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The Investigation of Photocatalysts and Iron Based Materials in the Oxidation and the Adsorption of Toxic Organic and Chromium Materials

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

THE INVESTIGATION OF PHOTOCATALYSTS AND IRON BASED MATERIALS
IN THE OXIDATION AND ADSORPTION OF TOXIC ORGANIC AND
CHROMIUM MATERIALS

A dissertation submitted in partial fulfillment of

the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

by

Wenjun Jiang

2013

To: Dean Kenneth G. Furton
College of Arts and Sciences

This dissertation, written by Wenjun Jiang, and entitled The Investigation of Photocatalysts and Iron Based Materials in the Oxidation and the Adsorption of Toxic Organic and Chromium Materials, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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Florida International University, 2013

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DEDICATION

I dedicate this dissertation to all my beloved mentors, my parents, Ms. Dianshi Lv and Mr. Zuoyu Jiang, my wife Min Cai, and my son Alex Jiang. Without their unconditional support and love, this dissertation could not be completed.

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ABSTRACT OF THE DISSERTATION

THE INVESTIGATION OF PHOTOCATALYSTS AND IRON BASED MATERIALS
IN THE OXIDATION AND ADSORPTION OF TOXIC ORGANIC AND
CHROMIUM MATERIALS

by

Wenjun Jiang

Florida International University, 2013

Miami, Florida

Professor Kevin E. O'Shea, Major Professor

The presences of heavy metals, organic contaminants and natural toxins in natural water bodies pose a serious threat to the environment and the health of living organisms. Therefore, there is a critical need to identify sustainable and environmentally friendly water treatment processes. In this dissertation, I focus on the fundamental studies of advanced oxidation processes and magnetic nano-materials as promising new technologies for water treatments.

Advanced oxidation processes employ reactive oxygen species (ROS) which can lead to the mineralization of a number of pollutants and toxins. The rates of formation, steady-state concentrations, and kinetic parameters of hydroxyl radical and singlet oxygen produced by various TiO_2 photocatalysts under UV or visible irradiations were measured using selective chemical probes. Hydroxyl radical is the dominant ROS, and its generation is dependent on experimental conditions. The optimal condition for generation of hydroxyl radical by of TiO_2 coated glass microspheres is studied by response surface methodology, and the optimal conditions are applied for the degradation

of dimethyl phthalate. Singlet oxygen ($^1\text{O}_2$) also plays an important role for advanced processes, so the degradation of microcystin-LR by rose bengal, an $^1\text{O}_2$ sensitizer was studied. The measured bimolecular reaction rate constant between MC-LR and $^1\text{O}_2$ is $\sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$ based on competition kinetics with furfuryl alcohol.

The typical adsorbent needs separation after the treatment, while magnetic iron oxides can be easily removed by a magnetic field. Maghemite and humic acid coated magnetite ($\text{HA-Fe}_3\text{O}_4$) were synthesized, characterized and applied for chromium(VI) removal. The adsorption of chromium(VI) by maghemite and $\text{HA-Fe}_3\text{O}_4$ follow a pseudo-second-order kinetic process. The adsorption of chromium(VI) by maghemite is accurately modeled using adsorption isotherms, and solution pH and presence of humic acid influence adsorption. Humic acid coated magnetite can adsorb and reduce chromium(VI) to non-toxic chromium (III), and the reaction is not highly dependent on solution pH. The functional groups associated with humic acid act as ligands lead to the Cr(III) complex via a coupled reduction-complexation mechanism. Extended X-ray absorption fine structure spectroscopy demonstrates the Cr(III) in the Cr-loaded $\text{HA-Fe}_3\text{O}_4$ materials has six neighboring oxygen atoms in an octahedral geometry with average bond lengths of $1.98 \text{ \AA}$.

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1 General Introduction

1.1 Global water treatment challenges

Access to clean water is a serious global problem. An estimated 22 % of the world's populations do not have the access to clean drinking water (Nordstrom, 2002). Waterborne diseases, especially in the developing countries, are widely spread through contaminated drinking water (Montgomery et al., 2007), and more than 1.5 million children die from diarrheal disease and lack of access to clean drinking water annually (Fenwick, 2006). Two-thirds of the global population will have severe water shortages in the next 10-15 years (Malmqvist et al., 2002), because the increasing level of heavy metals, organic contaminants and natural toxins introduced into natural water bodies through population growth, industrialization and anthropogenic activities (Bove et al., 2002; Olness, 1995). The consumption of contaminated water can result in both chronic and acute effects on human beings and wildlife (Berg et al., 2001; Bove et al., 1995; Chorus et al., 1999). With the demand for clean water increasing and the availability decreasing, water management is a critical challenge for sustainable drinking water supplies in the 21st century (Gatrell et al., 2009; Levine et al., 2004; Viessman et al., 2009). The identification and development of effective economic technologies for water purification is a global challenge.

1.1.1 Chromium contamination

The most problematic heavy metal contaminants include aluminum (Al), arsenic (As), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), and silver (Ag) (Nordberg et al., 2007). Heavy metals can lead to adverse biological consequences at trace levels. The cleanup of heavy metals from natural water bodies is particularly challenging because they are generally persistent under typical environmental conditions and can accumulate

in the biological systems. In addition, the toxicities of heavy metals are often highly dependent on their chemical forms and oxidation state.

Chromium, which can enter the environment through natural and industrial processes, is one of the common heavy metals and receives significant attention. The annual chromium production was approximately 13 million tons in 1999, and 140 thousand ton of Cr(VI) was produced in 1985 (Anger et al., 2000). Metal chromium(0) is primarily used in steel and other alloy industries. Chromium compounds are widely used in refractory and chemical industries, wood preservatives (Hingston et al., 2001), leather-tanning (Agrawal et al., 2006), manufacture of dyes and pigments (Wang et al., 1991), and chrome plating of metals (Barnhart, 1997b). Thus, chromium is discharged into the environment via a variety of industrial processes, and an estimated 2 million tons chromium are introduced into hydrosphere from natural sources annually (Chernousov et al., 2003).

Chromium, the first element in group 6 of the periodic table of the elements, is the 21st most abundance element in the earth's crust, and the average concentration of chromium in USA's soils is ~ 40 ppm (Barnhart, 1997a). Chromium can exist in several different oxidation states (0, +2, +3, +4, +6). A number of chromium oxides exist and they are summarized in **Table 1.1** (Bell et al., 1975; Firouzabadi et al., 1986; Jaleel et al., 1983; Richard et al., 1991; Stomberg, 1962). The metal form of chromium(0) is not found in nature, and the Cr(II) (chromous) ion is unstable in water and readily oxidized to Cr(III) in nature (Ardon et al., 1959). Cr(III) and Cr(VI) are the predominantly oxidation states observed in aqueous media. The mobility, toxicity, environmental fate and behavior of chromium are highly dependent on the oxidation state. Chromium(III) has

lower water solubility than Cr(VI) and more readily adsorbed onto solid substrates (Saliba et al., 2000; Wehrli et al., 1990; Wu et al., 2008). Chromium(III) is an essential nutrient for humans (Anderson, 1997). Chromium(III) plays an important role in glucose and protein metabolism (Morris et al., 1992) and can enhance the action of insulin (Mertz, 1993). The recommended dietary intakes of chromium is 50-200 micrograms per day for adults ("US Food Nutrition Board. Recommended Dietary Allowances", 1989). However, Cr(III) may be toxic at higher concentration (Stearns et al., 1995). Chromium(VI) is ~ 500-1000 times more toxic than Cr(III) and is a serious threat to the environment and human health. In addition, Cr(VI) is more soluble, and the more stable chemical form in oxygenated aqueous solution (Bartlett et al., 1976). The pK_{a1} and pK_{a2} of chromic acid (H_2CrO_4) are 0.74 and 6.50, respectively. Chromic acid, chromate, bichromate, hydrogen dichromate ($pK_a = 1.8$) and dichromate (as shown in **Figure 1.1**) in aqueous solution are in equilibrium. The chemical equilibrium is described by **Eqs. 1.1-1.5** (Brito et al., 1997; Hoffmann et al., 2001; Swinehart et al., 1964). The chromate and dichromate compounds are strong oxidizing agents (Bokare et al., 2010; Reitsema et al., 1962).

Table 1.1 The chromium oxides

Name	Chemical formula	Structure
chromium(II) oxide	CrO	$\text{Cr(II)}=\text{O}$
chromium(III) oxide	Cr ₂ O ₃	
chromium(IV) oxide	CrO ₂	$\text{O}=\text{Cr(IV)}=\text{O}$
chromium(VI) oxide	CrO ₃	
chromium(VI) oxide peroxide	CrO ₅

Figure 1.1 The structures of Cr(VI) species: (a) chromic acid, (b) bichromate, (c) chromate, (d) dichromate and (e) hydrogen dichromate.

The reduction of Cr(VI) to Cr(III) is critical to reduce the health risk associated with chromium contaminated water. The exposure to Cr(VI) is the main source of the acute and chronic biological effects of Cr (Gochfeld, 1991). The exposure to Cr(VI) compounds can result in carcinomas of the respiratory organs (Léonard et al., 1980; Satoh et al., 1994), mutations (Hepburn et al., 2003), and DNA damage (Peterson-Roth et al., 2005). The World Health Organization recommended maximum allowable limit for total chromium in drinking water at 50 ppb (Fowler et al., 2011).

1.1.2 The organic water contaminants

Great varieties of organic contaminants are introduced into water bodies via paper-making, pharmacy, printing and textile industries. Persistent organic pollutants (POPs), phthalate acid esters (PAEs), chlorinated hydrocarbon, pharmaceuticals and personal care products are common pollutants in drinking water sources. Estimated 4×10^8 kg of organic pesticides are used in USA annually, and $\sim 9 \times 10^8$ kg of industrial organic contaminants were discharged into atmosphere in 1989 in the USA (Simonich et al., 1995). Even in the treated water, 72 microconstituents were detected in USA (Wang et al., 2013). Organic compounds encompass diverse structural features, and some of them can pose hazardous biological activities on living organisms (Aksu, 2005).

