Evaluation Of Sonocatalytic Degradation Of Ibuprofen And Sulfamethoxazole In The Presence Of Various Catalysts

Yasir Alhamadani
University of South Carolina

Follow this and additional works at: https://scholarcommons.sc.edu/etd
Part of the Civil Engineering Commons

Recommended Citation

This Open Access Dissertation is brought to you by Scholar Commons. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact dillarda@mailbox.sc.edu.
EVALUATION OF SONOCATALYTIC DEGRADATION OF IBUPROFEN AND SULFAMETHOXAZOLE IN THE PRESENCE OF VARIOUS CATALYSTS

By

Yasir Alhamadani

Bachelor of Science and Engineering
Al-Mustansiriya University, 2007

Master of Science
University of Science Malaysia, 2010

Master of Science
University of South Carolina, 2016

Submitted in Partial Fulfillment of the Requirements
For the Degree of Doctor of Philosophy in
Civil Engineering
College of Engineering and Computing
University of South Carolina
2018

Accepted by:
Yeomin Yoon, Major Professor
Joseph R.V. Flora, Committee Member
Shamia Hoque, Committee Member
Jang Min, Committee Member

Cheryl L. Addy, Vice Provost and Dean of the Graduate School
DEDICATION

Foremost, I am highly grateful to God for His blessing that continue to flow into my life, and because of You, I made this through against all odds.

I dedicate my dissertation work to my family and many friends. First of all, a special feeling of gratitude to my parents, brothers, sisters and friends for constant support, encouragement, and interest in what I am doing. Special thanks to my children, my son and daughter, Elyas and Talia. You are the light of my life.

For the last, to my lovely wife, Maryam, who stands with me for days and nights, handling and taking all the responsibilities while I were spending my time in the lab and office to finish my Ph.D. You are my rock in everything and certainly through these five years of experience. Without your faith, belief, smiles, hugs, and love, I would have not overcome trials and submitted this dissertation. Thank you for understanding how important this was to me and for supporting me every step of the way.

My love and gratitude goes out to you all.
ACKNOWLEDGEMENTS

This dissertation could not have been completed without the great support that I have received from so many people over the years. I wish to offer my most heartfelt thanks to the following people:

To my advisor, Dr. Yeomin Yoon. Thank you for the advice, support, and willingness that allowed me to pursue research on topics for which I am truly passionate. I see the same drive and passion in your own research efforts, and I thank you for letting me do the same.

To Dr. Flora, who supports me and advised my research. I learned from you how to think “out of the box” and deeply understand any process, thank you very much. Also, I would like to thank my friend Linkel for his support in molecular modeling. In addition, special thank goes to Dr. Jang, who was willing to serve as dissertation committee.

I would also like to thank Dr. Hoque, Dr. Berge, and Dr. Saleh for guiding my research for the past several years and helping me to develop my background in physiology and water chemistry.

To my mentor and friend Chanil, who became from day one in my study as a mentor and friend. I have always been able to turn to you when I have needed a listening ear and a dissenting opinion. You are a great friend and successful mentor. His help and support were very important to fulfill this dissertation. Thank you for being part of this.
Special thanks to Dr. Im for his help and guide which was the foundation of every success in this program. Many thanks to my friends in the environmental engineering group Seawoon, Liang, Ife, Hamid, Feroza, Malu, and Dahae, for their encouragements which help me to focus on my work. My research would not have been possible without their help.

I would also like to thank my parents, and sister, they were always supporting me and encouraging me with their best wishes.

Finally, I would like to thank my wife, Maryam who stood with me and took care of my children Elyas and Talia during my study, Thank you my love, friend, and wife.

To anyone that may I have forgotten. I apologize. Thank you as well.
ABSTRACT

Over the last two decades, large quantities of products, such as medicines, disinfectants, and personal care products, have been released into surface waters and wastewater treatment facilities by the pharmaceutical and chemical industries which have come to the attention of scientists with regard to their impacts on life in lakes, rivers, and groundwater. Among various types of treatment processes, ultrasonic (US) treatment process was used in this study to investigate the effect catalysts and removal of selected pharmaceutical’s (PhACs) compounds (ibuprofen (IBP) and sulfamethoxazole (SMX)). Carbon nanomaterials (CNMs) have become candidates for numerous applications in nanocomposites, microelectric devices, sensors, energy storage, microelectronics, biomedicines, and mechanical resonators. However, a key challenge is how to enhance the dispersion and stabilization of CNMs in water. The stabilization and dispersion of target CNMs was reviewed to address the effects of water quality conditions (pH, ionic strength, and temperature), natural/synthetic dispersing agents, and the effects of ultrasonication, acidification, and/or UV irradiation on dispersion and stabilization. Sonocatalytic degradation experiments were carried out to determine the removal effects on IBP and SMX in the presence of various types of catalysts including single walled carbon nanotubes (SWNTs), glass beads, and two fly ashes (Belews Creek fly ash and Wateree Station fly ash). In addition, the removal of the IBP/SMX and the production of hydrogen peroxide H$_2$O$_2$ was measured in the absence and the presence of the mentioned catalysts under different conditions; pH (3.5, 7, and 9.5), frequency (28, 580, and 1000)
kHz), temperature (15, 25, 35, and 55°C) and power intensity (0.045, 0.09, 0.135, and 0.18 WmL$^{-1}$). Furthermore, the adsorption analysis between these pharmaceuticals and SWNTs was performed by molecular modeling and validated with the experimental results. Overall, the sonocatalytic degradation of IBP and SMX fitted pseudo first-order rate kinetics and the synergistic indices of all the reactions were determined to compare the efficiency of the catalysts.
# Table of Contents

**DEDICATION** ................................................................................................................................. iii

**ACKNOWLEDGEMENTS** .................................................................................................................. iv

**ABSTRACT** ........................................................................................................................................ vi

**LIST OF TABLES** .............................................................................................................................. x

**LIST OF FIGURES** ............................................................................................................................. xi

**CHAPTER 1 INTRODUCTION AND MOTIVATION** ........................................................................... 1

**CHAPTER 2 OBJECTIVES AND SCOPE** ............................................................................................ 5

**CHAPTER 3 STABILIZATION AND DISPERSION OF CARBON NANOATERIALS IN AQUEOUS SOLUTIONS: A REVIEW** ................................................................. 7

3.1 INTRODUCTION .............................................................................................................................. 8

3.2 CNM SYNTHESIS .......................................................................................................................... 11

3.3 STABILIZATION/DISPERSION OF CNMs ....................................................................................... 13

3.4 ULTRASONICATION ....................................................................................................................... 29

3.5 ACIDIFICATION AND UV IRRADIATION .................................................................................... 30

3.6 APPLICATIONS FOR ADSORPTION IN WATER AND WASTEWATER TREATMENT ...... 33

3.7 CONCLUSIONS AND AREAS FOR FUTURE RESEARCH .......................................................... 39

**CHAPTER 4 SONOCATALYTIC DEGRADATION COUPLED WITH SINGLE-WALLED CARBON NANOTUBES FOR REMOVAL OF IBUPROFEN AND SULFAMETHOXAZOLE** ........ 45

4.1 INTRODUCTION .............................................................................................................................. 46

4.2 MATERIALS AND METHODS ......................................................................................................... 50
4.3 RESULTS AND DISCUSSION .................................................................................54

4.4 BINDING ENERGIES OF PHACs ON THE SWNTs ..............................................70

4.5 CONCLUSIONS .....................................................................................................71

CHAPTER 5 SONOCATALYTICAL DEGRADATION ENHANCEMENT FOR IBUPROFEN AND SULFAMETHOXAZOLE IN THE PRESENCE OF GLASS BEADS AND SINGLE-WALLED CARBON NANOTUBES ...........................................................73

5.1 INTRODUCTION .....................................................................................................74

5.2 MATERIALS AND METHODS ............................................................................77

5.3 RESULTS AND DISCUSSION ............................................................................79

5.4 CONCLUSIONS .....................................................................................................97

CHAPTER 6 SONOCATALYTIC REMOVAL OF IBUPROFEN AND SULFAMETHOXAZOLE IN THE PRESENCE OF DIFFERENT FLY ASH SOURCES .........................................................99

6.1 INTRODUCTION ..................................................................................................100

6.2 MATERIALS AND METHODS ...........................................................................103

6.3 RESULTS AND DISCUSSION ...........................................................................105

6.4 CONCLUSIONS ..................................................................................................122

CHAPTER 7 OVERALL CONCLUSIONS ...................................................................127

REFERENCES ...........................................................................................................132

APPENDIX A – PRINTABLE AUTHORSHIP LICENSE .............................................182
LIST OF TABLES

Table 3.1. Physical properties of different carbon nanomaterials .................................................14

Table 3.2. Summary of stabilization and dispersion for selected CNMs.................................34

Table 3.3 Summary of selected EDC/PPCP and dye removal by CNMs (modified from (Jung et al.2015)) ........................................................ .........................................................40

Table 4.1. Properties of ibuprofen and sulfamethoxazole. ..............................................................51

Table 4.2. Degradation efficiencies of PhACs and coefficient of determination ($R^2$) at different solution temperatures (pH 7, contact time = 60 min, and 1000 kHz) ...............57

Table 4.3. Pseudo-first order ($k_1$) rate constants, coefficient of determination ($R^2$), and synergistic index values within 10 and 60 min in different reactions (15 ± 1°C, pH 7, and 1000 kHz). ..........................................................66

Table 5.1. Pseudo-first order ($k_1$) degradation rate constants, coefficient of determination ($R^2$), and synergistic index values within 60 min for 28/1000-kHz US/GBs US/SWNTs, and US/GBs+SWNTs reactions at pH 7, power 0.18 W/mL, and temperature 15 ± 1°C .................................................................95

Table 6.1. XRF chemical composition analysis of BFA and WFA ..............................................108

Table 6.2 Determination of the pseudo-first order ($k_1$) removal rate constants, coefficient of determination ($R^2$), and synergistic index values for all the reactions.. .................123
LIST OF FIGURES

Figure 3.1. Proposed adsorption influenced by CNM stabilization and dispersion........42

Figure 4.1. Schematic diagram of the ultrasonic system........................................52

Figure 4.2. Effect of temperature on (a) the degradation of IBP and SMX. H₂O₂ production in the presence of (b) IBP and (c) SMX at various temperatures, pH 7, 0.18 W/mL and 1000 kHz. Error bars are smaller than the symbols in most cases. ...............56

Figure 4.3. Effect of pH on the degradation of (a) IBP and (b) SMX, (c) degradation rate constants of IBP and SMX, and (d) H₂O₂ production for different reactions at 15 ± 1°C, 0.18 W/mL, and 1000 kHz. Error bars are smaller than the symbols…………………59

Figure 4.4. (a) Effect of SWNTs on H₂O₂ production in the absence and presence of IBP and SMX, (b) effect of SWNTs concentration on H₂O₂ production, (c) degradation of IBP and SMX under different reaction conditions, and (d) degradation rate constants of IBP and SMX of each reaction at 15 ± 1°C, pH 7, 0.18 W/mL, and 1000 kHz. Error bars are smaller than the symbols.................................63

Figure 4.5. Proposed mechanisms of US and US/SWNT processes. .........................64

Figure 4.6. Effect of ultrasonication on (a) hydrodynamic radius of SWNTs and (b) zeta potential of SWNTs at 15 ± 1°C, pH 7, 0.18 W/mL, and 1000 kHz…………………68

Figure 4.7. Visual examination of SWNTs solution with and without sonication: (a) SWNTs without ultrasonication and (b) SWNTs with ultrasonication. (SWNTs = 45 mg/L, pH = 7, and 1000 kHz).................................................................69

Figure 4.8. Molecular modeling of adsorption mechanisms of (a.1) IBP un-dissociated form, (a.2) IBP dissociated form, (b.1) SMX un-dissociation form, and (b.2) SMX dissociated form. ..................................................................................71

Figure 5.1. Effect of frequency on (a) IBP and SMX degradation and (b) H₂O₂ production in the presence of IBP and SMX. (pH = 7, temperature = 15 ± 1°C, and power = 0.18 W/mL) ..................................................................................81
Figure 5.2. Effect of power on IBP degradation at (a) 28 kHz and (b) 1000 kHz. Effect of power on H$_2$O$_2$ production at (c) 28 kHz and (d) 1000 kHz. (pH = 7, temperature = 15 ± 1°C, and power = 0.18 W/mL). ..........................................................83

Figure 5.3. Effect of power on SMX degradation at (a) 28 kHz and (b) 1000 kHz. Effect of power on H$_2$O$_2$ production at (c) 28 kHz and (d) 1000 kHz. (pH = 7, temperature = 15 ± 1°C, and power = 0.18 W/mL). ..........................................................85

Figure 5.4. H$_2$O$_2$ production in the presence of glass bead as a function of (a) GBs size at 28 kHz, (b) GBs size at 1000 kHz, (c) 0.1 mm GBs dose at 28 kHz, and (d) 0.1 mm GBs dose at 1000 kHz (pH = 7, power = 0.18 W/mL, and temperature = 15 ± 1°C). ...............87

Figure 5.5. Removal of IBP in the absence and presence of GBs and SWNTs at (a) 28 kHz, and (b) 1000 kHz. H$_2$O$_2$ production rate in the absence and presence of GBs and SWNTs at (c) 28 kHz and (d) 1000 kHz (GBs = 0.1 mm and 10 g/L, SWNTs = 45 mg/L, pH = 7, power = 0.18 W/mL, and temperature = 15 ± 1°C). ..................................................89

Figure 5.6. Removal of SMX in the absence and presence of GBs and SWNTs at (a) 28 kHz, and (b) 1000 kHz. H$_2$O$_2$ production rate in the absence and presence of GBs and SWNTs at (c) 28 kHz and (d) 1000 kHz (GBs = 0.1 mm and 10 g/L, SWNTs = 45 mg/L, pH = 7, power = 0.18 W/mL, and temperature = 15 ± 1°C). ..................................................91

Figure 5.7. H$_2$O$_2$ production in the absence and presence of GBs and SWNTs with/without IBP at (a) 28 kHz, and (b) 1000 kHz, and with/without SMX at (c) 28 kHz, and (d) 1000 kHz. (GBs = 0.1 mm and 10 g/L, SWNTs = 45 mg/L, pH = 7, power = 0.18 W/mL, and temperature = 15 ± 1°C). ..................................................92

Figure 5.8. Proposed mechanisms of US and US/SWNT processes .................................93

Figure 5.9. Effect of CCl$_4$ (150 µM) and MeOH (150 mM) on (a) IBP and (b) SMX degradation rate (GBs = 0.1 mm and 10 g/L, SWNTs = 45 mg/L, pH = 7, power = 0.18 W/mL, and temperature = 15 ± 1°C). .................................................................96

Figure 6.1. Effect of ultrasonic frequency on H$_2$O$_2$ production in the presence of BFA and WFA; (a) BFA at 28 kHz, (b) BFA at 580 kHz, (c) BFA at 1000 kHz, (d) WFA at 28 kHz, (e) WFA at 580 kHz, and (f) WFA at 1000 kHz at pH 7 .........................107

Figure 6.2. Particle size distribution of BFA and WFA. .................................................109

Figure 6.3. Effect of ultrasonic frequency and pH on IBP and SMX removal; (a) IBP at pH 3.5, (b) IBP at pH 7, (c) IBP at pH 9.5, (d) SMX at pH 3.5, (e) SMX at pH 7, and (f) SMX at pH 9.5 ..........................................................110
Figure 6.4. Effect of ultrasonic frequency and pH on H2O2 production in the presence of IBP and SMX; (a) IBP at pH 3.5, (b) IBP at pH 7, (c) IBP at pH 9.5, (d) SMX at pH 3.5, (e) SMX at pH 7, and (d) SMX at pH 9.5..................................................114

Figure 6.5. Effect of ultrasonic frequency and pH on H2O2 production at (a) pH 3.5, (b) pH 7, and (c) pH 9.5.................................................................117

Figure 6.6. Effect of ultrasonic frequency and pH on IBP and SMX removal in the presence of BFA (45 mg/L); (a) IBP at pH 3.5, (b) IBP at pH 7, (c) IBP at pH 9.5, (d) SMX at pH 3.5, (e) SMX at pH 7, and (d) SMX at pH 9.5.................................118

Figure 6.7. Effect of ultrasonic frequency and pH on IBP and SMX removal in the presence of WFA (45 mg/L); (a) IBP at pH 3.5, (b) IBP at pH 7, (c) IBP at pH 9.5, (d) SMX at pH 3.5, (e) SMX at pH 7, and (d) SMX at pH 9.5...............................................119
CHAPTER 1
INTRODUCTION AND MOTIVATION

Pharmaceutical compounds (PhACs) in the water body have become an important issue in water and wastewater treatment facilities, because they are very complex compounds, occur at low concentrations, and yet have high impacts on aquatic life and human health (Halling-Sørensen et al. 1998; Heberer 2002). Their occurrence in the water body is due to several reasons, including irregular disposal of unused medications and expired drugs and veterinary medicines (Sirés and Brillas 2012; Snyder et al. 2003). Ibuprofen (IBP) and sulfamethoxazole (SMX) were selected as examples, due to their widespread occurrence in many United States rivers and wastewater treatment plant effluents (Kolpin et al. 2002). PhACs have been detected at between 0.002 and 24.6 µg L⁻¹ for ibuprofen (IBP) and 0.01 and 2 µg L⁻¹ for sulfamethoxazole (SMX) in the effluent of several sewage treatment plants (Buser, Poiger, and Müller 1999; Méndez-Arriaga et al. 2008) and surface waters (0.03–0.48 µg L⁻¹) (Hirsch et al. 1999; Beltrán et al. 2008).

Ultrasonic (US) treatment is one of the promising advanced oxidation processes that has the potential to produce hydroxyl radicals (OH⁺) in water, which are strong oxidizing agents (Hinge et al. 2016). The power of OH⁺ in water treatment lies in their ability to destroy and degrade complex, otherwise-hard-to-degrade, and toxic organic compounds and convert them ultimately to carbon dioxide and water (Zhao et al. 2016). The process of US treatment produces OH⁺ through the cavitation phenomenon and the
formation of high-intensity bubbles (Mischopoulou et al. 2016). Cavitation occurs very quickly, through the steps of nucleation, growth, and the collapse of cavitation bubbles in water, releasing large amounts of energy locally, generating hot spots, and producing hydrogen and OH\(^-\) due to the sonolysis of water (Hinge et al. 2016; Al-Hamadani et al. 2016). During this phenomenon, high temperatures (5000 K) and pressures (1000 atm) created inside cavitation bubbles lead to thermal dissociation of water molecules into H\(^-\) and OH\(^-\) (Li et al. 2016). The O\(_2\) dissolved in water reacts and forms OH\(^-\) and HO\(_2\)^*.

Additionally, the cavitation bubbles contain three zones: the gaseous zone, the gas–liquid transition zone, and the bulk liquid zone. In the gaseous zone, the temperature and pressure reach their maximum levels of 5000 K and 1000 atm, respectively. The zone is hydrophobic and volatile compounds can be degraded. Second, in the gas–liquid transition zone, the temperature reaches 2000 K. The zone is moderately hydrophobic and moderate degradation of volatile compounds can be achieved. The third zone is the bulk liquid zone, where the temperature is 300 K; hydrophilic and non-volatile compounds undergo degradation in this zone (Im et al. 2013a; Im et al. 2014; Riesz, Kondo, and Krishna 1990). Previous studies have indicated that US treatment has marked benefits, including safety, cleanliness, and ease of use; additionally, no carcinogenic by-products form during treatment (Al-Hamadani et al. 2016; Zhao et al. 2016).

Carbon nanomaterials (CNMs) are defined as carbon materials that have physical features with at least one dimension of 100 nm or less, and include carbon nanofilms and carbon nanocoatings (<100 nm in one dimension), carbon nanotubes and carbon nanowires (<100 nm in two dimensions), and CNMs (<100 nm in three dimensions) (Tiede et al. 2008). Among the three main groups (natural, incidental, and engineered)
into which CNMs are classified, engineered CNMs are produced intentionally and are fabricated from the “bottom up” (Perez, Farre, and Barcelo 2009). CNMs, including carbon nanotubes (CNTs), graphene oxides (GOs), and fullerenes, are widely used in various applications such as electro-optical devices, plastics, catalysts, and components in composites (Perez, Farre, and Barcelo 2009). Despite the significant growth in CNT use and sonocatalysis in water and wastewater treatment, much is still unknown, such as, for example, how sonocatalysis coupled with CNTs influences the transport of PhACs, while removal mechanisms (e.g., sorption of PhACs onto CNTs and thermal degradation/oxidation during sonocatalytic degradation) are relatively well known. Molecular-level simulations can also provide unique insight into the molecular interactions among PhACs and CNTs. Previous studies have clarified the adsorption process of contaminants onto carbon nanomaterials by applying the quantum chemistry and molecular dynamics simulations (Zhao and Johnson 2007; Arsawang et al. 2011; Mucksch and Urbassek 2011).

Many studies have shown that using catalysts in combination with sonochemical degradation (i.e., sonocatalytic degradation) has advantages over both conventional and advanced treatment processes (Kong et al. 2012; Madhavan et al. 2010). For that, single-wall carbon nanotubes (SWNTs) and inert glass beads (GBs) can be used, individually and in combination, to enhance the degradation of PhACs. SWNTs are a member of the carbon nanotube group that consist of a single rolled up graphene sheet, which has been recently shown to be a significant adsorbent, due to its unique physiochemical properties (Li, Ding, et al. 2003). The hydrophobicity, electrical conductivity, optical activity, and mechanical strength of SWNTs enhance the removal of various types of contaminants,
such as heavy metals, organic and inorganic matter, pharmaceuticals, personal care products, and endocrine-disrupting compounds (Qu, Alvarez, and Li 2013; Im et al. 2013a). However, such catalysts are relatively expensive for treating large volumes of wastewater. Thus, alternative low-cost catalysts need to be investigated for their ability to remove contaminants, such as pharmaceutical compounds. Fly ash was assessed in this study regarding its ability to enhance the sonodegradation of IBP and SMX. Fly ash is a by-product waste material generated in dry form in thermal power plants. Large amounts of fly ash are generated and dumped in landfills annually (Yu 2004; Janoš, Buchtová, and Rýznarová 2003; Mirshahghassemi, Cai, and Lead 2016). Thus, using fly ash in water and wastewater treatment is a good strategy to reduce environmental pollution. Fly ash’s chemical composition generally consists of aluminum oxide ($\text{Al}_2\text{O}_3$) and silicon dioxide ($\text{SiO}_2$) (in total, 60–80 wt%), in addition to some transition metal oxides (Li et al. 2016; Yu 2004). Previous studies have found fly ash to be a good adsorbent for various types of dyes (Wang and Wu 2006; Wang, Boyjoo, and Choueib 2005), and it has been used in photocatalytic applications, combined with TiO$_2$ (Wang et al. 2011).
CHAPTER 2

OBJECTIVES AND SCOPE

Sonocatalytic novelty of using both sonodegradation and single wall carbon nanotubes (SWNTs) adsorption processes is, at one level, a relatively simple approach that involves the combination of two existing technologies (i.e., adsorption and oxidation). Additionally, an enhancement catalyst such as glass bead glass beads (GBs) and fly ash were used to enhance the sonodegradation of ultrasonic treatment. Therefore, four objectives were set to this project as follow:

The first objective was to review and summarize the recent progress on the stabilization and dispersion of various carbon nanomaterials (CNMs) (such as carbon nanotubes, graphene oxides and fullerenes) in aqueous solutions. The stabilization and dispersion of target CNMs was reviewed and studied the effects of water quality conditions (pH, ionic strength, and temperature), natural/synthetic dispersing agents, and the effects of ultrasonication, acidification, and/or UV irradiation on dispersion and stabilization.

The second objective was to evaluate the degradation of selected pharmaceuticals (PhACs; ibuprofen (IBP) and sulfamethoxazole (SMX)) using an ultrasonic reactor at high frequency (1000 kHz) in the absence and presence of SWNTs, and to illustrate the adsorption mechanisms between PhACs and SWNTs by the molecular-level simulations.
The third objective was to determine the effects of GBs and SWNTs on IBP and SMX removal using low and high ultrasonic frequencies (28 and 1000 kHz). GBs were used as enhancement of the sonodegradation in this study, and the effect of low and high frequency was compared.

The fourth objective in this project was to evaluate the removal of IBP and SMX at different US frequency and pH conditions in the presence and absence of fly ash as a low-cost adsorbent.
CHAPTER 3

STABILIZATION AND DISPERSION OF CARBON NANOMATERIALS IN AQUEOUS SOLUTIONS: A REVIEW

Abstract

Carbon nanomaterials (CNMs) have become candidates for numerous applications in nanocomposites, microelectric devices, sensors, energy storage, microelectronics, biomedicines, and mechanical resonators. However, a key challenge is how to enhance the dispersion and stabilization of CNMs in water. Thus, this review summarizes recent progress on the stabilization and dispersion of various CNMs (such as carbon nanotubes, graphene (oxides), fullerenes) in aqueous solutions. The stabilization and dispersion of target CNMs is reviewed to address the effects of water quality conditions (pH, ionic strength, and temperature), natural/synthetic dispersing agents, and the effects of ultrasonication, acidification, and/or UV irradiation on dispersion and stabilization. Applications of CNMs are also briefly addressed regarding removing micropollutants by adsorption in water and wastewater treatment.

The outlook for future research challenges on CNMs is also discussed.

*Key words*: Carbon nanomaterials; carbon nanotubes; graphene oxides; fullerenes; dispersion; adsorption

### 3.1. Introduction

Carbon nanomaterials (CNMs) are defined as carbon materials that have physical features with at least one dimension of 100 nm or less, and include carbon nanofilms and carbon nanocoatings (<100 nm in one dimension), carbon nanotubes and carbon nanowires (<100 nm in two dimensions), and CNMs (<100 nm in three dimensions) (Tiede et al. 2008). Among the three main groups (natural, incidental, and engineered) into which CNMs are classified, engineered CNMs are produced intentionally and are fabricated from the “bottom up” (Perez, Farre, and Barcelo 2009). CNMs, including carbon nanotubes (CNTs), graphene oxides (GOs), and fullerenes, are widely used in various applications such as electro-optical devices, plastics, catalysts, and components in composites (Perez, Farre, and Barcelo 2009).

In particular, since their discovery in 1991, CNTs have shown such unusual mechanical, electrical, thermal, and chemical properties that they have become candidates for many applications, including nanocomposites, energy storage, microelectronics, and medical devices (Baughman, Zakhidov, and de Heer 2002; Valcarcel et al. 2005). Several studies anticipated the production of CNTs at millions of tons in 2010, and a $1 trillion worldwide market for nanoproducts by 2015 (Roco 2005; Ball 2001). Additionally, other CNMs, such as graphene and fullerenes, have drawn intense research interest and large-scale applications in various areas due to their unique physicochemical properties (Wiesner et al. 2006; Mascioli and Zhang 2003; Geim and Novoselov 2007; Rao et al. 2009). However, to maximize the advantage of CNMs
(e.g., as effective adsorbents in water), they should not form aggregates and must be well dispersed, so that dispersed and stabilized CNMs in solution can greatly increase the interaction of CNMs with, for example, contaminants in solutions.

