ca^{2+} concentration in the solution from 2.286 to 6.266 for Ca^{2+} concentration from 0 to 50 mg/L, respectively.

Figure 5.11 Freundlich model fitted to experimental results at different pH values with increasing Ca^{2+} in solutions (0, 20 and 50 ppm). (solid line: Freundlich plot; ■, ◇, ● : experimental results)

Table 5.7 Freundlich adsorption model parameters for the adsorption of HA on nano-structured TiO_2 microsphere.

No	pH Value	Ca^{2+} (mg/L)	R^2	$1/n$	K_d	τ
1	7	0	0.9894	0.332	2.286	0.143
2	7	20	0.9163	0.752	5.645	0.502
3	7	50	0.9679	0.920	6.266	0.975

Since HA adsorption on the nano-structured TiO_2 microsphere could be well described by both the Langmuir and Freundlich models, the experimental results therefore indicated that removal of HA followed a monolayer adsorption processes on the surfaces of the TiO_2 which displayed heterogeneous adsorption property. To support this statement, the HA adsorption was further modeled with Langmuir-Freundlich model.

5.5.3 Langmuir-Freundlich (L-F) Model

For high solution concentration, the isotherms were poorly modeled by the Langmuir equation. This is due to the fact that this model assumes a constant energy of adsorption at all sites and the molecules are adsorbed on definite sites on the surface of the adsorbent. While the Freundlich model does not use this assumption, it assumes an infinite supply of unreacted adsorption sites and therefore saturation behavior of the adsorbent cannot be determined. The L-F model behaves as a Langmuir equation at low concentrations and as a Freundlich equation at high concentrations. This isotherm model has been proven successful in modeling a number of other system involving the adsorption of simple organic compounds and polymers to heterogeneous materials (Yoon et al., 1996; Kilduff and Wigton, 1999; Umpley et al., 2001; Zimmerman et al., 2004).

Langmuir-Freundlich (L-F) isotherm is also known as the Sips equation (Zimmerman et al., 2004). This model describes an equilibrium relationship between the concentration of adsorbed compound and the equilibrium compound concentration in solution and can be expressed as:

$$S = \frac{NbC^m}{1 + bC^m} \quad (5.10)$$

Where S = concentration of adsorbed compound, C = equilibrium concentration (mg/L). N , b and m are three fitting coefficients that represent the adsorption capacity, the binding affinity of the compound, and the heterogeneity index, respectively. m varies from 0 to 1: $m = 1$ reflects a homogeneous material and $m < 1$, reflects the material's heterogeneous characteristic. As b approaches zero at low binding affinities, the equation reduces to the classical Freundlich equation. As the name implies, the L-F isotherm is a composite of Langmuir and Freundlich

isotherms and can reduce to either at its limits.

Figure 5.12 Fitted L-F isotherms at different pH solutions (3, 7 and 9). (solid line: L-F plot; ■, ◇, ● : experimental results)

Figure 5.13 Fitted L-F isotherms at different pH solution (3, 7 and 9) in the presence of Ca^{2+} . (solid line: L-F plot; ■, ◇, ● : experimental results)

Table 5.8 L-F fitting parameters for humic acid adsorption on nano-structured TiO₂ microsphere.

No	pH Value	Ionic strength	R ²	N	B	m
1	3	N/A	0.9958	31	0.600	1.00
2	7	N/A	0.9497	8	0.250	1.00
3	9	N/A	0.9015	13	0.045	1.00
4	3	Ca ²⁺	0.9399	155	0.200	0.95
5	7	Ca ²⁺	0.9926	170	0.040	0.95
6	9	Ca ²⁺	0.9632	200	0.060	0.95

L-F isotherm was used to predict the adsorption behavior of HA onto nano-structured TiO₂ microsphere. Of the model tested, the L-F model provided the best fit to the data with R² values more than 0.9 (Table 5.8). With the absence of cation in solution, the heterogeneous index, $m = 1$, the L-F isotherm could be reduced to Langmuir isotherm. The corresponding adsorption isotherm (Figure 5.12) was curved downward when plotted in log format, indicating the characteristic of saturation at high coverage as agreed by Umpley et al. (2001). The L-F parameter, N, the adsorption capacity was decreasing from 31 to 13 as pH values increased. These values were almost matching the values obtained from the Langmuir equation (Table 5.5). The binding affinity, b, increased from 0.045 to 0.6 as the pH values decreased from 9 to 3 respectively. This result revealed that the binding affinity between HA and nano-structured TiO₂ microsphere were greatly dependent on pH conditions.

On the other hand, the presence of Ca²⁺ in solutions would enhance the adsorption capacity tremendously by five to ten times. The m values obtained were less than 1, indicating a heterogeneous surface of adsorbent. Thus, it could verify that the Langmuir equation was not applicable to model the adsorption behavior of HA onto TiO₂ microsphere when the cation existed in solution. The corresponding adsorption

isotherms in Figure 5.13 shows the linear adsorption isotherm when plotted in log format, which was typical for a heterogeneous system. From the results obtained, in the case of absence of Ca^{2+} cation, the adsorption process was probably dominated by a monolayer adsorption process. Multilayer adsorption might occur when Ca^{2+} was present in the solution.

As a conclusion, Langmuir or Freundlich isotherms could be used to accurately model the adsorption behavior of HA on nano-structured TiO_2 microsphere at different solution conditions (pH or cation strength), despite the limitations of each model. The L-F isotherm was capable to model the adsorption behavior of HA in any conditions. In the absence of cation in solutions, the L-F isotherm reduced to the Langmuir isotherm. On the other hand, the L-F isotherm could be effectively reduced to Freundlich isotherm when $m < 1$, yielding a straight line in the log plot. Thus, the LF fit overlays directly on the Langmuir fit when the cation was absent in solution.

5.6 Adsorption Kinetics of Humic Acid on Nano-structured TiO₂ Microsphere

The kinetics of adsorption was used to establish the time course of HA uptake onto nano-structured TiO₂ microsphere. It was generally agreed by many researchers that the adsorption of HA on a solid surface involved two important processes (Avena and Koopal, 1999; Zhang and Bai, 2003):

- 1) Transport from the bulk solution to the subsurface plane adjacent to the surface
- 2) Attachment to the surface

Rearrangements in the adsorbed layer due to reformation and polydispersity effects and/ or other slow adsorption processes that might become evident at relatively long times could be neglected in the initial stages of the adsorption process. As the adsorbent surface was bare in the initial stage, the adsorption kinetic transport of HA from the bulk solution to the surface of TiO₂ microsphere could be governed by the diffusion of HA molecules from the bulk solution to the surface of TiO₂ microsphere. The HA would attach on TiO₂ microsphere surface instantly. The amount of adsorption controlled by the diffusion process could be derived from the Fickian diffusion model (Siqueira et al., 1996) as:

$$q(t) = 2CoS\sqrt{Dt/\pi} = kt^{\frac{1}{2}} \quad (5.11)$$

Where $q(t)$ is the amount adsorbed per unit surface area of the TiO₂ microsphere at time t , Co is the initial concentration of the HA in the bulk solution, S is the specific surface area of TiO₂ microsphere, D is the diffusion coefficient and k is a constant. The adsorption process is considered diffusion controlled if step 1 is much slower than step 2. The diffusion controlled adsorption model has been successfully applied to HA adsorption on different adsorbents (Zhang and Bai, 2002; Deng and

Bai, 2004; Lorenc-Grabowska and Gryglewicz, 2005).

When there was a large number of HA molecules were adsorbed on the surface of TiO₂ microsphere. Further adsorption could only take place if the arriving HA molecules could find available adsorption sites. Hence the later stage of the adsorption process could most likely be an attachment-controlled process. In addition, when a layer of HA was adsorbed on the surface, the electrostatic repulsion between the adsorbed layer and the incoming HA molecules hindered the transport of HA from the bulk solution to the subsurface. A simplified model for the attachment-controlled adsorption may be given as (Siqueira et al., 1996; Deng and Bai, 2004):

$$\Gamma(t) = \Gamma_e [1 - \exp(-t/\tau)] \quad (5.12)$$

Where $\Gamma(t)$ and Γ_e are the amount adsorbed per unit surface area of TiO₂ microsphere at time t and at adsorption equilibrium, and τ is a parameter depicting the possible conformation change of adsorbed HA. Equation 5.12 can be revised to:

$$-\ln[(q_e - q_t)/q_e] = \frac{1}{\tau} t \quad (5.13)$$

Equation 5.13 suggests that under an attachment-controlled adsorption process, $-\ln[(q_e - q_t)/q_e]$ versus t would generate a straight line.

5.6.1 Diffusion-Controlled Adsorption Kinetics

Equation 5.11 indicates that $q(t)$ versus $t^{0.5}$ would follow a linear relationship under a diffusion-controlled adsorption mechanism. Figure 5.14 shows the plots at different pH values. A linear relationship was observed at each pH conditions at the

initial stage lasted about 1 min. The results suggest that the adsorption of HA onto TiO_2 microsphere in the initial stage followed a diffusion controlled adsorption kinetics. Decreasing pH caused an increase on the adsorption rate (increase of the slope). The linear dependence was significant at pH 3. The HA molecules were immediately adsorbed as the HA molecules arrived at the subsurface. Figure 5.15 shows the plots for HA adsorption at increasing Ca^{2+} concentration. Similarly, a linear relationship was observed in the initial stage of HA adsorption.

Figure 5.14 Adsorption kinetics of HA on nano-structured TiO_2 microsphere at pH 3, 7 and 9.

Figure 5.15 Adsorption kinetics of HA at pH 7 in different Ca^{2+} concentration.

5.6.2 Attachment-Controlled Adsorption Kinetics

At the later stage of adsorption, the plot of $-\ln[(q_e - q_t)/q_e]$ versus time $\cdot t$ is also observed to generate a straight line for the experimental adsorption data in each pH values (Figure 5.16) and increasing Ca^{2+} concentration (Figure 5.17), verifying that HA adsorption onto TiO_2 microsphere in the later stage obeys attachment-controlled adsorption kinetics. As shown in Figure 5.16 and 5.17, the attachment-controlled adsorption kinetics dominated the most part of the adsorption process. The adsorption rate of HA were significantly affected by solution chemistry. pH condition and cation strength were found to have significant effect on the adsorption kinetics of HA onto nano-structured TiO_2 microsphere.

Figure 5.16 Adsorption kinetics of HA on nano-structured TiO₂ microsphere at pH 3, 7 and 9.

Figure 5.17 Adsorption kinetics of HA at pH 7 in different Ca²⁺ concentration.

5.7 Molecular Size Analysis of HA Molecules

The adsorption extent and rate of HA molecules on nano-structured TiO₂ microsphere was greatly dependent on pH and cation strength. It was revealed that the adsorption extent and rate increased as pH decreased and in the presence of cation strength. It could be explained the by the size of HA molecules. The molecular weight (MW) distributions of HA molecules were determined by high performance size exclusion chromatography (HPSEC). The sizes of HA were referred to as apparent molecular weight. The molecular size region in which the highest percentage of the molecules located between 100 000 – 30 000 at 43% which was similar to the results reported by Kerc et al. (2004). Table 5.9 shows the distribution percentage of HA molecules at different MW range from Figure 3.3. Most of the HA molecules were located above 10 000 MW. However the pH conditions would alter the molecular size of HA molecule in solutions. The highest percentage, 56% of molecules was located between 1 000 000 – 100 000 at pH 9 reduced to 12% as pH value decreased to 3 (Table 5.9). Hence the MW fraction of 100 000 – 10 000 was increased from 35% to 73% when pH values was decreased from 9 to 3, respectively. The molecular size of HA molecule decreased with decreasing pH values. This was in agreement with Ghosh and Schnitzer (1980). HA molecules could change from a large, flexible and linear shape at high pH to a small, rigid and spherical shape at low pH.