The presence of highly toxic POPs in natural water bodies are especially problematic because they are resistant to natural degradation and can have serious biological impacts. The common sources of POPs are pesticides and pharmaceuticals compounds. Persistent organic pollutants can bioaccumulate in food chain, thus they may pose adverse effects on human health and wildlife (Jones et al., 1999). Pharmaceuticals are emerging contaminants because of their increasing use in human and

veterinary medicine. The most common pharmaceutical contaminants in environment are antibiotics, anti-inflammatory drugs, lipid regulators, steroids and related hormones, beta-blockers, cancer therapeutics, diuretics and antiepileptics (Nikolaou et al., 2007). Phthalate acid esters represent another widespread pollutant. Phthalate acid esters are used in most plastics as plasticizers and often leach into environment (Bauer et al., 1997; Stales et al., 1997). The uptake of phthalate acid esters by mice has significant effects on body weight and liver weight (Lamb Iv et al., 1987).

While POPs, pharmaceuticals and PAEs are synthetic organic compounds, there are a group of natural toxins produced by algae which also possess a serious threat to drinking water sources. The incidences of cyanobacterial blooms in freshwater bodies have increased as a result of the eutrophication and global warming (Heisler et al., 2008). The cyanobacteria are detected in various habitats, and cyanobacterial blooms become an international problem as a consequence of water eutrophication (Pelaez et al., 2010). Exposure to cyanobacterial toxins can have lethal effects on human being and wildlife. For the purpose of this dissertation, we focus on the specific family of microcystins cyanotoxin.

Microcystins are produced by cyanobacteria and pose serious chronic and acute toxic effects on human beings and animals. Microcystins are cyclic heptapeptides which have seven amino acids connected by peptide bond: γ -linked D-glutamic acid, D-alanine, β -linked D-erythro- β -methylaspartic acid, N-methyldehydroalanine and a unique C₂₀ β -amino acid, (2S, 3S, 8S, 9S), 3-amino-9-methoxy-2, 6, 8- trimethyl-10-phenyldeca-4 (E), 6(E)-dienoic acid (Adda) and two variable L-amino acids (R₁ and R₂ as shown in **Figure. 1. 2**). Adda is not toxic alone, but it is critical to the toxicity of microcystins. While

approximately 80 different variants of microcystins have been identified, microcystin-LR (MC-LR) is one of the most toxic and problematic variants. The two variable L-amino acids of MC-LR are leucine (L) and arginine (R). The lethal dose for 50 % mice of MC-LR is $\sim 50 \mu\text{g/kg}$ and World Health Organization guideline of $1 \mu\text{g/L}$ MC-LR has been adopted as the drink water standard in 1998 (WHO, 1998). The concentration of MC-LR may exceed the drinking water guideline of $1 \mu\text{g/L}$, especially during the lysis of cyanobacteria leading to the closure of specific water bodies. Although there are a number of natural processes that can contribute to the reduction of MC-LR levels in water: dilution, adsorption, thermal degradation, photolysis and biodegradation (Chen et al., 2010), specific effective water treatments are needed for the removal MC-LR.

Figure 1.2 The structure of microcystin

Table 1.2 The common microcystins variants

Name	R ₁	R ₂
MC-LR	Arginine	Leucine
MC-LA	Alanine	Leucine
MC-RR	Arginine	Arginine
MC-YR	Arginine	Tyrosine

Conventional methods are often not effective for the removal of microcystins. The degradation of MC-LR by various advanced oxidation process has been extensively studied, including TiO₂ photocatalysis (Lawton et al., 1999), ultrasound (Song et al., 2005), sulfate radical (Antoniou et al., 2010), Fenton and photo-Fenton process (Bandala et al., 2004), hydrogen peroxide enhanced process (Cornish et al., 2000) and ozone (Shawwa et al., 2001).

1.2 Innovative water treatment techniques

Because of the diversity of contaminants in water, the conventional water treatment techniques are not effective for emerging contaminants. Multistep drinking water purification systems may be effective but typically have costly high-energy requirements and/or heavy doses of chemical additives. Advanced oxidation process and iron oxide materials have distinct advantages and exhibit excellent potential for the drinking water treatment.

1.2.1 Advanced oxidation processes (AOP)

Semiconductor photocatalysis has shown tremendous promise for the environmental remediation of an extensive number of pollutants and toxins in water and air streams (Serpone et al., 2012). Titanium dioxide is a typical semiconductor

photocatalyst, since it is low-cost, readily available, and chemical stable. Photoexcitation of a semiconductor material can promote an electron from the valence band (VB) to the conduction band (CB) resulting in an electron-hole pair. In competition with recombination the electron can act as a reducing entity and the hole as an oxidizing entity. The VB and CB positions are critical to the effectiveness and economic feasibility of semiconductor photocatalytic materials for water purification. The energy difference between the VB and CB dictates the wavelength of irradiation required for photoexcitation. Large band gaps require higher energy UV irradiation, while semiconductor materials with smaller band gaps can be photoexcited with lower energy visible light irradiation (Hoffmann et al., 1995). Photoexcitation with visible light has a significant economic advantage because of the high cost associated with generating the UV light required for activating materials with large band gaps. Doping of TiO_2 materials can extend the absorbance into the visible light range, but the semiconductor photocatalytic reaction pathways initiated by UV and visible light involve significantly different processes (Choi et al., 2007). Another critical factor is the oxidation and reduction potential of the hole and electron (band position). The VB and CB positions as well as band gaps energy of a number of common semiconductor catalysts are summarized in **Figure 1.3** (Choi, 2006).

Figure 1.3 VB and CB positions, band gaps for a number of common semiconductor materials at pH 0. The energy scale is referenced by normal hydrogen electrode (NHE)

A variety of reactive oxygen species (ROS) can be produced during semiconductor photocatalysis. ROS are central to the semiconductor photocatalytic and advanced oxidative water treatment technologies (Serpone et al., 2012). Hydroxyl radical ($\bullet\text{OH}$), superoxide anion radical ($\text{O}_2^{\bullet-}$), singlet oxygen ($^1\text{O}_2$) and hydrogen peroxide (H_2O_2), can be produced (as shown in **Figure. 1. 4**) during semiconductor photocatalysis but the production and role of the different ROS are dependent on the photocatalyst, reaction conditions and target compound. Ultraviolet (UV) TiO_2 photocatalysis has been extensively studied and hydroxyl radical is generally believed to be responsible for the primary degradation of target pollutants (Buxton et al., 1988). Visible light initiated (VLA) photocatalysis typically does not possess the oxidation potential required for the direct formation of hydroxyl radical and thus superoxide anion radical and singlet oxygen appear to play important roles in the degradation processes associated with VLA photocatalysis (Hoffmann et al., 1995). Ultimately, the VB and CB positions are critical to the effective production of ROS and the economic feasibility of

semiconductor photocatalytic materials for water purification (Linsebigler et al., 1995).

Figure 1.4 Representation of ROS generation during UV TiO₂ photocatalysis

Among the ROS, $\bullet\text{OH}$ is the most powerful oxidant and primarily responsible for the degradation processes during UV photocatalysis in aqueous solution (Sun et al., 2008) and advance oxidation technologies (O'Shea et al., 2012). Hydroxyl radical reacts by addition, hydrogen and electron transfer processes with most organic compounds and many inorganic substrates often at nearly diffusion-controlled rates (Buxton et al., 1988). Singlet oxygen, superoxide anion radical, and hydrogen peroxide have lower oxidation potentials than hydroxyl radical, however these species can still lead to the remediation of a variety of pollutants and toxins. The lower oxidation of these species can lead to better selectivity, which can be advantageous for treatment of solutions containing innocuous substrates such as dissolved organic matter, which can compete for and quench hydroxyl radical. Hydrogen peroxide and singlet oxygen are generally formed as secondary oxidants but their specific impact in the UV and VLA semiconductor photocatalysis are still not clear. Singlet oxygen can be produced through a photosensitized process and

from the reduction of superoxide anion radical, while hydrogen peroxide can be generated from disproportionation of superoxide anion radical and combination of two hydroxyl radicals. Hydrogen peroxide is commonly employed for remediation through UV/H₂O₂ disinfection processes, Fenton-type reactions and Haber-Weiss reactions. O₂•⁻ can act as a oxidizing or reducing agent depending on the reactivity of the target substrate. The role of O₂•⁻ especially in VLA photocatalysis is not well understood (Li et al., 2012).

Accurate determination of ROS can be challenging because of their high reactivities, short lifetimes and the requirement for specialized equipment. Direct measurement of •OH is not feasible given the short wavelength absorbance and short lifetime. Common methods for detection and measurement of hydroxyl radical include monitoring of initial reaction products, use of trapping agents and competition kinetics (Song et al., 2009). The formation of hydroxyl radical products with absorbance from ~260-700 nm can be directly monitored by transient absorption spectroscopy and absolute rate constants can be extracted by varying the concentration of substrate. Trapping experiments and competition kinetics employ probe compounds with known hydroxyl radical selectivity and reactivities. Formic acid and t-butanol have been added as hydroxyl radical inhibitors during photocatalysis to access the role of hydroxyl radical in the observed degradation of a target compound. A decrease in the degradation upon addition of a hydroxyl radical inhibitor implies hydroxyl radical plays an important role in the degradation process. While inhibitors are effective for a qualitative assessment, trapping of hydroxyl radical can provide an accurate determination of the concentration and production rate of hydroxyl radical. Hydroxyl radical spin traps produce a spin

adducts which can be measured by electron spin resonance (ESR) spectroscopy (Fu et al., 2006; Schwarz et al., 1997). Terephthalic acid and coumarin react with hydroxyl radical to yield adducts with characteristic fluorescence (Ishibashi et al., 2000b; Louit et al., 2005). These fluorescence probes are easy to use and excellent for quantification of hydroxyl radical in a variety of systems.