Difficulties in the stabilization and dispersion of CNMs originate from their propensity to aggregate, particularly in aqueous systems, due to substantial van der Waals attractions and specific hydrophobic interaction between CNMs (Saleh, Pfefferle, and Elimelech 2010; Girifalco, Hodak, and Lee 2000; Ma et al. 2010; Pang et al. 2009). Researchers have used novel and unique approaches to address such challenges in the aggregation or bundling of CNMs, including covalent and non-covalent functionalization schemes (Lu et al. 2010; Chen et al. 2003; Datsyuk et al. 2009; Dou, Xin, and Xu 2009; Duan, Wang, and Collins 2011; Lee et al. 2007; Rozhkova 2013). Generally, chemical functionalization is based on the covalent linkage of functional entities onto the carbon support of CNTs (Ma et al. 2010). For example, for CNTs, direct covalent sidewall functionalization is associated with a change in hybridization from sp\(^2\) to sp\(^3\), leading to a partial loss of their optical, electrical, and thermal properties (Dyke and Tour 2004; Balasubramanian and Burghard 2005). Defect functionalization is another method for the covalent functionalization of CNMs. Acids, such as HNO\(_3\), H\(_2\)SO\(_4\), or a mixture thereof (Hirsch and Vostrowsky 2005; Prezhdo, Kamat, and Schatz 2011), and strong oxidants, such as KMnO\(_4\) (Banerjee, Hemraj-Benny, and Wong 2005), ozone (Sham and Kim 2006), and reactive plasma (Felten et al. 2005), can create defect functionalization on CNMs.

While covalent methods can provide valuable functional groups on the CNM surface, these methods have two main disadvantages (Ma et al. 2010): (i) During the
functionalization reaction, particularly along with damaging ultrasonication and/or oxidation processes, many defects are inevitably created on the CNM surfaces, and in some extreme cases, CNMs may be fragmented into smaller pieces, and (ii) concentrated acids or strong oxidants are frequently used for CNM functionalization, which are environmentally unfriendly. Thus, non-covalent functionalization is an alternative method for changing the interfacial properties of CNMs. The suspension of CNMs (a typical example of non-covalent treatment) in the presence of various polymers causes the wrapping of polymer around the CNMs to form super-molecular complexes of CNMs (Dror, Pyckhout-Hintzen, and Cohen 2005; Etika, Cox, and Grunlan 2010; Jofre et al. 2007; Mountrichas, Tagmatarchis, and Pispas 2007). The polymer wrapping process is achieved through van der Waals interactions and \( \pi-\pi \) stacking between CNMs and polymer chains containing aromatic rings (Ma et al. 2010).

While the stabilization and dispersion of CNMs in aqueous solutions have been studied widely (Suttipong et al. 2013; Tummala et al. 2010; Xiao et al. 2007; Zhang, Tjiu, et al. 2011), a broader analysis of CNM stabilization and dispersion in water is essential, because the unique properties of CNMs in terms of size, shape, surface area, volume, morphology, functional groups, and functionalization of CNMs affect their stabilization and degree of dispersion in water. Thus, this review provides a comprehensive analysis of the aqueous stabilization and dispersion of CNMs, particularly CNTs, GOs, and fullerenes, under various water quality conditions, natural/synthetic dispersing agents, and ultrasonication, acidification, and/or UV irradiation conditions. Additionally, this review briefly surveys recent publications on the synthesis and potential applications of CNMs for micropollutant removal in water and wastewater.
3.2 CNM synthesis

Kroto et al. developed the chemistry of fullerenes in the mid-1980s (Kroto et al. 1985). Fullerenes are geometric cage-like structures of carbon atoms that are composed of hexagonal and pentagonal faces (Thostenson, Ren, and Chou 2001). C\textsubscript{60} was the first closed and convex structure. A few years later, CNTs that are now one of the widely known CNMs were discovered by Iijima, who described a multi-walled CNTs (MWNTs) preparation process after a random event during the testing of a new arc evaporation method for C\textsubscript{60} carbon molecule fabrication in 1991 (Iijima 1991). While MWNTs that have diameters from 2 to 100 nm and lengths of tens of microns consist of an array of such cylinders, formed concentrically and separated by 0.35 nm, similar to the basal plane separation in graphite (Iijima 1991), single-walled nanotubes (SWNTs) consist of a single sheet of graphene rolled seamlessly to form a cylinder with diameter of the order of 1 nm and lengths of up to centimeters (Bethune et al. 1993; Coleman et al. 2006).

CNTs can be fabricated by various methods. For example, high-temperature preparation techniques, such as arc discharge, were originally used to fabricate CNTs (Iijima and Ichihashi 1993). The arc discharge synthesis of CNTs is simple in circumstances where all the growth conditions are ensured for MWNTs (Prasek et al. 2011). It has been reported that MWNTs can be synthesized using an arc discharge technique under He, ethanol, acetone, and hexane atmospheres at various pressures (150-500 Torr) (Shimotani et al. 2001), and arc discharges in the three organic atmospheres (ethanol, acetone, hexane) produced more MWNTs, at least double, than those in the He atmosphere. Additionally, arc discharge is commonly used for the deposition of some non-standard CNTs. Unlike standard MWNTs deposition using a gas
atmosphere, a previous study showed a high-yield synthesis of MWNTs by arc discharge in liquid nitrogen, suggesting that this technique may be a practical option for the large-scale synthesis of MWNTs with high purity (Jung et al. 2003). Unlike MWNTs, SWNTs are synthesized with a transition metal catalyst in the arc discharge deposition process, typically in a hydrogen or argon atmosphere, using a composite anode (a composition of graphite and a metal, such as Ni, Fe, Co, Pd, Ag, or Pt, or mixtures of Co, Fe, or Ni with other elements like Co-Ni, Fe-Ni, Fe-No, Co-Cu, Ni-Cu, or Ni-Ti) (Prasek et al. 2011).

High-temperature preparation methods, such as arc discharge, are currently being replaced by laser ablation (Batani, Vinci, and Bleiner 2014; Mubarak et al. 2014; Saeed and Ibrahim 2013) and low-temperature chemical vapor deposition (e.g., < 800°C) (Jin et al. 2015; Ma et al. 2014; Wang et al. 2014), because the orientation, alignment, nanotube length, diameter, purity, and density of CNTs can be controlled precisely with these new techniques (He et al. 2010). However, for most of those techniques, supporting gases and a vacuum are required. Because gas-phase methods are volumetric, they are appropriate for applications such as composite materials that require large quantities of nanotubes and industrial-scale fabrication methods to make them economically practicable (Prasek et al. 2011). However, the disadvantages of gas-phase synthesis methods are low catalyst production, where only a small percentage of the catalysts form nanotubes, short catalyst lifetimes, and low catalyst number density (Unrau, Axelbaum, and Lo 2010). While many researchers have reported mechanical properties of CNMs (e.g., CNTs, GOs, fullerenes) that exceed those of any previously existing material, some defects are always present when high-quality CNMs are produced. Their physical properties suffer due to the presence of defects, with thermal, electronic, and mechanical properties differing
significantly from those expected for ‘pristine’ CNMs, such as CNTs (Coleman et al. 2006).

3.3. Stabilization/dispersion of CNMs

Because CNMs hold potential for delivering unique multifunctional characteristics and mechanical properties, understanding CNM properties is important, particularly when CNMs are used under different stabilization and dispersion conditions in numerous different fields. Table 3.1 summarizes the properties of various CNMs, including fullerenes, MWNTs, and SWNTs, compared with diamond and graphite (Koo 2006; Coleman, Khan, and Gun'ko 2006). Clearly, CNTs have numerous advantages over other carbon materials in terms of their electrical and thermal properties. These CNM properties have great potential for many applications in various areas, including field emissions, conducting plastics, thermal conductors, energy storage, conductive adhesives, thermal interface materials, structural materials, fibers, catalyst supports, biological applications, air and water filtration, and ceramics (Coleman, Khan, and Gun'ko 2006; Thostenson, Ren, and Chou 2001; Ajayan, Schadler, and Braun 2003). However, the stabilization/dispersion problem of CNMs has been one of the major concerns. In particular, the difficulty in stabilizing CNMs is due to their propensity to aggregate, particularly in aqueous systems, due to non-specific hydrophobic interactions between tubes, as well as substantial van der Waals attractions (Saleh, Pfefferle, and Elimelech 2010; Girifalco, Hodak, and Lee 2000; Collins et al. 2011; Li, Mueller, et al. 2008; Zhang et al. 2014). Additionally, because the physicochemical environmental conditions of the water (pH, ionic strength, temperature, and natural organic matter present) influence CNM properties, they also significantly affect the stabilization and dispersion of CNMs.
Table 3.1 Physical properties of different carbon nanomaterials (modified from (Ma et al. 2010)).

<table>
<thead>
<tr>
<th>CNM property</th>
<th>CNM material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diamond</td>
</tr>
<tr>
<td>Specific gravity (g cm(^{-3}))</td>
<td>3.5</td>
</tr>
<tr>
<td>Electrical conductivity (S cm(^{-1}))</td>
<td>10(^{-2}) – 10(^{-15})</td>
</tr>
<tr>
<td>Electron mobility (cm(^2) v(^{-1}) s(^{-1}))</td>
<td>1,800</td>
</tr>
<tr>
<td>Thermal conductivity (W m(^{-1}) K(^{-1}))</td>
<td>900 – 2,320</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (K(^{-1}))</td>
<td>(1 – 3) \times 10(^{-6})</td>
</tr>
<tr>
<td>Thermal stability in air (°C)</td>
<td>&lt;600</td>
</tr>
</tbody>
</table>

\(^a\)in-plane; \(^b\)c-axis; NG = negligible

3.3.1 Water quality

3.3.1.1 pH

Huyng et al. reported that adsorption of Suwannee River natural organic matter (SRNOM) to MWNTs increased as pH decreased, due to a denser and more coiled conformation of the NOM under acidic conditions (Hyung and Kim 2008). In a separate study, when comparing the solubilizing ability of SRNOM under different pH conditions, SRNOM was a more effective dispersant at pH 3.5 than at pH 7 (Alpatova et al. 2010), consistent with the findings of a previous study (Hyung and Kim 2008). Both carboxylic and phenolic groups of SRNOM deprotonate as the pH increases, resulting in higher electrostatic repulsion between SWNTs and SRNOM molecules and, thus, in a lower amount of SRNOM adsorbed on the SWNT surface. Additionally, the ‘better’ dispersion of SWNTs at pH 3.5 could be attributable in part to steric hindrance due to the SRNOM, when a higher surface density of NOM on the surface of SWNT bundles results in higher
repulsion between SWNTs (Alpatova et al. 2010). In a separate study, highly O-MWNTs showed a higher dispersion stability than low O-MWNTs at pH 1.5-11.0 (Bai et al. 2014). The higher suspension concentration of high O-MWNTs could be attributed to the increased electrostatic repulsion on their surfaces, according to the electrostatic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Smith, Wepasnick, Schrote, Bertele, et al. 2009). This is presumably because the high O-MWNTs showed a more negative charge than low O-MWNTs at corresponding pH levels. Four different pH-responsive polymers (weak polyelectrolytes), poly(acrylic acid), poly(methacrylic acid), poly(allylamine), and branched polyethyleneimine), were used as stabilizers in water (Etika, Cox, and Grunlan 2010). This non-covalent functionalization of SWNTs resulted in suspensions where the dispersion state could be altered simply by changing the pH. This was presumably because the weak polyelectrolytes can be positively charged (polycations) or negatively charged (polyanions) or, as in the case of proteins, have groups that can be either positively or negatively charged (amphoteric) depending on the pH. Larger chain extension occurred in poly(acrylic acid) at high pH due to self-repulsion of the negatively charged carboxylates on its backbone (Etika, Cox, and Grunlan 2010).

While hydrogen bonds may form due to the polyethoxyl moiety of surfactants (e.g., the Triton X-series) and hydroxyl/carboxylic groups on CNT surfaces (Chen, Duan, and Zhu 2007; Lin and Xing 2008a), a recent study showed hydrophobic and π-π interactions to be the dominant mechanisms for the adsorption of the surfactants by MWNTs due to the insignificant effects of electrostatic interactions and hydrogen bonds (Bai et al. 2010). This was confirmed because constant adsorption within the pH range of 2-12 would exclude hydrogen bonding as a major mechanism regulating the adsorption of
The surfactants onto MWNTs. The adsorbed amount on MWNTs would be expected to
decrease with increasing pH due to the transition from -COOH to -COO⁻ on the surface
of the MWNTs, if hydrogen bond was a major mechanism of surfactant adsorption on
MWNTs.

Aggregation experiments were conducted to examine the role of pH in the
stability of sonicated and stirred C₆₀ nanoparticles at pH 2-12 in the presence of KCl
(Chen and Elimelech 2009). Both nanoparticles showed the fastest aggregation at pH 2,
because they were least negatively charged at that pH. This is consistent with previous
studies with other CNMs. The nanoparticles became more negatively charged and
underwent slower aggregation as the pH was increased. The attachment efficiencies of
the sonicated fullerene nanoparticles were calculated to be 0.92 and 0.38 at pH 2 and 5.5,
respectively, obtained by determining the initial slopes of the aggregation profiles.
However, the aggregation was too slow at pH 12 to determine the attachment efficiency
precisely. In the case of the stirred fullerene nanoparticles, the attachment efficiencies
were determined to be 0.82, 0.64, and 0.12 at pH 2, 5.5, and 12, respectively (Chen and
Elimelech 2009). Homogeneous aqueous particles of graphene were prepared by
chemical reduction of GO in the presence of chitosan (Fang et al. 2010). The amino
groups of chitosan are protonated at low pH and the chitosan “clouds” are greatly
extended. Thus, the reduced GO sheets were strongly dispersed due to intersheet
electrostatic repulsion. However, the chitosan clouds became deprotonated and intersheet
electrostatic repulsion was reduced with an increase in the pH; at the same time,
intermolecular association (e.g., hydrogen bonding) of chitosan molecules became
dominant, so that the reduced GO became aggregated (Fang et al. 2010).
3.3.1.2 Ionic strength

The stability of CNMs can also be influenced by the presence of background ions in water. The optical density (OD; i.e., controlled by both the particle size and the particle concentration of CNMs) of a MWNT suspension was stable at low NaCl and CaCl$_2$ concentrations (Bai et al. 2014). However, the OD of the MWNT suspension decreased suddenly, to less than 1%, at ionic concentrations in excess of a certain value, consistent with the electrostatic DLVO theory (Smith, Wepasnick, Schrote, Bertele, et al. 2009). For acidified MWNTs, the critical coagulation concentration (CCC) values for NaCl and CaCl$_2$ ranged from 2.0 to 108.1 mM and from 0.11 to 0.48 mM, respectively (Bai et al. 2014). The CCC is defined as the ionic concentration at which the amount of suspended MWNTs equals 50% of the original amount in the absence of ions (Lin et al. 2009).

The effect of NaCl concentration on the aggregation kinetics of aqueous colloidal suspensions of C$_{60}$ (aqu/C$_{60}$) clearly showed that at a NaCl concentration of 50 mM and below, aqu/C$_{60}$ aggregation took place slowly due to electrostatic stabilization (Bouchard, Ma, and Issacson 2009). In this study, at NaCl concentrations ≤ 100 mM, aqu/C$_{60}$ aggregate charge was adequate to impede aggregation (reaction-limited kinetics), while at NaCl concentrations ≥ 300 mM, no additional increase in aggregation was obtained, indicating that electrostatic repulsive forces had been successfully shielded, the energy barrier to aggregation eliminated, and that aggregation was then diffusion-limited. Similar trends were obtained at relatively low ionic strengths of 0, 0.01, and 0.1 M NaCl; the n-C$_{60}$ remaining in suspension was characterized by a narrow size distribution with mean diameters (168, 298, and 680 nm, respectively) that increased with increasing ionic strength (Brant, Lecoanet, and Wiesner 2005). However, at the highest ionic strength of
1.0 M NaCl, a larger intensity-weighted mean diameter of 897 nm was observed. This suggests that the same phenomenon governs the transport and deposition of n-C_{60} clusters in porous media, where increases in electrolyte concentration resulted in an increased affinity between the fullerene colloids and the collector surfaces, thus resulting in reduced colloid mobility (Brant, Lecoanet, and Wiesner 2005). nC_{60} was differentially stabilized under varying ionic strength conditions with different wastewater samples (Yang et al. 2013). After 1 h, the nC_{60} retained its initial size (~150 nm) at an added ionic strength of ≤ 50 mM, but clear aggregation occurred in all samples at ≥ 100 mM, similar to the reported threshold destabilization concentration of < 120 mM for nC_{60} in pure water (Chen and Elimelech 2006). The nC_{60} aggregates in deionized (DI) water were obviously larger than those in waste-water samples at 100 and 500 mM. At 500 mM, the size decreased in the order of DI water (~750 nm, DOC < 0.1 mg/L) > secondary effluent (~500 nm, DOC = 3.4 mg L^{-1}) > aeration tank liquor (~400 nm, DOC = 5.8 mg L^{-1}) > primary effluent (~200 nm, DOC = 26.9 mg L^{-1}), the opposite of the DOC concentration (Yang et al. 2013).

GO is a common precursor of graphene and other similar CNMs used in ultracapacitors and is accessible from graphite in one facile step (Shen et al. 2011). Acik et al. found that both the anion and cation moieties of ammonium-based ionic liquids intercalated into GO influenced the degree of thermal expansion and exfoliation upon thermal annealing of the resulting intercalation compounds (Acik et al. 2012). While GO-ionic liquid was readily dispersed in DI water, after annealing at 500°C and redispersing in DI water, the particle size was reduced, improving the colloidal properties.
3.3.1.3 Temperature

Colloidal stability and dispersion of CNMs vary significantly depending on the temperature of water. Colloidal stability of purified forms of arc-discharge SWNTs decreased significantly at 40°C, compared with lower temperatures (20°C, 4°C) in waste water (pH 7; conductivity = 2,290 µS cm⁻¹, total organic carbon = 2.38 mg L⁻¹) (Adeleye and Keller 2014). However, SWNTs were more stable at 20°C than 4°C; 36% of the SWNTs suspended after sonication had settled out after 48 h at 40°C, compared with 31% and 24% sedimentation at 4°C and 20°C, respectively. The increase in temperature corresponds to energy input into the SWNT suspension, causing disruption of weak interaction forces, increased Brownian motion/collisions, and decreased zeta potential (Zhou, Bennett, and Keller 2012). These findings suggest that the stability of SWNTs in the natural environment may be affected as ambient temperatures change, particularly with rapid temperature fluxes (e.g., those due to sunrise and sunset) (Adeleye and Keller 2014). SWNTs were well dispersed in pure water with a thermo-responsive amphiphilic PNIPAM₁₅₀-F₁₀₈-PNIPAM₁₅₀ pentablock terpolymer (Wu, Guo, and Feng 2014). In this study, the temperature was increased to 50°C, and the hybrids showed a largely bundled and networked microstructure, suggesting that intermolecular hydrogen bonding between the polymers and water molecules was predominant at low temperatures, and that the terpolymer chains were extended and soluble in water, leading to SWNTs being soluble in water. However, at higher temperatures, the intramolecular hydrogen bonding between C=O and N-H groups resulted in a dense and collapsed conformation of the terpolymer chains, making it more difficult for SWNTs to remain soluble in water (Zhang and Wang 2009).
3.3.2. Natural and synthetic dispersing agent

3.3.2.1 Natural dispersing agent

Natural organic matter: The stability and dispersion of CNMs may be enhanced in water bodies with significant amounts of NOM, such as humic acid, extracellular polymeric substances (EPS), or alginate, because, for example, the hydrophobic surfaces of CNTs makes them interact readily with NOM, which is abundant in the environment (Saleh, Pfefferle, and Elimelech 2010). Additionally, improved CNT stability was observed in the presence of SRNOM (Hyung et al. 2007). EPS stabilized SWNTs more effectively than SRNOM when EPS, as confirmed verified by the CCC shifting about 100 mM in NaCl (Adeleye and Keller 2014). It is known that EPS contains some hydrophobic polysaccharides with large surface areas with which it can interact with other hydrophobic materials (Flemming, Neu, and Wozniak 2007), such as CNMs, leading to steric repulsion between CNMs. Additionally, functional groups present in EPS—such as hydroxyl, phosphoryl, and carboxylic groups (Pal and Paul 2008)—can increase electrostatic repulsion due to the enhanced negative charges on CNMs. The suspendability of both SWNTs and MWNTs increased with increasing their diameter in tannic acid (TA, containing a large number of aromatic functional groups) solution without the aid of sonication (Lin and Xing 2008b). Sorption affinity of CNTs for TA increased with decreasing CNT diameter, positively related to the surface area. This was presumably because (i) TA molecules may be adsorbed first onto CNTs with aromatic rings, binding to the surface carbon rings via \( \pi-\pi \) interactions, until forming a monolayer and (ii) the TA monolayer then further sorbed dissolved TA via hydrogen bonds and other polar interactions.
In the absence of Suwannee River humic acid (SRHA), the effects of monovalent and divalent electrolytes (NaCl, MgCl₂, and CaCl₂) on the aggregation performance of C₆₀ nanoparticles was consistent with the DLVO theory of colloidal stability (Chen and Elimelech 2007). However, in the presence of SRHA and NaCl, MgCl₂, or CaCl₂ electrolytes, the adsorbed humic acid on the C₆₀ nanoparticles resulted in electrostatic repulsion, which successfully dispersed the nanoparticle suspension. This behavior caused a dramatic drop in the rate of aggregation, an increase in the CCC, and an attained value of less than unity for the inverse stability ratio at high MgCl₂ and CaCl₂ concentrations. The sorption study of humic and fulvic acids with MWNTs has shown that MWNT sorption capacity for humics is greater than that for fulvics (Hyung and Kim 2008), similarly to the findings of Terashima and Nagao (Terashima and Nagao 2007) in their study of NOM-C₆₀ suspensions. The stronger affinity observed for humics was attributed to their stronger aromatic character, which resulted in enhanced π-π interactions with the surface of the MWNT (Wang, Tao, and Xing 2009).

Other natural dispersing agents: SWNTs were dispersed in the presence of two natural dispersants (gum Arabic (GA) ~250 kDa, a complex mixture of saccharides and glycoproteins obtained from the acacia tree, and amylose, molecular weight not specified, a polymeric form of glucose). The effective hydrodynamic diameter ($D_h$) after dispersion was 950 nm for GA and 661 nm for amylose (Alpatova et al. 2010). For the amylose-dispersed SWNTs, a slight decrease in the effective size was observed due to settling of larger and unstable SWNT aggregates, which left behind more consistently sized, smaller amylose-stabilized SWNT clusters. However, the aqueous suspension of GA contained GA colloids of a size that was (i) comparable to the size of dispersed SWNTs and (ii)
decreased during 4 weeks of settling. In that study, the concentration of SWNTs in the suspension was negatively correlated with the effective hydrodynamic size of the SWNTs. The use of GA for the stabilization of SWNT dispersions provides several advantages. For example, disruption of the interrope packing, leading to dispersion of the SWNTs, will allow the testing of isolated tube properties and comparison to theoretical estimates (Bandyopadhyaya et al. 2002). Additionally, from a practical point of view, the GA molecules that adsorb to the SWNTs may act as bond promoters, leading to the formation of highly adhesive interfaces between individual tubes and a polymeric matrix (De-Gennes 1990).

The properties of bovine serum albumin (BSA), such as electric charge and conformation, affect the exfoliation dynamics in a similar way, because they affect SWNT recoveries; a bulkier protein conformation results in more rapid exfoliation and higher SWNT recoveries (Edri and Regev 2009). Additionally, a higher BSA-to-SWNT ratio results in lower recoveries and slower dynamics, suggesting that entropic consideration may be involved in the exfoliation-stabilization process of SWNTs. In a separate study, specific interactions of underivatized C$_{60}$ as an aggregate suspension in water with clay minerals (montmorillonite and kaolinite) were investigated (Fortner et al. 2012). The findings indicated that C$_{60}$, as a water-stable aggregate, interacted with the clays. The degree of interaction was found to be a function of available surface charge in relation to the net negative surface charge of nC$_{60}$. 


3.3.2.2 Synthetic dispersing agents

3.3.2.2.1 Surfactants

Surfactants can enhance the stabilization of CNMs in water through their adsorption. A synthetic dispersing agent (Triton X-100) effectively disperses SWNTs; the effective $D_h$ after dispersion was 209 nm (Alpatova et al. 2010). Additionally, the effective size of SWNTs dispersed using Triton X-100 remained somewhat stable with increasing settling time over 48 h. Several Triton X-series surfactants with relatively short hydrophilic chains showed higher dispersibility of MWNTs, which could be influenced by surfactant adsorption and, also, presumably, through the formation of larger micelles, both in the surfactant solution and on the MWNT surface at surfactant concentrations greater than the critical micelle concentration (Bai et al. 2010). This study also suggested that hydrophobic and $\pi-\pi$ interactions between the surfactants and MWNTs were the dominant mechanism of adsorption. An optimum surfactant value was determined as the point at which the relative concentration of CNTs dispersed was maximized, before flocculation-inducing attractive depletion interactions began to dominate. The optimum surfactant concentrations for arc SWNT dispersion were nearly 1.6% sodium deoxycholate (SD), 0.5% sodium dodecylbenzene sulfonate (SDBS), 3% Triton X-405, 2% Brij S-100, 5% Pluronic F-127, and 3% PVP-55 (Blanch, Lenehan, and Quinton 2010). In that study, the concentration of the surfactant was found to be a more significant parameter on the resulting dispersion than the ratio of surfactant to SWNTs by mass for both SD and SDBS, presumably because this determines the concentration of micelles in the solution volume.
For ionic surfactants, dispersions are understood to be stabilized by electrostatic repulsion between the hydrophilic head groups, and both cationic and anionic surfactants are able to sufficiently disperse CNTs, with neither showing superiority (Vaisman, Wagner, and Marom 2006), while a recent study reported that the counter-ion basically balances the electrostatic forces (Xu, Yang, and Yang 2010). A low-molecular-weight surfactant (sodium dodecyl sulfate, SDS) used in the first stage for the debundling of the double-walled CNTs showed that the average size of aggregates (213-524 nm) by number was approximately one order of magnitude higher than SDS-stabilized and substituted carbon nanotubes (20.3 nm) (Datsyuk et al. 2009). Molecular modeling simulations from an energy perspective showed that a CNT tube can be dispersed by a sufficient number of SDS surfactant molecules due to the binding energy between the surfactants and the CNT (Duan, Wang, and Collins 2011). In that study, with the help of ultrasonication, a sufficient number of SDS molecules penetrated into an initial gap between a single tube and other nanotubes in the bundle. Thus, the gap became enlarged until complete dispersion due to additional congregation of surfactants at the gap site.

The first stable graphene dispersion was produced by reducing an aqueous GO dispersion with hydrazine hydrate in the presence of the amphiphilic surfactant poly-(sodium 4-styrenesulfonate (PSS) (Stankovich, Piner, Chen, et al. 2006). In this approach, the newly reduced graphene was stabilized via association with the hydrophobic backbone of PSS, while the hydrophilic sulfonate side groups sustained the whole graphene-PSS complex in water. In contrast to PSS-stabilized graphene, where only the hydrophilic sulfonate side groups are exposed to water, in this case both the
hydrophobic styrene and hydrophilic acrylamide moieties can interact with the solvent, allowing for good dispersion in water or xylene (Compton and Nguyen 2010).