Table 5.9 Percentage of molecular weight of HA at different pH values

Molecular weight	pH 3	pH 7	pH 9
> 1 000 000	-	-	6
1 000 000 – 100 000	12	21	56
100 000 – 10 000	73	69	35
10 000 – 1 000	13	8	1
< 1 000	2	2	2

The fraction of molecular size of HA molecules also decreased associated with the presence of Ca^{2+} in solutions. Table 5.10 displays the percentage of HA molecules at different molecular size range from Figure 3.4. As Ca^{2+} ion present in solution, the percentage of molecular size between 10 000 – 1000 was increased from 8% to 28% at pH 7. The percentage of molecular size at this range was approaching 45% as pH values decreased to 3. Hence it was revealed that ionic strength would reduce the molecular size of HA molecules in solutions as agreed by Ghosh and Schinitzer (1980).

Table 5.10 Percentage of molecular weight of HA at different pH values (with the presence of Ca^{2+}).

Molecular weight	pH 3	pH 7	pH 9
1 000 000 – 100 000	6	8	12
100 000 – 10 000	48	63	74
10 000 – 1 000	45	28	14
< 1 000	1	1	-

HA molecules would change to a small, rigid and spherical shape at low pH and increasing Ca^{2+} concentration, hence the diffusivity would increase with decreasing pH as agreed by Vermeer et al. (1998) and Wang et al. (2001b). The diffusivity of HA increased remarkably at low pH with the presence of Ca^{2+} . The smaller size HA molecules could diffuse faster to the subsurface of TiO_2 microsphere and subsequently increase the adsorption rate. Furthermore, HA molecules were assumed to fit their shape easily and conform into the adsorbed HA layer in acidic condition associated with the presence of Ca^{2+} (Zhang and Bai, 2002). Hence HA molecules could adsorb in more compactly packing state on TiO_2 microsphere. It explained the adsorption extent of HA was increased dramatically in acidic condition associated with the presence of Ca^{2+} in solution.

5.8 Conclusion

The adsorption of HA on nano-structured TiO₂ microsphere was rather a complex process that depended on the nature of the adsorbent surface, the nature of adsorbate and the solution condition. From the results obtained, it was found that the adsorption extent and rate of HA was greatly affected by solution chemistry (pH and cation strength). The adsorption extent and rate of HA would increase in acidic condition with increasing cation strength. L-F model could be used to accurately model the adsorption behavior of HA at any condition. L-F model was reduced to Langmuir model in binary system and reduced to Freundlich model in ternary system. It was found that the adsorption kinetics of HA on nano-structured TiO₂ microsphere followed two important stages: diffusion of HA from bulk solution to the surface of nano-structured TiO₂ microsphere, and attachment to the surface of nano-structured TiO₂ microsphere. The attachment controlled adsorption dominated the adsorption process at the later stage. This is because the diffusion process was very fast. It was revealed that the increased adsorption extent and rate was due to the size of HA molecules which were greatly dependent on pH and cation strength. The size of HA molecules decreased as the pH values decreased and in the presence of Ca²⁺ in solution. The smaller size HA molecules could diffuse faster to the subsurface of TiO₂ microsphere and subsequently increase the adsorption rate. Moreover the smaller size HA molecules could adsorb more compactly on the surface of TiO₂ microsphere and therefore the adsorption extent was increased as well.

CHAPTER 6

ADSORPTION MECHANISM OF HUMIC ACID ON NANO-STRUCTURED TITANIUM DIOXIDE MICROSPHERE

6.1 Introduction

In general the adsorption of HA on metal oxides is observed with decreasing pH and increasing cation strength (Vermeer et al., 1998). Nevertheless, the adsorption behavior of HA on metal oxides was not clearly defined by many researchers. It is due to the fact that the different nature of the adsorbent surface and adsorbate, and the solution condition. Furthermore, the roles played by various mechanisms which have been proposed to explain the interaction between HA and metal oxides such as electrostatic interaction (Vermeer and Koopal, 1998), ligand exchange (Gu et al., 1994), hydrophobic interaction (Chi and Amy, 2004), cation bridging (Engebretson and Wandruszka, 1998), entropic effect, hydrogen bonding etc., were less well understood. Different metal oxides and experimental conditions used by the individuals could attribute to the heterogeneity and complexity of HA and adsorbent surfaces. Because of these, different association mechanisms may be operative simultaneously and to varying degrees. Hence this chapter was undertaken to elucidate the interaction mechanisms between HA and nano-structured TiO₂ microsphere surface by using zeta potential measurement and x-ray photoelectron spectroscopy (XPS) techniques.

Zeta potential measurement is commonly used to qualitatively illustrate the charge distribution of compounds as a function of the solution pH or ionic strength. The information of surface charge of HA molecules and metal oxides could be easily obtained by zeta potential measurement (Bai and Zhang, 2001; Moriguchi et al., 2006). While XPS spectroscopy is a more sophisticated technique in identifying the elemental composition and oxidation states of a solid material surface. XPS spectroscopy is a surface analysis technique (the analyzed depth is of some nanometers under the sample surface), well adapted to derive information on the chemical environment of one atom. The principle of the technique lies in measuring the binding energy (BE) of core electrons ejected from this atom under photo-

ionisation. The measured BE enables to determine the nature of the chemical bonds in which the atom is implied (ionic or covalent character, nature of associated ligands). To investigate the adsorption of HA onto TiO₂ microsphere surface, XPS core-level peaks will derive the information for the chemical structure of organic solids by fitting peak intensity and position features. From the spectrum, the description of the chemical bonds and the organic functional groups implied in HA/trace elements association was useful to explain the interaction mechanism of HA on TiO₂ microsphere.

Few XPS data are available in the field of humic substances studies. Nefedov et al. (1998) utilized XPS to identify the surface complexes formed by uranyl, calcium ions with natural and synthetic HA. They discovered that the COOH group of HA interacted with uranyl ions and calcium ions to form complex. Schild et al. (2000) used XPS to investigate the Th(IV)-humate complexes and showed that chemical shifts were similar to Th(IV) complexes with an ion exchanger containing only carboxylic functional groups, suggesting that Th(IV) was predominantly bound to carboxylic groups of HA.

On the other hand, the interaction of small molecules with TiO₂ surface was studied extensively by XPS. Many researchers examined the interaction of small molecular probes such as CO, N₂O, H₂O, HCOOH, O₂ and H₂ on TiO₂ single-crystal surfaces in an attempt to understand the reactivity of these defect sites (Wang et al., 1996; Farfan-Arribas and Madix, 2002). Ti³⁺ and Ti²⁺ (the defects population of TiO₂) were found to alter the characteristics of the adsorption of some molecules, promoting dissociative over molecular adsorption. Several adsorbates might involve in redox reactions with the surface, in which the reduced Ti³⁺ is oxidized by the adsorbates to Ti⁴⁺. Beside this, the adsorption of ammonia on TiO₂ rutile powders by means of XPS was investigated by several researchers (Siu et al., 2000; Farfan-

Arribas and Madix, 2003). Erdem et al. (2001) used XPS to characterize the surface of TiO_2 encapsulated with polymer.

From the above literature, it was found that the surface analysis of HA adsorption on TiO_2 was not available. The adsorption of HA onto TiO_2 microsphere might strongly dependent upon the type and concentration of reactive sites (i.e. hydroxyls or defects) on TiO_2 particle surface. Furthermore, acid-base interactions between functional groups of HA and surface hydroxyls groups of TiO_2 microsphere surfaces was also of interest.

6.2 Adsorption Capacity of Mesoporous Phase

The investigation of surface area occupied by HA molecules was carried out to provide the direct information concerning the adsorption state of HA at different pH values. Approximately 10% reduction of BET surface area was observed after the adsorption test (Table 6.1). The reduction of BET surface area was further increased to about 17% in the ternary system. The decrease of BET surface area of adsorbed nano-structured TiO₂ microsphere was in agreement with Terashima et al. (2004). In addition, the total pore volume was reduced tremendously after the adsorption process. More than 90% of the pore volume was diminished after the adsorption process. Both surface area and pore volume reductions suggested that at least partial filling of the mesopores. However, these pore volume reductions cannot be used to evaluate the sorption mechanisms since changes in molecular associations must occur upon drying of the samples (Zimmerman et al., 2004).

Table 6.1 Reduction of BET surface area and total pore volume of nano-structured TiO₂ microsphere after adsorption.

Sample	Reduction of BET Surface Area, %	Total pore volume reduction, %
pH 3	11.14	90.69
pH 7	10.15	92.14
pH 9	12.60	91.40
pH 3 with Ca ²⁺	15.29	92.22
pH 7 with Ca ²⁺	17.57	91.81
pH 9 with Ca ²⁺	17.16	92.15

6.3 Zeta Potential Analysis

6.3.1 Binary System

Zeta potential analysis was useful in providing information on the charge distribution of compounds in solution. In this study, zeta potential measurement was carried out to qualitatively describe the charge distribution of HA and nano-structured TiO₂ microsphere at different pH condition.

Figure 6.1 Zeta potentials of humic acid, TiO₂ microsphere in ultrapure water and TiO₂ microsphere in HA solution (HA = 20 mg/L, TiO₂ microsphere dosage = 1 g/L).

Figure 6.1 displays the zeta potentials of HA solution at 20ppm, TiO₂ microsphere in ultra pure water and TiO₂ adsorbed with HA. The results obtained clearly denoted the distribution of surface charge of each component in the binary system. It was observed that the HA molecules became more negatively charged as pH value increased due to the ionization of carboxylic and phenolic groups. The dissociation of carboxylic groups usually takes place at pH > 4 whereas the phenolic groups undergo dissociation at pH > 8 (Bai and Zhang, 2001). A majority of phenolic

groups will only be ionized above pH 9 (Palmer et al., 2002). This ionization would lead to an increase of negative charge on the HA molecules. At low pH value, HA became less negatively charged since these functional groups were mostly protonated which subsequent led to reduction of tangentially intra-molecular electrical repulsion. Under neutral pH condition, HA could be considered as an anion that was partially charged due to the deprotonation of the carboxylic groups present at the periphery of the molecules. The titration method (Chapter 3) used for quantifying functional groups revealed that the carboxylic group of HA was 5.8 meq/g and 8.1 meq/g at pH 7 and pH 3, respectively. While the phenolic group of HA was 3.8 meq/g and 0.2 meq/g at pH 7 and pH 3, respectively. The results revealed that carboxylic group was the dominant functional group of HA in the adsorption process at neutral and acidic condition.

Figure 6.1 also clearly indicates that pH would have also affected the nature of nano-structured TiO₂ microsphere. TiO₂ microsphere was found to be an amphoteric material which the surface charge would change at different pH condition. The surface of TiO₂ microsphere became charged when particles were dispersed in aqueous system (Illés and Tombácz, 2004). Figure 6.1 clearly depicted that TiO₂ microsphere was positively charged in acidic condition but negatively charged in basic condition. The surface of TiO₂ microsphere could be protonated or deprotonated by adsorption of H⁺ and OH⁻, respectively as shown below:

pH condition was important in determining the dominant species of TiO₂ microsphere in the solution. The positively charged TiO₂ microsphere surface

hydroxyls were mainly TiOH_2^+ (Equation 6.1) and negatively charged TiO_2 microsphere surface hydroxyls were TiO^- (Equation 6.2) in acidic and basic solution, respectively. The point of zero charge (PZC) was obtained at pH 6.5 which was similar to the value reported by Bekbölet et al. (2002). The PZC was a reference point for surface charging of TiO_2 in aqueous medium.