Singlet oxygen is an excited state unlike the other ROS mentioned earlier. While it requires specialized equipment it is possible to measure the presence of singlet oxygen directly on the basis of phosphorescence at 1270 nm of the $^1\Delta_g$ state (Nosaka et al., 2004). Another challenge in measuring singlet oxygen during photocatalysis is its short lifetime in aqueous media. Azide, 1,4-diazabicyclo[2.2.2]octane (DABCO), and furfuryl alcohol are used to probe singlet oxygen reactions. Addition of these probes to the reaction solution will quench singlet oxygen and inhibit reactions with target substrates. The generation rate and steady-state concentration of 1O_2 can be measured by using furfuryl alcohol as a probe (Haag et al., 1986). Thus, simple addition of a singlet oxygen quencher can provide qualitative evidence for the involvement of singlet oxygen. The role of 1O_2 during photocatalysis can be probed by conducting experiments in water and in heavy water (D_2O). The lifetime of singlet oxygen in D_2O is ~ 20 times longer than in H_2O , thus singlet oxygen mediated processes are dramatically enhanced in D_2O compared to H_2O .

The production of H_2O_2 can be achieved using simple reliable colorimetric methods based on peroxidic-type reactions, i.e., the I_3^- method is based on the spectrophotometric determination of formed I_3^- , when H_2O_2 is mixed with a concentrated I^- solution. The dimerization of p-hydroxyphenyl acetic acid and enzymatic-colorimetric

method are also employed for H_2O_2 measurement (Miller et al., 1988). Catalyse has also been used to assess the involvement of hydrogen peroxide in oxidative and biological systems. The involvement of superoxide anion radical can be assessed using competition kinetics employing benzoquinone and superoxide dismutase. Electron spin resonance spectroscopy using a spin trap (Diaz-Urbe et al., 2010), a luminal chemiluminescent probe compound (Hirakawa et al., 1999), the combination of reduction of 2,3-bis (2-methoxy-4-nitro-5-sulfohenyl)-2H-tetrazolium-5-carboxanilide and superoxide dismutase method have been used to monitor the production of superoxide anion radical (Auffan et al., 2010). While there are an extensive number of techniques for measuring and assessing the production of ROS, semiconductor photocatalysis involves heterogeneous systems, which can complicate measurements and limit the use of spectroscopic methods. Accurately determining the production and understanding the interplay among ROS generated under specific semiconductor photocatalytic condition is critical for practical water treatment applications.

1.2.2 Iron oxide materials

Use of the common adsorbents, including activated carbon, agricultural products, industrial by-products and biosorbents, can involve a time-consuming and sometimes costly separation process following a treatment (Babel et al., 2003; Owlad et al., 2009). The advantage of magnetic materials is the easy separation by an external magnetic field (Ambashta et al., 2010). The common iron oxides are summarized in **Table 1.3** (Cornell et al., 2003). These iron oxide materials are low-cost and readily available. The bare magnetic iron oxide and functionalized magnetic iron oxides materials can be employed for water treatments.

Table 1.3 The common iron oxides

Iron oxide	Chemical formula	Structural type	Crystal system
Hematite	$\alpha\text{-Fe}_2\text{O}_3$	Corundum	Hexagonal
Magnetite	Fe_3O_4	Inverse spinel	Cubic
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$	Defect spinel	Cubic or Tetragonal
Wüstite	$\text{Fe}_{(1-x)}\text{O}$		Cubic

Iron oxides materials have widely used for toxic heavy metals removal. Magnetite particles has been employed for the chromium(VI) removal from water, and the X-ray absorption near edge structure spectroscopy indicates that chromium(VI) was adsorbed and reduced to nontoxic species chromium(III) (Polizzotto et al., 2005). Amorphous iron oxide, maghemite, and magnetite, exhibit excellent adsorption capacity of arsenic species in aqueous solution (Dixit et al., 2003; Tuutijärvi et al., 2009). Mercury(II), lead(II), cadmium(II) and copper(II) are also can be removed from the aqueous solution by magnetic iron oxide materials (J.-f. Liu et al., 2008).

Another attractive feature of iron oxides is the ability to initiate oxidation processes through the decomposition of hydrogen peroxide generating $\bullet\text{OH}$ in presence of Fe(II) or Fe(III) (Kwan et al., 2003). The Fe(II) containing materials, it can act via the well-known Fenton reaction:

Fe(II) can be formed slowly from Fe(III) in the presence of hydrogen peroxide :

The deprotonation of HO₂ (pK_a = 4.8) yields O₂⁻, which initiates reduction of Fe(III) :

The generated Fe(II) initiates **Eq. 1.6**. Thus, the iron oxide can initiate the generation of •OH and degrade the contaminants in presence of hydrogen peroxide. The technique may combine the advantage of magnetic iron oxide and hydroxyl radical mediated degradation, resulting in an improvement of performance for the contaminant treatment (Valentine et al., 1998).

In order to improve its efficient purification technology, a number of magnetic iron-containing materials were synthesized and employed for water treatment. The silica-coated magnetite core material exhibits a good performance for removal of MC-LR due to the magnetic properties and unique microstructure (Deng et al., 2008). The other synthetic strategy is magnetic composite material. For example, magnetic MnO₂-Fe₂O₃ composite shows an excellent adsorption of azo-dye from water (Wu et al., 2005). The clay-maghemite composite has a high adsorption capacity for the heavy metals (Oliveira et al., 2003). The activated carbon-magnetite composite was employed for adsorption of volatile organic compounds from water and the experimental results demonstrates that magnetic iron oxide core does not change the adsorption behavior of activated carbon (Oliveira et al., 2002).

1.3 General objective of dissertation projects

The generation of reactive oxygen species by various TiO₂ catalysts was monitored. Since the hydroxyl radical is the dominant reactive oxygen species, the optimization conditions for hydroxyl radical generation by TiO₂ coated glass

photospheres were evaluated, and the optimal conditions were applied for the degradation of dimethyl phthalate. Conventional water treatment methods are often not effective or not practical for the removal of MC-LR. In the present study, we employed rose bengal, a singlet oxygen sensitizer, to study the photo-oxidative destruction of MC-LR. Two magnetic iron oxide nanoparticles, maghemite and humic acid coated magnetite, were synthesized and characterized for the removal of chromium(VI) from water.

2 Quantification of Hydroxyl Radical and Singlet Oxygen Formation by Various TiO_2 Photocatalysts

2.1 Abstract

The formation rate, steady-state concentration, and other kinetics parameters of hydroxyl radical and singlet oxygen by various TiO₂ photocatalysts under UV or visible irradiations were measured using selective chemical probes in our study. The generation of hydroxyl radical is highly dependent on the irradiation wavelength, and the steady-state concentration of hydroxyl radical is lower by 3-4 orders of magnitude than singlet oxygen. The lower steady-state concentration of hydroxyl radical is mainly because hydroxyl radical reacts with most organic compounds at nearly diffusion-controlled rates. There is modest effect of type of TiO₂ material and irradiation wavelength on the singlet oxygen formation kinetic parameters. It may be the results of generation mechanisms of hydroxyl radical and singlet oxygen: the hydroxyl radical is generated by an electron transfer mechanism and singlet oxygen is generated by an energy transfer followed by an inter-system crossing.

2.2 Keywords

Reactive oxygen species, TiO₂, Photocatalysis, Hydroxyl radical, Singlet oxygen

2.3 Introduction

Advanced oxidation processes involve the generation of reactive oxygen species (ROS). Since ROS are capable of initiating a wide range of reactions, the technique has been applied to degrade and/or mineralize a variety of contaminants (Hoffmann et al., 1995; Linsebigler et al., 1995).

Among the ROS, hydroxyl radical ($\bullet\text{OH}$) is the most powerful oxidant in aqueous solution. In general, $\bullet\text{OH}$ is considered to be the dominant ROS produced during UV TiO₂ photocatalysis. Hydroxyl radical reacts with most organic compounds at or near the

diffusion-controlled rate. The predominant reaction pathways of $\bullet\text{OH}$ with organic compounds include the addition to double bonds, triple bonds, and aromatic rings, hydrogen-atom abstraction, and electron transfer processes (Buxton et al., 1988). Since $\bullet\text{OH}$ is critical for effective degradation of organic contaminants by TiO_2 photocatalysis, we used terephthalate acid (TA) as a $\bullet\text{OH}$ trap to determine the rates of generation, steady-state concentrations and rate constants of $\bullet\text{OH}$ employing different TiO_2 materials. TA selectively reacts with $\bullet\text{OH}$ to produce 2-hydroxy terephthalic acid (35 % yield) which can be readily and accurately measured using fluorescence (Fang et al., 1996). The mechanism is described in **Scheme 2.1**.

Scheme 2.1 Reaction of TA with $\bullet\text{OH}$

Although $\bullet\text{OH}$ is considered predominant for the treatment of pollutants/toxins by UV TiO_2 photocatalysis, visible light activated (VLA) TiO_2 photocatalysis appears to involve different ROS and the formation of singlet oxygen ($^1\text{O}_2$) has been reported (Rengifo-Herrera et al., 2009; Stylidi et al., 2004). Singlet oxygen is an excited state of molecular oxygen, which reacts with alkenes, conjugated and aromatic systems by ene-type, [2+2] cycloaddition, and Diels-Alder reaction pathways (Kearns, 1971).