3.3.2.2 Solvent

MWNTs supramolecularly functionalized with pyrene-derivatized hydrolyzed poly(styrene-co-maleic anhydride) in aqueous solution exhibited good dispersibility in pure water due to the electrostatic repulsion force between tubes (Gao et al. 2009). They also showed reasonable dispersibility, when the conjugate was dispersed in mixed solvents of water/ethanol at volume ratios of 75/25 and 50/50. This was presumably because the electrostatic repulsion plus the steric barrier provided by these less bound polymer coils allowed good dispersibility of the conjugates in the mixed solvents. However, the dispersibility of the conjugates in the mixed solvent with excess ethanol or pure ethanol became unstable; the polymer chains were collapsed (Gao et al. 2009). A simple method to stabilize SWNT dispersions was developed with N-methyl-2-pyrrolidone (NMP) and polyvinylpyrrolidone (PVP) (Hasan et al. 2007). A significant population of isolated SWNTs, as well as small bundles of SWNTs in NMP, was obtained by ultrasonic treatment followed by vacuum filtration through glass-fiber filters. Slow microscopic aggregation of nanotubes was observed over a period of 3 weeks, due presumably to the addition of PVP that dramatically improved the stability. In addition, PVP also spontaneously “debundled” some nanotube aggregates, increasing the isolated SWNT population without further ultrasonic treatment. In a separate study, addition of fluoroalcohols in solution increased the SWNT dispersion by more than an order of magnitude, presumably due to the decreased hydrophobic interaction among SWNTs
(Hirano et al. 2009). This approach allows the production of biofunctional CNTs, such as one-dimensional nanobiosensors and drug carriers that can penetrate cells.

Because many of the potential applications are hindered by the degree of fullerenes’ stabilization and dispersion in many solvents (Ruoff et al. 1993), there is a need to identify means of increasing the solubility of C\textsubscript{60} and other fullerenes in such solvents as water and polar organic liquids. Molecular dynamics simulations of the water-induced repulsion between C\textsubscript{60} fullerenes in water revealed that energy plays a dominant role (Li, Bedrov, and Smith 2005). As two fullerenes are brought together in aqueous solution, water molecules are expelled from the vicinity of the fullerenes, causing a loss of energetically favorable C\textsubscript{60}-water interactions. The simulations have also suggested that the magnitude of this energy loss is reduced by the presence of water molecules that interact with both fullerenes simultaneously. C\textsubscript{60} and C\textsubscript{70} fullerenes can be dispersed in various solvents (e.g., benzene, toluene, xylene, 1-methylnaphthalene, chloroform, acetonitrile, ethanol, acetone, N-methyl-2-pyrrolidinone) (Alargova, Deguchi, and Tsujii 2001). In that study, the particle size varied slightly from solvent to solvent, but remained in the 150-280-nm range. The most interesting findings were that the colloidal dispersions were constant for more than 10 months in the absence of any stabilizer. Electrophoretic mobility measurements showed that the surface of the particles was negatively charged, suggesting that the repulsive electrostatic interactions between particles played a significant role in the colloid stability of fullerene dispersions. C\textsubscript{60} particles ($D_h = 60$-$70$ nm) were stabilized from ultrapure and tap water into toluene to facilitate liquid chromatography coupled with mass spectrometry: evaporation of the sample to dryness, extraction using 20\% NaCl into toluene, and then solid-phase
extraction (Chen, Westerhoff, and Herckes 2008). Stable aqueous suspensions of colloidal C_{60} nanoparticles free of toxic organic solvents were prepared by two methods: ethanol-to-water solvent exchange and extended mixing in water (Dhawan et al. 2006). The extended mixing method resulted in the formation of larger ($D_h = 178$ nm) and less negatively charged (zeta potential = -13.5 mV) nC_{60} particles than nC_{60} particles prepared by the ethanol to water solvent exchange ($D_h = 122$ nm, zeta potential -31.6 mV).

The first reported strategy for preparing colloidal dispersions of GO in organic solvents used modification with organic isocyanates (Stankovich, Piner, Nguyen, et al. 2006), where the surface- and edge-bound hydroxyl and carboxyl groups of GO were converted into amide and carbamate groups, respectively. The isocyanate-modified sheets then became dispersible in polar organic solvents, such as dimethyl sulfoxide, N,N-dimethylformamide (DMF), and N-methylpyrrolidone, but not in water. However, diisocyanate functionalized GO can be coupled to an amphiphilic oligoester to produce amphiphilic GO that was dispersible in both water and DMF (Xu et al. 2008).

### 3.3.2.2.3 Other synthetic dispersing agents

Among various dispersion methods, surfactants are widely used to enhance the dispersibility of CNMs in aqueous phases. Numerous studies have investigated the effects of surfactants on the dispersibility of CNMs and the mechanism(s) thereof (Blanch, Lenehan, and Quinton 2010; Datsyuk et al. 2009; Islam et al. 2003; Matarredona et al. 2003; Wang, Han, et al. 2012; Xiao et al. 2007; Yu et al. 2007; Bai et al. 2010). Antonietti et al. reported that a nanolatex copolymer (25-30 nm) of an imidazolium bromide acrylate provided effective waterborne dispersions of SWNTs and both thermally and electrically conducting coatings that adhered to plastics (Antonietti et al.
This study demonstrated that SWNTs were readily dispersed as waterborne latex dispersions at 0.5% by weight. Additionally, the findings suggested that such SWNT nanolatexes could be employed in useful applications due to the excellent adhesion to a variety of substrates provided by the nanolatex. Previous experimental findings have shown that a good SWNT dispersion occurs with poly(ethylene glycol-\(bl\)-propylene sulfide) concentrations well above the block copolymer CCC and it has also been demonstrated that the driving force for the dispersion of SWNTs is not the presence of micelles in solution, but rather the achievement of a high degree of SWNT surface coverage (Di Meo et al. 2010). SWNTs dispersed by the new dispersant (a charged rod-like nanoparticle that was a cylindrical micelle wrapped by negatively charged polymers, fabricated by the aqueous free radical polymerization of a polymerizable cationic surfactant, cetyltrimethylammonium 4-vinylbenzoate, in the presence of sodium 4-styrenesulfonate) was fully dried and easily re-dispersed in water, providing enhanced processability of SWNTs (Doe et al. 2008).

Stable aqueous dispersions of fullerenes (60 nm in diameter), \(C_{60}\) and \(C_{70}\), were prepared by simply injecting into water a saturated solution of fullerene in tetrahydofuran (THF), followed by THF removal by purging with gaseous nitrogen (Deguchi, Alargova, and Tsujii 2001). In addition to electrostatic repulsion, other possible mechanisms include clathrate formation and charge transfer. Fullerenes are known to form clathrate crystals with simple organic solvent molecules such as \(n\)-pentane, diethyl ether, and 1,3-dibromopropane (Kamaras et al. 1993). Aqueous-dispersed graphene was prepared successfully using 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion as a stabilizer (Hao et al. 2008). The adsorbed TCNQ anions lead to the solubility of graphene in polar
solvents. According to the report (Li, Wang, et al. 2008), 0.5 wt% of the expanded graphite could be converted into small pieces of single- and few-layer graphene.

3.4. Ultrasonication

Ultrasonication significantly enhances the dispersion and debundling of SWNTs (Huang and Terentjev 2008). This is presumably because the implosion of cavities creates high temperatures, causes pressure differences, and imparts shear forces on SWNT surfaces, and has been reported to bring about complex reactive intermediates on the surfaces of these helicoids (Benedict, Pehrsson, and Zhao 2005). Thus, these surface reactive groups overcome van der Waals interaction between SWNTs, leading to a well-dispersed aqueous suspension (Huang and Terentjev 2008). However, the effectiveness of SWNT dispersion requires a succession of these cavitation events (Huang and Terentjev 2008), because the cavity size can influence the stability of SWNTs, which is governed mainly by the frequency of ultrasonication, where low frequencies produce larger cavities and vice versa (Hilding et al. 2003). Ultrasonication treatment of SWNTs affected debundling and shortening of their clusters, which could be evidenced by the slight variation in the SWNT hydrodynamic radius, determined by dynamic light scattering (DLS), from 164±22 to 139±16 nm, with an increase in energy input from 0 to 100 kJ (Zaib, Khan, Yoon, et al. 2012); these values are comparable with the previously reported hydrodynamic radii of SWNTs (~150 nm) (Jaisi et al. 2008). In that study, the ‘average’ hydrodynamic radii of the SWNT clusters was obtained from averaging the radii values collected for 25 min for each energy input (Zaib, Khan, Yoon, et al. 2012). A sonication-mediated effect on GO dispersion was also observed by comparing the average hydrodynamic radii of the GO clusters before and after sonication at 24 W (Nam et al.
The DLS data in the sonicated GO solution showed a significant reduction in the average hydrodynamic radius versus that of pristine GO; 21,950.4 nm for pristine GO and 165.4 nm for sonicated GO. Joseph et al. measured the average hydrodynamic radius of SWNTs by DLS, and suggested that smaller distributed SWNTs had a more dispersed state in bulk-layer solution than larger SWNTs (Joseph, Zaib, et al. 2011). CNMs are readily dispersible in water using sonication, which results in a greater adsorptive surface area than that of the aggregated form (Hyung et al. 2007; Machida, Mochimaru, and Tatsumoto 2006).

The nanoparticles prepared by sonication in toluene were much less stable than those prepared by prolonged stirring of bulk fullerene in water, as evident from their significantly higher CCC (40 and 166 mM KCl, respectively) (Chen and Elimelech 2009). This suggests that the method of fullerene release into natural aquatic systems (either dissolved in an organic solvent or directly as bulk material) significantly influences the colloidal stability of fullerene nanoparticles formed in such systems. In addition, heteroaggregation between fullerene nanoparticles and these colloidal particles would play a predominant role in controlling the fate, transport, and bioavailability of fullerene nanoparticles, because naturally occurring aquatic colloidal particles would be expected to be at much higher concentrations than the fullerene nanoparticles (Chen and Elimelech 2009).

3.5. Acidification and UV irradiation

Among the various surface functionalization techniques, acidification/oxidization of CNMs has been studied widely, because surface CNMs can be significantly influenced by oxidation, which then affects the aggregation kinetics, morphological characteristics,
and adsorption capacity of CNMs. It is widely known that oxygen-containing functional groups enhance the stabilization of CNMs in suspension. Increased concentrations of protic oxygen functional groups have generally resulted in CNT suspensions that were more resistant to electrolyte-induced aggregation (Shieh et al. 2007). More quantitative structure-property relationships linking surface chemistry to colloidal behavior were developed by Smith et al. using a series of oxidized MWNTs (Smith, Wepasnick, Schrote, Cho, et al. 2009). In that study, while the other oxygen-containing functionalities were also found to contribute to stabilization, negatively charged surface carboxyl groups played a major role in stabilizing CNT suspensions. The oxygen content of MWNTs increases during oxidation with concentrated HNO$_3$ and H$_2$SO$_4$, resulting in a decrease in the settling rate, from 0.277 to 0.01 (OD) min$^{-1}$ (Bai et al. 2010). Because Simmons et al. had recently developed stable aqueous dispersions of SWNTs by a non-covalent functionalization of the nanotube sidewalls with 1-pyrenecarboxylic acid (PCA) (Simmons et al. 2009), this scalable and facile technique has been applied to graphene with PCA that exfoliates single-, few-, and multi-layered graphene flakes into stable aqueous dispersions (Shih et al. 2010). The findings showed that the PCA containing hydrophilic -COOH groups facilitated forming stable aqueous dispersions of graphene, in a manner similar to that of graphene oxide, but without degrading the sp$^2$ structure. Poly(acrylic acid) (PAA) was used to control the level of SWNT dispersion in aqueous mixtures (Grunlan, Liu, and Kim 2006). At low pH, PAA-stabilized suspensions containing 0.1 wt % SWNT had a water-like viscosity, whereas the mixture thickened as the pH was increased. This phenomenon was reversed when the pH was lowered again. Because C$_{60}$ and NOM are ultraviolet (UV) light-sensitive (Rao et al. 1993; Cooper and
Zika 1983), solar irradiation may also play a significant role in the dispersion of C\textsubscript{60} in the natural aqueous environment. Dispersion of C\textsubscript{60} was greatly enhanced and nC\textsubscript{60} particle size decreased very rapidly in the presence of NOM when experiments were performed under sunlight (Li et al. 2009). This is presumably associated with the surface erosion or dissolution-recrystallization process as a result of NOM interacting with C\textsubscript{60} molecules at the surface of the primary crystals, catalyzed by sunlight. The decrease in particle size was accompanied by an increase in the electrophoretic mobility of the nC\textsubscript{60} particles, indicating that the surface charge density of the secondary crystals was greater than the primary crystals as a result of interactions with NOM (Li et al. 2009). In a separate study, the size distribution of the C\textsubscript{60} particles was monitored as a function of UV irradiation time (Zhang, Sun, et al. 2013). In the initial stages of the light irradiation procedure (0, 6, 12, and 24 h), the particle size distribution showed no clear shift, and the average diameter remained nearly constant at 117, 118, 118, and 116 nm, respectively. However, with longer reaction times (0, 48, 96, 144, and 192 h), the size distributions shifted towards the smaller size range, where the average diameter was inversely related to irradiation time (117, 107, 88, 66, and 51 nm, respectively). Additionally, the rate of average size change was 12.4, 18.9, and 23.7 nm every 48 h for 50, 100, and 150 mW cm\textsuperscript{-2}, respectively, indicating that the size reduction rate was proportional to light intensity. Based on previous reports on photo-induced C\textsubscript{60} oxidation and its conversion to water-soluble intermediates in the presence of oxygen, it was assumed that this phenomenon might be caused by photoetching of the C\textsubscript{60} (Bagrov et al. 2008; Hou and Jafvert 2009). Table 3.2 summarizes the stabilization and dispersion for selected CNMs and their hydrodynamic sizes in water.
3.6. Applications for adsorption in water and wastewater treatment

Numerous studies have reported that CNMs have high adsorption capacities for heavy metals (Li et al. 2005; Ge et al. 2014; Salam, Al-Zhrani, and Kosa 2014), methyl orange (Derakhshan and Moradi 2014), red dye (Baghapour, Pourfadakari, and Mahvi 2014), phenols (Chen, Chen, and Zhu 2008), pharmaceuticals (Heo et al. 2012; Im et al. 2013b; Nam et al. 2015), and other organic chemicals (Yang, Zhu, and Xing 2006; Gai et al. 2011). Among numerous contaminants found in water and waste water, over the last decade, many studies have reported on the behavior of endocrine-disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs) in drinking water treatment (Benotti et al. 2009; Westerhoff et al. 2005; Yoon et al. 2006; Yoon et al. 2007; Snyder et al. 2007) and waste-water treatment processes (Ryu, Yoon, and Oh 2011; Yoon et al. 2010; Ren et al. 2011; Andersen et al. 2003).

Conventional water treatment plants that typically consist of coagulation followed by flocculation, sedimentation, filtration, and disinfection, can remove only a very small percentage of the EDCs and PPCPs in aqueous solutions (Joseph et al. 2013; Westerhoff et al. 2005). In addition, ‘conventional’ biological processes, such as activated sludge, biofiltration, and soil aquifer treatment processes, also show very limited EDC/PPCP removal, depending on several factors, including the physicochemical properties of the pollutants (e.g., pKa and hydrophobicity) and the type of wastewater treatment technology used (e.g., dilution of waste-water effluent, rainfall, and temperature) (Alexy, Kumpel, and Kummerer 2004; Al-Rajab et al. 2009; Bester and Schafer 2009; Blair et al. 2013; Del Rio et al. 2013; Kasprzyk-Hordern, Dinsdale, and Guwy 2009; Kistemann et al. 2008; Meyer and Bester 2004; Maeng et al. 2011; Snyder et al. 2004).
Table 3.2 Summary of stabilization and dispersion for selected CNMs.

<table>
<thead>
<tr>
<th>CNMs</th>
<th>Stabilization/dispersion</th>
<th>Water type</th>
<th>Hydrodynamic size ($D_h$)</th>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs</td>
<td>Surfactants (4 Triton X-series)</td>
<td>Synthetic water at various pH conditions</td>
<td>Dispersed/stabilized</td>
<td>Colloidal stabilization</td>
<td>(Bai et al. 2010)</td>
</tr>
<tr>
<td>MWNTs</td>
<td>Humic substances</td>
<td>Synthetic water</td>
<td>250 nm (Aldrich humic acid, 450 nm (Catlin humic substance)</td>
<td>Colloidal stabilization</td>
<td>(Chappell et al. 2009)</td>
</tr>
<tr>
<td></td>
<td>Surfactant (SDS)</td>
<td>Synthetic water</td>
<td>20.3 nm after surfactant substitution</td>
<td>Colloidal stabilization</td>
<td>(Datsyuk et al. 2009)</td>
</tr>
<tr>
<td>-COOH</td>
<td>Microwave accelerated reaction</td>
<td>Synthetic water w/ NaCl, NaOAc, MgCl$_2$ at 100 mM</td>
<td>~200 nm (NaCl, NaOAc), ~450 nm (MgCl$_2$ )</td>
<td>Colloidal stabilization</td>
<td>(Ntim et al. 2011)</td>
</tr>
<tr>
<td>-PVP*</td>
<td>Microwave accelerated reaction</td>
<td>Synthetic water w/ NaCl, NaOAc, MgCl$_2$ at 100 mM</td>
<td>~250 nm (NaCl, NaOAc), ~350 nm (MgCl$_2$ )</td>
<td>Colloidal stabilization</td>
<td>(Ntim et al. 2011)</td>
</tr>
<tr>
<td>NaCl</td>
<td>Microwave accelerated reaction</td>
<td>Synthetic water at pH 6 and 64 mM NaCl</td>
<td>~200/400/800 nm with increasing surface oxygen con. 4.3/7.6/9.5%, respectively</td>
<td>Colloidal stabilization</td>
<td>(Smith, Wepasnick, Schrote, Cho, et al. 2009)</td>
</tr>
<tr>
<td>SWNTs</td>
<td>NOM, temperature, and extracellular polymeric substances after sonication</td>
<td>Freshwater, seawater, stormwater, wastewater, groundwater</td>
<td>1.49x10$^4$ nm (SWNT-DI), 246 nm (SWNT-NOM), 252 nm (SWNT-EPS)</td>
<td>Colloidal stabilization</td>
<td>(Adeleye and Keller 2014)</td>
</tr>
<tr>
<td></td>
<td>Natural (gum arabic, amylose, SRNOM and synthetic (polyvinyl pyrrolidone, Triton X-100) dispersing agents</td>
<td>Synthetic water at pH 3.5 and 7</td>
<td>950, 666, 348/301 (pH3.5/7), 306, 209 nm, respectively</td>
<td>Colloidal stabilization</td>
<td>(Alpatova et al. 2010)</td>
</tr>
<tr>
<td>25-30 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Joseph, Zaib, et al. 2011)</td>
</tr>
<tr>
<td>Ultrasonication</td>
<td>Synthetic water</td>
<td>278-328 nm</td>
<td>Colloidal stabilization</td>
<td>(Antonietti et al. 2010)</td>
<td>(Schwyzer et al. 2013)</td>
</tr>
<tr>
<td>18-100 kJ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrophilic and hydrophobic NOM</td>
<td>Mimic landfill leachate</td>
<td>~200 nm w/ humic acid and ~500 nm w/ glucose</td>
<td>Colloidal stabilization – adsorption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRHA</td>
<td>Synthetic water varying Ca, pH</td>
<td>~150-350 nm with increasing Ca$^{2+}$ (0-2 mM), ~300 nm (pH 5-8)</td>
<td>Colloidal stabilization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>------------------</td>
<td>-----------------------------------------------------------------------------------------------------------------</td>
<td>------------------------</td>
<td>-------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>Synthetic and tap water</td>
<td>60-70 nm</td>
<td>Colloidal stabilization for detection</td>
<td>(Chen, Westerhoff, and Herckes 2008)</td>
<td></td>
</tr>
<tr>
<td>Ethanol, water mixing for nC₆₀</td>
<td>Synthetic water</td>
<td>122 nm (ethanol), 178 nm (water mixing)</td>
<td>Colloidal stabilization - toxicity</td>
<td>(Dhawan et al. 2006)</td>
<td></td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>Synthetic and tap water</td>
<td>60 nm</td>
<td>Colloidal stabilization</td>
<td>(Deguchi, Alargova, and Tsujii 2001)</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>High salt synthetic water (0, 0.01, 0.1, 1 M)</td>
<td>168, 298, 680, 897 nm, respectively</td>
<td>Colloidal stabilization</td>
<td>(Brant, Lecoanet, and Wiesner 2005)</td>
<td></td>
</tr>
<tr>
<td>HA, NaCl, MgCl₂</td>
<td>Synthetic water; 10 mg L⁻¹ HA, 0.3 M NaCl, 0.1 M MgCl₂</td>
<td>~300 nm (DI), ~600 nm (NaCl), ~700 nm (MgCl₂), ~150 nm (HA), ~1,500 nm (HA+NaCl), ~2,000 nm (HA+MgCl₂)</td>
<td>Colloidal stabilization</td>
<td>(Chae et al. 2012)</td>
<td></td>
</tr>
<tr>
<td>SRHA</td>
<td>Synthetic water; 1 mg L⁻¹ HA, 650 Mm NaCl, 40 Mm CaCl₂</td>
<td>~180 nm (NaCl+no HA), ~140 nm (HA+NaCl), ~160 nm (CaCl₂+no HA), ~220 nm (HA+CaCl₂)</td>
<td>Colloidal stabilization</td>
<td>(Chen and Elimelech 2007)</td>
<td></td>
</tr>
<tr>
<td>SRHA</td>
<td>Synthetic water; 2 mg L⁻¹, 1.5/2.4/5.7/50 mM Ca²⁺</td>
<td>~90 nm (HA only), ~110/500/700/700 nm (HA+Ca²⁺), respectively</td>
<td>Colloidal stabilization</td>
<td>(Mashayekhi et al. 2012)</td>
<td></td>
</tr>
<tr>
<td>1 h Mixing at 500 mM NaCl</td>
<td>DI, secondary effluent (SE), aeration tank liquor (ATL), primary effluent (PE)</td>
<td>~750 nm (DI), ~500 nm (SE), ~400 nm (ATL), ~200 nm (PE)</td>
<td>Colloidal stabilization</td>
<td>(Yang et al. 2013)</td>
<td></td>
</tr>
<tr>
<td>UV irradiation</td>
<td>Synthetic water</td>
<td>117-51 nm (0-192 h), 12.4/18.9/23.7 nm for 50/100/150 mW cm²</td>
<td>Colloidal stabilization</td>
<td>(Zhang, Sun, et al. 2013)</td>
<td></td>
</tr>
<tr>
<td>Graphene (oxides)</td>
<td>Ionic liquids</td>
<td>High ammonium salts Reduced</td>
<td>Electrochemical energy storage Conductometric</td>
<td>(Acik et al. 2012)</td>
<td></td>
</tr>
<tr>
<td>1-pyrenecarboxylic acid</td>
<td>Synthetic water at pH 3.5</td>
<td>Dispersed/stabilized</td>
<td>Conductometric</td>
<td>(Shih et al. 2010)</td>
<td></td>
</tr>
<tr>
<td>Ultrasonication</td>
<td>Synthetic water</td>
<td>43,900 nm for pristine GO, 330 nm for sonicated GO</td>
<td>Sensors/ultracapacitors with colloidal stabilization for adsorption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------------</td>
<td>--------------------------------------------------</td>
<td>---------------------------------------------------------------</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Polyvinyl pyrrolidone
Compared with ‘conventional’ adsorbents (granular and powdered activated carbon) frequently used in water treatment plants, much less is known about the behavior of EDCs and PPCPs with CNMs. The adsorption properties of CNMs depend on various factors, including adsorption site, surface area, purity, and surface functional groups (Agnihotri et al. 2006). Because the adsorption site and surface area are primary parameters influencing EDC/PPCP adsorption, the dispersion of CNMs facilitates rapid adsorption, because small, dispersed particles would provide additional sites for adsorption (Im et al. 2013b; Zaib, Khan, Yoon, et al. 2012). It is also known that oxygen-containing functional groups (-OH, -C=O, and -COOH) of CNMs influence the maximum adsorption capacity. These functional groups can be added purposely during dispersion and stabilization processes, including with acids (Nishikiori et al. 2014; Shulga et al. 2011; Zaib, Khan, et al. 2012b), ozone (Peng et al. 2011; Yim and Johnson 2009), and plasma (Kolacyak et al. 2011). Water quality parameters including pH, background ions, and temperature influence the adsorption process significantly due to their effects on the stability and chemical form of EDCs and PPCPs.

A decrease in the sorption potential of the CNTs at higher pH values occurred for bisphenol A (BPA, a well-known EDC) in wastewater (Bohdziewicz and Kaminska 2013). Due to its high pKa (9.6-10.2) (Yoon et al. 2003), it releases a proton and forms bisphenolate anions in alkaline wastewater. Reduction of adsorption of BPA when pH > pKa was clearly observed, due to increasing repulsion forces and a reduction in π-π interactions between bisphenolate anions and the surface of the MWNTs-COOH (Bohdziewicz and Kaminska 2013). Like CNTs, over a wide range of pH values
(pH 3-11) the removal of compounds (e.g., diclofenac, DCF, and sulfamethoxazole, SMX) by GO was greater under acidic conditions (pH < pKa) than at basic pH (pH > pKa). DCF (pKa, 4.15) and SMX (pKa, 5.7) have neutral ion species at acidic pH and can have greater affinity with GO in adsorption than at basic pH values (Teixido et al. 2011; Llinas et al. 2007). Increases in the NaCl concentration, from 0 to 320 mM, did not significantly change the SWNT adsorption of BPA or 17α-ethyl estradiol (EE2) in either leachate solution (Joseph, Zaib, et al. 2011). However, while using the old leachate conditions (high hydrophobic DOC = 293 mg L⁻¹ HA), an increase in the Ca²⁺ concentration from 0 to 150 mM increased the adsorption of BPA and EE2, by 12% and 19%, respectively. This was presumably due to a “salting-out” effect, referring to the reduced solubility of organic compounds in aqueous salt solutions (Xie, Shiu, and Mackay 1997). In another study, 19.4, 15.4, and 14.3 mg g⁻¹ of BPA were adsorbed on SWNTs, while 8.0, 6.4, and 5.1 mg g⁻¹ were adsorbed on t-SWNTs at 280, 295, and 315 K, respectively (Zaib, Khan, et al. 2012b). This decrease in BPA sorption with increasing temperature can be attributed to the associated exothermic reaction mechanism described previously (Feng et al. 2010).

The adsorption of the herbicides diuron and dichlobenil on MWNTs increased with increasing surface areas and pore volumes of MWNTs (Chen et al. 2011). The adsorption of atrazine by surfactant-dispersed SWNTs and MWNTs showed that surfactant treatment reduced atrazine adsorption significantly (Shi et al. 2010).