On the other hand, the zeta potential of adsorbed TiO_2 microsphere was presented in Figure 6.1. The most obvious difference between clean TiO_2 microsphere and adsorbed TiO_2 microsphere was that the zeta potentials of TiO_2 adsorbed with HA were mostly negative and thus evidenced that HA was adsorbed on the surface of TiO_2 microsphere. A negative potential profile was developed around TiO_2 microsphere at all pH values after attaining adsorption equilibrium. Adsorption of HA therefore not only neutralized the positive charges but also reversed the surface charges of the TiO_2 microsphere. All the HA adsorbed particles became uniform and negatively charged due to the excess acidic groups of adsorbed macroions (Au et al., 1999; Tombácz et al., 2004). The charge reversal of TiO_2 microsphere from positive to negative at lower pH value indicated that the bound organic polyanions had smeared out the differences between the surface properties of oxides because of covering the most reactive conditionally charged Ti-OH sites. The surface charge compensation might lead to electrostatic repulsion between the free HA molecules and the HA/ TiO_2 complex that would strongly inhibit further adsorption of the negative charged HA. The prohibition from further adsorption would therefore indicate that the adsorption of HA onto TiO_2 microsphere followed Langmuir adsorption model, which emphasized on monolayer coverage.

It was revealed that the main factor in initiating the adsorption process was of electrostatic origin as agreed by other researchers (Bai and Zhang, 2001; Bekbölet et al., 2002; Deng and Bai, 2004). At $\text{pH} < 7$, the adsorption was promoted by the

electrostatic attraction between the negatively charged HA and positively charged TiO_2 microsphere. At $\text{pH} > 7$, the situation was reversed, both negatively charged HA and TiO_2 microsphere generated a strong electrostatic barrier which would inhibit the adsorption process. Nevertheless, HA adsorption also occurred above PZC indicated that adsorption other than the electrostatic interaction between HA and TiO_2 microsphere surface must exist. Hence it was revealed that the neutral surface species of TiO_2 ($-\text{TiOH}$) would interact with the deprotonated functional groups of HA (L^-) via ligand exchange to form surface complexes:

Equation 6.3 describes that the adsorption of HA was due to specific interactions via a ligand exchange between a surface hydroxyls and deprotonated functional group of HA. The oxides or hydroxides surfaces have been shown to promote strong binding of carboxylated, aromatic HA through a ligand exchange mechanism (Chorover and Amistadi, 2001). Vermeer et al. (1998) also supported that the adsorption of a surface hydroxyl or bound water molecule and the oxygen of carboxylic group of HA was via a ligand exchange. Ligand exchange was rationalized to occur above PZC of TiO_2 microsphere by considering the electrostatic effect was trivial.

6.3.2 Ternary System

Cation strength played an important role in enhancing the HA adsorption extent on TiO_2 microsphere and this was in agreement with Au et al. (1999), Vermeer et al. (1998), Avena and Koopal (1999) and Li et al. (2002). It was known that HA would coagulate drastically at low ionic strength (the presence of divalent cations such as Ca^{2+} and Mg^{2+}) in solution (Hong and Elimelech, 1997; Wall and Choppin, 2003).

The presence of Ca^{2+} could increase the coulombic attraction between negative charged HA and oxide surfaces and also decrease lateral electrostatic repulsion among negative charged HA which could subsequently draw the HA molecules together. Zeta potential measurement was carried out to study the effect of Ca^{2+} on the electrical property of TiO_2 microsphere and HA.

Figure 6.2 Zeta potentials of nano-structured TiO_2 microsphere in the absence and in the presence of Ca^{2+} in ultrapure water. (TiO_2 microsphere dosage = 1g/L, Ca^{2+} = 1.25 mM)

The effect of Ca^{2+} on the electrical properties of nano-structured TiO_2 microsphere is shown in Figure 6.2. It was clear that the negative zeta potential of TiO_2 microsphere approximated the balance between attraction and repulsive force at $\text{pH} > 7$ in the presence of Ca^{2+} ; it could be due to the decrease of Ti-O^- species, the dominant species in basic solution. Ca^{2+} clearly affected the surface speciation by screening electrostatic interactions involved in the surface ionization reactions as suggested by Au et al. (1999). At a given pH, the positively charged surface species (TiOH_2^+) increased with increasing ionic strength, whereas the negatively charged species (Ti-O^-) decreased with increasing cation strength. Apparently the reduction

of negative charge of TiO₂ microsphere would enhance the adsorption of HA on TiO₂ microsphere. In addition, the point of zero charge was slightly shifted to 7.

Figure 6.3 Zeta potentials of humic acid at a concentration of 20mg/L in the presence of Ca²⁺.

Figure 6.3 displays the zeta potential profiles of HA at both low and high Ca²⁺ concentration. It was observed that the negative zeta potential of HA was reduced by 10 mV in the presence of Ca²⁺ in solution. It was known that HA molecules gained its negative charge with increasing pH, but the negative charge could be neutralized with increasing Ca²⁺ concentration. Nevertheless the overall charge profile remained negative even though the Ca²⁺ concentration increased to 10 mM. It was obvious that Ca²⁺ only partially neutralize the negative surface charge of HA. The decrease of negative charge of HA was expected to reduce the repulsive barrier which subsequently lead to the decrease of inter-particle repulsion and create a less electrically stable system which finally leading to aggregation of HA in solution (Hong and Elimelech, 1997; Wall and Choppin, 2003).

Figure 6.4 Zeta potentials of post-adsorption of nano-structured TiO₂ microsphere in HA solution. (HA = 20 mg/L, TiO₂ microsphere dosage = 1 g/L, Ca²⁺ = 1.25 mM)

Figure 6.4 shows the zeta potentials of post-adsorption of nano-structured TiO₂ microsphere in HA solution. Consistently the charge profile of post-adsorption TiO₂ microsphere remained negative although Ca²⁺ was present in the solution. Nevertheless the surface charge compensation did not restrict from further adsorption of HA on TiO₂ microsphere. Hence Ca²⁺ might engage in intramolecular bridging interaction as agreed by Engebretson and Wandruszka (1998) who did a study on the effect of Mg²⁺ on HA complexation. So the presence of Ca²⁺ was postulated to promote the multilayer adsorption of HA molecules on TiO₂ microsphere due to the bridging effect. There was a function of Ca²⁺ bridging between the HA molecules in solution and also between the adsorbed HA molecules and free molecules in solution as agreed by Yoon et al. (1998) and Li et al. (2002). For this reason, the adsorption behavior of HA with the presence of Ca²⁺ could be well described by Freundlich isotherm. Furthermore, the bridging interactions between Ca²⁺ and the HA molecules could increase the hydrophobicity of HA and decrease the electrostatic repulsion between HA and TiO₂ microsphere surfaces

which would enhance the adsorption of HA molecules on TiO_2 (Engelbrecht and Wandruszka, 1998; Piccolo, 2001; Chi and Amy, 2004).

In summary, pH condition dominated the surface species of nano-structured TiO_2 microsphere which could trigger the interaction between HA molecules and TiO_2 microsphere. The interaction was initiated by electrostatic attraction and/or ligand exchange, subject to pH condition, and finally led to surface complexation. Surface complex was formed between the functional group of HA and surface hydroxyls of TiO_2 microsphere to create a stable molecular entity. The presence of Ca^{2+} was indeed enhance the interaction between HA molecules and TiO_2 microsphere but was not clearly clarified by zeta potential analysis. In view of this, XPS analysis was used to further investigate the surface complexation and also the Ca^{2+} bridging effect involved in the adsorption process.

6.4 Surface Analysis Using X-ray Photoelectron Spectroscopy (XPS)

6.4.1 XPS Analysis on Nano-structured TiO₂ Microsphere

The survey scan indicated that nano-structured TiO₂ microsphere contained the Ti 2p and O 1s peaks. C 1s peak was also detected in addition to the Ti 2p and O 1s peaks. Figure 6.5 shows a Ti 2p XPS spectrum for nano-structured TiO₂ microsphere. The Ti 2p_{1/2} and Ti 2p_{3/2} spin-orbital splitting photoelectrons were located at binding energies of 464.6 and 458.9 eV, respectively. The peak separation of 5.7 eV between Ti 2p_{1/2} and Ti 2p_{3/2} signals was in excellent agreement with the reported literature values (Demri et al., 1997).

Figure 6.5 Ti 2p XPS spectra of nano-structured TiO₂ microsphere.

The O 1s signal for nano-structured TiO₂ microsphere is shown in Figure 6.6, indicating an intense peak at 530.1 eV with two pronounced sub-peaks. The most intense peak at 530.1 eV was attributed to O²⁻, the oxygen in the metal oxide. While the lower intensity peak at 531.9 eV was assigned to hydroxyl (OH) species on the surface and the relatively small peak at 533.1 eV could be attributed to adsorbed

molecular water and /or to the oxygen present in the organic contamination.

Figure 6.6 XPS spectra of the O 1s peak of nano-structured TiO_2 microsphere.

A comparison of literature values for observed O^{2-} and OH peaks reported by other researchers is summarized in Table 6.2. The binding energy between O^{2-} and OH was 1.8 eV and between the OH and chemisorbed water was 1.3 eV, respectively. These results were agreeable with Simmons and Beard (Table 6.2). The binding energy difference of 71.2 eV between the observed peaks positions of Ti $2p_{3/2}$ and O 1s (Oxide) was also in excellent agreement with the reported literature values of 72.7-71.2 eV as shown in Table 6.3.

Table 6.2 Comparison of the assignment of the peaks for OH and bulk O²⁻ with literature values.

Reference	Bulk O ²⁻	OH	Difference eV
Simmons and Beard (1987)	529.7	531.5	1.8
Sanjines et al. (1994)	530.0	531.5	1.5
Raikar et al. (1995)	529.5	531.0	1.5
McCafferty and Wightman (1998)	530.6	532.4	1.8
Erdem et al. (2001)	530.6	531.9	1.3
Current work	530.1	531.9	1.8

Table 6.3 Comparison of the assignment of the peaks for Ti and bulk O²⁻ with literature values.

Reference	Bulk O ²⁻	Ti 2p _{3/2}	Difference eV
Sanjines et al. (1994)	530.0	458.7	71.3
Raikar et al. (1995)	530.9	458.2	72.7
Erdem et al. (2001)	530.6	459.3	71.3
Current work	530.1	458.9	71.2

A typical high-resolution C 1s spectrum for nano-structured TiO₂ microsphere is shown in Figure 6.7. The spectrum was resolved into three components. The most intense peak at 285 eV was attributed to carbon in –CH₂–CH₂–CH₂– and the peaks at 286.2 and 289 eV were oxidized carbon. The result obtained was similar with Simmons and Beard (1987). Unequivocal identification of the specific organic compounds that was present on these specimens was not possible. However the carbon spectrum did indicate that the organic compounds contain polar groups. The polar groups could account for the propensity of the adsorption of organic contamination observed on the hydrated oxides of the TiO₂ specimens after exposure to the atmosphere.

Figure 6.7 XPS spectra for C 1s of nano-structured TiO₂ microsphere.