To access the formation and reaction of $^1\text{O}_2$ under VLA TiO_2 photocatalysis, furfuryl alcohol (FFA) is employed as a $^1\text{O}_2$ trap (Haag et al., 1984). Furfuryl alcohol reacts with $^1\text{O}_2$ with the bimolecular rate constant of $k = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Haag et al.,

1986). The generation of $^1\text{O}_2$ is monitored by the loss of FFA, and the mechanism is described in **Scheme 2.2**.

Scheme 2.2 Mechanism of reaction of FFA with $^1\text{O}_2$

Considering the band gap of TiO_2 is 3.2 eV (anatase TiO_2), UV light is required to activate the photocatalysis process. Visible light reaching the earth's surface represents $\sim 45\%$ of the solar spectrum, whereas only $\sim 5\%$ is in the UV region. The use of an external UV light source is expensive. Fortunately, doped TiO_2 materials have been developed to lower band gap, thus, visible light can be utilized for the activation of TiO_2 photocatalysis (Pelaez et al., 2009). TiO_2 photocatalysis involves the generation of ROS as a primary step followed by subsequent reactions with contaminants. The majority of publications focus on the degradations efficiency and removal effectiveness. The present study investigates the generation of ROS by various TiO_2 materials.

The objective of this study is to quantify the formations of $\bullet\text{OH}$ and $^1\text{O}_2$ by various TiO_2 materials under visible and UV irradiation. The productions of $\bullet\text{OH}$ and $^1\text{O}_2$ by different TiO_2 materials can be compared and used to access the potential applications for the degradation of a wide varieties of pollutants and toxins.

2.4 Materials and methods

2.4.1 Materials

Furfuryl alcohol (98%), and HPLC-grade methanol were purchased from Acros Organics. Terephthalate acid (disodium salt) was purchased from Sigma-Aldrich. Hollow glass microspheres coated with photocatalytic TiO_2 (HGM- TiO_2) was obtained from Microsphere Technology Limited (Limerick, Ireland). 2-hydroxy terephthalic acid (2-HTA) was synthesized for calibration by using a published method (Mason et al., 1994). All the compounds were used as received without any further purification. Millipore filtered water ($18 \text{ M}\Omega \cdot \text{cm}$) was used for the preparation of all solutions.

2.4.2 Determination of hydroxyl radical and singlet oxygen

Terephthalate acid is used to scavenge $\bullet\text{OH}$ and to produce 2-HTA. TiO_2 was prepared as a suspension (0.10 g/L) in 100 mL TA solution. The suspension was magnetically stirred and purged with oxygen for 15 min (unless otherwise stated) prior to and during irradiation, in order to establish the adsorption/desorption equilibrium. The illumination of TiO_2 suspension was conducted in a Rayonet photochemical reactor (Southern New England Ultra Violet Company, www.rayonet.org, model RPR-100) equipped with a cooling fan and four lamps. Samples (3.0 mL) were taken from the suspension at the given time intervals and immediately filtered through a $0.45 \mu\text{m}$ filter. 2-hydroxy terephthalic acid was excited at 315 nm and fluorescence measured at 425 nm

(Ishibashi et al., 2000b), using a Horiba FluoroMax 3 spectrofluorometer. The instrument was calibrated using standard solutions of 2-HTA from 0.01-15 μM (**Figure 2.1**).

Figure 2.1 Calibration curve of 2-HTA

Furfuryl alcohol was employed to determine the generation of singlet oxygen. Twenty mL TiO_2 suspension (0.25 g/L) with FFA (20 μM) was magnetically stirred and purged with oxygen for 15 min prior to and during the irradiation in a Rayonet photochemical reactor (12 lamps). A 1.0 mL sample was taken from the suspension at the given time intervals and immediately filtered through a 0.45 μm filter.

The concentration of FFA residual was measured using a Varian ProStar HPLC system equipped with a ProStar 410 autosampler and a ProStar 335 photodiode array detector. FFA was analyzed as the following HPLC conditions: C18 column of 250 $\times$ 4.6 mm Luna 5 μm , mobile phase of 20 % methanol and 80% water, 50 μL injection volume

and detection wavelength at 219 nm. The flow rate was 1 mL·min⁻¹ at room temperature. **Figure 2.2** was the calibration curve of measurement of singlet oxygen with FFA.

Figure 2.2 Calibration curve of FFA

2.5 Results and discussion

2.5.1 Hydroxyl radical formation

The preparation of doped TiO₂ materials was described in the previous publications (Choi et al., 2007; Han et al., 2011; Pelaez et al., 2009) and the band gap energies of different TiO₂ materials are summarized in **Table 2.1**. Doped TiO₂ materials are attractive, because solar energy is available for photocatalysis without the need of external radiation resource. **Figure. 2.3** and **2.4** show the yield of hydroxyl radical as a function of time by various TiO₂ materials under 350 and 419 nm irradiations. The yield increases in an approximately linear relationship with time. Wavelength of irradiation is a major factor affecting the yield of hydroxyl radical. It is shown that hydroxyl radical

yield increases with the increase of irradiation energy. The effect of irradiation wavelength was not the same for different TiO₂ materials.

The generation of •OH fits pseudo-zero order kinetics model with k_0 as a pseudo-zero order rate constant. The coefficients of determination (R^2) ≥ 0.939 indicate they follow pseudo-zero order kinetics well. It occurs because the photocatalyst was not consumed during irradiation, and there was excessive TA (1000 μM) present in TiO₂ suspension and the loss of TA is negligible during photocatalysis. Therefore, zero-order kinetics was applied to describe the generation of hydroxyl radical well. The •OH formation rate (r_{OH}) is equal to the rate constant (k_0) for zero-order kinetics model.

$$d[\bullet\text{OH}]/dt = k_0 \quad (2.1)$$

$$d[\bullet\text{OH}]/dt = k_{\text{OH}+\text{TA}} \times [\text{TA}] \times [\bullet\text{OH}] \quad (2.2)$$

where $k_{\text{OH}+\text{TA}} = 1.98 \times 10^{11} \text{ M}^{-1} \text{ min}^{-1}$ (Fang et al., 1996)

Since hydroxyl radical reacts with most organic compounds at or near the diffusion limit rate, the steady-state concentration of hydroxyl radical is extremely low (Buxton et al., 1988). The •OH formation rate is in the $10^{-1} \mu\text{M}/\text{min}$ range, while the steady state concentration of •OH is $\sim 0.7\text{-}2$ femtomole/L (10^{-15} M , fM) level upon 350 nm irradiation (**Table 2.2**). For 419 nm (**Table 2.3**), the •OH formation rate is $10^{-2} \mu\text{M}/\text{min}$ level, and the steady state concentration is $\sim 10^{-1}\text{-}10^{-2}$ fM. The wavelength of irradiation source plays a critical role in •OH formation.

Table 2.1 Band gap energy of TiO₂ materials

	HGM-TiO ₂	S TiO ₂	NF TiO ₂	Brookite TiO ₂	PF TiO ₂
Band gap		2.94	2.75	3.4	2.68
Energy (eV)		(Han et al., 2011)		(Hu et al., 2009)

Figure 2.3 Hydroxyl radical yields by various TiO_2 under 350 nm illumination

Figure 2.4 Hydroxyl radical yield by various TiO_2 under 419 nm illumination

Table 2.2 Kinetic constant of •OH under 350 nm irradiation

Catalyst	k_0 ($\mu\text{M}/\text{min}$)	R^2	$[\cdot\text{OH}]_{ss}$ (fM)
NF TiO ₂	0.27	0.991	1.4
HGM-TiO ₂	0.43	0.982	2.2
S TiO ₂	0.28	0.992	1.4
Brookite TiO ₂	0.22	0.981	1.1
PF TiO ₂	0.15	0.999	0.76

Table 2.3 Kinetic constants of •OH under 419 nm irradiation

Catalyst	k_0 ($\mu\text{M}/\text{min}$)	R^2	$[\cdot\text{OH}]_{ss}$ (fM)
NF TiO ₂	0.043	0.996	0.22
S TiO ₂	0.023	0.984	0.12
HGM-TiO ₂	0.022	0.985	0.11
PF TiO ₂	0.006	0.939	0.03
Brookite TiO ₂	0.004	0.969	0.02

2.5.2 Formation of singlet oxygen

In order to assess the efficiency of ¹O₂ generation upon visible light irradiation, ¹O₂ was identified and quantified using FFA as a scavenger compound since the generation of ¹O₂ was correlated to the loss of FFA. The disappearance of FFA was measured as a function of time. The loss of FFA follows the pseudo-first order kinetic model. The pseudo-first order kinetic model can be expressed as:

$$-\frac{d[C]}{dt} = k_1[C] \quad (2.3)$$

After integration, the equation becomes

$$\ln \frac{C}{C_0} = -k_1 t \quad (2.4)$$

where k_1 is the rate constant of pseudo-first order model (s^{-1}), and t is the time (s). Rate constants can be derived from the linear plots of $\ln C/C_0$ against time. The measurement of 1O_2 is performed upon visible light irradiation, so the reaction of FFA with hydroxyl radical is negligible. The steady state concentration of 1O_2 is derived from k_1/k_{FFA} , where k_{FFA} is the rate constant of FFA and 1O_2 ($1.2 \times 10^8 M^{-1} s^{-1}$) (Coelho et al., 2011). Singlet oxygen may be deactivated to return to its ground state by collision with water ($2.5 \times 10^5 s^{-1}$), so the formation rate of 1O_2 (r_{so}) is $2.5 \times 10^5 \times [^1O_2]_{ss}$ (Vione et al., 2010). The kinetic parameters of 1O_2 generation of various TiO_2 materials upon 419 and 450 nm irradiations are given in **Table 2.4** and **2.5**. The R^2 indicates that the formation of 1O_2 fits the pseudo-first order model well under 419 and 450 nm irradiations. These kinetic parameters vary among catalysts. The steady state concentration of 1O_2 is $\sim$ picomole/L ($10^{-12} M$, pM) level and the formation rate of 1O_2 is $\sim 10^{-7} M s^{-1}$. Therefore, they have the same order of magnitude, implying that photocatalysts have the similar photoactivity of 1O_2 generation and 1O_2 may exhibit a similar contribution to TiO_2 photocatalysis. 1O_2 is generated by an energy transfer followed by an inter-system crossing, so the mechanism is different from $\cdot OH$ generation. The steady state concentration of 1O_2 is higher by 3-4 orders of magnitude than $\cdot OH$, which is analogous to the generation of 1O_2 and $\cdot OH$ by dissolved organic matter upon UV irradiation (Vione et al., 2010). The higher 1O_2 steady state concentration is likely due to higher 1O_2 formation rate.