The modified CNTs may have become more hydrophilic, because the hydrophilic fraction of the surfactant micelles faces the water, inhibiting the adsorption of atrazine to a great degree. The surfactant treatment enhanced the dispersion of MWNTs, and thus an
adsorption surface area increase would be expected (Shi et al. 2010). In a separate study for the sorption of divalent metal ions (Cd\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), Pb\(^{2+}\), and Zn\(^{2+}\)) from aqueous solution, it was shown that the sorption mechanisms appeared to be due mainly to chemical interactions between the metal ions and the surface functional groups (-OH, -C=O, and -COOH) of the CNTs (Rao, Lu, and Su 2007). The functional groups when oxidized by NaOCl, HNO\(_3\), KMnO\(_4\), or H\(_2\)O\(_2\), significantly enhanced the sorption capacities of the CNTs (Lu and Liu 2006; Li, Wang, et al. 2003; Lu and Chiu 2006; Li et al. 2006). A separate study showed that three antibiotics (sulfamethoxazole, tetracycline, tylosin) interacted with the polarized electron-depleted or electron-rich regions on the graphitized carbon surfaces of KOH-activated SWNTs and MWNTs via the mechanism of \(\pi-\pi\) electron donor-acceptor interactions (Ji et al. 2010). Removal information by CNMs on selected representative classes of EDCs/PPCPs and dyes is summarized based on literature reports in Table 3.3. In addition, based on this review, we proposed possible adsorption influenced by CNM stabilization and dispersion, as shown in Fig. 3.1.

3.7. Conclusions and areas for future research

Enhanced dispersion and stabilization of CNMs in water greatly improves their physicochemical properties. Thus, a critical challenge is the development of methods to promote and increase the dispersion and stabilization of CNMs in water. This review summarizes the dispersion and stabilization of target CNMs (CNTs, GOs, fullerenes) under different water quality conditions and in the presence of various dispersing agents. While dispersion degree depends on the dispersing agent, generally, CNMs aggregate more at low pHs, due mainly to relatively less negative charge under those conditions.
<table>
<thead>
<tr>
<th>EDC/PPCP class &amp; dye</th>
<th>Adsorbent</th>
<th>Stabilization/ dispersion/ purification</th>
<th>Surface area (m² g⁻¹)</th>
<th>Cₒ (μg L⁻¹)</th>
<th>qₘ (mg g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Analgesics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>SWNTs, MWNTs, MWNTs-O</td>
<td>HNO₃, sonication</td>
<td>1020, 283, 287</td>
<td>50-2000</td>
<td>232, 81, 19</td>
<td>Cho, Huang, and Schwab 2011</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>MWNTs</td>
<td>None</td>
<td>162</td>
<td>NA</td>
<td>41.4, 22.3</td>
<td>Sotelo et al. 2012</td>
</tr>
<tr>
<td></td>
<td>GO</td>
<td>Sonication</td>
<td>2,960</td>
<td>500 (w/o sonication), 545 (w/ sonication)</td>
<td>(Nam et al. 2015)</td>
<td></td>
</tr>
<tr>
<td><strong>Antibiotics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxytetracycline</td>
<td>MWNTs</td>
<td>HNO₃/H₂SO₄</td>
<td>58-357</td>
<td>2,500</td>
<td>41-7,910ᵃ</td>
<td>(Oleszczuk, Pan, and Xing 2009)</td>
</tr>
<tr>
<td>Sulfapyridine</td>
<td>MWNTs</td>
<td>None</td>
<td>300</td>
<td>210-7,300</td>
<td>10⁷⁻¹⁰⁶ᵇ</td>
<td>Ji et al. 2009</td>
</tr>
<tr>
<td></td>
<td>MWNTs</td>
<td>None</td>
<td>174</td>
<td>100,000</td>
<td>600-800ᵇ</td>
<td>Xia et al. 2013</td>
</tr>
<tr>
<td>Sulfadimethoxine</td>
<td>MWNTs</td>
<td>None</td>
<td>174</td>
<td>100,000</td>
<td>1,300-1,500ᵇ</td>
<td>Xia et al. 2013</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>MWNTs</td>
<td>None</td>
<td>300</td>
<td>380-2,500</td>
<td>10⁷⁻¹⁰⁶ᵇ</td>
<td>Ji et al. 2009</td>
</tr>
<tr>
<td></td>
<td>SWNTs, MWNTs</td>
<td>KOH</td>
<td>410-653, 157-422</td>
<td>810-48,000</td>
<td>38,900-83,400, 3,780-24,100ᵇ</td>
<td>Ji et al. 2010</td>
</tr>
<tr>
<td>Tylosin</td>
<td>MWNTs</td>
<td>KOH</td>
<td>157-422</td>
<td>2,900-174,000</td>
<td>11,300-33,900ᵇ</td>
<td>Ji et al. 2010</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>MWNTs-COOH</td>
<td>None</td>
<td>200-400</td>
<td>90,000</td>
<td>13.9ᶜ</td>
<td>(Cai and Larese-Casanova 2014)</td>
</tr>
<tr>
<td></td>
<td>GO</td>
<td>None</td>
<td>720</td>
<td>90,000</td>
<td>94.1ᶜ</td>
<td>(Cai and Larese-Casanova 2014)</td>
</tr>
<tr>
<td>Antiseptics</td>
<td>Triclosan</td>
<td>SWNTs</td>
<td>HNO$_3$/H$_2$SO$_4$</td>
<td>58-357</td>
<td>2.500</td>
<td>30-190$^{a}$</td>
</tr>
<tr>
<td>MWNTs</td>
<td>None</td>
<td>10-20,000</td>
<td>130</td>
<td>(Lerman et al. 2013)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MWNTs/Al$_2$O$_3$</td>
<td>None</td>
<td>237</td>
<td>3.658</td>
<td>37.2</td>
<td>(Wei et al. 2013)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SWNTs</td>
<td>None</td>
<td>281</td>
<td>1,000-12,000</td>
<td>155-166</td>
</tr>
<tr>
<td></td>
<td>Bisphenol A</td>
<td>SWNTs, MWNTs, MWNTs-COOH</td>
<td>HNO$_3$/H$_2$SO$_4$</td>
<td>467, 456, 338</td>
<td>1000</td>
<td>58.7, 18.7, 21.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SWNTs</td>
<td>None</td>
<td>407</td>
<td>2,280</td>
<td>22.6-44.8</td>
</tr>
<tr>
<td></td>
<td>Bisphenol A</td>
<td>SWNTs, acid treated</td>
<td>H$_2$SO$_4$</td>
<td>407</td>
<td>228</td>
<td>52.8, 41.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SWNTs</td>
<td>None</td>
<td>407</td>
<td>228</td>
<td>13.4-16.1</td>
</tr>
<tr>
<td></td>
<td>Bisphenol A</td>
<td>SWNTs, MWNTs, MWNTs-OH, MWNTs-COOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hormones</td>
<td>17a-ethinyl estradiol</td>
<td>SWNTs</td>
<td>None</td>
<td>407, 233</td>
<td>2,960</td>
<td>24.9-120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SWNTs</td>
<td>H$_2$SO$_4$</td>
<td>407</td>
<td>296</td>
<td>115, 101 (w/ acid)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SWNTs</td>
<td>None</td>
<td>407</td>
<td>296</td>
<td>35.6-35.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SWNTs, MWNTs</td>
<td>HNO$_3$/H$_2$SO$_4$</td>
<td>541, 174</td>
<td>300-3,300</td>
<td>276, 119</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SWNTs, MWNTs, DWNTs</td>
<td>None</td>
<td>418, 176, 619</td>
<td>1,000</td>
<td>1.13, 0.29, 1.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SWNTs</td>
<td>None</td>
<td>364</td>
<td>20,000</td>
<td>10.0-13.6</td>
</tr>
<tr>
<td></td>
<td>Perchlorate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pesticides/herbicides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Atrazine</td>
<td>SWNTs</td>
<td>HCl</td>
<td>407</td>
<td>100</td>
<td>4.97$^{c}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MWNTs-O (0.85, 2.16, 7.07%)</td>
<td>None</td>
<td>167, 178, 185</td>
<td>1,000-8,000</td>
<td>60.3, 33.3, 24.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MWNTs</td>
<td>None</td>
<td>189</td>
<td>1,000-30,000</td>
<td>61-67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Magnetic MWNTs</td>
<td>None</td>
<td>163</td>
<td>5,000</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Adsorbent</td>
<td>Method</td>
<td>$q_m$ (mg g$^{-1}$)</td>
<td>$K_F$ (mg g$^{-1}$)</td>
<td>Source</td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-----------</td>
<td>------------</td>
<td>---------------------</td>
<td>---------------------</td>
<td>-----------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Diuron</strong></td>
<td>SWNTs, MWNTs</td>
<td>None</td>
<td>167,300</td>
<td>3,110</td>
<td>(Yan et al. 2008)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fullerenes</td>
<td>Hand-ground</td>
<td>4.3</td>
<td>NA</td>
<td>(Yan et al. 2008)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MWNTs-O</td>
<td>None</td>
<td>162, 159, 157, 161</td>
<td>600-22,000</td>
<td>(Gai et al. 2011)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1.52, 2.66, 7.58%)</td>
<td>None</td>
<td></td>
<td></td>
<td>(Chen et al. 2011)</td>
<td></td>
</tr>
<tr>
<td><strong>Dichlobenil</strong></td>
<td>MWNTs-O</td>
<td>None</td>
<td>159, 157, 161</td>
<td>600-13,000</td>
<td>(Chen et al. 2011)</td>
<td></td>
</tr>
<tr>
<td><strong>Isoproturon</strong></td>
<td>MWNTs</td>
<td>None</td>
<td>162</td>
<td>NA</td>
<td>(Sotelo et al. 2012)</td>
<td></td>
</tr>
<tr>
<td><strong>Stimulant</strong></td>
<td>Caffeine</td>
<td>MWNTs</td>
<td>None</td>
<td>162</td>
<td>(Sotelo et al. 2012)</td>
<td></td>
</tr>
<tr>
<td><strong>Dyes</strong></td>
<td>Methylene blue</td>
<td>GO</td>
<td>42.5</td>
<td>200,000</td>
<td>(Wu et al. 2014)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reactive blue 29</td>
<td>MWNTs</td>
<td>None</td>
<td>NA</td>
<td>(Dehghani et al. 2013)</td>
<td></td>
</tr>
</tbody>
</table>

$c_0$ = EDC/PPCP initial concentration; WW = wastewater; NA = not available; $q_m$ = maximum sorption capacity; $^a$sorption capacity from Polanyi-Manes; $^b$distribution coefficient (L kg$^{-1}$) calculated from the Freundlich model; $^c$K$_F$ = capacity factor (μg g$^{-1}$)/(m$^3$ mg$^{-1}$) for the Freundlich model.

**Fig. 3.1** Proposed adsorption influenced by CNM stabilization and dispersion.
The dispersion of CNMs can also be influenced significantly by the presence of background ions in water. CNM aggregation increases with increasing ionic strength. However, once ionic strength becomes high, no additional increases in aggregation occur, indicating that electrostatic repulsive forces are successfully shielded. CNM stability increases with increasing temperature, presumably due to disruption of weak interaction forces, increased Brownian motion/collisions, and decreased zeta potential.

Among various natural and synthetic dispersing agents, NOM has been studied widely. The stability and dispersion of CNMs is significantly enhanced in water bodies with NOM, because, for example, the hydrophobic surfaces of CNMs facilitate their interaction with NOM, which is abundant in the environment. Surfactants also enhance the stabilization of CNMs in water through their adsorption. Typically, CNMs are dispersed due to hydrophobic and π-π interactions between the surfactants and CNMs, which are the dominant mechanism of their adsorption. For ionic surfactants, dispersions of CNMs are stabilized by electrostatic repulsion between the hydrophilic head groups, and both cationic and anionic surfactants are able to sufficiently disperse CNMs, with neither showing superiority. Ultrasonication significantly enhances the dispersion and stabilization of CNMs, presumably due to the implosion of cavities creating high temperatures that cause pressure differences, and impart shear forces on CNM surfaces. The modified CNMs associated with dispersion and stabilization can enhance the sorption capacity for the removal of EDCs and PPCPs in water and waste-water treatment.

While there are many studies on dispersion and stabilization of CNMs in water, many further data are required to understand the relevance of natural and synthetic
dispersing agents in water and how these agents enhance the dispersion and stabilization of CNMs under different water quality conditions. It is also important to gain information as to the toxicological impact of CNMs in water, because CNMs can be introduced into the natural water environment. Standardized analytical methods for detection of various CNMs that can be found in water in the near future are important. Development of appropriate analytical methods can provide tools to understand the fate and transport of these CNMs in the environment. To adopt CNMs in water and waste-water treatment, much is still unknown as to the transport of inorganic and organic contaminants in CNMs. Thus, many additional data are required to better understand contaminant removal by CNMs in water. In addition, while CNMs have shown potential as superior sorbents to remove selected contaminants from aqueous solution, their relatively high unit cost currently limits their practical use.

**Acknowledgement**

This research was supported by the Korea Ministry of Environment, ‘GAIA Project, 2015000540003’.
CHAPTER 4

SONOCATALYTIC DEGRADATION COUPLED WITH SINGLE-WALLED CARBON NANOTUBES FOR REMOVAL OF IBUPROFEN AND SULFAMETHOXAZOLE

Abstract

This study examined the degradation of pharmaceuticals (PhACs), ibuprofen (IBP) and sulfamethoxazole (SMX) using an ultrasonic (US) reactor at a 1000 kHz frequency in the absence and presence of single walled carbon nanotubes (SWNTs). In the absence of SWNTs, maximum degradation of PhACs were achieved under high temperature; 55 > 35 > 25 > 15°C. In addition, the relatively higher degradation of IBP and SMX was obtained under acidic condition at pH 3.5 than pH 7 and 9.5; >99%, 79%, and 72% for IBP and >99%, 75%, and 65% for SMX, respectively. However, H$_2$O$_2$ production increased from 77 µM (no SWNTs) to 115 µM in the presence of SWNTs (45 mg/L) at pH 7. In addition, the removal of IBP and SMX significantly increased under US/SWNTs reaction conditions than US and SWNTs only reactions. The removal of IBP and SMX was 57% and 48% under SWNTs (adsorption) reactions, 77% and 70% under US reactions, and 97% and 92% under US/SWNTs reactions, respectively. This study

evaluated the effect of temperature, pH, SWNTs, and physiochemical properties of selected PhACs under US process. In addition, the adsorption molecular modeling was validated with the experimental results.

Keywords: ibuprofen; sulfamethoxazole; sonocatalytical degradation; single-walled carbon nanotubes; molecular modeling

4.1. Introduction

Since the prevalent use of pharmaceutical (PhACs) products was identified as an environmental problem, numerous studies have focused on the sources, occurrence, and impact of these compounds in the aquatic environment (Kolpin et al. 2002; Snyder et al. 2003). Previous studies have reported that the concentrations of PhACs in surface water and wastewater effluent vary, with ranges from ng/L to µg/L, creating unique challenges in water treatment processes that typically can remove only 10-20% of those compounds (Rivera-Utrilla et al. 2013; Lishman et al. 2006). Ibuprofen (IBP), a non-steroidal anti-inflammatory analgesic, has been detected between 0.002 and 24.6 µg/L in the effluent of several sewage treatment plants (Buser, Poiger, and Müller 1999; Méndez-Arriaga et al. 2008). Sulfamethoxazole (SMX) has also been found with many other PhACs in wastewater treatment plant effluents (0.01-2 µg/L) and in surface waters (0.03-0.48 µg/L) (Hirsch et al. 1999; Méndez-Arriaga et al. 2008). Previous studies of selected group of micropollutants, such as pesticides and herbicides, have shown that coagulation, sedimentation, and filtration achieve only minimal levels of removal (Adams et al. 2002; Westerhoff et al. 2005). However, addition of common disinfectants (e.g., chlorine or ozone) can result in the reaction and transformation of these compounds (Snyder et al. 2003; Westerhoff et al. 2005; Lei and Snyder 2007). The rate constants and oxidation
mechanisms that accompany the use of chlorine (Westerhoff et al. 2005; Huerta-Fontela, Galceran, and Ventura 2007) and ozone (Westerhoff et al. 2005; Beltran et al. 2010) have been quantified for quite a large number of PhACs.

Advanced oxidation processes (AOPs) are the most appropriate way of treatment to deal with these complex compounds (Huber et al. 2003; Klavarioti, Mantzavinos, and Kassinos 2009). Generally, among AOPs, the use of sonocatalysis in combination with TiO$_2$, ZnO, glass bead, sand, steel beads, and Al$_2$O$_3$ represents a relatively new and effective technique for degrading contaminants (Bejarano-Perez and Suarez-Herrera 2008; Kaur and Singh 2007; Wang et al. 2008; Shimizu et al. 2007). Ultrasonic (US) treatment is one of the recent AOPs technologies that can oxidize various complex organic pollutants (Koseoglu-Imer et al. 2013). The closest technology to the sonocatalytic degradation, is the photocatalytic degradation, which was used in the past to degrade organic and coloring pollutants (Zhang et al. 2016; Turki et al. 2015; Sivakumar et al. 2010). However, main differences between the photocatalytic degradation and the sonocatalytic degradation is that the ultrasonic waves have stronger penetrating power - resulting of the sonoluminescence and hot spot which are very effective in degrading complex contaminants - than the photocatalytic waves, which made the photocatalytic process unsuitable for the treatment of complex compounds (Zhou et al. 2015; Zhang et al. 2016; Harichandran and Prasad 2016). In addition, advantages of using US technology include ease of use and safety, short contact time, that it works without any additives to oxidize the contaminants, and there are minimal by-products generated after treatment (Mahvi 2009; Hao et al. 2003; Teo, Xu, and Yang 2001). However, Gogate et al. (Gogate, Sivakumar, and Pandit 2004) indicated that the presence of solid particles in the
ultrasound system has the potential to increase the intensity of cavitation and decrease the energy transmitted, which increase the ultrasonic efficiency. Because an increase in the intensity will result in a decrease in the collapse pressure for single cavity and increase the number of cavitational bubbles lead to an enhancement in the sonochemical activity (Sivakumar and Pandit 2001).

Carbon nanotubes (CNTs) are considered as attractive adsorbents for the removal of heavy metals, organic and inorganic matter, pharmaceuticals, personal care products, and endocrine-disrupting compounds (Jung et al. 2013). Their ability to adsorb various types of contaminant is due to the unique properties of CNTs, including their electrical conductivity, optical activity, and mechanical strength. Additionally, two studies have shown that nanoparticle-CNT hybrid materials and CNTs can be used as catalysts (Yang, Zhu, and Xing 2006; Wang, Li, et al. 2012; Al-Hamadani et al. 2015). Other solid particles such as loquat seeds (Hamdaoui 2011), corn-cob-activated carbon (Milenković, Bojić, and Veljković 2013), and granular activated carbon are commonly applied during US reactions to improve the generation of OH$^-$ via increasing the presence of cavitation bubbles but also physically adsorb the pollutant onto the surface of the particles (Zhao et al. 2011). Recent studies show very attractive results using sonocatalytic removal for dye in aqueous system such as; Soltani et al., (2016) who used ultrasonic with ZnO and found great removals of decolorization of methylene blue (MB) dye in the aqueous phase (Soltani, Safari, and Mashayekhi 2016). Also, a separated study has reported that SonoFenton methods effectively decolorize DR81 dye in waste water (Harichandran and Prasad 2016).
Despite the significant growth in CNT use and sonocatalysis in water and wastewater treatment, much is still unknown, such as, for example, how sonocatalysis coupled with CNTs influences the transport of PhACs, while removal mechanisms (e.g., sorption of PhACs onto CNTs and thermal degradation/oxidation during sonocatalytic degradation) are relatively well known. Molecular-level simulations can also provide unique insight into the molecular interactions among PhACs and CNTs. Previous studies have clarified the adsorption process of contaminants onto carbon nanomaterials by applying the quantum chemistry and molecular dynamics simulations (Zhao and Johnson 2007; Arsawang et al. 2011; Mucksch and Urbassek 2011).

The main objectives of this study were to evaluate the removal efficiency of two PhACs (IBP and SMX) under US irradiation, to estimate the effect of US coupled with single-walled carbon nanotubes (SWNTs) on the removal of IBP and SMX, and to illustrate the mechanism of US/SWNTs via molecular modeling. Sonocatalytic novelty of a sonodegradation process combined with CNT adsorption is, at one level, a relatively simple approach that involves the combination of two existing technologies (i.e., oxidation and adsorption). In addition, limited work has been reported on the adsorption behavior of PhACs on SWNT at the molecular level. Therefore, the adsorption of IBP/SMX on SWNTs was simulated in this study in order to validate the modeling with the experiment data to better understand the mechanism of dispersed SWNT particles. The processes were carried out as a function of temperature (15, 25, 35, and 55°C) and pH (3.5, 7, and 9.5) at a frequency of 1000 kHz. We hypothesized that sonocatalytic degradation coupled with SWNTs for the target PhACs would be enhanced for two reasons: (i) IBP and SMX removal due to adsorption will be enhanced, because
ultrasonication greatly enhances the dispersion and debundling of SWNTs, providing more adsorption sites for IBP and SMX, and (ii) SWNTs will act as a catalyst to enhance and promote sonochemical reactions.

4.2. Materials and methods

4.2.1. Chemicals

High-purity IBP (C_{13}H_{18}O_{2}, > 98%) and SMX (C_{10}H_{11}N_{3}O_{3}S, > 98%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). The target PhAC characteristics are summarized in Table 4.1, from the SRC PhysProp Database (SRC 2006). Potassium hydrogen phthalate (C_{8}H_{5}K_{4}O_{4}, 99.95%), potassium iodide (KI, 99%), ammonium molybdate tetrahydrate (H_{24}Mo_{7}N_{6}O_{24}·4H_{2}O), and H_{2}O_{2} (30% w/v used to measure H_{2}O_{2} production), were also purchased from Sigma-Aldrich. High purity SWNTs having a length of 5-30 µm and an outer diameter of 1-4 nm and were obtained from Cheap Tubes, Inc. (Brattleboro, VT, USA). Stock solutions of IBP, SMX, and SWNTs were prepared in ultrapure deionized (DI) water.

4.2.2. Apparatus

In this study, US and US/SWNTs experiments were conducted in a US generator (Ultech, Dalseo, Daegu, South Korea) having a double-jacketed stainless steel reservoir (L×W×H, 15×10×20 cm) with a water-cooled (Fisher Scientific Inc., Pittsburgh, PA, USA) at a fixed frequency of 1000 kHz with applied power of 180±3 W at various temperatures. The contact time of 60 min was employed to determine the effect SWNTs (0, 5, 15, and 45 mg/L (ppm)) on sonodegradation, as well as in the absence and presence of PhACs at 10 µM. Fig. 4.1 shows a diagram of the experimental set-up. Batch adsorption experiments were conducted to assess the adsorption capacity of SWNTs
Table 4.1 Properties of ibuprofen and sulfamethoxazole studied in this paper.

<table>
<thead>
<tr>
<th>Pharmaceuticals</th>
<th>Ibuprofen (IBP)</th>
<th>Sulfamethoxazole (SMX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classification</td>
<td>Analgesic</td>
<td>Analgesic</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>206.3</td>
<td>253.3</td>
</tr>
<tr>
<td>(g/mol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pK&lt;sub&gt;a&lt;/sub&gt;</td>
<td>4.52</td>
<td>5.81</td>
</tr>
<tr>
<td>LogK&lt;sub&gt;ow&lt;/sub&gt;</td>
<td>3.84</td>
<td>0.79</td>
</tr>
<tr>
<td>Water solubility</td>
<td>0.049</td>
<td>0.459</td>
</tr>
<tr>
<td>(g/L at 25°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Henry’s law constant</td>
<td>1.50×10&lt;sup&gt;-7&lt;/sup&gt;</td>
<td>6.42×10&lt;sup&gt;-13&lt;/sup&gt;</td>
</tr>
<tr>
<td>(atm·m&lt;sup&gt;3&lt;/sup&gt;/mol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>0.000139</td>
<td>NA</td>
</tr>
<tr>
<td>(mmHg at 25 ºC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical structure</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

without sonication. SWNTs were hydrated for 24 hours in DI water prior to and added as a slurry to the sample reactor. Both US/SWNTs and adsorption experiments were conducted using 1000 mL of this initial solution. Samples taken periodically were filtered with 0.22 µm glass microfiber filters (Whatman, Little Chalfont, Buckinghamshire, UK) for additional analysis. To perform a complex and immediate analysis, high-performance liquid chromatography (HPLC, 1200 series; Agilent Technologies, Santa Clara, CA, USA) was employed to measure IBP and SMX. The mobile phase solvent profile of 40:60 (DI water:acetonitrile) for IBP and 50:50 (DI water:acetonitrile) for SMX was used. Separation was achieved under the following conditions: a LiChrosorb RP-18 analytical column (4.6 mm × 100 mm i.d., 5 µm particles, Atlantis; Waters, Milford, MA, USA);
Fig. 4.1 Schematic diagram of the ultrasonic system.

A flow rate of 1.0 mL/min for IBP and 0.75 mL/min for SMX with a 100 µL sample loop; a detection wavelength of 210 nm for both compounds.

4.2.3. Analysis

The KI dosimetry method was employed to determine the H₂O₂ concentration using an ultraviolet-visible (UV-vis) spectrophotometer (Agilent Technologies) at 350 nm during US reactions (Kormann, Bahnemann, and Hoffmann 1988). A Zeta potential analyzer (ZetaPLAS, Brookhaven Instruments Corporation, Holtsville, NY, USA) was
employed to determine zeta potentials of SWNTs before and after sonication. The zeta was calculated with the electrophoretic mobility ($\mu$) values using the Smoluchowski approach:

$$\mu = \frac{\xi \varepsilon V}{4\pi \eta d}$$ (4.1)

where $\xi$ is the zeta potential, $\varepsilon$ is the dielectric constant of the medium (water), $V$ is the applied voltage, $\eta$ is the viscosity of the suspension, and $d$ is the electrode separation (Saleh, Pfefferle, and Elimelech 2008).

The average hydrodynamic radii of the SWNT clusters and their size distribution were determined with a robust dynamic light scattering and static light scattering DLS/SLS instrument (ALV/CGS-3, Langen, Germany), equipped with a 22 mW He-Ne laser at 632 nm (equivalent to an 800 mW laser at 532 nm) and a sensitive high-QE APD detector with photomultipliers. The average cluster size of a SWNT suspension before and after sonication was determined for a 0-90° scattering angle. The measured distribution data was used to calculate the average hydrodynamic diameter of SWNT particles.