6.4.2 XPS Analysis on Adsorbed Nano-structured TiO₂ Microsphere

The nature of the sites where adsorption took place was investigated by means of XPS. A survey scan was carried out to identify the component existed on the surface of adsorbed nano-structured TiO₂ microsphere. It indicate that the adsorbed HA on TiO₂ microsphere surface was mainly comprised of carbon and oxygen. The nitrogen atoms in the HA were undetectable. The results was agreeable with Bai and Zhang (2001) that the nitrogen component in the HA was indeed very small and that no protonated nitrogen atoms were detected. Although elemental analysis showed that there was about 1.23% of nitrogen atom in the HA, the major components contributed to the adsorption of HA onto TiO₂ microsphere were mainly C and O (Chapter 3).

Figure 6.8 XPS spectra of Ti 2p for the adsorbed nano-structured TiO_2 microsphere a) at pH 7, b) at pH 3, c) at pH 7 associated with Ca^{2+} .

Figure 6.8(a-c) shows the Ti 2p spectrum of saturated TiO₂ microsphere at different experimental condition. It could be observed from the spectra of a clean nano-structured TiO₂ microsphere that the most intense peak at both Ti 2p_{3/2} and Ti 2p_{1/2} was corresponding to the major species of Ti⁴⁺ (Figure 6.5). The area of Ti⁴⁺ was substantially reduced after the adsorption process indicating that the surface of TiO₂ microsphere was covered by adsorbed compound or hydroxyls groups. A shoulder located towards the higher binding energy for both peak Ti 2p_{3/2} and Ti 2p_{1/2}, was observed in Figures 6.8 (a-c). The shoulder might belong to a newly formed Ti-bounded compound with higher binding energy after the adsorption process. It was proposed that the functional group of HA adsorbed dissociatively on TiO₂ microsphere surface. The carboxylic group would most likely bond through the oxygen atom to the surface Ti⁴⁺ cations. The adsorption occurred through the formation of a R-C(O)O-Ti bond with the surface Ti⁴⁺ cations. The same phenomenon was observed by Farfan-Arribas and Madix (2003) who studied the adsorption of amines on TiO₂ surface. Concurrently, the carboxylic acid proton dissociated from the carboxyl group presumably bound to surface oxygen, forming a hydroxide group. The proposed adsorption scheme:

Every carboxylic group adsorbed was accompanied by one hydroxide group, hence the concentration of hydroxide group increased simultaneously as depicted in O 1s spectrum. It was possible for the newly formed compound, R-C(O)O-Ti to recombine with -OH groups. However it was assumed that adsorption might not

completely reversible because of competition with the reaction of hydroxyl groups to form water:

The water generated at the same time would react with the surface Ti cations to form surface hydroxyl group (-TiOH). The water generated could also oxidize Ti^{3+} to Ti^{4+} (Wang et al., 1996), therefore it explained that Ti^{3+} species was not observed in the spectrum. The adsorption of HA on TiO_2 microsphere surface was not via the redox reactions which was suggested by other researchers that the adsorbate would bind with the bridging oxygen vacancy produced from the Ti^{3+} defects (Wang et al., 1996; Hebenstreit et al., 2000; Farfan-Arribas and Madix, 2003). In fact, Ti^{3+} defects were not detected at the low energy shoulder in Figures 6.8 (a-c). Hence it was proposed that the carboxylic group formed a bond to Ti^{4+} rather than replacing bridging oxygen atoms produced from Ti^{3+} defects. The detection of the newly formed Ti-bounded compound with higher binding energy confirmed that surface complexation was the eventual process in the adsorption of HA on TiO_2 microsphere surface. However, once the Ca^{2+} was added into the solution, different surface complexation phenomenon was observed. Figure 6.8c indicates that Ti did not form any bonding with Ca^{2+} .

Figure 6.9 Decomposition of O 1s spectrum for adsorbed nano-structured TiO_2 microsphere a) at pH 7, b) at pH 3, c) at pH 7 with Ca^{2+} .

Figure 6.9 illustrates the decomposition of O 1s spectrum for the adsorbed TiO₂ microsphere. The O 1s peak for the adsorbed TiO₂ microsphere was composed of 4 peaks which were attributed to the signals from oxygen in metal oxide (O²⁻) at 530.1 eV, oxygen in carboxylic functional groups at ~ 530.7 eV, oxygen in hydroxyl groups (OH⁻) at ~ 531.9 eV, water (H₂O) or organic contaminations at ~ 533.1 eV. It was also suggested that the ester oxygen in carboxyl groups gave O 1s peak at ~ 533 eV or at the same approximate location of the chemisorbed H₂O peak in the O 1s spectrum (McCafferty and Wightman, 1998). The results revealed that carboxylic group of HA played an important role in the adsorption of HA on TiO₂ microsphere surface and further verified that the formation of Ti-bounded compounds through surface Ti⁴⁺ cations and oxygen of carboxylic group. In fact, the concentration of carboxylic group could reflect the amount of HA molecules adsorbed on the TiO₂ microsphere surface. The ratio of oxygen in carboxyl groups to oxygen in metal oxide ($I_{\text{COO}}/I_{\text{O}}$) increased substantially in acidic condition and in the presence of Ca²⁺. The $I_{\text{COO}}/I_{\text{O}}$ at pH 7 was 0.022, the value increased to 0.049 at pH 3 and finally increased to 0.074 associated with the presence of Ca²⁺ at pH 7.

Figure 6.10 Decomposition of C 1s spectrum for adsorbed nano-structured TiO_2 microsphere a) at pH 7, b) at pH 3, c) at pH 7 with Ca^{2+} .

Table 6.4 Binding energies, assignments and quantitative data for chemical peaks under the C 1s envelopes for HA adsorbed on nano-structured TiO₂ microsphere.

Peak	Assignment	BE (eV)
1	Aromatic C-C/C-H	284.6
2	Aliphatic C-C/C-H	285.0
3	C-O	286.2
4	C=O	287.6
5	C(O)O	289.2

Decomposition of C 1s spectrum for adsorbed TiO₂ microsphere is displayed in Figures 6.10 (a-c). The C 1s binding energies of different carbon components that corresponded to the HA in this study is summarized in Table 6.4. A reasonably good consistency between the peak positions of the different carbons emerged. The great ability of HA to sequester metal ions is mainly due to the presence of two types of sites, carboxylic and phenolic groups. However the existence of phenolic groups could not be deduced from the spectra. It could not be distinguished from non-aromatic hydroxyl and moreover they overlap with ether carbons that differ of only 0.1 eV from alcohols (Monteil-Rivera et al., 2000). As agreed from the titration method, the concentration of phenolic acid was indeed low in the HA solution, moreover it would only dissociated at pH > 8. As well, the O/C atomic ratio for HA was 1.18, indicating higher amounts of COOH and/or carbohydrates in HA. Hence COOH was recognized as an important functional group that will form surface complex with metal oxides in this study. From the reconvolution of the peaks, the functional groups of HA that could be identified from the samples was COOH functional group. Other important groups of HA including aromatic C-H, aliphatic C-H, C-O, C=O could also be identified from the peaks. The concentration of these groups increased at pH 3 and pH 7 in the presence of Ca²⁺, this observation verified that the adsorption extent increased at these conditions. The results obtained were applicable to justify the adsorption carboxylic group of HA on TiO₂ microsphere

surface as discussed in the previous section.

Figure 6.11 High resolution Ca 2p spectrum of adsorbed nano-structured TiO_2 microsphere in the presence of Ca^{2+} at pH 7.

The Ca 2p XPS spectrum obtained after HA adsorption on TiO_2 microsphere surface is shown in Figure 6.11. Ca $2p_{3/2}$ and Ca $2p_{1/2}$ were centered at 347.6 eV and 350.9 eV, respectively, indicating the presence of Ca^{2+} on TiO_2 microsphere surface. The spin-orbit splitting difference was 3.3 eV which was agreeable with the binding energy reported of the most calcium compounds, particularly from CaO (Demri et al., 1997). The formation of CaO could also be verified from the O 1s peak at about binding energy of 533.1 eV (Figure 6.9c). The intensity of this peak increased remarkably as shown in Figure 6.9c. During the adsorption process, Ca^{2+} could coagulate HA in bulk solution by reducing the lateral repulsion of between HA molecules and subsequently attached on the surface of TiO_2 microsphere. Hence CaO was detected on the surface of TiO_2 microsphere after drying.

It was verified from the Ti 2p spectrum that Ca^{2+} was not directly contact on TiO_2 microsphere surface. Although Zhang et al. (1998) suggested that Ca has a strong chemical interaction between O and Ti. Normally a shoulder would appear in the

lower binding energy side of the peak of Ti 2p showing the formation of Ti_2O_3 when the metal ions were adsorbed on the surface of TiO_2 (Zhang and Henrich, 1992; Dake and Rad, 1993; Demri et al., 1997). Neither Ti^{3+} nor Ti_2O_3 was detected in Ti 2p spectrum revealed that Ca^{2+} did not react with TiO_2 . At the same time, the concentration of oxygen of carboxylic group on the adsorbed TiO_2 was increased substantially by 3 times when Ca^{2+} was present in the solution. It was proposed that Ca^{2+} could also bind through the oxygen in carboxylic group (the bridging effect) and subsequently attached on the surface of TiO_2 microsphere.

Hence it was believed that the interaction between HA molecules and Ca^{2+} was essentially coulombic, involving charge neutralization and electrostatic bridging of anionic groups of HA by Ca^{2+} . This largely intramolecular effect caused various portion of the HA molecules to be drawn together, enhancing the establishment of hydrophobic regions (Engelbreton and Wandruszka, 1998). The system slowly proceeded to form stable complex and finally attached on the surface of TiO_2 microsphere.

6.5 Conclusion

The adsorption mechanism of HA on nano-structured TiO_2 microsphere was studied based on the zeta potential and XPS analyses. Both electrostatic interaction and ligand exchange were revealed as the important step in explaining the interaction between HA and nano-structured TiO_2 microsphere. The interaction between HA and nano-structured TiO_2 microsphere would finally lead to surface complexation. XPS analysis confirmed that surface complex was formed on the surface of nano-structured TiO_2 microsphere after reaching adsorption equilibrium. The carboxylic group of HA was detected on the nano-structured TiO_2 microsphere surface after the

adsorption process. A newly formed Ti-bounded compound was detected after the adsorption process. This proved the validity of surface complexation mechanism. The oxygen of carboxylic group was bonded with surface Ti^{4+} cations, forming surface complex on the surface of nano-structured TiO_2 microsphere as shown in Scheme 1. In the ternary system, Ca^{2+} could coagulate the HA molecules; it could also bind with the oxygen of carboxylic group and subsequently attached on the surface of nano-structured TiO_2 microsphere as shown in Scheme 2. Carboxylic group could also bind with surface Ti^{4+} cations simultaneously in ternary system; nevertheless it was believed that the reaction between carboxylic group and Ca^{2+} was much faster than former process. Hence the presence of Ca^{2+} will help to enhance the adsorption kinetic and extent of HA on TiO_2 microsphere.

Scheme 6.1 Formation of surface complex on the surface of nano-structured TiO_2 microsphere.

Scheme 6.2 Formation of surface complex on the surface of nano-structured TiO_2 microsphere in the presence of Ca^{2+} .