Table 2.4 Kinetic parameters of $^1\text{O}_2$ upon 419 nm irradiation

Catalyst	k_1 (s^{-1})	R^2	$[^1\text{O}_2]_{\text{ss}}$ (pM)	r_{so} ($\mu\text{M s}^{-1}$)
S-TiO ₂	1.36×10^{-4}	0.993	1.13	0.28
PF-TiO ₂	9.88×10^{-5}	0.989	0.82	0.20
NF-TiO ₂	2.30×10^{-4}	0.977	1.92	0.48
HGM-TiO ₂	1.81×10^{-4}	0.990	1.51	0.38
Brookite TiO ₂	2.89×10^{-4}	0.950	2.41	0.60

Table 2.5 Kinetic parameters of $^1\text{O}_2$ upon 450 nm irradiation

Catalyst	k_1 (s^{-1})	R^2	$[^1\text{O}_2]_{\text{ss}}$ (pM)	r_{so} ($\mu\text{M s}^{-1}$)
S-TiO ₂	1.03×10^{-4}	0.985	0.86	0.22
PF-TiO ₂	1.61×10^{-4}	0.972	1.34	0.34
NF-TiO ₂	1.80×10^{-4}	0.999	1.50	0.38
HGM-TiO ₂	2.06×10^{-4}	0.996	1.72	0.43
Brookite TiO ₂	3.15×10^{-4}	0.961	2.62	0.66

2.6 Conclusions

The formation of $\bullet\text{OH}$ and $^1\text{O}_2$ by various TiO₂ materials were measured using probes methods the transformation of TA into 2-HTA and degradation of FFA, respectively. The generation of $\bullet\text{OH}$ upon is relative more efficient upon UV irradiation. The difference is mainly related to their formation mechanisms. The $\bullet\text{OH}$ generation follows pseudo-zero order kinetics, and it is pseudo-first order kinetics for $^1\text{O}_2$ formation. Because of the extremely high reaction rate of $\bullet\text{OH}$, its steady-state concentration is lower by 3-4 orders of magnitude than singlet oxygen.

3 Optimization of Photocatalytic Performance of TiO₂ Coated Glass Microspheres
Using Response Surface Methodology and the Application for Degradation of
Dimethyl Phthalate

3.1 Abstract

Hollow glass microspheres coated with photocatalytic TiO_2 (HGM- TiO_2), recently became commercially available and have the distinct advantages of easy separation and recovery after treatment. With this in mind, we determined the optimum conditions for hydroxyl radical generation from HGM- TiO_2 photocatalysis using response surface methodology (RSM). The hydroxyl radical yield and its average generation rate are critical parameters for practical applications of TiO_2 photocatalysis. In this study, terephthalic acid was used as a hydroxyl radical trap because of the selective formation of the readily detectable hydroxyl radical adduct, 2-hydroxy terephthalic acid. Three independent variables, including loading of HGM- TiO_2 , concentration of terephthalic acid and irradiation time, were investigated. The 3D response surface graphs of hydroxyl radical yield and average hydroxyl radical generation rate indicated that optimum conditions of loading of HGM- TiO_2 , concentration of terephthalate acid and irradiation time were 8.0 g/L, 4.0 mM, and 20 min, respectively. Under these optimized conditions, we measured the photocatalysis employing HGM- TiO_2 for the remediation of dimethyl phthalate (DMP), as a representative compound for problematic phthalate acid esters. HGM- TiO_2 photocatalysis leads to the rapid destruction of DMP and there is a linear correlation between the DMP destruction and hydroxyl radical production. The results of our study demonstrate RSM can be used to readily determine the optimal conditions for hydroxyl radical production and the subsequent treatment of target compounds may be correlated to the hydroxyl radical production during HGM- TiO_2 photocatalysis.

3.2 Key words

Advanced oxidation; Photocatalysis; FTIR; Response surface methodology; Dimethyl phthalate remediation

3.3 Introduction

Access to clean water is a global problem and one of the primary causes of human health problems worldwide (O'Shea et al., 2012). TiO₂ photocatalysis is an attractive method for the purification of water, due to its abilities to effectively degrade a tremendous variety of toxins and pollutants (Hoffmann et al., 1995). The degradation processes are initiated at the surface of TiO₂ (Fox et al., 1993). When TiO₂ is photoexcited by photons with energy equal to or greater than the band gap, an electron is promoted from the valence band to the empty conduction band, resulting in an electron-hole pair. Electron-hole pairs can recombine or migrate to the surface and react with the adsorbed species on TiO₂ surface. The process can generate a variety of reactive oxygen species (ROS), including hydroxyl radical, hydrogen peroxide, singlet oxygen, and superoxide anion radical. Among the ROS, hydroxyl radical is generally responsible for the degradation during UV TiO₂ photocatalysis in aqueous solution (Linsebigler et al., 1995). The processes initiated during TiO₂ photocatalysis are represented in **Eqs. 3.1-3.8**. Hydroxyl radical is capable of reacting with most organic compounds and many inorganic compounds often at nearly diffusion controlled rates. Hydroxyl radical is a powerful electrophile and reacts with organic substances mainly by the addition to double and triple bonds, and aromatic rings, hydrogen-atom abstraction from C_(sp3)-H bonds, and electron transfer pathways (Buxton et al., 1988). Since the performance of TiO₂ photocatalysis for water treatment processes is highly dependent on hydroxyl radical, it is

critical to evaluate and optimize experimental conditions for maximizing hydroxyl radical generation during TiO₂ photocatalysis.

In an attempt to improve the performance of UV TiO₂ photocatalysis, a variety of TiO₂ materials have been developed, including surface modification (Kado et al., 2011), TiO₂ films (Yogi et al., 2008), doped TiO₂ (Graham et al., 2010), TiO₂ nanotubes (Z. Liu et al., 2008), porous TiO₂ microspheres (Wang et al., 2009) and microspheric cores covered with TiO₂ shell/film (Li et al., 2008). Among these means, microspheric cores covered with nano- or micro- sized shells are novel fabricated composite materials and have received significant attention (Jackson et al., 1991). As an important composite material, HGM-TiO₂, recently became commercially available and has the major advantages of easy separation and recovery. Thus, HGM-TiO₂ is promising for use in industrial wastewater treatment plants and gaseous pollutants reduction, due to unique properties, such as low density (0.22 g/cm³), buoyancy, and transparency to visible light.

However, detailed studies on the photocatalytic performance and applications of HGM-TiO₂ have received limited attention.

An excellent study on the optimization of the experimental conditions to produce the highest •OH yield during photocatalysis using suspensions of Degussa P25 TiO₂ has been reported (Eremia et al., 2008), but to the best of our knowledge there are no reports on optimized conditions for HGM-TiO₂ photocatalysis. The •OH generation rate is also an important parameter, since a high generation rate results in rapid degradation and short reaction times to achieve specific treatment objectives. The specific experimental conditions are critical to generation rate and yield of •OH during HGM-TiO₂ photocatalysis. For example, as the concentration of catalyst increases, the photodegradation efficiency can increase to a maximum at a specific catalyst loading above which light scattering and screening may reduce the TiO₂ photocatalytic efficiency. Terephthalic acid (TA) was employed to trap •OH effectively and selectively. Although quenching and inter filter effects may occur at high TA concentrations, these issues are not significant under dilute concentrations (Ishibashi et al., 2000a). Another important factor is irradiation time. Since there are significant costs associated with generation of UV light, it is important to evaluate the treatment time required to achieve desired levels of degradation. From our study, •OH yield increases, whereas •OH generation rate decreases under extended irradiation time. Photocatalytic deactivation can occur when the intermediate products compete for radical species (•OH) leading to inhibition of the photocatalytic performance (Cao et al., 2000). Therefore, it is critical to determine the optimal yield and rate of •OH generation, as a function of loading of HGM-TiO₂, concentration of TA and irradiation time.

The classical one-variable-at-a-time methodology does not enable the study of combined effects of two or more variables on a measured response. Probing each variable independently is also labor intensive and time consuming. Thus, RSM was originally developed by Box and Wilson (Box et al., 1951), to access the interactions of various variables simultaneously and provide an empirical description of effects of variables and their interactions on a measured response. The RSM has successfully applied to determine the optimal conditions for a variety of processes (Arslan-Alaton et al., 2009). Herein, RSM is used to optimize yield and average generation rate of $\bullet\text{OH}$ by HGM-TiO₂ photocatalysis. A central composite design was used to investigate the effects of three independent variables, namely loading of HGM-TiO₂, concentration of TA, and reaction time coded at five levels.

The RSM results were used to guide the application of HGM-TiO₂ photocatalysis in the photocatalytic degradation of DMP, as a model for problematic phthalate acid esters which have wide spread use and an annual production of approximately 4 million tons (Lin et al., 2003). The US Environmental Protection Agency and European Union have classified these compounds as priority pollutants (Hansen et al., 1999) because of the significant threat they pose on reproductive and behavioral health of humans and wildlife at low concentrations (Matsumoto et al., 2008). HGM-TiO₂ photocatalysis leads to the rapid destruction of DMP and there is a linear correlation between the DMP destruction and hydroxyl radical production. The results of our study demonstrate RSM can be used to readily determine the optimal conditions for hydroxyl radical production and the subsequent treatment of target compounds can be correlated to the hydroxyl radical production during HGM-TiO₂ photocatalysis.