4.2.4. Molecular modeling for solutes and adsorbents

The original molecular structures of each SWNTs and the PhACs were produced using Gaussview (Dennington et al. 2003) and improved using dispersion-corrected density functional theory (DFT-D) (Grimme et al. 2010; Grimme, Ehrlich, and Goerigk 2011) with the B3LYP5 functional and the 6-31G basis set in TeraChem (Kastner et al. 2009; Ufimtsev and Martinez 2009). The geometries of the SWNTs-PhACs complexes (SWNTs-IBP and SWNTs-SMX) were improved by following geometry optimization processes described in previous studies (Zaib, Khan, et al. 2012a). The adsorption of IBP
and SMX onto SWNTs in aqueous solution was measured using the SMD continuum solvation model applied in GAMESS (Schmidt et al. 1993; Gordon and Schmidt 2005; Gordon et al. 2007; Smith, Slipchenko, and Gordon 2008). Aqueous phase energy calculations were conducted at the DFT-D/B3LYP5/6-31++G(d,p) level, and the binding energies ($\Delta E$) between the SWNTs and PhACs were calculated as:

$$\Delta E = E(\text{SWNTs} + \text{PhACs}) - E(\text{SWNTs}) - E(\text{PhACs})$$  (4.2)

A negative value of the binding energy shows a positive interaction and a constant SWNTs-PhACs system. Aqueous phase binding energies were determined by considering the dissociated (pH > pKa) and un-dissociated (pH < pKa) forms of the PhACs to demonstrate the effect of pH on the adsorption mechanism.

4.3. Results and discussion

4.3.1. Effect of temperature on PhAC degradation and H$_2$O$_2$ formation

4.3.1.1. PhAC degradation

Temperature is an important factor in the US process because sonication produces cavitation bubbles that have high temperatures and vapor pressures over time. Thus, the effects of aqueous temperature on sonochemical reaction rate of selected PhACs were investigated at a 1000 kHz frequency with an US power of 180 ± 3 W. The pseudo-first-order rate ($k$) of IBP and SMX increased when the temperature increased from 15 to 55°C (Fig. 4.1). The increase in temperature affects the cavitation intensity due to the change in the physicochemical properties of the compound and the type of cavities formed, which can affect the kinetic rate constant for the degradation reaction (Golash and Gogate 2012). Four important parameters were affected when the temperature of the solution increased: (i) Cavitation energy decreased, (ii) the threshold limit of cavitation energy,
required to produce cavitation, decreased, (iii) the quantity of dissolved gas was reduced, leading to the transfer of organic molecules from bulk solution to the gas-liquid interface region, and (iv) the vapor pressure increased, causing cavitation bubbles to comprise more water vapor (Jiang, Petrier, and Waite 2006; Im et al. 2014). Previous studies have estimated the effect of temperature on different pharmaceuticals, such as acetaminophen, naproxen (Im et al. 2014) and diclofenac (Naddeo et al. 2010), and dyes, such as rhodamine B (Behnajady et al. 2008), and found a proportional relationship of the degradation rate to the temperature. Because the degradation rate is proportional to the temperature, the reaction can be assumed to follow the Arrhenius equation (Eq. (4.3)),

\[
-\ln k = -\ln A + \frac{E_a}{RT}
\]  

(4.3)

where \( k \) = pseudo-first-order rate constant (min\(^{-1}\)), \( A \) = Arrhenius coefficient, \( E_a \) = apparent activation energy (kJ/mol), \( R \) = the gas constant (8.314 J/mol.K), and \( T \) = temperature (K). Fig. 4.1a shows the correlation between \(-\ln k\) and \(1/T\), where the apparent activation energy was 17.49 kJ/mol \( (R^2 = 0.961) \) for IBP and 7.28 kJ/mol \( (R^2 = 0.977) \) for SMX at pH 7. These low apparent activation energy values indicate that the degradation of PhACs is influenced by diffusion (Im et al. 2014). This is presumably because the degradation rate apparently reflects IBP and SMX molecules in bulk solution moving to the gas-liquid interface region, where the temperatures and \( \text{OH}^- \) concentrations are high (Kim, Huang, and Chiu 2001; Im et al. 2014).

4.3.1.2. \( \text{H}_2\text{O}_2 \) formation

During US treatment, high temperatures (5000 K) and pressures (1000 atm) in the cavities created are reached in a very short time, leading to the dissociation of water
Fig. 4.2 Effect of temperature on (a) the degradation of IBP and SMX. H$_2$O$_2$ production in the presence of (b) IBP and (c) SMX at various temperatures, pH 7, 0.18 W/mL and 1000 kHz. Error bars are smaller than the symbols in most cases.

molecules to H' and OH' (Méndez-Arriaga et al. 2008; Guo et al. 2015). In this study, different temperatures (15, 25, 35, and 55°C) were studied to understand the effects of
temperature on PhACs degradation and H$_2$O$_2$ production. By increasing the temperature of the solution, from 15 to 55°C, the degradation of IBP and SMX increased (Table 4.2).

**Table 4.2** Degradation efficiencies of PhACs and coefficient of determination ($R^2$) at different solution temperatures (pH 7, contact time = 60 min, and 1000 kHz).

<table>
<thead>
<tr>
<th>°C</th>
<th>IBP degradation %</th>
<th>$R^2$</th>
<th>SMX degradation %</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>77.2</td>
<td>0.925</td>
<td>72.2</td>
<td>0.963</td>
</tr>
<tr>
<td>25</td>
<td>86.4</td>
<td>0.889</td>
<td>80.8</td>
<td>0.952</td>
</tr>
<tr>
<td>35</td>
<td>98.5</td>
<td>0.899</td>
<td>87.7</td>
<td>0.924</td>
</tr>
<tr>
<td>55</td>
<td>&gt;99</td>
<td>0.916</td>
<td>90.34</td>
<td>0.952</td>
</tr>
</tbody>
</table>

This could be explained by the properties of US process in generating hydroxyl radicals. However, the relationship between temperature and H$_2$O$_2$ production can be used as an indirect method of measuring OH$^\cdot$ concentration. When the temperature increased, the cavitation threshold decreased, leading to increased numbers of cavitation bubbles on sonolysis and thus increased OH$^\cdot$ production (Jiang, Petrier, and Waite 2006). When the temperature increased, the free OH$^\cdot$ increased for a particular limit, as shown in Figs. 4.2b for IBP and 4.2c for SMX due to the high collapse of cavitation bubbles, resulting in increased destruction of the compounds. In contrast, other studies found that the increase in the temperature has an adverse effect on the degradation rate because as temperature increased, the surface tension and viscosity of the solution increase, which make it easy to generate cavitation bubbles but lower cavitation intensity due to the increase in the vapour pressure of the liquid (Sivakumar, Tatake, and Pandit 2002).
4.3.2. Effects of pH on PhAC degradation and H₂O₂ formation

3.2.1. PhAC degradation

In US processes, pH is also an important factor, affecting the degradation of compounds (Lin and Ma 1999; Sivakumar and Muthukumar 2011). Consequently, experiments were performed at pH values of 3.5, 7, and 9.5 to better understand the effects of pH on the selected PhACs degradation. The pH values chosen were acidic conditions, pH 3.5, below the pKa values of IBP and SMX (4.52 and 5.81, respectively), above the pKa values at neutral conditions (pH 7), and clearly alkaline conditions at pH 9.5. Under acidic conditions at pH 3.5, complete degradation of both IBP and SMX was achieved within 50 and 60 min, respectively. However, the degradation decreased with increasing the pH to 7 and then 9.5, as shown in Figs. 4.3a for IBP and 4.3b for SMX. This could be explained by the acid-basic properties of each compound with its pKa value; below the pKa values of IBP and SMX, the compounds would be in their molecular forms, while above the pKa values, they would be in their ionic forms. Thus, at pH 3.5 the selected compounds have greater hydrophobic characteristics when their structures are in the molecular form and would accumulate at the boundary of cavitation bubbles, where the OH⁻ concentration is higher, leading to higher degradation. However, at pH values higher than their pKa values, the hydrophilicity and solubility would be superior because the compounds dissociate to their ionic forms and thus degradation will occur in the bulk liquid region where the OH⁻ concentration is lower; as a result degradation was slower.
Fig. 4.3 Effect of pH on the degradation of (a) IBP and (b) SMX, (c) degradation rate constants of IBP and SMX, and (d) H$_2$O$_2$ production for different reactions at 15 ± 1°C, 0.18 W/mL, and 1000 kHz. Error bars are smaller than the symbols. (Im et al. 2013a; Méndez-Arriaga et al. 2008; Soltani, Safari, and Mashayekhi 2016).

Moreover, Fig. 4.3c clearly shows that higher IBP and SMX degradation rate constants were achieved with decreasing pH value: pH 3.5 > pH 7 > pH 9.5. This is presumably because larger amounts of OH’ interact with IBP and SMX under lower pH conditions. In contrast, the lower oxidation potential was due to the smaller amounts of free OH’, which tend to recombine to form H$_2$O$_2$ at higher pH values. The difference in the removal
efficiencies of IBP and SMX is due to differences in their physicochemical properties (Her, Park, and Yoon 2011b), such as logK_{OW}, water solubility (S_W), vapor pressure, and Henry’s law constant. IBP has higher logK_{OW} (3.84) and lower solubility (0.049 g/L at 25°C) than SMX (logK_{OW} = 0.79, S_W = 0.459 g/L at 25°C) in water, as described in Table 4.1. Thus, higher degradation of IBP was achieved because OH’ induced reactions are likely the major degradation mechanism and the reaction occurs at the boundary of the cavitation bubbles where the more OH’ presents (Manickam et al. 2014). However, for the more hydrophilic and nonvolatile SMX, due its low logK_{OW} and high S_W, the reaction may occur more at the gas-liquid interface and the bulk liquid region where smaller amounts of free OH’ are present (Im et al. 2013a).

4.3.2.2. H_2O_2 formation

As previously described, H_2O_2 is likely the key parameter to understand the degradation mechanism of US. Thus, the concentrations of H_2O_2 for the selected pH values were measured to examine the degradation of IBP and SMX in the US process. The generation of H_2O_2 increased with increasing pH in the absence and presence of the compounds (Fig. 4.3d): pH 9.5 > pH 7 > pH 3.5. At the lower pH condition, where the uncombined OH’ concentration is maximal, the generated OH’ is more likely to react with PhACs than OH’ to produce H_2O_2. The generation of OH’ increases due to the decomposition of H_2O_2 at pH 3.5, which leads to more free radicals enhancing the oxidation of the IBP and SMX in the system (Harichandran and Prasad 2016). In contrast, the highest accretion of H_2O_2 was observed at the highest pH due to the more rapid recombination of OH’ being than attacking PhACs. Because at pH > pKa, high concentration of OH’ occurs that enhance the production of H_2O_2, also, less degradation
achieved because the hydrophilicity of the compounds dominate and reactions are likely to be carried out in the bulk liquid where the OH\(^-\) concentration is lower (Im et al. 2014).

To calculate the H\(_2\)O\(_2\) consumption required for the complete degradation of 10 µM IBP and 10 µM SMX, the following stoichiometric calculations were used (Eq. (4.4)) for IBP and (Eq. (4.5)) for SMX:

\[
C_{13}H_{18}O_2 + 33H_2O_2 \rightarrow 13CO_2 + 42H_2O
\]

(4.4)

\[
C_{10}H_{11}N_3O_3S + 33H_2O_2 \rightarrow 10CO_2 + 37H_2O + 3HNO_3 + SO_3
\]

(4.5)

Thus, from Eqs. (4) and (5), 165 µM H\(_2\)O\(_2\) for each reaction was required theoretically to fully degrade IBP and SMX in the system. However, H\(_2\)O\(_2\) generated via ultrasonication at the different pH values in the absence of PhACs was considerably less than 165 µM.

As shown in Fig. 2d, a maximum 87 µM H\(_2\)O\(_2\) was achieved at pH 9.5 in the absence of PhACs. Although the US did not provide sufficient amounts of H\(_2\)O\(_2\) to completely remove the selected PhACs based on Eqs. (4.4) and (4.5), complete degradation of IBP and SMX was achieved at pH 3.5 within 50 and 60 min, respectively. This could be explained by H\(_2\)O\(_2\) acting as both a hydroxyl scavenger (Eq. (4.6)) and as a hydroxyl source (Eq. (4.7)) under sonochemical conditions. Thus, the remaining H\(_2\)O\(_2\) concentration was not quantified exactly based on the experimentally determined H\(_2\)O\(_2\) concentration during the reactions.

\[
H_2O_2 + OH^- \rightarrow H_2O + HO_2^- \quad [k = 2.7 \times 10^7 \text{ 1/M.s}]
\]

(4.6)

\[
H_2O_2 + H^- \rightarrow OH^- + H_2O \quad [k = 9.0 \times 10^7 \text{ 1/M.s}]
\]

(4.7)
4.3.3. Effect of SWNTs on PhAC removal and H$_2$O$_2$ formation

4.3.3.1. H$_2$O$_2$ formation

To evaluate the effect of solid surfaces on the US process, SWNTs at various initial concentrations were added to aqueous samples at pH 7. Under 1000 kHz ultrasonication, H$_2$O$_2$ production was determined in the presence of 0, 5, 15, and 45 mg/L SWNTs to determine the optimum concentration that generates the greatest quantity of free OH$^\cdot$. Figs. 3a and 3b show that H$_2$O$_2$ production increased with increased initial concentrations of SWNTs. The increase in H$_2$O$_2$ production was because the dispersed SWNTs particles tended to act as additional nuclei for the pyrolysis of water molecules and formation of OH$^\cdot$ and can thus be used to quantify the effectiveness of reactors in generating the desired cavitation intensity (Her, Park, and Yoon 2011b; Im et al. 2013a). Therefore, 45 mg/L was used for PhACs removal due to the higher oxidation activities caused by the higher number of free OH$^\cdot$ in the system. In the absence of PhACs, higher concentrations of H$_2$O$_2$ were achieved with increasing SWNTs in the US/SWNTs reaction than with US alone and the concentration of H$_2$O$_2$ in the presence of PhACs decreased. This could explain the difference in H$_2$O$_2$ concentrations in the absence and presence of PhACs; it is due to the amount of free OH$^\cdot$ that interact with IBP and SMX.

4.3.3.2. PhACs removal

Fig. 4.4c shows higher removal of IBP and SMX under US/SWNTs reaction conditions versus US and SWNTs only reactions. Moreover, the removal rate constants of IBP and SMX were higher under US/SWNTs reactions, followed by US and SWNTs only reactions, as shown in Fig. 4.4d. This could be explained in two ways: (i)
removal increased in the presence of SWNTs due to an increase in the number of free OH$^-$ because the dispersed particles acted as additional nuclei for the pyrolysis of water molecules and formation of OH$^-$, leading to an increase in the oxidation activities; and (ii) the dispersed particles increased the adsorption capacity of SWNTs because ultrasonication of CNT dispersions is used to break up CNT agglomerates in solution, which would also lead to increased adsorption activities for the compounds.
Fig. 4.5 Proposed mechanisms of US and US/SWNT processes.

(Im et al. 2013a; Krause et al. 2010; Zhang et al. 2016). This indicates that SWNTs play a major role due to their interaction with PhACs during US processes. To understand the removal of PhACs and H₂O₂ production mechanism, the mechanisms of US and US/SWNT processes were proposed in Fig. 4.5. Fig. 4.5 shows the possible mechanisms and the interaction of OH⁻/PhACs and SWNTs/PhACs in the aqueous system. The adsorption was enhanced due to the dispersion of SWNTs, resulting in more adsorption sites due to the ultrasonication activity. Therefore, the combinations of these oxidation and adsorption in the US/SWNTs process are the main focus of this study.

Furthermore, to understand the effect of SWNTs during US reaction, synergism was assessed based on Eq. (4.8), which was adapted from Madhavan et al. (Madhavan et
al. 2010). The synergy index is determined by assessing the difference between the rate constants obtained under US/SWNT and the sum of those obtained under separate SWNT adsorption and US reactions, as summarized in Table 4.3.

$$Synergy = \frac{k_{(US+SWNTs)}}{k_{(US)} + k_{(SWNTs)}}$$ (4.8)

A synergy index > 1 indicates that the combined US/SWNT process exceeds the sum of the separate US and SWNT adsorption processes. The deceasing synergy index values for IBP from 1.71 at 10 min to 1.17 at 60 min and for SMX from 1.47 at 10 min to 1.12 at 60 min indicated that SWNTs played a more important role at the beginning of the process in terms of adsorption. The results in Figs. 3c and 3d suggest higher removal of IBP than SMX in all reactions (US, SWNTs, and US/SWNT). As described previously, under US reaction conditions, higher removal of IBP was obtained due to the high logK_{OW} and low solubility versus SMX.

In the adsorption reaction, the removal of IBP also was higher due to the strong hydrophobicity and lower water solubility compared to the logK_{OW} and water solubility of SMX. The hydrophobicity of compounds can be expressed by their octanol–water partition coefficients (logK_{OW}), an important factor in evaluating adsorption capacity (Yu, Peldszus, and Huck 2008). A higher logK_{OW} value indicates higher sorption affinity to the adsorbent material: the SWNTs in this study. However, in the adsorption reaction, the removal rate of SMX was faster than IBP in the first 30 min (Fig. 4.4c). In the first 30 min, the repulsion between SMX and the SWNTs decreased due to the complexation or iron pair of SMX with SWNTs ions at pH 7, which results in an increase in the
adsorption of SMX onto the SWNTs (Zhang et al. 2010). Thus, SMX adsorption rate on SWNTs increased until reaching equilibrium. In addition, the adsorbed cations may make sites available for cation association, leading to an increased removal rate for the first 30 min (Zhang, Pan, et al. 2011). However, the size exclusion (pore size) of SWNTs and the volume of SMX (204.6 Å³), which is less than the IBP volume (211.8 Å³), could be another factor enhancing the affinity of SMX molecules than IBP (Pan et al. 2013). Taken together, these results indicate that the removal of PhACs was dependent on their physicochemical properties.

Table 4.3 Pseudo-first order ($k_j$) rate constants, coefficient of determination ($R^2$), and synergistic index values within 10 and 60 min in different reactions (15 ± 1°C, pH 7, and 1000 kHz).

<table>
<thead>
<tr>
<th>Processes</th>
<th>SWNTs (mg/L)</th>
<th>$k_j$ (×10⁻² 1/min)</th>
<th>$k_j$ (×10⁻² 1/min)</th>
<th>$R^2$</th>
<th>$k_j$ (×10⁻² 1/min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>US only</td>
<td></td>
<td>3.73 2.53</td>
<td>1.85 0.939 1.35 0.980</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWNTs (adsorption)</td>
<td>45</td>
<td>3.11 2.62</td>
<td>0.99 0.985 1.03 0.940</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>US/SWNTs</td>
<td>45</td>
<td>11.7 7.58</td>
<td>3.25 0.953 2.68 0.962</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Synergistic index values</th>
<th>IBP</th>
<th>SMX</th>
<th>IBP</th>
<th>SMX</th>
</tr>
</thead>
<tbody>
<tr>
<td>US</td>
<td>45</td>
<td>1.71 1.47</td>
<td>1.17 1.12</td>
<td></td>
</tr>
</tbody>
</table>

4.3.4. Effect of US on SWNTs

To understand the effects of US on SWNTs, the hydrodynamic radii of the SWNTs were measured by DLS before ultrasonication, after 10 min, and after 60 min of
ultrasonication. Fig. 4.6a shows a significant decrease in the hydrodynamic radius of SWNTs from 140 nm before ultrasonication to 80 and 70 nm after 10- and 60-min ultrasonication, respectively. Moreover, Fig. 4.7 shows the effects of ultrasonication on the dispersion and stabilization on SWNTs (45 mg/L). Clearly, SWNTs after treatment were found in small agglomerates or bundles versus before treatment, indicating that ultrasonication played a major role in dispersing the SWNTs. The dispersion of SWNTs takes place, which reduces the negatively charged state of SWNTs, as shown in Fig. 4.6b. Dreyer et al. (Dreyer and Bielawski 2012) reported that sonication can enhance the exfoliation of graphite oxide (GO), causing ‘destruction’ of GO platelets. Thus, GO may undergo greater graphite exfoliation during sonication, losing more surface functional groups and negative charges due to the breakup of aggregated GO clusters. Bai et al. (Bai et al. 2017) also reported that due to the harsh condition provided by the ultrasonic irradiation, a mechanical shear stress would be introduced to the individual layers of GO due to Van der Waals interactions and π-π bonding, which simplifies the exfoliation GO sheets. This result is consistent with other reports of CNTs by Krause et al. (Krause et al. 2010) and with SWNTs by Niyogi et al. (Niyogi et al. 2003). These findings may support the idea of high removal of IBP and SMX in the presence of SWNTs during US treatment due to the high dispersion of SWNTs. This leads to an increased SWNT surface area, which enhances the adsorption process and increases OH\(^-\) generation, thus enhancing the oxidation process.

Furthermore, the zeta potential of SWNTs before sonication, and after 10 and 60 min ultrasonication was determined to estimate the effect of ultrasonication on the surface charge of SWNTs. SWNTs were examined for surface charge using zeta potential
Fig. 4.6 Effect of ultrasonication on (a) hydrodynamic radius of SWNTs and (b) zeta potential of SWNTs at 15 ± 1°C, pH 7, 0.18 W/mL, and 1000 kHz.
Fig. 4.7 Visual examination of SWNTs solution with and without sonication: (a) SWNTs without ultrasonication and (b) SWNTs with ultrasonication. (SWNTs = 45 mg/L, pH = 7, and 1000 kHz).

measurements over the pH range of 3.5-9.5. Fig. 4.6b shows the decrease in surface charge of the SWNTs particles with increasing ultrasonication time. For example, at pH 7, the zeta potential negatively decreased from -18 mV before sonication to 5 and 22 mV after sonication for 10 and 60 min, respectively. This can be explained by the behavior of surface functionalization; the presence of oxygen-containing functional groups, such as carboxyl, hydroxyl, and carbonyl, on the surface of SWNTs negatively
increases the zeta potential (Li, Boggs, et al. 2008). Due to the sonication, the SWNTs’ loss of negatively charged functional groups over a wide range of pH values indicates a decrease in the amount of functional groups, because OH\(^-\) on the surface of SWNTs is protonated and becomes OH\(_2^+\). Thus, a positively charged surface is created due to the high concentration of protonated functional groups produced during sonication (Jung et al. 2013).

4.4. Binding energies of PhACs on the SWNTs

The adsorption of un-dissociated PhACs onto SWNTs is mainly due to \(\pi-\pi\) and van der Waals interactions between the adsorbent and the PhACs. In its un-dissociated form, SMX interacts favorably with SWNTs compared to IBP (–23.1 vs. –14.5 kcal/mol) because of its larger molecular structure and greater surface area exposure to the SWNTs. As shown in Fig. 4.8, both rings in SMX are oriented towards the surface of the SWNTs, thus maximizing \(\pi-\pi\) interactions between SMX and the adsorbent. However, considering that IBP has a higher log\(_{\text{OW}}\) (3.84) and lower solubility (0.049 g/L at 25°C) than SMX (log\(_{\text{OW}}\) = 0.79, SW = 0.459 g/L at 25°C) in water, which are the main factors affecting the adsorption mechanism, the hydrophobicity effect could play a major role in the adsorption of PhACs onto SWNTs (Jung et al. 2015).

In the dissociated form, the binding of IBP onto SWNTs was greater than that of SMX (–11.2 vs. –5.8 kcal/mol), which was consistent with the trend of the adsorption experiment where IBP removal was higher than SMX at pH 7 (see Fig. 4.4d). In the dissociated form, the negative charge on the SMX is on the N atom in the middle of the SMX molecule, causing both rings to be oriented away from the surface of the SWNTs and reducing the \(\pi-\pi\) interactions between SMX and the adsorbent. In contrast, the
negative charge on IBP is on the carboxylic group at the edge of IBP molecule, which still allowed interaction of the IBP ring with the SWNTs to be intact. Thus, the net reduction in binding energy is larger for SMX than for IBP. The binding energies are still favorable because the binding strength is dominated by π–π and van der Waals interactions between the molecules and the adsorbent.

4.5. Conclusions

Sonocatalytical degradation of two target PhACs (IBP and SMX) having different physicochemical properties was carried out in the absence and presence of SWNTs at a
frequency of 1000 kHz. While the degradation of IBP and SMX depended on temperature and pH, the maximum degradation efficiencies of IBP and SMX were achieved under optimum pH of 3.5 and temperature 35°C in the absence of SWNTs. However, the removal of IBP and SMX was enhanced when SWNTs were added to the system. Higher removal was obtained under US/SWNT than the sum of those obtained under SWNTs and US- only reactions. The role of SWNTs in this study approved our hypothesis referring to the enhancement of the oxidation and adsorption activities when SWNTs are added to the system due to the dispersion of SWNTs under US irradiation. In addition, H$_2$O$_2$ formation significantly increased in the presence of SWNTs, indicating that the SWNTs dispersed particles performed as additional nuclei for the pyrolysis of water molecules and formation of OH$. Higher removal of IBP was achieved than that of SMX under US reaction, SWNTs adsorption, and US/SWNTs reactions due to their chemical properties. Furthermore, results of DFT-D calculations were consistent with the experimental results and provided insight on the adsorption of IBP and SMX onto SWNTs in aqueous system at different pH levels.

Acknowledgments

This research was supported by the Korea Ministry of Environment, ‘GAIA Project, 2015000540003’. This research was also supported by the Ministry of Higher Education and Scientific Research of Iraq and the Iraqi Cultural Office in Washington D.C.
CHAPTER 5

SONOCATALYTICAL DEGRADATION ENHANCEMENT FOR IBUPROFEN AND
SULFAMETHOXAZOLE IN THE PRESENCE OF GLASS BEADS AND SINGLE-WALLED
CARBON NANOTUBES

Abstract

Sonocatalytic degradation experiments were carried out to determine the effects of glass beads (GBs) and single-walled carbon nanotubes (SWNTs) on ibuprofen (IBP) and sulfamethoxazole (SMX) removal using low and high ultrasonic frequencies (28 and 1000 kHz). In the absence of catalysts, the sonochemical degradation at pH 7, optimum power of 0.18 W mL\(^{-1}\), and a temperature of 15°C was higher (79% and 72%) at 1000 kHz than at 28 kHz (45% and 33%) for IBP and SMX, respectively. At the low frequency (28 kHz) \(\text{H}_2\text{O}_2\) production increased significantly, from 10 µM (no GBs) to 86 µM in the presence of GBs (0.1 mm, 10 g L\(^{-1}\)); however, no enhancement was achieved at 1000 kHz. In contrast, the \(\text{H}_2\text{O}_2\) production increased from 10 µM (no SWNTs) to 31 µM at 28

\(^3\) Reprinted here with permission of publisher: Al-Hamadani et al., Sonocatalytical degradation enhancement for ibuprofen and sulfamethoxazole in the presence of glass beads and single-walled carbon nanotubes Ultrasonics Sonochemistry 32 (2016): 440-448.
kHz and from 82 µM (no SWNTs) to 111 µM at 1000 kHz in the presence of SWNTs (45 mg L⁻¹). Thus, maximum removals of IBP and SMX were obtained in the presence of a combination of GBs and SWNTs at the low frequency (94% and 88%) for 60 min contact time; however, >99% and 97% removals were achieved for 40 and 60 min contact times at the high frequency for IBP and SMX, respectively. The results indicate that both IBP and SMX degradation followed pseudo-first-order kinetics. Additionally, the enhanced removal of IBP and SMX in the presence of catalysts was because GBs and SWNTs increased the number of free OH⁻ radicals due to ultrasonic irradiation and the adsorption capacity increase with SWNT dispersion.