CHAPTER 7

PHOTOCATALYTIC DEGRADATION OF HUMIC ACID BY NANO-STRUCTURED TITANIUM DIOXIDE MICROSPHERE

7.1 Introduction

HA is one of the main contaminants in drinking water production. The prepared nano-structured TiO₂ microsphere provides an alternative for the removal of HA in water. The removal of HA using TiO₂ PCO process had been studied extensively by many researchers and reviewed in Chapter 2. These studies merely investigated the PCO degradation rate of HA under several operational parameters. Chapter 5 clearly revealed that HA could be effectively adsorbed on the surface of TiO₂ microsphere. The sorption of organic substrates at the surface of TiO₂ photocatalyst plays a prominent role as the PCO mainly occurs at the surface of the catalysts. Most of the researchers agreed that degradation of HA had higher efficiency in acidic medium due to strong adsorption of substances on the surface of TiO₂ catalysts. The presence of cation in water could provide favorable condition for the adsorption of HA onto TiO₂ surface and subsequently enhance the degradation process. It was agreed that the adsorption parameters showed that there was to a certain extent dependency between the adsorption characteristics and the PCO degradation rate. Therefore this chapter mainly discussed the PCO degradation of HA by nano-structured TiO₂ microsphere. The effects of initial HA concentration, pH condition and the presence of Ca²⁺ in the solution on the PCO degradation efficiency of HA were studied extensively. The PCO degradation rate of HA by nano-structured TiO₂ microsphere was analyzed with Langmuir-Hinselwood kinetics model and pseudo first order kinetic model. The role of pre-adsorption of HA on nano-structured TiO₂ microsphere in the PCO degradation efficiency was also elucidated.

7.2 Kinetics of photocatalytic degradation of humic acid by nano-structured TiO₂ microsphere

Several studies indicated that the PCO rate of various organic contaminants over illuminated TiO₂ could be explained by the Langmuir-Hinselwood (L-H) kinetic expression (Matthews, 1988; Ollis and Al-Ekabi, 1993; Hoffmann et al., 1995; Chen and Jenq, 1998; Topalov et al., 2000; Lewandowski and Ollis, 2003). The Langmuir-Hinshelwood rate form is expressed as:

$$\frac{dC}{dt} = -\frac{k_{L-H} K_{ads} C}{1 + K_{ads} C} \quad (7.1)$$

where C = concentration of the reactant (mg/L), t = illumination time (min), k_{L-H} = reaction rate constant (mg/L.min) and K_{ads} = adsorption coefficient of the reactant (L/mg).

Equation 7.1 could be rewritten as

$$-\left(1 + \frac{1}{K_{ads} C}\right) dC = k_{L-H} dt \quad (7.2)$$

Integration of Equation 7.2 yields Equation 7.3:

$$\ln\left(\frac{C_o}{C}\right) + K_{ads} (C_o - C) = k_{L-H} K_{ads} t \quad (7.3)$$

Then the half life, $t_{1/2}$ (min) is derived as

$$t_{1/2} = \left(\frac{0.693}{k_{L-H} K_{ads}}\right) + \left(\frac{0.5}{k_{L-H}}\right) C_o \quad (7.4)$$

Therefore a plot of $t_{1/2}$ versus C_o should give a straight line with a slope of $0.5/k_{L-H}$

and intercept of $0.693/k_{L-H}K_{ads}$ through which the coefficients k_{L-H} and K_{ads} could be calculated.

Equation 7.1 also could be rearranged into Equation 7.5, considering $v = -dC/dt$,

$$\frac{1}{v} = \frac{1}{k_{L-H}K_{ads}} \frac{1}{C} + \frac{1}{k_{L-H}} \quad (7.5)$$

A linear plot of $1/v$ versus $1/C$ could be obtained from Equation 7.5. From the slope and the intercept of this linear plot, the corresponding rate constant, k_{L-H} and the adsorption/desorption constant, K_{ads} could then be determined.

L-H rate law successfully explains the kinetics of the reactions occurring while both species are adsorbed; a free radical species reacts with the adsorbed substrate or a surface bound radical reacts with a free substrate in solution. The values of k_{L-H} and K_{ads} are used to explain the coefficients defining the rate determining reaction events and pre-equilibrium adsorption within an adsorbed monolayer at the oxide surface and the aqueous solution interface. The effect of light intensity is incorporated in k_{L-H} and K_{ads} to specifically express the equilibrium constant for fast adsorption-desorption processes between surface monolayer and bulk solution (Bekbölet et al., 2002). However, it was agreeable that the photocatalytic degradation of various organic compounds at low concentration obeyed Pseudo first order reaction kinetics (Bekbölet et al., 1998). When the initial concentration C_0 is very small, Equation 7.3 reduced to Equation 7.6:

$$\ln\left(\frac{C_0}{C}\right) = k_{L-H}K_{ads}t = K't \quad (7.6)$$

Therefore, a plot of $\ln(C_0/C)$ versus illumination time should produce a straight line which its slope equals to the pseudo first-order constant, K' (min^{-1}). Therefore the

half life, $t_{1/2}$ (min) is:

$$t_{1/2} = \frac{0.693}{K'} \quad (7.7)$$

7.2.1 Effect of initial concentration

The experimental procedure of PCO degradation process was described in Chapter 3. Three different initial HA concentration (5, 20 and 50 mg/L) were conducted to elaborate the effect of initial concentration on the PCO rate. For this series of experiments the catalyst loading was kept constant at 1g/L and the pH of the HA solution was kept in neutral condition. The experimental results are shown in Figure 7.1 wherein the dotted line region indicates the adsorption of HA in the dark for 2 hrs before the UV light irradiation. Approximately 65%, 29% and 11% of HA was removed in dark adsorption for the initial concentration of 5, 20 and 50 mg/L, respectively. More than 98% of HA was successfully degraded at the end of the PCO process. The UV irradiation time required to reach its total degradation increased as the initial concentration increased. Thus, 20 min was required to totally degrade an initial amount of HA at 5 mg/L, the time was increased to 40 min and 60 min at initial HA concentration of 20 mg/L and 50 mg/L, respectively. This behavior was expected since the ratio of HA molecules/active sites of TiO_2 was increasing, leading to a slower overall disappearance of the HA.

Figure 7.1 Effect of initial humic acid concentration on PCO degradation after attaining adsorption equilibrium.

Table 7.1 Effect of initial HA concentration on the Pseudo first order kinetic parameters

Initial HA Concentration (mg/L)	Rate (mgL ⁻¹ min ⁻¹)	K' (min ⁻¹)	t _{1/2} (min)	R ²
5	1.123	0.225	3	0.7683
20	1.990	0.100	7	0.9896
50	2.600	0.052	13	0.9556

Table 7.2 Effect of initial concentration on the L-H kinetic parameters

Initial HA Concentration (mg/L)	Rate (mgL ⁻¹ min ⁻¹)	k _{L-H} (min ⁻¹)	K _{ads} (Lmg ⁻¹)	t _{1/2} (min)	R ²
5	2.027	2.499	0.859	1	0.8171
20	1.156	1.195	1.500	9	0.9008
50	1.146	1.155	2.384	22	0.7777

The experimental results were modeled with Pseudo first order kinetic (Equation 7.6) and the half life value was calculated using Equation 7.7. Table 7.1 shows that the degradation rate increased with increasing HA concentration while the Pseudo

first order kinetic constant, K' decreased as the initial HA concentration increased. The experimental results were also modeled with L-H kinetic model (Equation 7.5) and the half life value was calculated using Equation 7.4 and shown in Table 7.2. The reaction rate constant, k_{L-H} decreased as the initial HA concentration increased which was in accordance with the results reported by Chen and Ray (1999), Li et al. (2002) and Pizarro et al. (2005).

Table 7.3 Calculated half-life values from Pseudo first order kinetic model L-H kinetic model and observed half life values from experimental data at different initial HA concentration.

Initial HA concentration (mg/L)	$t_{1/2}$ from Pseudo first order kinetic model (min)	$t_{1/2}$ from L-H kinetic model (min)	$t_{1/2}$ from experimental data (min)
5	3	1	2
20	7	9	7
50	13	22	22

Pseudo first order kinetic model and L-H kinetic model could be used to explain the PCO degradation of HA by nano-structured TiO_2 microsphere. The calculated half life values from Pseudo first order kinetic model L-H kinetic model were summarized in Table 7.3. The observed half life values for photocatalytic degradation process of HA concentration at 5, 20 and 50 mg/L were approximately 2, 7 and 22 min, respectively. The half life values obtained from the L-H kinetic model were almost in accordance with the observed values. The half life values obtained from the Pseudo first order kinetic model was found fitting well with the observed half life values at low initial HA concentration. This finding was in agreement with Bekbölet et al. (1998).

L-H kinetic model is commonly used to interpret the heterogeneous photocatalytic degradation of organic compound. When the initial concentration of organic

contaminants is low, the L-H rate form reduced to an apparent first-order kinetics form. The rate of photocatalytic degradation of HA was reported to obey the Pseudo first order kinetic model as well as the L-H kinetic model.

In PCO process, the generation and migration of the photogenerated electron-hole pair, and the reaction between photogenerated hole (or hydroxyl radical) and organic compounds are two processes that occur in series. At low concentration, the latter dominated the process, and therefore first order kinetic model as well as L-H kinetic model was sufficient to explain the removal rate of HA. Pseudo first order kinetic model explained a simple reaction. The degradation rate constant decreased with the increasing of initial concentration of HA when other parameters were kept unchanged. However Pseudo first order kinetic model could not sufficiently explain the removal rate of HA at high HA initial concentration. The calculated half life value was faster than the observed value.

On the contrary, at high concentration, the generation and migration of the photogenerated electron-hole pair for PCO reaction became the governing step, L-H kinetic model would be more appropriate to be used. From Table 7.2, the K_{ads} values calculated from L-H kinetic model increased as the HA concentration increased. It implied that the surface of TiO_2 microsphere was getting saturated by HA, which could actually block the active sites for PCO process on the TiO_2 surface; and also surface recombination of photogenerated holes and electrons through the adsorbed HA. Hence the reaction rate constant decreased as the initial concentration increased.

7.2.2 Effect of pH

In order to elaborate the effect of pH on PCO degradation of HA, the concentration of HA was fixed at 20 mg/L with catalyst loading at 1 g/L. A blank study was carried out, it can be seen that about 38% of HA was degraded by UV light in the absence of nano-structured TiO₂ microsphere at neutral pH (Figure 7.2). The removal efficiency of HA was greatly enhanced in the presence of nano-structured TiO₂ microsphere. Figure 7.2 shows the PCO degradation rate of HA at pH 7 and pH 3. The dotted line region indicates the HA adsorption in the dark for 2 hrs before UV light was turned on. The PCO degradation of HA achieved 98% and 97% removal efficiencies at pH 7 and pH 3, respectively after 45 min of UV light irradiation.

Figure 7.2 Effect of pH on photocatalytic degradation of HA after reaching adsorption equilibrium. (HA concentration = 20 mg/L, TiO₂ dosage = 1 g/L)

Table 7.4 Effect of pH on the L-H kinetic parameters

pH	Rate (mgL ⁻¹ min ⁻¹)	k _{L-H} (min ⁻¹)	K _{ads} (Lmg ⁻¹)	t _{1/2} (min)	R ²
3	2.150	2.583	0.741	5	0.8684
7	1.156	1.195	1.499	9	0.9008

The PCO degradation of HA was fitted using L-H kinetic model. Table 7.4 shows the L-H kinetic parameters of PCO photodegradation of HA at pH 7 and pH 3. The removal rate of HA was higher at pH 3. The reaction rate constant was 1.195 min⁻¹ (R² = 0.9008) and 2.583 min⁻¹ (R² = 0.8684) at pH 7 and pH 3, respectively. The PCO degradation rate constant increased by almost half as the pH value was reduced to 3. The half life value observed from graph at pH 7 and pH 3 was 7 min and 1 min, respectively. While the half life value calculated using L-H kinetic model was 9 min and 5 min at pH 7 and pH 3, respectively. This result was in accordance with most of the researchers that the degradation efficiency of HA was better in acidic medium due to strong adsorption of HA on the surface of TiO₂ catalysts (Zhou and Banks, 1993; Eggins et al, 1997; Chen and Jenq, 1998; Li et al., 2002; Qiao et al., 2002). However, it was found that PCO degradation of HA at pH 3 could not be fitted by Pseudo first order kinetic model.