3.4 Materials and methods

3.4.1 Chemicals

HGM-TiO₂ material was obtained from Microsphere Technology Limited (Limerick, Ireland). The characterization information of this material (including median diameter, particle size) is available from the company website <http://www.microspheretechnology.com/photospheres.php>. TA (disodium salt) and DMP were purchased from Aldrich. HPLC grade methanol was obtained from Fisher. 2-hydroxy terephthalic acid (2-HTA) was synthesized for calibration by using a published method (Mason et al., 1994). All the chemicals were used without further purification and all solutions were made with Millipore filtered water (18 MΩ · cm).

3.4.2 Fourier transform infrared spectroscopy (FTIR)

The TA and DMP loaded HGM-TiO₂ were prepared by adding 1.0 g HGM-TiO₂ into 100 mL solution with 1.0 g TA or DMP. The suspension was put on an orbit shaker at 300 RPM for half an hour. Solid samples for FTIR were separated, and dried in a vacuum oven at room temperature. FTIR was collected using Perkin Elmer Spectrum 100 FTIR spectrometer.

3.4.3 Photocatalytic and analytical methods

HGM-TiO₂ suspension was prepared by suspending HGM-TiO₂ into 100 mL TA aqueous solution in a Pyrex cylindrical reactor (12×1 inch, ~150 mL capacity, with a vented Teflon screw top). The suspension was magnetically stirred and purged with oxygen gently for 15 min prior to radiation and during the reaction, in order to maintain the adsorption/desorption equilibrium. The suspensions were irradiated in a Rayonet photochemical reactor (Southern New England Ultra Violet Company, www.rayonet.org,

model RPR-100), equipped with a cooling fan on the bottom and four phosphor-coated low-pressure mercury lamps (RPR 350 nm, 8.34×10^{-9} Einstein mL⁻¹ s⁻¹). Samples (3 mL) were taken from the suspension at given time intervals and immediately filtered through a 0.45 µm PTFE filter to remove suspended particles prior to analysis.

TA is used to selectively trap •OH and to produce 2-HTA with a percent yield of 35 % (Fang et al., 1996) (**Scheme 3.1**). The yield of •OH is quantified by fluorescent measurement of the generated 2-HTA. 2-HTA was excited at 315 nm to emit fluorescence at 425 nm (Ishibashi et al., 2000b), which was measured on a Horiba FluoroMax 3 spectrofluorometer.

Scheme 3.1. Reaction of TA with •OH

3.4.4 Experimental design and data analysis

To identify best combination of experimental parameters for optimal •OH generation, RSM was applied. Central composite design was employed for the optimal conditions. A full factorial 5-level experimental design with 3 variables needs to run $5^3 = 125$ experiments. However, as shown in **Table 3.1**, application of the central composite design reduces the number of required experiments to 20 (8 factor points, 6 axial points and 6 replications at the center points) (Parilti et al., 2011). Alpha (α) is the coded level of axial point from the center. The coded level is (x_i) defined by the following equation:

$$x_i = (X_i - X_0)/\Delta X_i \quad (3.9)$$

where, X_0 is the real value of the independent variable at the center point, X_i is the real value of the independent variable, and ΔX_i is the step changing value.

Table 3.1 Central composite design for RSM

Experiment entry	Variable in coded levels		
	x_1	x_2	x_3
1	-1	-1	-1
2	-1	-1	1
3	-1	1	-1
4	-1	1	1
5	1	1	1
6	1	1	-1
7	1	-1	1
8	1	-1	-1
9	0	0	α
10	0	0	$-\alpha$
11	0	α	0
12	0	$-\alpha$	0
13	α	0	0
14	$-\alpha$	0	0
15	0	0	0
16	0	0	0
17	0	0	0
18	0	0	0
19	0	0	0
20	0	0	0

In this study, the loading of HGM-TiO₂ (X₁), TA concentration (X₂) and irradiation time (X₃) were varied. The real levels and coded levels are showed in **Table 3.2**. The equation can quantitatively describe the predicted response as a function of three variables and the optima of three variables are obtained by surface response. Herein, Y is the yield of •OH or its average generation rate, which is defined by the following equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (3.10)$$

where Y is the predicted response, b₀ is the intercept, b₁, b₂ and b₃ are linear coefficients, b₁₂, b₁₃ and b₂₃ are squared coefficients, b₁₁, b₂₂ and b₃₃ are quadratic coefficients.

Table 3.2 Real and coded levels of three variables

Variable	Symbol coded	Coded level				
		- α (-2)	-1	0	1	α (2)
[HGM-TiO ₂] (g/L)	X ₁	2	4	6	8	10
[TA] (mM)	X ₂	1	2	3	4	5
Irradiation time (min)	X ₃	5	10	15	20	25

3.4.5 Degradation and analysis of DMP

The optimal conditions for the generation of •OH were employed for degradation of DMP. The concentration of DMP residual was analyzed using a Varian ProStar HPLC system equipped with a ProStar 410 autosampler and a ProStar 335 photodiode array detector with the stationary phase being a Luna RP C18 column of 250×4.6 mm I.D. (5 μm particle size). The mobile phase consisted of a mixture of water (50 %) and methanol (50 %), and detection wavelength was 230 nm. The flow rate was 1 mL min⁻¹ and the

injection volume is 30 μL at room temperature (Chen et al., 2009). The retention time of DMP is ~ 12.2 min under these HPLC conditions.

3.5 Results and discussions

3.5.1 FTIR

The FTIR spectra of were recorded in the range $600\text{--}4000\text{ cm}^{-1}$ to identify the functional groups of HGM-TiO₂ and access the adsorption of TA and DMP onto HGM-TiO₂ (**Figure 3.1**). For the neat HGM-TiO₂ sample, the infrared band at 3374 cm^{-1} shows the presence of OH stretching vibration (Burgos et al., 1999), while the IR band at 1631 cm^{-1} is ascribed to Si-H₂O adsorption (Ding et al., 2003; Wang et al., 2007). The peak at 1404 cm^{-1} corresponds to O-H bending mode (B. P. Singh et al., 2012), the band at 1019 cm^{-1} corresponds to Si-OH and Si-O-Ti vibration modes (Zhai et al., 1999) while a Ti-O-Ti band appears at 787 cm^{-1} . These assignments clearly demonstrate the HGM-TiO₂ contains characteristic bands associated with TiO₂ and glass (Minella et al., 2009). The DMP loaded HGM-TiO₂ materials exhibit a band at 2954 cm^{-1} corresponding to Csp³-H stretching (Ibarra et al., 1996), a band at 1727 cm^{-1} is assigned to C=O stretching (Khare et al., 2002), a C-O stretching band at 1289 cm^{-1} , a band at 743 cm^{-1} indicative of ortho-disubstituted benzene ring (Liu et al., 2006) and a band at 1434 cm^{-1} is assigned to C-H group (Matuana et al., 2001). For TA loaded HGM-TiO₂, the band at 1555 cm^{-1} corresponds to antisymmetric -CO₂ stretching (Liao et al., 2002), the band at 823 cm^{-1} is ascribed to =C-H bending of an aromatic ring (Pavia et al., 2009). The remaining bands are ascribed to HGM-TiO₂. The results demonstrate adsorption of DMP and TA onto the HGM-TiO₂ materials.

Figure 3.1 FTIR spectra of HGM-TiO₂, TA- and DMP- loaded onto HGM-TiO₂

3.5.2 Model fitting and 3-D response surface

The data of •OH yield and average rate of •OH generation are shown in **Table 3.3**. The experimental data were fitted to empirical second-order polynomial models by a regression function in Microsoft Excel 2007. The results indicate that the experimental and expected responses match well, and the experimental responses fit the second-order polynomials well. The empirical second-order polynomials were obtained as the following two equations:

$$Y_1 = -98.78 + 20.49X_1 + 41.91X_2 + 7.28 X_3 + 1.48X_1X_2 + 0.15X_1X_3 + 0.91X_2X_3 - 1.45X_1^2 - 8.39X_2^2 - 0.16X_3^2 \quad (3.11)$$

$$Y_2 = 6.71 + 2.02X_1 + 3.81X_2 - 0.93X_3 + 0.096X_1X_2 - 0.027X_1X_3 + 0.0015X_2X_3 - 0.10X_1^2 - 0.58X_2^2 + 0.022X_3^2 \quad (3.12)$$

where Y_1 is the predicted response of yield of generated $\bullet\text{OH}$ (μM) , Y_2 is the predicted average generation rate of $\bullet\text{OH}$ ($\mu\text{M}/\text{min}$), the variables of X_1 , X_2 and X_3 are the loading of HGM-TiO₂ (g/L), concentration of TA (mM) and irradiation time (min), respectively.