*Keywords*: ibuprofen; sulfamethoxazole; sonocatalytical degradation; glass beads; single-walled carbon nanotubes

5.1. Introduction

Pharmaceutical compounds (PhACs) in the water body have become an important issue in water and wastewater treatment facilities, because they are very complex compounds, occur at low concentrations, and yet have high impacts on aquatic life and human health (Halling-Sørensen et al. 1998; Heberer 2002). Their occurrence in the water body is due to several reasons, including irregular disposal of unused medications and expired drugs and veterinary medicines (Sirés and Brillas 2012; Snyder et al. 2003).

Ibuprofen (IBP) and sulfamethoxazole (SMX) were selected as examples, due to their widespread occurrence in many United States rivers and wastewater treatment plant effluents (Kolpin et al. 2002). PhACs have been detected at between 0.002 and 24.6 µg L⁻¹ for ibuprofen (IBP) and 0.01 and 2 µg L⁻¹ for sulfamethoxazole (SMX) in the effluent of
several sewage treatment plants (Buser, Poiger, and Müller 1999; Méndez-Arriaga et al. 2008) and surface waters (0.03–0.48 µg L\(^{-1}\)) (Hirsch et al. 1999; Beltrán et al. 2008).

Ultrasonication treatment has been noted recently as an advanced technique among oxidation processes, such as sonocatalysis, ozone/hydrogen peroxide (H\(_2\)O\(_2\)), ultraviolet (UV)/H\(_2\)O\(_2\), UV/TiO\(_2\), and Fenton/photo-Fenton, to remove complex organic and inorganic compounds from wastewater (Her, Park, and Yoon 2011a; Park, Her, and Yoon 2011b). The sonochemical reaction is based on the sonolysis of water, which produces OH\(^-\), H\(^+\), OOH\(^-\), OH\(^2-\), and H\(_2\)O\(_2\) via the nucleation, growth, and collapse of cavitation bubbles in water due to the high temperature and pressure resulting from ultrasound waves (Im et al. 2014; Im et al. 2013a). Previous studies have indicated significant advantages in using ultrasonic treatments, such as safety, cleanliness, energy conservation, and no or minimal secondary pollution products (Nalini et al. 2010; Madhavan et al. 2010).

Many studies have shown that using catalysts in combination with sonochemical degradation (i.e., sonocatalytic degradation) has advantages over both conventional and advanced treatment processes (Kong et al. 2012; Madhavan et al. 2010). For that, single-wall carbon nanotubes (SWNTs) and inert glass beads (GBs) can be used, individually and in combination, to enhance the degradation of PhACs. SWNTs are a member of the carbon nanotube group that consist of a single rolled up graphene sheet, which has been recently shown to be a significant adsorbent, due to its unique physiochemical properties (Li, Ding, et al. 2003). The hydrophobicity, electrical conductivity, optical activity, and mechanical strength of SWNTs enhance the removal of various types of contaminants, such as heavy metals, organic and inorganic matter, pharmaceuticals, personal care
products, and endocrine-disrupting compounds (Qu, Alvarez, and Li 2013; Im et al. 2013a). A few studies have demonstrated the effects of SWNTs as a catalyst with ultrasonic treatment and reported promising results in degrading complex contaminants (Im et al. 2013a). Im et al. reported that adding SWNTs to an ultrasonic system increased the generation of OH’, because the dispersed SWNTs particles acted as additional nuclei for the pyrolysis of water molecules, forming more OH’ (Im et al. 2013a). Several studies have also investigated the effects of glass beads (GBs) in sonication processes. The general outcome from these studies was significant enhancement of contaminant degradation and increased generation of OH’ radicals; however, these enhancements depended on the ultrasound frequency used (Her, Park, and Yoon 2011a; Kong et al. 2012; Suzuki, Maezawa, and Uchida 2000). Kong et al. found that the addition of GBs increased the OH’, associated with an increase in the number of collapsing bubbles at 28 kHz (Kong et al. 2012). However, a previous study reported that the addition of different sizes of GBs was not effective under 1000 kHz and yet some were very effective below 580 kHz, indicating that the size of the GB particles and the frequency of the ultrasound played major roles in OH’ production (Her, Park, and Yoon 2011a).

The effect of SWNTs was investigated in a previous study with acetaminophen and naproxen and showed significant improvement in adsorption and sonocatalytic reactions (Im et al. 2013a). However, the effects on sonochemical and adsorption reactions of combinations of GBs and SWNTs for IBP and SMX have not been reported previously. Thus, the objectives of this study were to estimate the effects of GBs and SWNTs individually and in combination under low frequency (28 kHz) and high frequency (1000 kHz) ultrasound. Processes were carried out as a function of frequency
(28 and 1000 kHz) and power (0.045, 0.09, 0.135, and 0.18 W mL\(^{-1}\)) at pH 7 and 15ºC. We hypothesized that the combination of SWNTs and GBs would enhance the degradation of the selected PhACs, IBP and SMX. We predicted that the presence of GBs would increase the generation of OH\(^{-}\) and enhance the oxidation reaction. In addition, the adsorption reaction would be enhanced due to the dispersion of SWNTs, which provide more adsorption sites.

5.2. Materials and methods

5.2.1. Chemicals and catalysts

The chemicals were used as-received without further purification and were purchased from commercial sources. Table 4.1 lists the characteristics of the target PhACs tested, from the SRC PhysProp Database (SRC 2006). The high-purity IBP (C\(_{13}\)H\(_{18}\)O\(_2\), >98%) and SMX (C\(_{10}\)H\(_{11}\)N\(_3\)O\(_3\)S, >98%) tested, as well as the potassium hydrogen phthalate (C\(_8\)H\(_5\)KO\(_4\), 99.95%), potassium iodide (KI, 99%), ammonium molybdate tetrahydrate (H\(_{24}\)Mo\(_7\)N\(_6\)O\(_{24}\)·4H\(_2\)O), and H\(_2\)O\(_2\) (30% w/v) were purchased from Sigma-Aldrich (St. Louis, MO, USA). GBs (0.05, 0.1, 0.5, 1, and 2 mm in diameter) were purchased from Goryeo-Ace Inc. (Seoul, South Korea). SWNTs (>90%) with an outer diameter of 1–4 nm and a length of 5–30 µm were purchased from Cheap Tubes, Inc. (Brattleboro, VT, USA). Stock solutions of IBP, SMX, and SWNTs were prepared in nanopure deionized (DI) water. The SWNT stock solutions were covered with aluminum foil and stored in a refrigerator.

5.2.2. Apparatus

The sonication experiments, using ultrasound (US) and US/(GB and/or SWNTs), were performed in a double-jacketed stainless steel reservoir (L:W:H, 15:10:20 cm) with
a water-cooled (Fisher Scientific Inc., Pittsburgh, PA, USA) US generator (Ultech, Dalseo, Daegu, South Korea), at frequencies of 28 kHz and 1000 kHz (applied power: 0.045, 0.09, 0.135, and 0.18 W mL⁻¹) and 15°C. The optimum size and dosage of the catalysts were selected depending on H₂O₂ production. For that, the optimum GB size was chosen among different sizes, 0.05, 0.1, 0.5, 1, and 2 mm. The optimum GB dose was chosen among 1, 2.5, 5, 10, and 20 g L⁻¹. In addition, the optimum dose of SWNTs was chosen from our previous study, 45 mg L⁻¹ (Im et al. 2013a). Batch adsorption experiments were used to evaluate the adsorption capacity of SWNTs without sonication. SWNTs were hydrated for 24 h in DI water and mixed with a magnetic stirrer at 300 rpm prior to being added to the reactor vessel. All US/(GB and/or SWNTs) and adsorption experiments were carried out using 1000 mL of this initial solution. Samples were taken periodically and immediately filtered with 0.22-µm glass microfiber filters (Whatman, Little Chalfont, Buckinghamshire, UK) for further analysis.

5.2.3. Analysis

Measurements of IBP and SMX concentrations were carried out using high-performance liquid chromatography (HPLC, 1200 series; Agilent Technologies, Santa Clara, CA, USA). To remove the GBs and SWNTs particles, all samples were filtered with 0.22-µm glass microfiber filters prior to analysis. The mobile phase was a mixture of 40%/60% (DI water/acetonitrile) for IBP and 50%/50% (DI water/acetonitrile) for SMX. Separation was achieved with a LiChrosorb RP-18 analytical column (4.6 mm × 100 mm i.d., 5-µm particles, Atlantis; Waters, Milford, MA, USA) with a 100-µL sample loop at a flow rate of 1.0 mL min⁻¹ for IBP and 0.75 mL min⁻¹ for SMX. The detection wavelength was 210 nm for both compounds. The H₂O₂ concentration was determined,
indicative of OH•, through the KI dosimetry method using an ultraviolet-visible (UV-vis) spectrophotometer (Agilent Technologies) at 350 nm during US reactions (Kormann, Bahnemann, and Hoffmann 1988).

5.3. Results and discussion

5.3.1 Effect of frequency on PhAC degradation and H₂O₂ formation

Under ultrasonic irradiation, frequency plays a major role in degrading PhACs. Thus, the effects of low and high frequency on the degradation of 10 µM IBP and SMX were studied at 28 and 1000 kHz with a US power of 180 ± 3 W at pH 7. As shown in Fig. 5.1a, the removal of both IBP and SMX increased significantly at the higher frequency (1000 kHz), which showed that the sonochemical degradation of an organic compound is frequency-dependent. Changes in bubble number, bubble size, cavitation threshold, and temperatures during cavitation bubble collapse are major factors affected by ultrasound frequency (Chiha et al. 2011). Thus, at the higher frequency, the generation of free OH• was promoted in the solution due to the increase in production and intensity of cavitation (Zhang, Gao, et al. 2011). In addition, the lifetime of the bubbles decreased at the high frequency; thus, under these conditions, free radicals tended to move quickly towards the bulk liquid, minimizing the likelihood of recombination (Zhang, Gao, et al. 2011; Park, Her, and Yoon 2011a). As a result, more reactions took place between the free radicals and targeted compounds, leading to the high removal of IBP and SMX at 1000 kHz.

Fig. 5.1b illustrates the production of OH• at high and low frequencies in the absence and presence of selected PhACs, to explain the effects of frequency on OH• radical production, which participate in many fast reduction/oxidation reactions. Due to
the high pressure and temperature resulting from ultrasonic irradiation, the water molecules dissociate into H’ and OH’ radicals (Eq. (5.1)). Then, the H’ radicals combine with O₂ producing OH’₂ (Eq. (5.2)). Finally, H₂O₂ is produced by the recombination of two OH’ and HO’₂, discharging O₂ (Eqs. (5.3) and (5.4)) as a result of diffusion at high temperature and pressure (Im et al. 2013a; Selli 2002), as explained in the following equations:

\[ \text{H}_2\text{O} \rightarrow \text{H}'+ \text{OH}' \quad k_1 = \text{unknown} \quad (5.1) \]
\[ \text{H}'+ \text{O}_2 \rightarrow \text{OH}'_2 \quad k_2 = 2.1 \times 10^{10} \text{ L M}^{-1}\text{s}^{-1} \quad (5.2) \]
\[ 2\text{HO}'_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad k_3 = 8.3 \times 10^{5} \text{ L M}^{-1}\text{s}^{-1} \quad (5.3) \]
\[ 2\text{OH}' \rightarrow \text{H}_2\text{O}_2 \quad k_4 = 2.1 \times 10^{10} \text{ L M}^{-1}\text{s}^{-1} \quad (5.4) \]

Obviously, the H₂O₂ concentration is higher at a higher frequency without PhACs than with PhACs due to the degradation of IBP and SMX that consumed the difference between the two conditions. IBP showed higher removal than SMX under the same experimental conditions due to their differing physicochemical properties, which play a major role in the reaction between IBP or SMX with OH’ (Nakada et al. 2007).

As shown in Table 4.1, IBP is relatively more hydrophobic due to its high log K\text{OW} (3.84) and low solubility (0.049 g L\text{⁻¹} at 25°C) than SMX (log K\text{OW} = 0.79 and S\text{W} = 0.459 g L\text{⁻¹} at 25°C) in water. Higher removal of IBP was achieved because high hydrophobic compounds tend to concentrate at the gas–liquid interface [24]. Therefore, the accumulated IBP on the gas–liquid interface and/or inside the gas bubble was effectively degraded by direct pyrolysis. However, for less hydrophobicity compounds such as SMX, the reactions may occur more likely at the gas–liquid interface and in the
Fig. 5.1 Effect of frequency on (a) IBP and SMX degradation and (b) \( \text{H}_2\text{O}_2 \) production in the presence of IBP and SMX. (pH = 7, temperature = 15 ± 1°C, and power = 0.18 W mL\(^{-1}\)).

bulk liquid region, where lower amounts of free OH\(^•\) are present (Park, Her, and Yoon 2011a; Goel et al. 2004). These results agree with previous studies of the sonodegradation of different contaminants such as acetaminophen and naproxen (Im et al. 2013a), 4-chlorophenol removal (Jiang, Petrier, and Waite 2006), a azo dyes (Eren and Ince 2010).
5.3.2. Effects of power on PhACs degradation and \( \text{H}_2\text{O}_2 \) formation

Due to the conditions that the US system provides to the solution (\( i.e., \) a temperature of 5000 K and pressure of 2000 atm), understanding the effect of power is necessary, because most of the power is transferred into heat, which is the major factor in the dissociation of water that produces the \( \text{OH}^- \) and \( \text{H}^- \) radicals (Méndez-Arriaga et al. 2008; Naddeo et al. 2009). Four power intensities were used (0.045, 0.09, 0.135, and 0.18 W mL\(^{-1}\)) and, as expected, the degradation of selected PhACs increased linearly as the power intensity increased (Figs. 5.2a/2b and 5.3a/3b). The increase in IBP and SMX degradation was attributed to the power increased, which resulted in (i) an increase in the number of cavitation bubbles leading to more \( \text{OH}^- \) radicals in the solution and (ii) an increase in the temperature, pressure, and the collapse time due to the increase in acoustic energy (Chiha et al. 2011; Golash and Gogate 2012; Naddeo et al. 2010). Additionally, due to the similar mechanism of power intensity and frequency in the US system, the effects of power on PhAC degradation and \( \text{H}_2\text{O}_2 \) production were investigated at low and high frequencies to determine the relationship between power and frequency. As shown in Figs. 5.2a and 5.2c for IBP, and Figs.5.3a and 5.3c for SMX, at low frequency, the effect of power on IBP and SMX degradation, as well as \( \text{H}_2\text{O}_2 \) production, was relatively insignificant compared with high frequency, perhaps because the bubble sizes are larger than those at high frequency and bubble collapse occurred insufficiently at the low frequency (28 kHz), resulting in less \( \text{OH}^- \) radical production and less degradation activity (Im et al. 2013a; Güyer and Ince 2011). In contrast, a significant increase in \( \text{H}_2\text{O}_2 \) production was obtained at the high frequency (1000 kHz), because the cavitation activity
Fig. 5.2 Effect of power on IBP degradation at (a) 28 kHz and (b) 1000 kHz. Effect of power on H$_2$O$_2$ production at (c) 28 kHz and (d) 1000 kHz. (pH = 7, temperature = 15 ± 1°C, and power = 0.18 W mL$^{-1}$).

and high-frequency effect increased with the applied power, as explained above (Lim et al. 2007). The results obtained are in good agreement with earlier investigations for IBP (Méndez-Arriaga et al. 2008), acetaminophen and naproxen (Im et al. 2014), and diclofenac (Madhavan et al. 2010).
5.3.3. Catalyst size and dose optimization

Multiple studies have indicated that sonocatalysis degradation rates increase for specific catalyst sizes and dosages. However, a lower degradation rate can result if the dose and size are below or higher than the optimum (Her, Park, and Yoon 2011a). The increase in the degradation rate in the sonication system in the presence of catalysts is generally due to the formation of OH’ radicals, which are very efficient oxidants that can degrade complex compounds. For example, the presence of SWNTs increase the concentration of H₂O₂, because the dispersion of SWNT particles tends to enhance the reaction of OH’ and HOO’ radicals in the liquid phase around cavitation bubbles (Im et al. 2013a; Zhang, Zhang, et al. 2011). Thus, the dispersion of SWNTs can be used to quantify the effectiveness of a reactor in generating the desired cavitation intensity. This is also because the dispersed particles act as additional nuclei for the pyrolysis of water molecules and the formation of OH’ (Her, Park, and Yoon 2011b; Im et al. 2013a). In addition, the presence of solid particles, such as GBs or TiO₂, in the ultrasonic system solution also has the potential to increase the number of cavitation bubbles. This can lead to an increase in the local temperature at cavity collapse, because the particles provide nucleation sites for the cavitation bubbles, resulting in a reduction of the cavitation threshold, due to surface roughness (Tuziuti et al. 2005; Taghizadeh and Abdollahi 2011; Zhang, Zhang, et al. 2011). This reduction in the cavitation threshold can enhance the pyrolysis of H₂O molecules to form OH’ radicals (Zhang, Zhang, et al. 2011).

Thus, size and dose optimization of GBs was determined by considering H₂O₂ production. In our previous work (Im et al. 2013a), the SWNTs optimum dose was 45 mg L⁻¹ among 0, 5, 15, and 45 mg L⁻¹ at pH 7 and 15°C, where
maximum H$_2$O$_2$ production was obtained. Various diameters of GBs were investigated (0.05, 0.1, 0.5, 1, and 2 mm) at low and high frequency at a dose of 5 g L$^{-1}$. At both frequencies, 28 kHz and 1000 kHz, the highest H$_2$O$_2$ production was obtained with the 0.1-mm GB size. In contrast, the lowest level of H$_2$O$_2$ production was obtained with the larger sizes, 1 and 2 mm (Figs. 5.4a and b). Although previous studies have suggested that the presence of solids would increase the reactivity of sonochemistry through the
addition of inert glass beads, in both our and those studies (Her, Park, and Yoon 2011a; Ahmed et al. 2011), H$_2$O$_2$ production was not linearly enhanced by the addition of various sizes of glass beads. Additionally, the optimum dose of GBs (at 0.1 mm) was compared with the absence of GBs and investigated under low and high frequency depending on H$_2$O$_2$ production (Figs. 5.4c and d). The results clearly showed that the optimum dose at low and high frequency was 10 g L$^{-1}$. Thus, the results indicated that the presence of GBs in the system was frequency-dependent. At the low frequency (28 kHz), the presence of GBs increased H$_2$O$_2$ production significantly; however, this was not true at the high frequency (1000 kHz), in which H$_2$O$_2$ production was about the same or lower than the level obtained with no added GBs. This may have resulted from the size and shape of the bubbles at low and high frequencies. As discussed in previous studies, the cavitation bubbles’ collapse on solid surfaces occurs in four different geometries: toroidal, spherical, symmetric, and asymmetric (Bai et al. 2008). At lower frequencies, the cavitation bubbles have more time to grow, which results in larger bubbles than those at a higher frequency (Tsochatzidis et al. 2001). Thus, at the low frequency (28 kHz), the presence of GBs enhanced H$_2$O$_2$ production, because there was minimal interference between the US wavelengths and GB particles and because the bubbles became larger than the GBs. In contrast, because the size of GB particles was similar to or bigger than the cavitation bubbles at the high frequency (1000 kHz), interference between the US wavelengths and GBs may occur, leading to a reduction in H$_2$O$_2$ production (Her et al. 2011; Her, Park, and Yoon 2011a). The results obtained agreed with the study of Her et al. who explored the effect of the size of cavitation bubbles and surface solids at different frequencies (Her, Park, and Yoon 2011a).
Fig. 5.4 $\text{H}_2\text{O}_2$ production in the presence of glass bead as a function of (a) GBs size at 28 kHz, (b) GBs size at 1000 kHz, (c) 0.1 mm GBs dose at 28 kHz, and (d) 0.1 mm GBs dose at 1000 kHz (pH = 7, power = 0.18 W mL$^{-1}$, and temperature = 15 ± 1°C).

5.3.4. Effect of catalysts on PhACs sono-degradation and adsorption

To further investigate the effects of the combination of GBs and SWNTs, the degradation of IBP and SMX in the absence and presence of the selected catalysts was considered. It was assumed that the removal of IBP and SMX, in the presence or absence of catalysts, was due to two major activities: sonochemical degradation activity due to US irradiation with or without catalysts and adsorption activity due the presence of
To demonstrate this, various sonication reactions were investigated, such as (PhACs/US), (PhACs/US+GBs), (PhACs/US+SWNTs), and (PhACs/US+GBs+SWNTs), in addition to the adsorption reaction of (PhACs/SWNTs). Figs. 5.5a and b show the removal of IBP, at 28 kHz and 1000 kHz, respectively, with the optimum catalysts loaded, GBs (0.1 mm and 10 g L\(^{-1}\)) and SWNTs (45 mg L\(^{-1}\)) in individual and combination forms. Overall, the removal was highest with the combination, where the effect of oxidation from the OH\(^-\) radicals and adsorption on the SWNTs took place. In more detail, at the low frequency, the sonochemical degradation results indicated that the removal followed the order of (IBP/US) < (IBP/US+GBs) < (IBP/US+SWNTs) < (IBP/US+GBs+SWNTs) (Fig. 5.5a), which was proportional to the H\(_2\)O\(_2\) production rate constant that followed the order of (IBP/US) < (IBP/US+SWNTs) < (IBP/US+GBs) < (IBP/US+GBs+SWNTs) (Fig. 5.5c). Despite that, the H\(_2\)O\(_2\) production rate constant of (IBP/US+GBs) appeared slightly higher than (IBP/US+SWNTs); however, the removal showed the reverse due to the adsorption that took place, in addition to the sonochemical degradation, from OH\(^-\) radicals. However, at the high frequency (1000 kHz), the sonochemical degradation of IBP showed a slightly different trend, in the order of (IBP/US+GBs) < (IBP/US) < (IBP/US+SWNTs) < (IBP/US+GBs+SWNTs) (Fig. 5.5b), which was also, proportional to the H\(_2\)O\(_2\) production rate constant, in the order of (IBP/US+GBs) < (IBP/US) < (IBP/US+SWNTs) < (IBP/US+GBs+SWNTs) (Fig. 5.5d). The presence of GBs negatively impacted the sonochemical degradation, as explained earlier, because interference between the US wavelengths and GBs may occur, leading to a reduction in H\(_2\)O\(_2\) production; this occurs because the size of the GB particles was
Fig. 5.5 Removal of IBP in the absence and presence of GBs and SWNTs at (a) 28 kHz, and (b) 1000 kHz. H₂O₂ production rate in the absence and presence of GBs and SWNTs at (c) 28 kHz and (d) 1000 kHz (GBs = 0.1 mm and 10 g L⁻¹, SWNTs = 45 mg L⁻¹, pH = 7, power = 0.18 W mL⁻¹, and temperature = 15 ± 1°C).

Similar to or bigger than the cavitation bubbles at the high frequency (1000 kHz) (Her et al. 2011; Her, Park, and Yoon 2011a). Similar sonochemical degradation results were achieved with SMX at low and high frequencies, but relatively less removal was obtained (Fig. 5.6). The order for SMX at 28 kHz was (SMX/US) < (SMX/US+SWNTs) < (SMX/US+GBs) < (SMX/US+GBs+SWNTs) (Fig. 5.6a), which is proportional to the H₂O₂ production rate constant, in the order of (SMX/US) < (SMX/US+SWNTs) < (SMX/US+GBs) < (SMX/US+GBs+SWNTs) (Fig. 5.6c). Fig. 5.7 shows the H₂O₂ production in all the reactions that were tested. Clearly, the concentration of H₂O₂ was
higher at high frequency than at low frequency in all the reactions because more
cavitational bubbles generated at high frequency increase the number of OH• in the
system (Im et al. 2013a; Tuziuti et al. 2005). In adsorption reaction, the removal of IBP
also was higher due to its strong hydrophobicity based on log \( K_{OW} \) compared to that of
SMX. A higher log \( K_{OW} \) value indicates higher sorption affinity to the SWNTs for
bisphenol A and 17-b estradiol (Yu, Peldszus, and Huck 2008). Ultrasonication
significantly enhances the dispersion and debundling of SWNTs, which provide more
adsorption sites. This is presumably because the implosion of cavities creates high
temperatures, causes pressure differences, and imparts shear forces on SWNT surfaces. In
addition, complex reactive intermediates having different functional groups can be
produced on the surfaces of these helicoids, which overcome van der Waals interaction
between SWNTs. (Al-Hamadani et al. 2015).

Therefore, the overall adsorption capacity of SWNTs was increased when
ultrasound irradiation was applied. Based on these results, we proposed possible
mechanisms in US and US/SWNTs process, as shown in Fig. 5.8. Thus, in all of these
reactions there are four major mechanisms that could cause the removal of IBP and SMX:
(i) In the absence of catalysts, the removal is due to the ultrasound irradiation, resulting in
\( \text{H}_2\text{O} \) pyrolysis, which generates OH• radicals that interact with these compounds
(Weavers, Malmstadt, and Hoffmann 2000). (ii) In the presence of GBs, the increase in
the number of cavitation bubbles leads to an increase in the temperature of inside the
Fig. 5.6 Removal of SMX in the absence and presence of GBs and SWNTs at (a) 28 kHz, and (b) 1000 kHz. \( \text{H}_2\text{O}_2 \) production rate in the absence and presence of GBs and SWNTs at (c) 28 kHz and (d) 1000 kHz (GBs = 0.1 mm and 10 g L\(^{-1} \), SWNTs = 45 mg L\(^{-1} \), pH = 7, power = 0.18 W mL\(^{-1} \), and temperature = 15 ± 1°C).