7.2.3 Effect of Ca²⁺

The concentration of HA and the catalyst loading was also fixed at 20 mg/L and 1g/L, respectively. The pH of the HA solution was also kept in neutral condition to elucidate the effect of Ca²⁺ on the PCO degradation of HA. Figure 7.3 depicts the effect of Ca²⁺ on the PCO degradation of HA. 98% of HA was photodegraded after 45 min of UV light irradiation either in the presence of Ca²⁺ or vice versa. The dotted line region indicates the HA adsorption in the dark for 2 hrs before UV light irradiation.

Figure 7.3 Effect of the presence of Ca^{2+} on photocatalytic degradation of HA after reaching adsorption equilibrium at pH 7. (HA concentration = 20 mg/L, TiO_2 microsphere dosage = 1 g/L)

Table 7.5 Effect of presence of Ca^{2+} on the L-H kinetic parameters (at pH 7).

Ca^{2+} (mgL^{-1})	Rate ($\text{mgL}^{-1}\text{min}^{-1}$)	$k_{\text{L-H}}$ (min^{-1})	K_{ads} (Lmg^{-1})	$t_{1/2}$ (min)	R^2
0	1.156	1.195	1.499	9	0.9008
50	6.135	8.764	0.117	2	0.9111

The L-H kinetic parameters revealed that the reaction constant rate was 8.764 min^{-1} and the half life value was 2 min ($R^2 = 0.9111$) as shown in Table 7.5. While the observed half life value was 1 min (Figure 7.3). The reaction constant rate of PCO degradation process increased tremendously when the Ca^{2+} was present in solution. However L-H kinetic model was not able to fit the experimental data obtained from PCO degradation of HA at pH 3 in the presence of Ca^{2+} . Similarly, the pseudo first order kinetic model was also not applicable when the Ca^{2+} was present in the solution. The presence of Ca^{2+} could enhance the adsorption of HA onto TiO_2 surface and subsequently enhance the PCO degradation process.

Nevertheless, the results obtained above were debatable. In this study, the PCO degradation rate of HA was determined directly using the decreased concentration of HA in solution, that was, $\Delta C = C_{\text{initial}} - C$, where C_{initial} was the concentration before UV irradiation and C was the concentration after irradiation at different time interval, both detected in the aqueous phase. L-H kinetic model actually explained the PCO degradation rate of HA on the surface of TiO_2 . Hence any change of the HA concentration in bulk solution might not represent the actual PCO degradation rate as HA was highly adsorbed on TiO_2 microsphere at pH 3 and in the presence of Ca^{2+} . Also, Figures 7.2 and 7.3 clearly indicates that the PCO degradation rate of HA was indeed slower in pH 3 and in the presence of Ca^{2+} , respectively. Majority of the HA was merely removed by adsorption process before PCO set off. This observation was contradicted with the results obtained from L-H kinetic model. Hence the role of adsorption of HA in the PCO degradation process was discussed in next section.

7.3 Role of Pre-adsorption of HA in Photocatalytic Oxidation Degradation Process

According to the principles of photocatalytic oxidation reaction, the main steps in the process occur on the surface of the solid semiconductor photocatalyst, hence the adsorption of organic compounds on the catalyst surface undoubtedly affects the reaction and high adsorption capacity usually favours the reaction. Many researchers, therefore, suggested that the preliminary adsorption of substrate on the catalyst surface was a prerequisite for highly efficient oxidation (Chen and Ray, 1999; Xu and Langford, 2001; Lee et al., 2003; Xie and Yuan, 2003; Robert et al., 2004). Hence the role of adsorption of substrate on the catalyst surface was debatable.

According to the report of Minero et al. (1992), if the reaction site was at the surface of the photocatalyst, the following processes could occur:

- a) Diffusion of the reactants from the bulk solution to the photocatalyst surface
- b) Diffusion of the reactants from the surface or the pore sites to the active sites at the surface of photocatalyst
- c) Photocatalytic reactions at the active sites
- d) Diffusion of photogenerated reactive species from the surface to the bulk solution
- e) Photocatalytic reactions in the bulk solution initiated by $\cdot\text{OH}$ radicals
- f) Photocatalytic reactions of the photogenerated reactive species

It had been identified from Chapter 5 that acidic pH condition and the presence of cation would significantly enhance the adsorption rate of HA on nano-structured TiO_2 microsphere. Hence processes (a) and (b) were accelerated in the aforementioned conditions. Subsequently it would be interesting to identify if the

pre-adsorption would really enhance the photodegradation rate of HA during the photocatalytic oxidation process.

7.3.1 Effect of pH

In order to indicate the influence of adsorption on the PCO degradation process, nano-structured TiO_2 microsphere was suspended in HA solution in the dark for 2 hrs before UV light was turned on. The adsorption of HA in dark was evaluated as shown in Figure 7.4. Approximately 29% and 81% of HA was removed by merely adsorption process in dark at pH 7 and pH 3, respectively. The great adsorption did not exhibit higher PCO degradation rate of HA as 97% of HA was PCO degraded regardless of pH condition. Therefore it proved that pH condition would enhance the adsorption process but not the PCO degradation process. It was contradicted with the results represented in section 7.2.2 and also other researchers who suggested that a strong adsorption of substances on the surface of TiO_2 catalysts at low pH values could enhance the reaction rate of photocatalytic oxidation.

Figure 7.4 Adsorption of HA in the dark for 2 hrs before PCO process.

To further support this statement, the amount of undegraded HA on the catalyst surface was evaluated. It was assumed that after PCO, the adsorption/desorption equilibrium was also reached immediately between the adsorbed HA and the HA in the bulk solution and that the adsorption parameters of $q_{\max}$ and K_a were the same as those determined in the dark (Xu and Langford, 2001). Hence the amount of HA left on the surface of TiO_2 microsphere after reaction, could be evaluated by the Langmuir adsorption equation:

$$q_e = \frac{q_{\max} C_e}{1/K_a + C_e} \quad (7.8)$$

where C_e is the concentration of HA detected in the aqueous phase after PCO. In this case, it was assumed that the interference from the intermediates was negligible because the PCO degradation was performed at low substrate conversion. Then the real initial rate of HA PCO degradation could be calculated using the decreased concentration of HA by TiO_2 microsphere PCO process and adsorption process.

At pH 3 (From Table 5.5),

$$q_e = \frac{33.557C_e}{1.631 + C_e} \quad (7.9)$$

At pH 7 (From Table 5.5),

$$q_e = \frac{6.949C_e}{3.115 + C_e} \quad (7.10)$$

The real initial rate was recalibrated and shown in Table 7.6. On the whole the recalibrated PCO degradation of HA was indeed slower as compared to the values displayed in Table 7.4. Although the reaction constant rate of pH 3 was still higher

than that of pH 7, it was interesting to find that the PCO degradation rate of HA at pH 3 ($0.754 \text{ mgL}^{-1}\text{min}^{-1}$) was almost similar with the value obtained at pH 7 ($0.711 \text{ mgL}^{-1}\text{min}^{-1}$). It explained that the removal rate of HA was similar at the end of PCO degradation process regardless pH condition. It was also noteworthy to discuss the K_{ads} values as shown in Table 7.6. The K_{ads} value obtained at pH 3 was indeed much slower than the value obtained pH 7. L-H kinetic model assumed that the number of surface adsorption sites was fixed at equilibrium and only one substrate may bind at each surface site. The surface coverage of TiO_2 was much higher at pH 3 than that at pH 7 as 81% of HA from solution was adsorbed on surface of TiO_2 (Figure 7.4) after reaching adsorption equilibrium. Hence the adsorption process was slow during the PCO process due to surface saturation.

Table 7.6 Effect of pH on the L-H kinetic parameters after recalibration.

pH	Rate ($\text{mgL}^{-1}\text{min}^{-1}$)	$k_{\text{L-H}}$ (min^{-1})	K_{ads} (Lmg^{-1})	R^2
3	0.754	2.067	0.029	0.8742
7	0.711	0.735	1.486	0.8614

On the other hand, it was found that the amount of HA left on TiO_2 surface was 0.83 mg/g and 5.55 mg/g at pH 7 and pH 3, respectively. Whereas the HA concentration remained in the solution was 0.42 mg/L and 0.56 mg/L at pH 7 and pH 3, respectively. Hence the actual removal percentage of HA by PCO degradation process at pH 7 and pH 3 was 94% and 69% after considering the amount of HA which still remained on the surface of TiO_2 microsphere. HA was merely adsorbed on TiO_2 but not fully degraded during the PCO process at pH 3.

7.3.2 Effect of Ca^{2+} ion

A clear depiction of HA adsorption in the dark for 2 hrs was shown in Figure 7.5. In the presence of Ca^{2+} in solution, there was about 83% of HA being removed by merely adsorption process in dark. High adsorption of HA was achieved in the presence of Ca^{2+} in solution, however the enhanced adsorption did not facilitate the subsequent photodegradation rate of HA as 98% of HA was removed at the end of PCO process. Dionasiou et al. (2000) reported that ionic strength in TiO_2 microsphere suspensions could influence the adsorption capacity but did not affect the rates of the PCO reactions significantly. However this result also contradicted with Li et al. (2002) who reported that the increase of cation strength in aqueous solution could provide a favorable condition for HA adsorption on the TiO_2 microsphere surface that could subsequently enhance the photooxidation rate. Hence the amount of undegraded HA on the catalyst surface was evaluated.

Figure 7.5 Adsorption of HA in dark for 2 hrs before PCO process at pH 7. (HA concentration = 20 mg/L, TiO_2 dosage = 1 g/L)

Table 7.7 Effect of Ca^{2+} on the L-H kinetic parameters after recalibration.

Ca^{2+} (mgL^{-1})	Rate ($\text{mgL}^{-1}\text{min}^{-1}$)	$k_{\text{L-H}}$ (min^{-1})	K_{ads} (Lmg^{-1})	R^2
0	0.711	0.735	1.486	0.8614
50	5.901	8.881	0.099	0.9104

The real reaction rate needed to be recalibrated. Freundlich model (from Table 5.6) was applied to obtain the amount adsorbed on the TiO_2 microsphere for calibration as Langmuir model was not applicable when Ca^{2+} was present in the solution.

$$q_e = \frac{6.266C_e^{0.92}}{42} \quad (7.11)$$

Similarly, the recalibrated removal rate of HA ($5.901 \text{ mgL}^{-1}\text{min}^{-1}$) was slightly lower than the original calculated value ($6.135 \text{ mgL}^{-1}\text{min}^{-1}$). At the end of the process, the amount of HA adsorbed on TiO_2 microsphere surface was 0.07 mg/g . While the HA remained in the solution was 0.46 mg/L . It revealed that almost 97% of HA was removed by PCO process. However this result was still debatable as L-H kinetic model considered monolayer adsorption during the PCO degradation process. Hence it was concluded that the existing model was not sufficient to explain PCO degradation kinetic of HA in a ternary system. The system became more complicated to be well fitted by the existing model. Further study needs to be carried out to understand the PCO degradation kinetic of HA in a ternary system.

7.3.3 Discussion

In this study, it was found that strong adsorption of HA on the surface of nano-structured TiO_2 microsphere did not actually enhanced the PCO degradation process. HA was merely adsorbed on TiO_2 but not fully degraded during the PCO

process at pH 3. The removal rate of HA at pH 3 and pH 7 was almost identical. It could be explained by two possibilities: (1) the blockage of sites for PCO process on the TiO_2 surface; and (2) surface recombination of photogenerated holes and electrons through the adsorbed HA.