Table 3.3 RSM central composite design and experimental and expected responses

X_1	X_2	X_3	Experimental Y_1	Predicted Y_1	Experimental Y_2	Predicted Y_2
6	3	5	95.8	99.4	19.17	18.28
6	3	15	176.7	176.5	11.78	11.80
6	3	25	228.2	221.6	9.13	9.73
2	3	15	108.0	114.1	7.20	7.39
10	3	15	202.1	192.4	13.47	13.02
6	1	15	115.0	114.7	7.67	7.63
6	5	15	174.4	171.1	11.63	11.34
4	2	10	107.0	103.1	10.70	11.11
4	2	20	152.0	152.1	7.60	7.36
8	2	10	131.5	133.3	13.15	14.08
8	2	20	178.0	188.3	8.90	9.25
4	4	10	120.9	116.3	12.09	12.57
4	4	20	179.5	183.5	8.97	8.85
8	4	10	152.6	158.3	15.26	16.30
8	4	20	221.9	231.5	11.09	11.50
6	3	15	175.9	176.5	11.72	11.80
6	3	15	177.4	176.5	11.83	11.80
6	3	15	176.9	176.5	11.79	11.80
6	3	15	176.0	176.5	11.73	11.80
6	3	15	177.5	176.5	11.83	11.80

In order to check the adequacy of the second-order models, the significance test and analysis of variance (ANOVA) were employed for the second-order models for •OH yield and the average •OH generation rate. The significance tests of estimated regression coefficients for •OH yield and average •OH generation rate are shown in **Table 3.4**. The probability value (P) of coefficients was greater than 0.05, indicating the term did not have a significant effect on the predicted response. Otherwise, it was rejected and this term influenced the predicted response at a significant confidence level. For **Eq. 3.11** and **3.12**, X_1 , X_2 , X_3 , X_1X_1 , X_2X_2 and X_3X_3 were significant terms for the predicted response, and X_1X_2 , X_1X_3 and X_2X_3 were insignificant terms. The determination coefficient (R^2) for •OH yield was calculated as 0.982, which can explain the variability of response at a 0.982 confidence level. Moreover, the adjusted R^2 value of 0.966 was also close to 1. For Y_2 , R^2 was 0.974 and adjusted R^2 was 0.951. Therefore, as well as the model for •OH yield, the predicted values had a good agreement with experimental data.

The response surface models were further analyzed by ANOVA and the output results are summarized in **Table 3.5**. The P value of regression model was less than 0.05, so the models were adequate to describe the variability of Y_1 and Y_2 as a function of X_1 , X_2 and X_3 . The linear and square effects were highly significant for the predicted responses, whereas the interaction effects were insignificant. In conclusion, both **Eq. 3.11** and **Eq. 3.12** are good approximations.

Table 3.4 Estimated regression coefficients for •OH yield and the average •OH generation rate

	•OH yield			average •OH generation rate		
Term	Coefficient	Std. Error	P	Coefficient	Std. Error	P
X ₁	20.49	6.71	0.012	2.02	0.60	0.007
X ₂	41.91	13.43	0.011	3.81	1.19	0.010
X ₃	7.28	2.69	0.022	-0.93	0.24	0.003
X ₁ X ₂	1.48	1.23	0.256	0.096	0.11	0.398
X ₁ X ₃	0.15	0.24	0.550	-0.027	0.022	0.236
X ₂ X ₃	0.91	0.49	0.093	0.0015	0.044	0.973
X ₁ X ₁	-1.45	0.35	0.002	-0.10	0.031	0.008
X ₂ X ₂	-8.39	1.38	0.000	-0.58	0.12	0.001
X ₃ X ₃	-0.16	0.055	0.015	0.022	0.0049	0.001

Table 3.5 ANOVA for the second-order models of •OH yield and average •OH generation rate

	•OH yield				average •OH generation rate			
Source	DF ^a	Sum of squares	F	P	DF	Sum of squares	F	P
Regression	9	26446.4	60.99	0.000	9	144.03	42.08	0.000
Linear	3	23932.0	5.02	0.022	3	118.47	19.02	0.000
Square	3	2260.3	15.64	0.000	3	24.65	21.61	0.000
Interaction	3	254.0	1.76	0.219	3	0.90	0.79	0.526
Residual error	10	481.8			10	3.80		
Total	19	26928.2			19	147.83		

^aDF is degree of freedom

To obtain the optimal conditions for $\bullet$ OH generation, the 3D response surface technique was employed to evaluate the effects of independent variables on Y_1 and Y_2 . **Figure 3.2** shows the effect of any two independent variables on the $\bullet$ OH yield and its average $\bullet$ OH generation rate, keeping the coded level of the third one at its central level (0). **Figure 3.2 a, c, d and f** demonstrate the effect of concentration of TA on Y_1 and Y_2 . Y_1 and Y_2 increase with increase in concentration of TA until Y_1 and Y_2 reach a highest value. The optimal value of concentration of TA for Y_1 and Y_2 is 4.0 mM. The effect of loading of HGM-TiO₂ on Y_1 and Y_2 is shown in **Figure 3.2 b, c, e and f**. The optimal value of concentration of HGM-TiO₂ on Y_1 and Y_2 is 8.0 g/L. **Figure 3.2 a, b, d and e** demonstrate the effect of irradiation time on Y_1 and Y_2 . $\bullet$ OH yield increases whereas the average $\bullet$ OH generation rate decreases with increase in irradiation time. The competition for hydroxyl radical between TA and the oxidation products and TA consumption are factors leading to the observed decrease in $\bullet$ OH generation rate. Although the overall $\bullet$ OH yields increase with irradiation time, the rate of $\bullet$ OH yield slowed significantly after 20 min. Thus, the optimal time for Y_1 and Y_2 is 20 min. In summary, the optimal conditions for the yield of $\bullet$ OH were 8.0 g/L HGM-TiO₂, 4.0 mM TA and 20 min for irradiation time.

Figure 3.2 Response surface showing of any two independent variables on the $\bullet\text{OH}$ yield (a, b, and c) and its average $\bullet\text{OH}$ generation rate (d, e, and f)

3.5.3 The degradation of DMP

The optimal conditions for the $\bullet\text{OH}$ generation were applied for the degradation of DMP. The initial concentration of DMP is 50 μM . The loss of DMP follows the pseudo-first order kinetic model. The pseudo-first order kinetic model can be expressed as (Ye et al., 2009):

$$d[C]/dt = -k[C] \quad (3.13)$$

After integration, the equation becomes

$$\ln(C_0/C) = kt \quad (3.14)$$

where k is the rate constant of pseudo-first order model (min^{-1}), t is time (min), C_0 is the initial concentration of DMP (μM) and C is the concentration of DMP (μM) at the specific time. Since R^2 of plot of $\ln C_0/C$ versus t is greater than 0.95, the experimental data fit the pseudo-first-order model nicely.

As shown in **Figure 3.3**, the rate constants for degradation of DMP increased with increase in loading of HGM-TiO₂, and reached the highest at 8.0 g/L HGM-TiO₂. No significant increase is observed at loading levels above 8.0 g/L HGM-TiO₂. At high loadings of HGM-TiO₂ (> 8.0 g/L), the rate does not change but the standard deviation becomes larger due to the light scattering and screening effects. Therefore, the loading of HGM-TiO₂ = 8.0 g/L was considered optimal. In order to assess the relationship between $\bullet\text{OH}$ yield and degradation of DMP, the plot of degraded DMP against $\bullet\text{OH}$ yield is demonstrated in **Figure 3.4**. The $\bullet\text{OH}$ yield derived from **Eq. 3.11** with the coded level of X_2 at the central level (0) and X_3 being 20 min, showing increased $\bullet\text{OH}$ yield as the increasing of loading of HGM-TiO₂ (2 to 10 g/L). After 20 min, DMP was eliminated in presence of ≥ 8.0 g/L HGM-TiO₂, in agreement with the optimal conditions of $\bullet\text{OH}$

generation. The linear relationship between $\bullet\text{OH}$ yield and DMP degradation indicates the $\bullet\text{OH}$ is responsible for degradation of DMP. The bimolecular reaction rate constants for the reaction of $\bullet\text{OH}$ with TA is $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Song et al., 2012), while it is $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for DMP (Haag et al., 1992). The rate constants are similar; however the trendline in **Figure 3.4** demonstrates the destruction of DMP correlates to the $\bullet\text{OH}$ yield, but not in a 1:1 ratio. The yield of $\bullet\text{OH}$ and TA adduct versus destruction of DMP may be related to the different adsorption properties of DMP versus TA on HGM-TiO₂. Since $\bullet\text{OH}$ is a relatively nonselective radical and is able to react with substance at nearly diffusion controlled rate, the oxidation products of DMP may be degraded further before they are released back to aqueous phase.

Figure 3.3 The rate constants of pseudo-first order kinetic model for degradation of DMP as a function of HGM-TiO₂ loading. The data at 10, 12 and 15 g/L were not used for the trend-line since the rate did not increase above 8.0 g/L. Error bars represent standard deviation of triplicate experiments. The insert is the molecular structure of DMP.

Figure 3.4. Plot of degraded DMP against •OH yield. Error bars represent standard deviation of triplicate experiments.

3.6 Conclusions

The FTIR spectra show that the HGM-TiO₂ exhibits adsorption of TA (•OH trap) and DMP (target compound). The loading of HGM-TiO₂, the concentration of TA and irradiation time affect •OH generation significantly. The optimum conditions of •OH generation by HGM-TiO₂ were measured using RSM. Statistical analyses indicate the empirical second-order polynomials can accurately describe the •OH yield and the average •OH generation rate. The 3D response surface graphs showed that the optimum conditions of loading of HGM-TiO₂, concentration of TA and irradiation time were 8.0 g/L, 4.0 mM, and 20 min, respectively. The optimal condition for •OH generation by HGM-TiO₂ has applied to the degradation of DMP. The degradation of DMP follows the pseudo-first order kinetic model nicely, and rate constant increased linearly as increasing of loading of HGM-TiO₂ up to 8.0 g/L. We have demonstrated RSM can be used to determine the optimal conditions for •OH generation. Employing the optimal conditions,

the problematic pollutant, DMP, is readily degraded. The effective application of RSM for determining optimal conditions for hydroxyl radical production and rapid destruction of DMP show HGM-TiO₂ photocatalysis is a promising material for water treatment.