Cavitational bubbles, which results in radical formation (Pang, Abdullah, and Bhatia 2011a; Papadaki et al. 2004). (iii) The presence of SWNTs increase the generation of OH\(^{•} \) radicals, due to sonication, in which the SWNT particles dispersed and acted as additional nuclei for the pyrolysis of water molecules, forming OH\(^{•} \). In addition, the adsorption activities were enhanced by sonication, because the dispersion of SWNTs leads to more adsorption sites, as well as an increase in the adsorption capacity (Papadaki et al. 2004). (iv) The presence of GBs and SWNTs results in an increase in OH\(^{•} \) radicals.
Fig. 5.7 $\text{H}_2\text{O}_2$ production in the absence and presence of GBs and SWNTs with/without IBP at (a) 28 kHz, and (b) 1000 kHz, and with/without SMX at (c) 28 kHz, and (d) 1000 kHz. (GBs = 0.1 mm and 10 g L$^{-1}$, SWNTs = 45 mg L$^{-1}$, pH = 7, power = 0.18 W mL$^{-1}$, and temperature = 15 ± 1°C).

due to (ii) and (iii) in addition to the enhancement of the adsorption activities due to (iii), resulting in the maximum removal of IBP and SMX under both frequencies. Taken together, the effect of the combination (GBs and SWNTs) on the removal was significant: >99% removal of IBP was obtained in 40 min (Fig. 4b). Moreover, 95% removal of SMX was obtained in 60 min (Fig. 5b). These results were summarized by determining the synergism of each reaction. Since this study focused on the effects of GBs and SWNTs individually and in combination on the removal of IBP and SMX at low and high
frequencies, three synergy indices were determined, based on the modified Eqs. (5–7) adapted from Madhavan et al. (Madhavan et al. 2010). The synergy index is signified by the normalized differences between the rate constants that result from the combined reactions divided by the sum of the rate constants. Therefore, in this case the synergy indices were calculated as the rate constants obtained under US/GBs in Eq. (5.5), US/SWNTs in Eq. (5.6), and US/GBs+SWNTs in Eq. (5.7), divided by the sum of those obtained from individual reactions, as summarized in Table 5.2.
A synergy index > 1 indicates that the combined US/GBs, US/SWNTs or US/GBs+SWNTs processes exceed the sum of the individual reactions. The result varied, depending on the frequencies and catalysts used (Table 5.2). The GBs brought about a greater improvement in the removal of IBP and SMX at low frequency than at high frequency, as explained earlier, in which the bubble size and the GBs’ size impacted the generation of OH\(^{•}\) radicals, which resulted in less removal at the high versus the low frequency, as illustrated in synergy index I. However, the SWNTs had the opposite impact; higher effectiveness was obtained at the higher frequency than the lower, as illustrated in synergy index II, because both the sonochemical reaction and adsorption were enhanced due to the dispersion of SWNTs. However, regardless of removal time for IBP and SMX, the combination of GBs and SWNTs was more effective at the low frequency, due to the increased reactivity between OH\(^{•}\) radicals and the selected PhACs than those at high frequency, as explained in synergy index III. This phenomenon may be due to the effect of size of the cavitation bubbles that were similar to or smaller than the GB size at the high frequency than those at the low frequency, which decreased the number of OH\(^{•}\) radicals generated for IBP and SMX removal, as explained earlier.

\[
Synergy \ index \ I = \frac{k_{(US+GBs)}}{k_{(US)} + k_{(GBs)}} \tag{5.5}
\]

\[
Synergy \ index \ II = \frac{k_{(US+SWNTs)}}{k_{(US)} + k_{(SWNTs)}} \tag{5.6}
\]

\[
Synergy \ index \ III = \frac{k_{(US+SWNTs+GBs)}}{k_{(US)} + k_{(GBs)} + k_{(SWNTs)}} \tag{5.7}
\]
Table 5.2 Pseudo-first order ($k_i$) degradation rate constants, coefficient of determination ($R^2$), and synergistic index values within 60 min for 28/1000-kHz US/GBs US/SWNTs, and US/GBs+SWNTs reactions at pH 7, power 0.18 W mL$^{-1}$, and temperature 15 ± 1°C.

<table>
<thead>
<tr>
<th>Process</th>
<th>28 kHz</th>
<th>1000 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IBP</td>
<td>SMX</td>
</tr>
<tr>
<td></td>
<td>$k_i$ (min$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>US only</td>
<td>0.84</td>
<td>0.97</td>
</tr>
<tr>
<td>US+GBs</td>
<td>0.99</td>
<td>0.96</td>
</tr>
<tr>
<td>SWNTs only</td>
<td>0.65</td>
<td>0.69</td>
</tr>
<tr>
<td>US+SWNTs</td>
<td>1.14</td>
<td>0.78</td>
</tr>
<tr>
<td>US+GBs+SWNTs</td>
<td>1.35</td>
<td>0.73</td>
</tr>
</tbody>
</table>

5.3.5. Effects of CCl$_4$ and MeOH on PhACs degradation

The addition of CCl$_4$ and MeOH, which are known as significant scavengers of H$^\cdot$ and OH$^\cdot$ radicals, respectively (Guo et al. 2010), was carried out to investigate the effectiveness of OH$^\cdot$ radicals in degrading IBP and SMX. As shown in Figs. 5.9a and b, in the presence of 150 µM CCl$_4$, the degradation rate constants of IBP and SMX were enhanced significantly in the presence and absence of the catalyst. These enhancements in the degradation rate of IBP and SMX show that OH$^\cdot$ radicals could be responsible for
Fig. 5.9 Effect of CCl₄ (150 µM) and MeOH (150 mM) on (a) IBP and (b) SMX degradation rate (GBs = 0.1 mm and 10 g L⁻¹, SWNTs = 45 mg L⁻¹, pH = 7, power = 0.18 W mL⁻¹, and temperature = 15 ± 1°C).

PhAC degradation, because the presence of CCl₄ decreased the H⁺ radicals, producing HCl and other by-product compounds such as C₂Cl₆ and C₂Cl₄. Under ultrasound irradiation, CCl₄ dissociates into CCl₃⁺, CCl₂⁺, and Cl⁺ radicals that have negligible interaction preference with OH⁺ radicals (Im et al. 2015; Sivakumar and Muthukumar 2011); thus, OH⁺ radicals were most likely the only radicals left in the solution. As such, the degradation of IBP and SMX was enhanced, because the reaction of OH⁺ radicals and
PhACs was predominant in the system (Im et al. 2015; BORGES, KORN, and COSTA LIMA 2002). Additionally, as demonstrated in Figs. 5.9a and b, the presence of the catalyst improved the degradation rate constant, because a higher concentration of OH’ radicals was generated that were then responsible for the decomposition of the selected compounds.

The effect of the addition of 150-mM MeOH, a known OH’ scavenger (Guo et al. 2010), was studied in the absence and presence of a catalyst for IBP and SMX (Figs. 5.9a and b). The degradation rate constant of both IBP and SMX decreased, because the OH’ radicals reacted with and were consumed by MeOH more than the PhACs; this provides an additional piece of evidence that free OH’ radicals are responsible for IBP and SMX removal (Im et al. 2014; Zheng, Maurin, and Tarr 2005).

5.4 Conclusions

The effects of the absence and presence of two catalysts (GBs and SWNTs) on the sonocatalytic degradation of IBP and SMX were studied at low and high ultrasound frequencies. One of the main factors in sonochemical degradation is the power intensity; maximum degradation of IBP and SMX was obtained at a power intensity of 0.18 W mL$^{-1}$. In the absence of catalysts, the removals of IBP and SMX were higher at a high frequency than at a low frequency, because more OH’ radicals were generated at 1000 kHz than at 28 kHz due to the increase in water molecule pyrolysis as a result of the ultrasound irradiation. The removals of IBP and SMX were enhanced significantly in the presence of GBs at the low frequency (28 kHz), whereas they were significantly reduced at high frequency (1000 kHz), because the GB particle size was similar to or larger than
the cavitation bubbles at the high frequency, leading to interference between the US wavelengths and GB particles resulting in a reduction in H$_2$O$_2$ production. Additionally, the presence of SWNTs was effective under low and high frequencies in both the sonochemical degradation mechanism and adsorption mechanism, because the dispersed SWNT particles acted as additional nuclei for the pyrolysis of water molecules and the formation of more OH$^\cdot$. Also, the dispersion of SWNTs, due to sonication, enhanced the adsorption process by providing more adsorption sites, leading to increased adsorption capacity. However, maximum removals of IBP and SMX were achieved at both frequencies when GBs and SWNTs were combined, as a result of the enhanced sonochemical degradation with OH$^\cdot$ formation, in addition to the adsorption process resulting from SWNT dispersion. IBP was more affected than SMX under all reactions; this was attributed to the physiochemical properties of IBP and SMX. The addition of CCl$_4$ and MeOH scavengers demonstrated that the major removal mechanisms were due to interactions between OH$^\cdot$ and the PhACs.

**Acknowledgments**

This research was supported by a grant (code 15IFIP-B088091-02) from Industrial Facilities & Infrastructure Research Program funded by Ministry of Land, Infrastructure and Transport of Korean government. This research was also supported by the Ministry of Higher Education and Scientific Research of Iraq and the Iraqi Cultural Office in Washington D.C.
CHAPTER 6

SONOCATALYTIC REMOVAL OF IBUPROFEN AND SULFAMETHOXAZOLE IN THE PRESENCE OF DIFFERENT FLY ASH SOURCES

Abstract

We examined the feasibility of using two types of fly ash (an industrial waste from thermal power plants) as a low-cost catalyst to enhance the ultrasonic (US) degradation of ibuprofen (IBP) and sulfamethoxazole (SMX). Two fly ashes, Belews Creek fly ash (BFA), from a power station in North Carolina, and Wateree Station fly ash (WFA), from a power station in South Carolina, were used. The results showed that >99% removal of IBP and SMX was achieved within 30 and 60 min of sonication, respectively, at 580 kHz and pH 3.5. Furthermore, the removal of IBP and SMX achieved, in terms of frequency, was in the order 580 kHz > 1000 kHz > 28 kHz, and in terms of pH, was in the order of pH 3.5 > pH 7 > pH 9.5. WFA showed significant enhancement in the removal of IBP and SMX, which reached >99% removal within 20 and 50 min, respectively, at 580 kHz and pH 3.5. This was presumably because WFA contains more silicon dioxide than BFA, which can enhance the formation of OH•

radicals during sonication. Additionally, WFA has finer particles than BFA, which can increase the adsorption capacity in removing IBP and SMX. The sonocatalytic degradation of IBP and SMX fitted pseudo first-order rate kinetics and the synergistic indices of all the reactions were determined to compare the efficiency of the fly ashes. Overall, the findings have showed that WFA combined with US has potential for treating organic pollutants, such as IBP and SMX, in water and wastewater.

Keywords: ibuprofen; sulfamethoxazole; sonocatalytical degradation; fly ash; water treatment

6.1. Introduction

Over the last two decades, large quantities of products, such as medicines, disinfectants, and personal care products, have been released into surface waters and wastewater treatment facilities by the pharmaceutical and chemical industries (Grassi et al. 2012). Increases in the concentrations of some pharmaceutical compounds, such as ibuprofen (IBP) and sulfamethoxazole (SMX), have come to the attention of scientists with regard to their impacts on life in lakes, rivers, and groundwater (Wong et al. 2016; Reguyal, Sarmah, and Gao 2017). Irregular disposal of unused medications, expired drugs, and veterinary medicines are the majors reasons why they end up in water bodies (Heberer 2002; Al-Hamadani et al. 2016). Concentrations of IBP and SMX in surface waters have been detected in the range of 30–480 ng L⁻¹ (Buser, Poiger, and Müller 1999; Hirsch et al. 1999), creating unique challenges, as conventional water treatment processes, including coagulation/sedimentation/filtration, typically can only remove 10–20% of these compounds (Halling-Sørensen et al. 1998; Lishman et al. 2006).
Consequently, efforts are needed to find effective processes to remove these contaminants from water to meet the important goal of providing safe drinking water.

Ultrasonic (US) treatment is one of the promising advanced oxidation processes that has the potential to produce hydroxyl radicals (OH•) in water, which are strong oxidizing agents (Hinge et al. 2016). The power of OH• in water treatment lies in their ability to destroy and degrade complex, otherwise-hard-to-degrade, and toxic organic compounds and convert them ultimately to carbon dioxide and water (Zhao et al. 2016). The process of US treatment produces OH• through the cavitation phenomenon and the formation of high-intensity bubbles (Mischopoulou et al. 2016). Cavitation occurs very quickly, through the steps of nucleation, growth, and the collapse of cavitation bubbles in water, releasing large amounts of energy locally, generating hot spots, and producing hydrogen and OH• due to the sonolysis of water (Hinge et al. 2016; Al-Hamadani et al. 2016). During this phenomenon, high temperatures (5000 K) and pressures (1000 atm) created inside cavitation bubbles lead to thermal dissociation of water molecules into H• and OH• (Li et al. 2016). The O₂ dissolved in water reacts and forms OH• and HO₂•.

Additionally, the cavitation bubbles contain three zones: the gaseous zone, the gas–liquid transition zone, and the bulk liquid zone. In the gaseous zone, the temperature and pressure reach their maximum levels of 5000 K and 1000 atm, respectively. The zone is hydrophobic and volatile compounds can be degraded. Second, in the gas–liquid transition zone, the temperature reaches 2000 K. The zone is moderately hydrophobic and moderate degradation of volatile compounds can be achieved. The third zone is the bulk liquid zone, where the temperature is 300 K; hydrophilic and non-volatile compounds undergo degradation in this zone (Im et al. 2013a; Im et al. 2014; Riesz, Kondo, and
Previous studies have indicated that US treatment has marked benefits, including safety, cleanliness, and ease of use; additionally, no carcinogenic by-products form during treatment (Al-Hamadani et al. 2016; Zhao et al. 2016).

Many studies have reported that sonochemical degradation can be enhanced by the presence of solid surfaces as catalysts, such as TiO\(_2\), quartz, glass beads, polyaluminum chloride, Al\(_2\)O\(_3\), and carbon nanotubes (Al-Hamadani et al. 2016; Im et al. 2014; Chong et al. 2017; Morosini et al. 2016). Because US treatment is highly energy-intensive, catalysts are needed to improve the removal efficiency and reduce the effective energy consumption (Chong et al. 2017). However, such catalysts are relatively expensive for treating large volumes of wastewater. Thus, alternative low-cost catalysts need to be investigated for their ability to remove contaminants, such as pharmaceutical compounds.

Fly ash was assessed in this study regarding its ability to enhance the sonodegradation of IBP and SMX. Fly ash is a by-product waste material generated in dry form in thermal power plants. Large amounts of fly ash are generated and dumped in landfills annually (Yu 2004; Janoš, Buchtová, and Rýznarová 2003; Mirshahghassemi, Cai, and Lead 2016). Thus, using fly ash in water and wastewater treatment is a good strategy to reduce environmental pollution. Fly ash’s chemical composition generally consists of aluminum oxide (Al\(_2\)O\(_3\)) and silicon dioxide (SiO\(_2\)) (in total, 60–80 wt%), in addition to some transition metal oxides (Li et al. 2016; Yu 2004). Previous studies have found fly ash to be a good adsorbent for various types of dyes (Wang and Wu 2006; Wang, Boyjoo, and Choueib 2005), and it has been used in photocatalytic applications, combined with TiO\(_2\) (Wang et al. 2011). However, only few studies have investigated the
use of fly ash as a catalyst under ultrasonic irradiation, despite its ability to enhance significantly the sonodegradation of acid orange 7 (Li et al. 2016). This suggests that fly ash may have the potential to enhance the removal of pharmaceutical compounds, such as IBP and SMX, under different frequency and pH conditions.

Thus, the objectives of this study were to evaluate the removal of IBP and SMX at different US frequency and pH conditions in the presence and absence of fly ash. Reactions were carried out as a function of frequency (28, 580, and 1000 kHz) and pH (3.5, 7, and 9.5) at a fixed power (0.18 W mL⁻¹) and temperature (15°C). The contribution of this work was to investigate an alternative low-cost catalyst (fly ash) that may enhance the removal of IBP and SMX. Two hypotheses were tested. First, fly ash should enhance the removal of IBP and SMX, due to the increased production of OH⁻ radicals (a strong oxidant). This is presumably because fly ash contains sufficient amounts of Al₂O₃ and SiO₂ that can react with the hydrogen peroxide and generate OH⁻ radicals. Second, US irradiation should enhance the adsorption activities of fly ash due to the dispersion resulting from the harsh conditions provided by US irradiation. This would be expected to lead to an increase in the adsorption sites on fly ash particles.

6.2. Materials and methods

6.2.1. Chemicals and fly ashes

Table 4.1 lists the characteristics of the selected target chemicals (IBP and SMX) from the SRC PhysProp database (SRC 2006). All chemicals were used as received with no further purification. High-purity IBP (C₁₃H₁₈O₂, > 98%), SMX (C₁₀H₁₁N₃O₃S, > 98%), potassium hydrogen phthalate (C₈H₅KO₄, 99.95%), potassium iodide (KI, 99%), and ammonium molybdate tetrahydrate (H₂₄Mo₇N₆O₂₄·4H₂O) were purchased from Sigma-
Aldrich (St. Louis, MO, USA). Two fly ashes, Belews Creek fly ash (BFA) from a power station in North Carolina and Wateree Station fly ash (WFA) from a power station in South Carolina, were investigated. The main difference between the two sources is that the Wateree Station source was subjected to a proprietary carbon burn-out process. The carbon burn-out process has been shown to be effective and efficient in producing a consistent, high-quality fly ash (Keppeler 2001). Stock solutions of IBP, SMX, BFA, and WFA were prepared in ultrapure deionized (DI) water.

6.2.2. Apparatus

The US process was performed in a double-jacketed stainless steel reactor (L × W × H: 15 × 10 × 20 cm) with a water-cooled (Fisher Scientific Inc., Pittsburgh, PA, USA) US generator (Ultech, Dalseo, Daegu, South Korea). The sonicator provided three test frequencies: 28, 580, and 1000 kHz. The applied power in all tests was 0.18 W mL⁻¹. Because BFA and WFA were used as catalysts, an optimum dose was determined based on H₂O₂ production at different fly ash dosages and frequencies. Adsorption experiments with the adsorbents (BFA and WFA) and adsorbates (IBP and SMX) were performed for 60 min, in a batch reactor with no US irradiation. BFA and WFA were hydrated for 24 h in DI water and stirred with a magnetic stirrer at 600 rpm prior to being added to the reactor vessel. The initial stock solution was 1000 mL, which was used in all experiments (US only, US with BFA/WFA, and the adsorption experiments). Samples were taken periodically and filtered through 0.22-μm glass microfiber filters to preserve uniformity and to eliminate larger fly ash particles that might interfere with the measurements.
6.2.3. Analysis

IBP and SMX concentrations before and after treatment were measured using high-performance liquid chromatography (HPLC, 1200 series; Agilent Technologies, Santa Clara, CA, USA). The mobile phase was a 40%:60% mixture of deionized water:acetonitrile for IBP and a 50%:50% deionized water:acetonitrile for SMX. Separation was achieved with a LiChrosorb RP-18 analytical column (4.6 mm × 100 mm i.d., 5 µm particles, Atlantis; Waters, Milford, MA, USA) with a 100-µL sample loop at a flow rate of 1.0 mL min⁻¹ for IBP and 0.75 mL min⁻¹ for SMX. The wavelength used to detect the compounds was 210 nm. The KI dosimetry method was used to determine the H₂O₂ concentration, as an indicator of OH⁺ free radicals in the system (Kormann, Bahnemann, and Hoffmann 1988), using a 350-nm wavelength and an ultraviolet-visible (UV-Vis) spectrophotometer (Agilent Technologies, Santa Clara, CA, USA). The elemental composition of BFA and WFA fly ash was determined by X-ray florescence (XRF) using fused bead analysis at the Holcim Inc. laboratory in Holly Hill, SC, USA.

6.3. Results and discussion

6.3.1. Dose optimization and characterization of BFA and WFA

Determining the optimum dose of fly ash is important in comparing the efficiency of BFA and WFA under US irradiation. The optimum dose was determined based on the H₂O₂ produced under irradiation; as a rule, the amount of H₂O₂ increases with the amount of OH⁺ radicals. Thus, H₂O₂ was measured as an indicator of OH⁺ radicals in the system (Nakui et al. 2007). Previous studies showed that the presence of solid surfaces can improve the sonodegradation of contaminants by increasing the formation rate of cavitation bubbles; the presence of solid particle in solution provides a nucleation site due
to surface roughness, leading to increased generation of OH\(^\cdot\) radicals in the system (Al-Hamadani et al. 2016; Chen et al. 2016). The optimum values of various doses (0, 5, 15, and 45 mg L\(^{-1}\)) of BFA and WFA were investigated at three frequencies (28, 580, and 1000 kHz) at pH 7, as shown in Fig. 6.1. The results clearly indicated that the maximum production rate of H\(_2\)O\(_2\) was achieved at 45 mg L\(^{-1}\) at all frequencies for both BFA and WFA. However, WFA showed higher H\(_2\)O\(_2\) production than BFA due to differences in the chemical properties between the fly ashes.

The elemental composition of BFA and WFA is summarized in Table 6.1. SiO\(_2\) was a major component in both fly ashes. SiO\(_2\) is also a main component of glass beads, which have been shown in previous studies to be effective in increasing the generation of OH\(^\cdot\) radicals in US processes (Nakai and Shirataki 2016; Al-Hamadani et al. 2016; Her, Park, and Yoon 2011a). The presence of Al\(_2\)O\(_3\) can also increase OH\(^\cdot\) because (i) the oxide would bind OH\(^\cdot\) radicals and thereby decrease the formation of H\(_2\)O\(_2\) and (ii) both SiO\(_2\) and Al\(_2\)O\(_3\) can react with the H\(_2\)O\(_2\) produced due to the sonication, and reproduce OH\(^\cdot\) radicals (ROTH, HIROKI, and LAVERNE 2011; Giamello et al. 1990). A third major constituent in the selected fly ashes was Fe\(_2\)O\(_3\). Fe\(_2\)O\(_3\) can also enhance the production of OH\(^\cdot\) radicals in an aqueous system by reaction with the H\(_2\)O\(_2\) produced; this in turn allows OH\(^\cdot\) to reform, leading to enhanced oxidation activity as described in Eqs. (6.1–3) (Nakui et al. 2009):

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\cdot + OH^- \quad (6.1)
\]

\[
Fe^{3+} + H_2O_2 \rightarrow Fe - O_2H^{2+} + H^+ \quad (6.2)
\]

\[
Fe - O_2H^{2+} \rightarrow Fe^{2+} + OOH^\cdot \quad (6.3)
\]
The decomposition of $\text{H}_2\text{O}_2$ in the presence of fly ash containing metal oxides can be described by the Haber-Weiss mechanism (Lin and Gurol 1998). In the Haber-Weiss

![Graph](image)

**Fig. 6.1** Effect of ultrasonic frequency on $\text{H}_2\text{O}_2$ production in the presence of BFA and WFA: (a) BFA at 28 kHz, (b) BFA at 580 kHz, (c) BFA at 1000 kHz, (d) WFA at 28 kHz, (e) WFA at 580 kHz, and (f) WFA at 1000 kHz at pH 7.
Table 6.1 XRF chemical composition analysis of BFA and WFA.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical formula</th>
<th>BFA wt.%</th>
<th>WFA wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon dioxide</td>
<td>SiO₂</td>
<td>48.9</td>
<td>58.4</td>
</tr>
<tr>
<td>Aluminum oxide</td>
<td>Al₂O₃</td>
<td>20.9</td>
<td>22.4</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>Fe₂O₃</td>
<td>6.9</td>
<td>6.6</td>
</tr>
<tr>
<td>Calcium oxide</td>
<td>CaO</td>
<td>3.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>MgO</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Sulfur trioxide</td>
<td>SO₃</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Sodium dioxide</td>
<td>Na₂O</td>
<td>5.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Potassium oxide</td>
<td>K₂O</td>
<td>2.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Total alkali</td>
<td>---</td>
<td>8.7</td>
<td>5.5</td>
</tr>
<tr>
<td>Diphosphorus pentoxide</td>
<td>P₂O₅</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>TiO₂</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Manganese oxide</td>
<td>MnO₂</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

mechanism, the principal role of H₂O₂ is the oxidation of the metal surface, which leads to the formation of hydroxyl radicals as described in Eq.6.4,

\[
S + H₂O₂ → S^+ + OH^+ + OH^− \tag{6.4}
\]

where S represents the uncharged metal surface (Weiss 1952).

Thus, Fe₂O₃ has the potential to produce more OH’ radicals by reacting with the H₂O₂ formed, leading to enhanced sonodegradation of the compounds. The remaining constituents in the fly ashes were not considered due to their trace amounts and their presumably minor or negligible effects on sonodegradation. Taken together, our results showed that WFA contained more SiO₂ than BFA (Table 6.1), which increased the production of OH’ radicals.
Because the fly ash consists of a wide range of particles sizes, it was important to define the particle size distributions of BFA and WFA (Fig. 6.2). WFA contained finer particles than BFA; the average particles size for BFA and WFA were 21.3 and 15.2 µm, respectively, indicating an average particle size difference of 29%. This could be responsible for the adsorption behavior of the fly ashes because smaller particles have more surface area and adsorption capacity for IBP and SMX.

![Particle size distribution of BFA and WFA](image)

**Fig. 6.2** Particle size distribution of BFA and WFA.

### 6.3.2. Effects of frequency and pH on IBP and SXM removal and H₂O₂ production

In the sonodegradation process, there are two important factors, frequency and pH, along with the physicochemical properties of the compounds, which play major roles in the degradation of contaminants. Fig. 6.3 shows the degradation of IBP and SMX at the three frequencies and three pH conditions (pH 3.5, 7, and 9.5). The concentration decrease followed a pseudo first-order kinetic law, and the removal of IBP was the
Fig. 6.3 Effect of ultrasonic frequency and pH on IBP and SMX removal; (a) IBP at pH 3.5, (b) IBP at pH 7, (c) IBP at pH 9.5, (d) SMX at pH 3.5, (e) SMX at pH 7, and (d) SMX at pH 9.5.

highest at 580 kHz (>99% at 30 min, >99% at 55 min, and 95% at 60 min at pH 3.5, 7, and 9.5, respectively) followed by 1000 kHz (98%, 77%, and 62% at pH 3.5, 7, and 9.5, respectively) at 60 min, and the significantly lower removal was obtained at 28 kHz.
(56%, 33%, and 22% at pH 3.5, 7, and 9.5, respectively) at 60 min. SMX removal showed a similar trend where maximum removal was obtained at 580 kHz (>99%, 90%, and 76% at pH 3.5, 7, and 9.5, respectively) at 60 min, followed by 1000 kHz (92%, 70%, and 47% at pH 3.5, 7, and 9.5, respectively) and 28 kHz (43%, 21%, and 19% at pH 3.5, 7, and 9.5, respectively) at 60 min.

The main factors at the different frequencies were the number of cavitation bubbles, bubble size, the cavitation threshold, and the lifetime of the bubbles before collapsing (Chiha et al. 2011; Al-Hamadani et al. 2016). At 28 kHz, fewer cavitation bubbles were produced, the growth period to collapse was high, and large bubbles formed (Balachandran et al. 2016); thus, fewer OH$^-$ free radicals were produced, leading to less degradation of IBP and SMX, due to the reduction in the oxidation activity in the system. In contrast, at higher frequencies, 580 and 1000 kHz, the number of cavitation bubbles increased and the lifetime of the bubbles to collapse decreased. Thus, free radicals tended to move quickly towards the bulk liquid (Im et al. 2014; Balachandran et al. 2016), reducing the possibility of OH$^-$ recombination and formation of H$_2$O$_2$; this resulted in increased removal of IBP and SMX (Park, Her, and Yoon 2011a). However, a lower degradation rate was achieved at 1000 kHz than 580 kHz, because the very high frequency would cause adverse effects such small cavitation bubbles formed, extremely short lifetime, and too low collapse for sufficient sonodegradation of the IBP and SMX (Güyer and Ince 2011; Pétrier and Francony 1997). Previous studies have shown similar trends confirming an optimal frequency of 300 kHz among ultrasound frequencies tested from 192 to 960 kHz (Petrier et al. 1992); Guyer and Nince found that the highest removal of diclofenac was achieved at 861 kHz, compared with 577 and 1145 kHz.
(Güyer and Ince 2011); and Im et al. found the degradation of acetaminophen and naproxen was maximal at 580 kHz, in comparison with 28 and 1000 kHz (Im et al. 2014).