As mentioned earlier, PCO process comprised of two processes: the generation and migration of the photogenerated electron-hole pair for surface reaction, and the reaction in bulk solution initiated by $\bullet\text{OH}$ radicals. At pH 7 without the presence of Ca^{2+} in solution, the former process actually governed the PCO degradation process as HA was not highly adsorbed on the surface TiO_2 microsphere as depicted in Figure 7.6a. However the latter process became dominating process when the HA was highly adsorbed on the surface of TiO_2 microsphere at pH 3 or in the presence of Ca^{2+} in solution as illustrated in Figure 7.6b. In acidic condition, the surface of TiO_2 was fully covered with HA that could block the active sites for PCO process. At the same time the well adsorbed HA molecules might facilitate the recombination of photogenerated electrons and holes (Cunningham et al., 1994; Liu et al., 2006).

Figure 7.6 Schematic diagram showing the PCO degradation of HA by nano-structured TiO_2 microsphere: a) Poorly adsorbed HA on TiO_2 microsphere at pH 7 or without the presence of Ca^{2+} ; b) Highly adsorbed HA on TiO_2 microsphere at pH 3 or associated with the presence of Ca^{2+} in solution.

As shown in Figure 7.6a, $\bullet\text{OH}$ radicals were generated by reactions of hole with surface OH groups and electron with adsorbed O_2 . In aqueous solution, there are always a layer of adsorbed hydroxyl (OH^-) and multiple layers of water molecules (Wang et al., 1998; Sakai et al., 1998; Lee et al., 2003) on the surface of TiO_2 which are important in producing $\bullet\text{OH}$ radicals. It was agreeable that the efficient PCO of organic substrates by UV/ TiO_2 driven photocatalysis was depend on the concentration of $\bullet\text{OH}$ radicals produced by PCO of surface hydroxyl groups and/or chemisorbed H_2O (Horikoshi et al., 2003). In order to generate $\bullet\text{OH}$, the electron/hole pairs were first photoexcited (Equation 7.12). The holes were ultimately trapped by surface HO^- groups (or H_2O) at the particle surface to yield $\bullet\text{OH}$ radicals (Equation 7.13). Dissolved oxygen molecules reacted with conduction band electrons (e^-) to yield superoxide radical anions, $\text{O}_2^-\bullet$, which on protonation would generate the hydroperoxy, $\bullet\text{OOH}$ radicals (Equation 7.15).

In addition, large amount of OH groups that present on the TiO_2 microsphere surface could also enhance the O_2 adsorption and consequently, its photoreactivity (Sclafani et al., 1990; Tsai and Cheng, 1997; Chhor et al., 2004). The OH groups would trap the holes in the valence band and then enhance the chemisorption of O_2 molecules in the conduction band. It would subsequently stabilize the holes in the valence band and prevent the electrons in the conduction band from recombination.

According to Figures 7.2 and 7.3, the high removal rate of HA (> 97 %) could be achieved regardless of the pH condition and cation strength. Undoubtedly the pH condition and cation strength could enhance the adsorption rate of HA on TiO₂ microsphere. In the case of high adsorption rate, the PCO process became the rate limiting step. Hence high adsorption did not accelerate the PCO rate. The HA was successfully photocatalyzed degraded regardless of operating conditions (pH and cation strength) investigated in this study. This finding was important for the application of TiO₂ microsphere photocatalysis in water treatment. It is not always practical to pre-adjust water pH from a neutral pH condition to a lower pH value and readjust it back after treatment. Thus TiO₂ photocatalysis possessed a potential to be an efficient technology in HA removal for water treatment process.

7.4 Extent of Mineralization

To study the mineralization of HA in the PCO reaction, TOC was also monitored against reaction time in various operating conditions as shown in Figure 7.7. On the whole, the TOC concentration was fluctuated throughout the PCO process. Nevertheless the removal trend at various conditions could be identified. The TOC removal was slow in the absence of TiO_2 microsphere. About 20 % of TOC was eliminated after 50 min of UV irradiation. The removal efficiency of TOC was about 70 % in neutral pH. The TOC removal was increased in acidic condition and further in the presence of Ca^{2+} in solution. The removal of TOC was 78 % in acidic condition. In the presence of Ca^{2+} , TOC concentration was reduced dramatically during the first 5 min. The removal of TOC reached 84% in the presence of Ca^{2+} at pH 7. The results indicated that a longer irradiation time was needed for a complete mineralization. The TOC removal was enhanced with the presence of Ca^{2+} . These results showed that the nano-structured TiO_2 microsphere could be applied in the real application for the removal of HA for drinking water production.

Figure 7.7 Removal of TOC vs irradiation time during PCO process. Conditions: HA=20 mg/L; $\text{TiO}_2 = 1$ g/L.

7.5 Recycling of Nano-structured TiO₂ Microsphere

The recycling of nano-structured TiO₂ microsphere in PCO degradation was investigated. HA concentration was fixed at 20 mg/L with TiO₂ microsphere loading of 1 g/L. The PCO process was carried out in neutral condition with UV irradiation time at 30 min each cycle for 5 cycles. It was found that the removal efficiency was ranged from 90 to 95% as shown in Figure 7.8. This result revealed that the photocatalytic activity of nano-structured TiO₂ microsphere hardly deteriorated regardless of recycling. Hence it could be reused for many times for the removal of HA in water treatment process.

Figure 7.8 Recycling of nano-structured TiO₂ microsphere in PCO degradation of HA. (HA=20 mg/L, TiO₂ microsphere = 1 g/L, pH 7)

7.6 Conclusion

In this study, Pseudo first order kinetic model was adequate to explain the PCO degradation study of diluted initial HA onto TiO₂ microsphere. L-H kinetic model was more appropriate to be used to explain the PCO degradation of HA by nano-structured TiO₂ microsphere. However L-H kinetic model was not adequate to explain the PCO degradation kinetic of HA on TiO₂ when Ca²⁺ was present in the solution due to its limitation. The current model needed to be further studied in order to explain the PCO degradation kinetic of HA on TiO₂ microsphere, particularly the adsorption constant.

It was shown in this study that strong adsorption of HA on nano-structured TiO₂ microsphere did not actually enhance the PCO process. The observed initial PCO rate that was contrary to the extent of dark adsorption was evidenced. The HA was successfully PCO degraded regardless of operating conditions (pH and cation strength). It was revealed that HA was merely adsorbed on TiO₂ but not fully degraded during the PCO process at pH 3 at the end of the PCO degradation process. The inhibition of PCO efficiency for well-adsorbed HA might be due to two possibilities: the blockage of active sites for PCO process on the TiO₂ microsphere surface and the surface recombination of photogenerated holes and electrons via adsorbed HA.

CHAPTER 8

CONCLUSION AND RECOMMENDATION

8.1 Conclusion

In this study, a novel nano-structured TiO_2 microsphere, photocatalyst with submicron particle size from 10 to 50 μm and crystal size of 10 nm was synthesized. The feasibility of this photocatalyst to be used in water treatment process was evaluated through various tests. The nano-structured TiO_2 microsphere could be used to remove humic acid, a sub-class of natural organic matter, via adsorption process and subsequently photocatalytic oxidation (PCO) process.

Nano-structured TiO_2 microsphere was synthesized via sol-gel spray coating technique using commercial P25 TiO_2 as the core. A titanium coating sol was prepared to bind the commercial P25 TiO_2 in forming the TiO_2 microsphere. The results showed that the anatase crystallite size of titanium coating sol was substantially affected by the mole ratio of ethanol to titanium alkoxide and also the calcination temperature. The anatase crystallite size of 10 nm was obtained at mole ratio of EtOH/alkoxide: 50/1 and calcinated temperature of 450°C. The resulting TiO_2 microsphere displayed a spherical shape with particle size ranged between 10 and 50 μm with BET surface area of 42 m^2/g that was identical to P25 TiO_2 . The photocatalytic activity was measured in the PCO degradation of phenol. The increase of photocatalytic activity of TiO_2 microsphere indicated that the actual photocatalytic rate was not dependent on the BET surface area but attributed to the quantum size effect induced by nano-sized anatase crystallite which has been embedded into the TiO_2 microsphere.

In the second phase of the study, the nano-structured TiO_2 microsphere was used to remove humic acid from water via adsorption process. The initial adsorption of HA on TiO_2 microsphere surface was rather a complex process depending on the nature of the adsorbent surface, the nature of adsorbate and the solution condition. From the experimental results obtained, it was found that the solution condition (pH and cation strength) could greatly affect the adsorption interaction between HA and TiO_2 microsphere. Apparently, the adsorption capacity of HA onto nano-structured TiO_2 microsphere increased substantially with decreasing pH values and increasing ionic strength. The regression analysis showed that the relationship between the

adsorption extent and solution chemistry (pH and Ca^{2+} concentration) could be expressed by a second order polynomial equation. The adsorption extent could reach saturation with high Ca^{2+} concentration at 50 mg/L at pH 3 in this study.

The adsorption behavior of HA on nano-structured TiO_2 microsphere in a binary system was well described by Langmuir model. Freundlich model was more suitable to describe the adsorption behavior when Ca^{2+} was present in the solution. The adsorption behavior of HA was actually condition dependent. In view of this, Langmuir-Freundlich (L-F) model was more adequate to model the adsorption behavior of HA on nano-structured TiO_2 microsphere. L-F model was able to be reduced to either Langmuir model in binary system or Freundlich model in ternary system accordingly. It was concluded that the adsorption behavior of HA on nano-structured TiO_2 microsphere in any condition could be well described by L-F model.

The adsorption rate of HA was greatly affected by solution condition (pH and cation strength). The adsorption rate of HA increased in acidic condition associated with the increasing of ionic strength. It was found that the adsorption of HA on nano-structured TiO_2 microsphere followed two important stages: (1) diffusion of HA from bulk solution to the surface of TiO_2 microsphere, and (2) attachment to the surface. In fact, the attachment controlled adsorption at the later stage dominated most part of the adsorption process since the diffusion process was very fast. It was revealed that the increased adsorption extent and rate was due to the size of HA molecules which were greatly dependent on pH and cation strength. The size of HA molecules decreased as the pH values decreased and in the presence of Ca^{2+} in solution. The smaller size HA molecules could diffuse faster to the subsurface of nano-structured TiO_2 microsphere and subsequently increase the adsorption rate. Moreover the smaller size HA molecules could adsorb more compactly on the surface of nano-structured TiO_2 microsphere and therefore the adsorption extent was increased as well.

The adsorption of HA on nano-structured TiO_2 microsphere surface showed interesting and complex behavior. Zeta potential analysis revealed that the

adsorption of HA was initiated by the electrostatic interaction and/or ligand exchange to form surface complex. The controlled step was subject to the pH condition. In acidic condition, the electrostatic interaction was rapid due to opposite charge between HA molecules and nano-structured TiO₂ microsphere. Ligand exchange process was rationalized to be the controlled step for surface complex formation by considering that the electrostatic effect was trivial. In neutral and basic condition, ligand exchange between functional group of HA and surface hydroxyls was suggested as the dominant adsorption mechanism.