The results and explanation above were also confirmed by evaluating the generation of H$_2$O$_2$ at the three frequencies with IBP and SMX (Fig. 6.4). Maximum H$_2$O$_2$ production was obtained at 580 kHz, followed by 1000 and 28 kHz. This supports the effects of the frequency on the degradation of IBP and SMX. The H$_2$O$_2$ concentrations were higher with SMX than IBP due to their physicochemical properties (Table 4.1). As shown in Table 4.1, IBP has more hydrophobic and less soluble properties (log Kow 3.84 and 0.049 g L$^{-1}$, respectively) than SMX (log Kow 0.79 and 0.5 g L$^{-1}$, respectively) as well as different pK$_a$ values (4.52 and 5.81 for IBP and SMX, respectively), which have combined effects on sonodegradation activity. Therefore, IBP had a tendency to consume more OH’ radicals than SMX from the system, leading to more degradation of IBP than SMX, resulting in more recombination of OH’ radicals to form H$_2$O$_2$. (Park, Her, and Yoon 2011a).

The second important factor influencing sonodegradation is the pH. Three pH values (3.5, 7, and 9.5) were investigated with the three frequencies to better understand the sonodegradation of IBP and SMX at a fixed power (0.18 W mL$^{-1}$). The removal of both IBP and SMX was highest under acidic conditions, pH 3.5, and it decreased at pH 7 and pH 9.5 (Fig. 6.3). The degradation of IBP and SMX decreased as pH increased because the physicochemical properties of the compounds would put them in their molecular forms when the pH was lower than the pK$_a$ values, while above the pK$_a$ values, they would be in ionic forms (Im et al. 2013a). The higher degradation of IBP and SMX under acidic conditions and US is because IBP and SMX, in their molecular forms, tend
to accumulate at the boundary of the cavitation bubbles where the concentration of OH’ radicals is maximal. In contrast, in their ionic forms, when the pH is higher than their pKₐ values, the compounds tend to move towards the bulk zone where the OH’ concentration is lower (Méndez-Arríaga et al. 2008; Soltani, Safari, and Mashayekhi 2016). Thus, under acidic conditions, more degradation of IBP and SMX was achieved because the reaction between the OH’ radicals and the IBP/SMX occurred in a zone with a higher density of OH’ radicals at the boundary of the cavitation bubbles and less under alkaline conditions because the reaction occurred in the bulk liquid zone, where fewer OH’ radicals are found.

The production of H₂O₂ was assessed at the selected pH values. Clearly, Fig. 6.4 shows that the generation of H₂O₂ followed a trend opposite to that of the degradation of IBP and SMX, in which the maximum H₂O₂ was produced at pH 9.5, followed by pH 7 and pH 3.5. This is because at low pH, the OH’ free radicals have a tendency to attach and react with IBP and SMX more than recombining to produce H₂O₂, and thus more degradation and less H₂O₂ were achieved than at higher pH conditions (Park, Her, and Yoon 2011a; Im et al. 2013a). In addition, in the absence of IBP and SMX, the production of H₂O₂ followed the order of 580 kHz > 1000 kHz > 28 kHz and pH 9.5 > pH 7 > pH 3.5 as shown in Fig. 6.5. The maximum H₂O₂ generated was achieved at 580 kHz (170 µM at pH 3.5, 211 µM at pH 7, and 232 µM at pH 9.5) followed by 1000 kHz (63 µM at pH 3.5, 81 µM at pH 7, and 105 µM at pH 9.5) and lowest H₂O₂ production was obtained at 28 kHz (12 µM at pH 3.5, 17 µM at pH 7, and 21 µM at pH 9.5).
**Fig. 6.4** Effect of ultrasonic frequency and pH on H$_2$O$_2$ production in the presence of IBP and SMX; (a) IBP at pH 3.5, (b) IBP at pH 7, (c) IBP at pH 9.5, (d) SMX at pH 3.5, (e) SMX at pH 7, and (f) SMX at pH 9.5.
6.3.3. Effects of frequency and pH on IBP and SMX removal in the presence of fly ash

The effect of the two types of fly ash, BFA and WFA, were investigated to estimate the enhancement of the sonodegradation of IBP and SMX under various ultrasound frequencies and pH conditions. Figs. 6.6 and 6.7 show the removal of IBP and SMX in the presence of BFA and WFA, respectively. As shown in both figures, the removal of IBP and SMX was enhanced significantly compared with the results in Fig. 6.3, which were obtained in the absence of fly ash. Several studies have linked sonochemical enhancement with the presence of different catalysts, including TiO₂, CNTs, quartz, glass beads, and Al₂O₃ (Morosini et al. 2016; Al-Hamadani et al. 2016; Pang, Abdullah, and Bhatia 2011b). Previous research has shown that the presence of solid surfaces in the system promotes an increase in the number of cavitation bubbles, resulting in enhanced sonodegradation. This occurs because surface roughness has a tendency to increase the local temperature of cavitation bubbles, leading to increased water pyrolysis, thus, generating more OH⁻, and redistributing the US irradiation field. In turn, the cavitation active volume increases, thus, decreasing the threshold energy for the bubbles to collapse (Iida et al. 2004; Al-Hamadani et al. 2016; Zhao et al. 2016). Generally, there are three reasons for the removal enhancement of IBP and SMX in the presence of fly ash: (i) sonochemical enhancement, due to the presence of solid surfaces that can increase the cavitation bubble production due to the surface roughness, (ii) due to the presence of metal oxides on the fly ash which can react with H₂O₂ to reproduce OH⁻, and (iii) adsorption enhancement, due to fly ash dispersion, which increases the adsorption sites. Sonochemical improvement may occur due to the following: the
presence of fly ash particles, which increases the number of cavitation bubbles, and bubble nucleation due to entrapped gas or impurities on particle surfaces, surface reactivity of the particles, or the surface steadiness of the bubbles at the boundary; all could cause the collapse of cavitation bubbles (Morosini et al. 2016; Lousada et al. 2013; Huo et al. 2010). Thus, the sonochemical degradation of IBP and SMX would be enhanced due to the presence of fly ash solid particles. Second, as shown in Table 1, the fly ash consists of many oxides that can react specifically with the H$_2$O$_2$ produced to regenerate the strong oxidant, OH$^\cdot$. As a result the degradation of IBP and SMX improves due to an increase in the oxidation process (Lousada et al. 2013; Morosini et al. 2016). In this, catalytic decomposition is one of possible main reactions between H$_2$O$_2$ and oxides (Hiroki and LaVerne 2005). Catalytic decomposition is important to understand in terms of the reasons for enhanced sonodegradation.

In catalytic decomposition, the H$_2$O$_2$ would be dissociated and form radical species that can bind to the surfaces where H$_2$O$_2$ undergoes decomposition; the radicals generated are stabilized by forming attachment states between the unpaired electron and the oxide surface (Hiroki and LaVerne 2005; Morosini et al. 2016; Lousada et al. 2013). The two main compounds in BFA and WFA are SiO$_2$ and Al$_2$O$_3$; SiO$_2$ and Al$_2$O$_3$ played major roles in this enhancement by dissociating the H$_2$O$_2$ produced via ultrasonication and regeneration of OH$^\cdot$ radicals, which are responsible for the removal of IBP and SMX (Hiroki and LaVerne 2005).
Fig. 6.5 Effect of ultrasonic frequency and pH on $\text{H}_2\text{O}_2$ production at (a) pH 3.5, (b) pH 7, and (c) pH 9.5.
Fig. 6.6 Effect of ultrasonic frequency and pH on IBP and SMX removal in the presence of BFA (45 mg L\(^{-1}\)): (a) IBP at pH 3.5, (b) IBP at pH 7, (c) IBP at pH 9.5, (d) SMX at pH 3.5, (e) SMX at pH 7, and (d) SMX at pH 9.5.
Fig. 6.7 Effect of ultrasonic frequency and pH on IBP and SMX removal in the presence of WFA (45 mg L$^{-1}$): (a) IBP at pH 3.5, (b) IBP at pH 7, (c) IBP at pH 9.5, (d) SMX at pH 3.5, (e) SMX at pH 7, and (f) SMX at pH 9.5.
The adsorption enhancement from the adsorption activity of the fly ash with the IBP and SMX is assumed to be enhanced by the US process. It is known that US irradiation is one of the best methods to disperse and stabilize adsorbents, leading to an increase in adsorption sites and consequently enhanced adsorption of IBP and SMX (Al-Hamadani et al. 2015). Under US irradiation, the fly ash particles would be expected to be dispersed because the collapse of cavities creates high temperatures, causes pressure differences, and imparts shear forces on particle surfaces; thus, more adsorption sites are created (Al-Hamadani et al. 2015; Wang, Boyjoo, and Choueib 2005). Accordingly, the removal of IBP and SMX was higher in the presence of WFA than BFA in the adsorption reaction. This is because WFA had finer particles than BFA (Fig. 6.2), providing more adsorption sites, which could be the main reason for the difference in removal between them.

As shown in Figs. 6.6 and 6.7, the removal of IBP and SMX in the presence of fly ash alone followed the order of pH 3.5 > pH 7 > pH 9.5 for both fly ashes. This is due to the physicochemical properties of IBP and SMX (Table 1S). The maximum hydrophobicity level was achieved when the pH value was lower than the pKₐ of the compounds (Grassi et al. 2012), as previously discussed. Consequently, the removal of IBP in all reactions was higher than SMX, due to the differences in physicochemical properties; particularly, IBP has a higher hydrophobicity and lower solubility than SMX (Al-Hamadani et al. 2016). A higher hydrophobicity indicates higher sorption affinity to the adsorbent (fly ash) (Nakui et al. 2009). The results here were consistent with previous studies of sonocatalytical degradation using fly ash, such as that by Li et al. (2016), who reported significant enhancement of acid orange 7 degradation using fly ash and
ultrasonication (Li et al. 2016). Li et al. (2015) compared the effects of different minerals in fly ash on the production of OH⁻ radicals (Li et al. 2015), and Hiroyuki et al. (2009) studied sonochemical and adsorption enhancement of hydrazine using coal ash (Nakui et al. 2009).

6.3.4 Evaluation of synergistic indices of the fly ashes under different frequency and pH conditions

The results of this study were summarized and analyzed by evaluating synergism in each reaction, to help in understanding the effects of frequency, pH, and fly ash as a catalyst under a US system. Table 6.2 provides a comprehensive evaluation and comparison on the effect of the three frequencies (28, 580, 1000 kHz), the three pH conditions (3.5, 7, 9.5), and the presence or absence of BFA and WFA on the removal of IBP and SMX.

The synergistic indices of each process were determined from normalized differences between the rates constants obtained from the combined effects or process divided by the sum of the rate constants of the processes individually, as shown in Eqs. (6.5) and (6.6), adopted from (Madhavan et al. 2010):

\[
\text{Synergy index I} = \frac{k_1 (\text{US+BFA})}{k_1 (\text{US})+k_1 (\text{BFA})} \tag{6.5}
\]

\[
\text{Synergy index II} = \frac{k_1 (\text{US+WFA})}{k_1 (\text{US})+k_1 (\text{WFA})} \tag{6.6}
\]

where \(k_1\) is the pseudo-first order reaction rate, ‘US’ indicates the US effect alone with no catalyst, ‘BFA’ the adsorption effect of BFA alone, with no US effect, and ‘WFA’ is the adsorption effect of WFA alone, with no US effect. Synergy index I evaluates the removal efficiency in the presence of BFA on the removal of IBP and SMX, while
synergy index II evaluates the removal efficiency in the presence of WFA. A synergy index > 1 indicates that the combined reactions (i.e., US+BFW; US+WFA) process exceeds the sum of the individual reactions (i.e., US alone; BFA and WFA alone). As shown in Table 6.2, the synergy indices II (in the presence of WFA) were always greater than 1 and higher than those of synergy indices I (in the presence of BFA). This indicates that WFA had better ability to remove the selected pharmaceuticals compounds (IBP and SMX). As explained earlier, (i) WFA contains more SiO$_2$ (Table 6.1), which can enhance the generation of OH$^-$ radicals in the system, leading to increased oxidizing of IBP and SMX; and (ii) the particle size distribution (Fig. 6.2) showed that WFA had more particles with smaller sizes than BFA; therefore, WFA had a higher specific surface area and more adsorption sites than BFA, leading to an increase in the adsorption capacity for IBP/SMX on the WFA surface.

6.4 Conclusions

In this study, the removal of IBP and SMX in the absence and presence of two fly ashes (BFA and WFA) was conducted at three frequencies (28, 580, 1000 kHz) and three pH values (3.5, 7, 9.5) with fixed conditions of power (0.18 W mL$^{-1}$), temperature (15°C), and contact time (60 min). The removal trends for IBP and SMX followed a pseudo first-order kinetic law in all reactions. The removal of IBP and SMX was enhanced significantly in the presence of fly ash under all conditions tested.
Table 6.2. Determination of the pseudo-first order ($k_1$) removal rate constants, coefficient of determination ($R^2$), and synergistic index values for all the reactions.

<table>
<thead>
<tr>
<th>Process</th>
<th>pH 3.5</th>
<th></th>
<th></th>
<th></th>
<th>pH 7</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>IBP</td>
<td>SMX</td>
<td></td>
<td>US only</td>
<td>IBP</td>
<td>SMX</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_1$</td>
<td>$R^2$</td>
<td>$k_1$</td>
<td>$R^2$</td>
<td>$k_1$</td>
<td>$R^2$</td>
<td>$k_1$</td>
</tr>
<tr>
<td>Frequency</td>
<td>28 kHz</td>
<td>580 kHz</td>
<td>1000 kHz</td>
<td>28 kHz</td>
<td>580 kHz</td>
<td>1000 kHz</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_1$</td>
<td>$R^2$</td>
<td>$k_1$</td>
<td>$R^2$</td>
<td>$k_1$</td>
<td>$R^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>US only</td>
<td>0.527</td>
<td>0.943</td>
<td>4.37</td>
<td>0.977</td>
<td>2.28</td>
<td>0.945</td>
<td>0.360</td>
<td>0.964</td>
</tr>
<tr>
<td>BFA w/US</td>
<td>2.01</td>
<td>0.997</td>
<td>5.81</td>
<td>0.995</td>
<td>4.10</td>
<td>0.990</td>
<td>0.814</td>
<td>0.974</td>
</tr>
<tr>
<td>WFA w/US</td>
<td>5.28</td>
<td>0.996</td>
<td>10.3</td>
<td>0.999</td>
<td>8.34</td>
<td>0.998</td>
<td>2.01</td>
<td>0.907</td>
</tr>
<tr>
<td>BFA w/o US</td>
<td>0.604</td>
<td>0.963</td>
<td></td>
<td></td>
<td>0.450</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WFA w/o US</td>
<td>1.23</td>
<td>0.615</td>
<td></td>
<td></td>
<td>0.633</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synergy index I (BFA)</td>
<td>1.78</td>
<td>1.31</td>
<td>1.42</td>
<td>1.01</td>
<td>1.42</td>
<td>1.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synergy index II (WFA)</td>
<td>3.01</td>
<td>1.84</td>
<td>2.38</td>
<td>2.01</td>
<td>2.06</td>
<td>1.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 7</td>
<td>US only</td>
<td>0.299</td>
<td>0.996</td>
<td>3.18</td>
<td>0.993</td>
<td>1.10</td>
<td>0.962</td>
<td>0.218</td>
</tr>
<tr>
<td></td>
<td>$k_1$</td>
<td>$R^2$</td>
<td>$k_1$</td>
<td>$R^2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BFA w/US</td>
<td>1.01</td>
<td>0.935</td>
<td>4.88</td>
<td>0.995</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WFA w/US</td>
<td>2.81</td>
<td>0.972</td>
<td>6.20</td>
<td>0.996</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BFA w/o US</td>
<td>0.497</td>
<td>0.984</td>
<td>0.327</td>
<td>0.986</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WFA w/o US</td>
<td>0.926</td>
<td>0.685</td>
<td>0.502</td>
<td>0.976</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

|                |       |       |       |       |
| Synergy index I| 1.27  | 1.33  | 1.37  | 1.01  |
| (BFA)          |       |       |       | 1.35  |
| Synergy index II| 2.29| 1.51  | 2.36  | 1.71  |
| (WFA)          |       |       |       | 2.02  |

| pH 9.5 |
|----------------|------|------|------|------|
| US only     | 0.280| 0.938| 2.19 | 0.992|
| BFA w/US   | 0.875| 0.920| 2.60 | 0.984|
| WFA w/US   | 1.86 | 0.981| 3.03 | 0.982|
| BFA w/o US | 0.340| 0.987| 0.249| 0.970|
| WFA w/o US | 0.599| 0.720| 0.335| 0.985|

|                |       |       |       |       |       |
| Synergy index I| 1.41  | 1.03  | 1.48  | 0.942 | 1.04  |
|                |       |       |       |       | 1.23  |
| Synergy index II (WFA) | 2.12 | 1.09 | 1.86 | 1.44 | 1.55 | 1.49 |
The ‘best’ results for the removal of IBP and SMX were obtained at 580 kHz in the presence of WFA. The removal enhancement could be presumably achieved because (i) the presence of solid surfaces (fly ash) can increase the production of OH\(^-\) radicals, increasing the reactions between OH\(^-\) and IBP and SMX; (ii) the presence of certain oxides such as SiO\(_2\), Al\(_2\)O\(_3\), and Fe\(_2\)O\(_3\) can enhance the oxidation process, because they can react with the H\(_2\)O\(_2\) produced from the ultrasonication and regenerate OH\(^-\) radicals, leading to increased oxidation activity; and (iii) ultrasonic irradiation can disperse the fly ash, which reduces the effective particle size and leads to an increase in the surface area of the fly ash, enhancing adsorption activity.

**Acknowledgments**

This research was supported by a Grant (code 17IFIP-B088091-04) from Industrial Facilities & Infrastructure Research Program funded by Ministry of Land, Infrastructure and Transport of Korean government. The authors also thank Holcim Inc. (Mr. Eddie Deaver) for their donation of fly ash samples.
CHAPTER 7

OVERALL CONCLUSIONS

In conclusion, this study evaluated the effect of ultrasonication treatment to remove selected pharmaceutical compounds (IBP and SMX) under different frequency, pH, temperature, and power condition. Also, evaluate various types of catalysts such as single-walled carbon nanotube, glass beads, and two types of fly ashes.

Carbon nano material dispersion and stabilization

Enhanced dispersion and stabilization of CNMs in water greatly improves their physicochemical properties. Thus, a critical challenge is the development of methods to promote and increase the dispersion and stabilization of CNMs in water. This review summarizes the dispersion and stabilization of target CNMs (CNTs, GOs, fullerenes) under different water quality conditions and in the presence of various dispersing agents. While dispersion degree depends on the dispersing agent, generally, CNMs aggregate more at low pHs, due mainly to relatively less negative charge under those conditions. The dispersion of CNMs can also be influenced significantly by the presence of background ions in water. CNM aggregation increases with increasing ionic strength. However, once ionic strength becomes high, no additional increases in aggregation occur, indicating that electrostatic repulsive forces are successfully shielded. CNM stability increases with increasing temperature, presumably due to disruption of weak interaction forces, increased Brownian motion/collisions, and decreased zeta potential.
Among various natural and synthetic dispersing agents, NOM has been studied widely. The stability and dispersion of CNMs is significantly enhanced in water bodies with NOM, because, for example, the hydrophobic surfaces of CNMs facilitate their interaction with NOM, which is abundant in the environment. Surfactants also enhance the stabilization of CNMs in water through their adsorption. Typically, CNMs are dispersed due to hydrophobic and π-π interactions between the surfactants and CNMs, which are the dominant mechanism of their adsorption. For ionic surfactants, dispersions of CNMs are stabilized by electrostatic repulsion between the hydrophilic head groups, and both cationic and anionic surfactants are able to sufficiently disperse CNMs, with neither showing superiority. Ultrasonication significantly enhances the dispersion and stabilization of CNMs, presumably due to the implosion of cavities creating high temperatures that cause pressure differences, and impart shear forces on CNM surfaces. The modified CNMs associated with dispersion and stabilization can enhance the sorption capacity for the removal of EDCs and PPCPs in water and waste-water treatment.

While there are many studies on dispersion and stabilization of CNMs in water, many further data are required to understand the relevance of natural and synthetic dispersing agents in water and how these agents enhance the dispersion and stabilization of CNMs under different water quality conditions. It is also important to gain information as to the toxicological impact of CNMs in water, because CNMs can be introduced into the natural water environment. Standardized analytical methods for detection of various CNMs that can be found in water in the near future are important. Development of appropriate analytical methods can provide tools to understand the fate and transport of
these CNMs in the environment. To adopt CNMs in water and waste-water treatment, much is still unknown as to the transport of inorganic and organic contaminants in CNMs. Thus, many additional data are required to better understand contaminant removal by CNMs in water. In addition, while CNMs have shown potential as superior sorbents to remove selected contaminants from aqueous solution, their relatively high unit cost currently limits their practical use.

**Sonocatalytical degradation of IBP and SMX in the absence and presence of SWNTs**

Sonocatalytical degradation of two target PhACs (IBP and SMX) having different physicochemical properties was carried out in the absence and presence of SWNTs at a frequency of 1000 kHz. While the degradation of IBP and SMX depended on temperature and pH, the maximum degradation efficiencies of IBP and SMX were achieved under optimum pH of 3.5 and temperature 35°C in the absence of SWNTs. However, the removal of IBP and SMX was enhanced when SWNTs were added to the system. Higher removal was obtained under US/SWNT than the sum of those obtained under SWNTs and US- only reactions. The role of SWNTs in this study approved our hypothesis referring to the enhancement of the oxidation and adsorption activities when SWNTs are added to the system due to the dispersion of SWNTs under US irradiation. In addition, \( \text{H}_2\text{O}_2 \) formation significantly increased in the presence of SWNTs, indicating that the SWNTs dispersed particles performed as additional nuclei for the pyrolysis of water molecules and formation of \( \text{OH}^- \). Higher removal of IBP was achieved than that of SMX under US reaction, SWNTs adsorption, and US/SWNTs reactions due to their chemical properties. Furthermore, results of DFT-D calculations were consistent with the
experimental results and provided insight on the adsorption of IBP and SMX onto SWNTs in aqueous system at different pH levels.

**Sonocatalytical enhancement in the absence and presence of two catalysts (GBs and SWNTs) IBP and SMX removal**

The effects of the absence and presence of two catalysts (GBs and SWNTs) on the sonocatalytic degradation of IBP and SMX were studied at low and high ultrasound frequencies. One of the main factors in sonochemical degradation is the power intensity; maximum degradation of IBP and SMX was obtained at a power intensity of 0.18 W mL\(^{-1}\). In the absence of catalysts, the removals of IBP and SMX were higher at a high frequency than at a low frequency, because more OH\(^-\) radicals were generated at 1000 kHz than at 28 kHz due to the increase in water molecule pyrolysis as a result of the ultrasound irradiation. The removals of IBP and SMX were enhanced significantly in the presence of GBs at the low frequency (28 kHz), whereas they were significantly reduced at high frequency (1000 kHz), because the GB particle size was similar to or larger than the cavitation bubbles at the high frequency, leading to interference between the US wavelengths and GB particles resulting in a reduction in H\(_2\)O\(_2\) production. Additionally, the presence of SWNTs was effective under low and high frequencies in both the sonochemical degradation mechanism and adsorption mechanism, because the dispersed SWNT particles acted as additional nuclei for the pyrolysis of water molecules and the formation of more OH\(^-\). Also, the dispersion of SWNTs, due to sonication, enhanced the adsorption process by providing more adsorption sites, leading to increased adsorption capacity. However, maximum removals of IBP and SMX were achieved at both frequencies when GBs and SWNTs were combined, as a result of the enhanced
sonochemical degradation with OH• formation, in addition to the adsorption process resulting from SWNT dispersion. IBP was more affected than SMX under all reactions; this was attributed to the physiochemical properties of IBP and SMX. The addition of CCl₄ and MeOH scavengers demonstrated that the major removal mechanisms were due to interactions between OH• and the PhACs.

The removal of IBP and SMX in the absence and presence of two fly ashes (BFA and WFA)

In this study, the removal of IBP and SMX in the absence and presence of two fly ashes (BFA and WFA) was conducted at three frequencies (28, 580, 1000 kHz) and three pH values (3.5, 7, 9.5) with fixed conditions of power (0.18 W mL⁻¹), temperature (15°C), and contact time (60 min). The removal trends for IBP and SMX followed a pseudo first-order kinetic law in all reactions. The removal of IBP and SMX was enhanced significantly in the presence of fly ash under all conditions tested. The ‘best’ results for the removal of IBP and SMX were obtained at 580 kHz in the presence of WFA. The removal enhancement could be presumably achieved because (i) the presence of solid surfaces (fly ash) can increase the production of OH• radicals, increasing the reactions between OH• and IBP and SMX; (ii) the presence of certain oxides such as SiO₂, Al₂O₃, and Fe₂O₃ can enhance the oxidation process, because they can react with the H₂O₂ produced from the ultrasonication and regenerate OH• radicals, leading to increased oxidation activity; and (iii) ultrasonic irradiation can disperse the fly ash, which reduces the effective particle size and leads to an increase in the surface area of the fly ash, enhancing adsorption activity.
REFERENCES


Dhawan, A., J. S. Taurozzi, A. K. Pandey, W. Shan, S. M. Miller, S. A. Hashsham, and V. V. Tarabara. 2006. Stable colloidal dispersions of C-60 fullerenes in water:
Evidence for genotoxicity. *Environmental science & technology* 40 (23):7394-7401.


decomposition of volatile and non-volatile organic compounds—a comparative

novel sonochemical reactor with capacity of 7.5 l. Separation and Purification


GAMESS a decade later. Theory and applications of computational chemistry:
The first forty years, Dykstra, C.E., Frenking, G., Kim, K.S., Scuseria, G.E.(editors). Elsevier
Amsterdam:1167–1189.

2007. The effective fragment potential: A general method for predicting

contaminants from water and wastewater by adsorption process. In Emerging
compounds removal from wastewater, 15-37: Springer.

Grimme, S., J. Antony, S. Ehrlich, and H. Krieg. 2010. A consistent and accurate ab
initio parameterization of density functional dispersion correction (DFT-D) for

Grimme, S., S. Ehrlich, and L. Goerigk. 2011. Effect of the damping function in


Im, J.-K., J. Yoon, N. Her, J. Han, K.-D. Zoh, and Y. Yoon. 2015. Sonocatalytic-TiO₂ nanotube, Fenton, and CCl₄ reactions for enhanced oxidation, and their applications to acetaminophen and naproxen degradation. *Separation and Purification Technology* 141:1-9.


during wastewater treatment and its impact on the quality of receiving waters.


Lou, J. C., Y. S. Hsu, K. L. Hsu, M. S. Chou, and J. Y. Han. 2014. Comparing the removal of perchlorate when using single-walled carbon nanotubes (SWCNTs) or


Zhou, D., S. W. Bennett, and A. A. Keller. 2012. Increased Mobility of Metal Oxide Nanoparticles Due to Photo and Thermal Induced Disagglomeration. Plos One 7 (5).

APPENDIX A – PRINTABLE AUTHORSHIP LICENSE

Please note that, as the author of this Elsevier article, you retain the right to include it in a thesis or dissertation, provided it is not published commercially. Permission is not required, but please ensure that you reference the journal as the original source. For more information on this and on your other retained rights, please visit: https://www.elsevier.com/about/our-business/policies/copyright#Author-rights