A Ti-bounded compound was formed on the surface of nano-structured TiO₂ microsphere after reaching adsorption equilibrium. Surface complexation mechanism was proposed as the eventual stage in the adsorption process. The adsorption occurred through the formation of a R-C(O)O-Ti bond with the surface Ti⁴⁺ cations. In the ternary system, Ca²⁺ could coagulate HA molecules by reducing the lateral repulsion between HA molecules. The presence of Ca²⁺ was also postulated to promote the multilayer adsorption of HA molecules on nano-structured TiO₂ microsphere due to the bridging effect. Ca²⁺ could have bind with the oxygen of carboxylic group and subsequently attached on the surface of nano-structured TiO₂ microsphere.

In the third phase of study, the PCO degradation of HA by nano-structured TiO₂ microsphere was studied. The effects of initial concentration, pH condition and the presence of Ca²⁺ on the PCO degradation kinetic were elucidated. L-H kinetic model was used to explain the PCO degradation of HA by nano-structured TiO₂ microsphere. However L-H kinetic model was not adequate to explain the PCO degradation kinetic of HA on TiO₂ when Ca²⁺ was present in the solution due to its limitation. The current model needed to be further studied in order to explain the PCO degradation kinetic of HA on nano-structured TiO₂ microsphere.

It was shown in this study that strong adsorption of HA on nano-structured TiO₂ microsphere did not actually enhance the PCO process. The HA was successfully photocatalyzed degraded regardless of operating conditions (pH and cation

strength). It was revealed that HA was merely adsorbed on TiO_2 but not fully degraded during the PCO process at pH 3 at the end of the PCO degradation process. Surface reaction actually governed the PCO degradation process when HA was not highly adsorbed on the surface of nano-structured TiO_2 microsphere at pH 7 without the presence of Ca^{2+} in solution. However the hydroxyl radicals reaction became the dominating process when HA was highly adsorbed on the surface of nano-structured TiO_2 microsphere at pH 3 or in the presence of Ca^{2+} in solution. In acidic condition, the surface of TiO_2 microsphere was fully covered with HA that could block the active sites for PCO process. At the same time the well adsorbed HA molecules might facilitate the recombination of photogenerated electrons and holes.

A novel nano-structured TiO_2 microsphere with a large particle size (10 -50 μm), porous structure, BET surface area of 42 m^2/g , nano crystal size (~ 10 nm) and also high photocatalytic activity was developed in this study. It showed the promising results in removing HA from water. The unique properties of this photocatalyst could solve the engineering problem by promoting a better separation and recovery for commercial application. The application of TiO_2 photocatalysis in water treatment process would be more comprehensive with this novel material.

8.2 Recommendation

Further characterization studies like transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) are helpful to confirm the formation of “P25 core” coated with TiO_2 nanoparticle materials. It could be carried out in future study.

Some recommendations which were not taken into account in this study were essential in view of TiO_2 microsphere's potential for water treatment application. Humic acid used in this study was commercial HA powder, the established HA such as that from IHSS (International humic substances society) could be used for future study to reflect the actual water treatment conditions. In addition, continuous adsorption study could be carried in future study for engineering application.

potential. Besides Ca^{2+} , the effect of other cations like Mg^{2+} and Al^{3+} were equally important in evaluate the performance of TiO_2 microsphere for HA removal. It could be carried out in future study.

XPS analysis had its limitation in detecting phenolic functional group of HA in this study. Although the concentration of this functional group was indeed low from the HA characterization result, it was known to be one of the significant functional group of HA. Nuclear magnetic resonance (NMR) analysis was proposed to study the role of phenolic group in the adsorption process for future study.

In the PCO process, the kinetic of photodegradation of HA on TiO_2 microsphere was unclear due to strong adsorptive effect of HA. The current model was not sufficient to explain the PCO degradation kinetic of HA on nano-structured TiO_2 microsphere in a ternary system. It was recommended to conduct further study to model the complex kinetic of this process. The study of intermediate compound or final product of HA in the PCO process was not included in the scope of study. The investigation of intermediate compound or final product in the PCO process could be carried out in future study. Finally, the potential of nano-structured TiO_2 microsphere should further verified using the real raw water and the large scale pilot test for future study.

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Appendix A: Extinction coefficient for humic acid at different pH

In this study, the extinction coefficient for humic acid at different pH was determined as shown in Figures A1, A2 and A3. The concentration of humic acid was calculated based on the extinction coefficient obtained from these figures.

Figure A1 Extinction coefficient of humic acid at pH 3.

Figure A2 Extinction coefficient of humic acid at pH 7.

Figure A3 Extinction coefficient of humic acid at pH 9

Appendix B: Statistical Analysis: Analysis of Variance (ANOVA)

a) Statistical analysis for Single-factor experiment of fixed effect model

i) Formal statistical hypotheses tested are:

$$H_0 : \mu_1 = \mu_2 = \dots = \mu_a$$

H_1 : At least one mean is different

ii) The ANOVA sum of squares identity:

$$SS_T = SS_{Treatments} + SS_E$$

$$\text{Total sum of squares: } SS_T = \sum_{i=1}^a \sum_{j=1}^n (y_{ij} - \bar{y}_{..})^2$$

$$\text{Treatment of sum of squares: } SS_{Treatment} = n \sum_{i=1}^a (\bar{y}_{i.} - \bar{y}_{..})^2$$

$$\text{Error sum of squares: } SS_E = \sum_{i=1}^a \sum_{j=1}^n (y_{ij} - \bar{y}_{i.})^2$$

Where a = factor levels or treatments, n = replicates for each factor levels or treatments. A large value of $SS_{Treatments}$ reflects large differences in treatment means. A small value of $SS_{Treatments}$ likely indicates no differences in treatment means.

iii) While sums of squares cannot be directly compared to test the hypothesis of equal means, mean squares can be compared:

$$\text{Mean square} = (\text{sum of squares}) / (\text{degree of freedom})$$

Degree of freedom, df:

$$df_{Total} = df_{Treatments} + df_{Error}$$

$$an-1 \qquad a-1 \qquad a(n-1)$$

Mean square for treatments: $MS_{Treatments} = \frac{SS_{Treatments}}{a - 1}$

Error mean square: $MS_E = \frac{SS_E}{a(n - 1)}$

If the treatment means are equal, the treatment and error mean square will be theoretically equal. If treatment means differ, the treatment mean square will be larger than the error mean square.

iv) If the null hypothesis H_0 is true, the ratio

$$F_o = \frac{SS_{Treatments} / (a - 1)}{SS_E / [a(n - 1)]} = \frac{MS_{Treatments}}{MS_E}$$

has an F-distribution with $a-1$ and $a(n-1)$ degrees of freedom. MS_E is an unbiased estimator of σ^2 , whether or not H_0 is true. Also, under the null hypothesis, $MS_{Treatments}$ is an unbiased estimator of σ^2 . However, if the null hypothesis is false, the expected value of $MS_{Treatments}$ is greater than σ^2 . Therefore under the alternative hypothesis, the expected value of the numerator of the test statistic, F_0 is greater than the expected value of the denominator. Hence H_0 will be rejected if the statistics is large. This implies an upper-tail, one-tail critical region. Therefore H_0 is rejected if $f_o > f_{\alpha, a-1, a(n-1)}$ where f_o is the computed value of F_o .

Table B1 The ANOVA table for a single-factor experiment, fixed effect model

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F_o
Treatments	$SS_{Treatments}$	$a - 1$	$MS_{Treatments}$	$\frac{MS_{Treatments}}{MS_E}$
Error	SS_E	$a(n - 1)$	MS_E	
Total	SS_T	$an - 1$		

b) Statistical analysis for two-factor experiment of fixed-effects model

i) The hypotheses that will be tested are as follows:

1. $H_0 : \tau_1 = \tau_2 = \dots = \tau_a = 0$ (no main effect of factor A)

$H_1 : \text{At least one } \tau_i \neq 0$

2. $H_0 : \beta_1 = \beta_2 = \dots = \beta_b = 0$ (no main effect of factor B)

$H_1 : \text{At least one } \beta_j \neq 0$

3. $H_0 : (\tau\beta)_{11} = (\tau\beta)_{12} = \dots = (\tau\beta)_{ab} = 0$ (no interaction)

$H_1 : \text{At least one } (\tau\beta)_{ij} \neq 0$

ii) The two-factor AVONA sum of squares identity:

$$SS_T = SS_A + SS_B + SS_{AB} + SS_E$$

$$\begin{aligned} \sum_{i=1}^a \sum_{j=1}^b \sum_{k=1}^n (y_{ijk} - \bar{y}_{...})^2 &= bn \sum_{i=1}^a (\bar{y}_{i..} - \bar{y}_{...})^2 + an \sum_{j=1}^b (\bar{y}_{.j.} - \bar{y}_{...})^2 \\ &\quad + n \sum_{i=1}^a \sum_{j=1}^b (\bar{y}_{ij.} - \bar{y}_{i..} - \bar{y}_{.j.} + \bar{y}_{...})^2 + \sum_{i=1}^a \sum_{j=1}^b \sum_{k=1}^n (y_{ijk} - \bar{y}_{ij.})^2 \end{aligned}$$

SS_T = Total sum of squares

SS_A = Sum of squares for the row factor A

SS_B = Sum of squares for the column factor B

SS_{AB} = Sum of squares for the interaction between A and B

SS_E = Error sum of squares

Degree of freedom, df

$$SS_T = SS_A + SS_B + SS_{AB} + SS_E$$

$$(abn-1) \quad (a-1) \quad (b-1) \quad (a-1)(b-1) \quad ab(n-1)$$

iii) Mean Squares for A, B, the interaction and error:

$$MS_A = \frac{SS_A}{a-1}$$

$$MS_B = \frac{SS_B}{b - 1}$$

$$MS_{AB} = \frac{SS_{AB}}{(a - 1)(b - 1)}$$

$$MS_E = \frac{SS_E}{ab(n - 1)}$$

iv) To test that the row factor effects are all equal to zero ($H_0: \tau_i = 0$), use

$$F_0 = \frac{MS_A}{MS_E} \quad \text{Reject null hypothesis at the } \alpha \text{ level of significance if } f_0 > f_{\alpha, a-1, ab(n-1)}$$

To test that the column factor effects are equal to zero ($H_0: \beta_j = 0$), use

$$F_0 = \frac{MS_B}{MS_E} \quad \text{Reject null hypothesis at the } \alpha \text{ level of significance if } f_0 > f_{\alpha, b-1, ab(n-1)}$$

To test the hypothesis $H_0: (\tau\beta)_{ij} = 0$

$$F_0 = \frac{MS_{AB}}{MS_E}$$

Reject null hypothesis at the α level of significance if $f_0 > f_{\alpha, (a-1)(b-1), ab(n-1)}$

Table B2 The ANOVA table for a two-factor experiment, fixed effect model

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Fo
A Treatments	SS _A	a - 1	MS _A	$\frac{MS_A}{MS_E}$
B Treatments	SS _B	b - 1	MS _B	$\frac{MS_B}{MS_E}$
Interaction	SS _{AB}	(a-1)(b-1)	MS _{AB}	$\frac{MS_{AB}}{MS_E}$
Error	SS _E	ab(n - 1)	MS _E	
Total	SS _T	abn - 1		

C) Residual Analysis

The analysis of variance assumes that the observations are normally and independently distributed with the same variance for each treatment or factor level. These assumptions should be checked by examining the residuals. A residual is the difference between an observation y_{ij} and its estimated (or fitted) value from the statistical model being studied.

Appendix C: Average particle size of TiO₂ microsphere in aqueous system

The particle size analysis in aqueous system was carried out using Mastersizer at constant stirring speed of 3000 rpm. The result showed the average particle size was remained at 25 μ m in a well mixed aqueous system versus time.

Figure C1 Average particle size of TiO₂ microsphere in aqueous system versus time.