4 Photocatalytic Degradation of Microcystin-LR by Rose Bengal: the Role of Singlet Oxygen

4.1 Abstract

We used rose bengal (RB), a singlet oxygen ($^1\text{O}_2$) sensitizer, to study the photo-oxidative destruction of microcystin-LR (MC-LR). Under photolysis by visible or solar light no measureable degradation of MC-LR was observed in the absence of RB, however the concentration of MC-LR is significantly reduced under the same conditions in the presence of RB. The degradation of MC-LR in presence of 500 μM RB follows the pseudo-first order kinetic model nicely. These results indicate RB can be used as a photosensitizer (catalyst) to effectively degrade MC-LR. Rate of degradation increase three fold under oxygen-saturated condition compared to argon-saturated condition, demonstrating that photo-oxidation is the predominant degradation process. Under argon saturation the degradation is likely because of the energy transfer between the RB^* and MC-LR. Since the lifetime of $^1\text{O}_2$ in D_2O is longer than in H_2O , the degradation of MC-LR is enhanced in D_2O . The measured bimolecular reaction rate constant between MC-LR and $^1\text{O}_2$ is $3.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ using competition kinetics with furfuryl alcohol.

4.2 Key Words

Microcystin-LR, Rose bengal, Singlet oxygen, Photodegradation

4.3 Introduction

An emerging environmental issue is the increased occurrence of cyanobacteria (blue-green algae) in fresh water, and the bloom-forming cyanobacteria can produce and release cyanobacterial toxin in freshwater bodies, and microcystin (cyclic heptapeptides) is the most common toxin. The microcystins are reported to be potential tumor promoters. While approximately 80 variants of microcystins have been isolated and identified, microcystin-LR (MC-LR) is one of the most toxic and problematic variants

(structure of MC-LR shown in **Figure 4.1**). Therefore, the World Health Organization recommended 1 µg/L as a guideline of MC-LR.

Figure 4.1 Molecular structures of rose bengal (top) and MC-LR (bottom)

Conventional water treatment methods are often not effective or not practical for the removal of MC-LR. However, advanced oxidation processes (AOP) can be effective under specific conditions. Advanced oxidation processes involves the generation of

reactive oxygen species (ROS), including hydroxyl radical, superoxide anion radical, singlet oxygen and hydrogen peroxide. Hydroxyl radical ($\bullet\text{OH}$) is a strong oxidant and studied well for treatment of MC-LR (Song et al., 2009). Singlet oxygen ($^1\text{O}_2$) is another important ROS (Kearns, 1971), which can react with unsaturated organic compounds via ene-type reaction, [2+2] cycloaddition, and Diels-Alder reaction (Changseok et al., 2013). $^1\text{O}_2$ can be generated in the natural surface water in presence of dissolved organic matter (DOM) upon irradiation, since DOM is photoexcited to $^1\text{DOM}^*$, followed by intersystem crossing to $^3\text{DOM}^*$ and an energy transfer process between $^3\text{DOM}^*$ and triplet molecular oxygen ($^3\text{O}_2$). The biological activities of microcystins are associated with Adda (Carmichael et al., 1999). Robertson *et al.* proposed that the double bonds on the Adda moiety of MC-LR was susceptible to $^1\text{O}_2$ (Robertson et al., 1999), so $^1\text{O}_2$ can play an important role in the environmental fate and detoxification of MC-LR. However, the knowledge of role of singlet oxygen during MC-LR destruction is very limited. In this study, rose bengal (RB, shown in **Fig. 1**), $^1\text{O}_2$ sensitizer, is employed to study the photo-oxidative destruction of MC-LR.

The main objective of current study was to conduct the kinetic study of the reaction of $^1\text{O}_2$ and MC-LR. The UV-vis absorbance spectrum of RB in water shows that it has a strong absorption of UV and visible light and the increased degradation of MC-LR in D_2O indicates that $^1\text{O}_2$ plays a critical role in photodegradation of MC-LR. The results can also help understand the photochemical transformation of MC-LR by DOM in natural environments.

4.4 Experimental section

4.4.1 Materials

Microcystin-LR was isolated and purified using a published method (Song et al., 2007). HPLC grade acetonitrile was purchased from Fisher. Furfuryl alcohol (FFA) and trifluoroacetic acid (TFA) were purchased from Acros Organics. All the solutions were prepared with Millipore filtered water ($18 \text{ M}\Omega \cdot \text{cm}$).

4.4.2 Experimental

The UV-vis absorbance spectrum of rose Bengal in water was collected using a Cary 100-Bio UV/visible light spectrophotometer (Varian, Sugar Land, Tex). Rose bengal was employed as the sensitizer. Rose bengal concentration employed for our studies was $500 \text{ }\mu\text{M}$ and $[\text{MC-LR}]_0 = 5 \text{ ppm}$ unless otherwise stated. The solution was prepared in a Pyrex cylindrical reactor ($\sim 1 \times 4 \text{ inch}$, $\sim 20 \text{ mL}$ capacities, with a vented Teflon screw top). The solution was purged with desired gas gently for 15 min prior to radiation and during the reaction, in order to saturate solution with desired gas. The solution was irradiated in a Rayonet photochemical reactor (Southern New England Ultra Violet Company, www.rayonet.org, model RPR-100), equipped with a cooling fan on the bottom and four phosphor-coated low-pressure mercury lamps (RPR 350 nm, $8.34 \times 10^{-9} \text{ Einstein mL}^{-1} \text{ s}^{-1}$). Aliquots were taken from the solution at given time intervals for analysis.

4.4.3 Bimolecular reaction rate constant MC-LR and $^1\text{O}_2$

The solution containing $50 \text{ }\mu\text{M}$ MC-LR, $50 \text{ }\mu\text{M}$ FFA and $500 \text{ }\mu\text{M}$ RB was employed for determination of $^1\text{O}_2$ bimolecular reaction rate constant. Samples were measured at specific time intervals by HPLC.

4.4.4 Analytical method

The concentration of MC-LR residual and FFA were analyzed using a Varian ProStar HPLC system equipped with a ProStar 410 autosampler and a ProStar 335 photodiode array detector with the stationary phase being a Luna RP C18 column of 250×4.6 mm I.D. (5 µm particle size). The mobile phase consisted of a mixture of (A) 0.05 % (v/v) trifluoroacetic acid (TFA) in acetonitrile (40 %) and (B) 0.1 % (v/v) TFA aqueous solutions (60 %) (Antoniou et al., 2008). The flow rate was 1 mL min⁻¹ and the injection volume is 30 µL at room temperature. Detection wavelength was 238 nm, and it is 219 nm for FFA. The retention time of MC-LR is ~ 8.9 min and it is ~ 4.1 min for 219 nm under these conditions.

4.5 Results and discussion

4.5.1 Degradation of MC-LR by rose bengal

When MC-LR solution is irradiated in absence of rose bengal (RB), no measureable degradation was observed in oxygen or argon saturation distilled water, implying that the direct photolysis had no effect on degradation of MC-LR. It is consistent with previous report the irradiation alone had no effect on the degradation of MC-LR (Robertson et al., 1999). Therefore, the sensitizer is necessary for this process.

In this study, we employed RB, a singlet oxygen (¹O₂) sensitizer, to study the photo-oxidative destruction of MC-LR. The UV-Vis absorption spectrum of RB (**Figure 4.2**) demonstrated a strong adsorption peak in the green region of the visible spectrum (495-565 nm), so ¹O₂ can be generated via visible light irradiation of RB. The photoexcited RB* can interact with fundamental-state triplet oxygen, leading to the formation of ¹O₂. ¹O₂ is reactive oxygen species, which can react with unsaturated

organic compounds via ene-type reaction, [2+2] cycloaddition, and Diels-Alder reaction. Thus, singlet oxygen mediated process may play an important role for degradation of MC-LR. Energy transfer is the other probable photocatalytic mechanism: degradation occurs by the interaction photoexcited RB* with MC-LR.

To study the role of energy transfer on degradation of MC-LR, the solution containing rose Bengal and MC-LR is purged with argon to eliminate the $^1\text{O}_2$ generation.

Figure 4.2 UV-vis absorbance spectrum of 20 μM RB in water

The degradation of MC-LR in presence of 500 μM RB follows the pseudo-first order kinetic model. The pseudo-first order kinetic model can be expressed as:

$$d[\text{C}]/dt = -k[\text{C}] \quad (4.3)$$

After integration, the equation becomes

$$\ln(\text{C}_0/\text{C}) = kt \quad (4.4)$$

where k is the rate constant of pseudo-first order model (min^{-1}), t is time (min), C_0 is the initial concentration of MC-LR (ppm) and C is the concentration of MC-LR (ppm) at the specific time. Coefficient of determination (R^2) of plot of $\ln(\text{C}/\text{C}_0)$ versus t is close to 1,

indicating that the degradation fits the pseudo-first order kinetics nicely. These results indicate RB can be used as a photosensitizer (catalyst) to effectively degrade MC-LR. Rate of degradation increase three fold under oxygen saturated conditions compared to argon-saturated conditions (**Table 4.1**), demonstrating that photo-oxidation is the predominant degradation process. Under argon saturation the degradation is likely due to the energy transfer between the RB^* and MC-LR. These results are in general consistent with the interactions between $^1\text{O}_2$ and aquatic fulvic acids in presence of RB. There are two pathways: $^1\text{O}_2$ process and non- $^1\text{O}_2$ process, and the $^1\text{O}_2$ process is predominant (Cory et al., 2008).

To investigate the role of singlet oxygen on degradation of MC-LR, reaction is conducted in D_2O . The quantum yield of RB in D_2O is as same as in H_2O (DeRosa et al., 2002), but the life time of $^1\text{O}_2$ in D_2O is ~ 20 times longer in H_2O . Therefore, the $^1\text{O}_2$ mediated degradation is generally enhanced in D_2O . The degradation of MC-LR in D_2O is evaluated. On the basis of the $R^2 \geq 97\%$ of plot of $\ln([\text{MC-LR}]/[\text{MC-LR}]_0)$ against time, it follows pseudo-first order kinetic model nicely in oxygen-saturated D_2O . A significant increase of rate constant from 0.036 ± 0.007 to $0.073 \pm 0.017 \text{ min}^{-1}$ is observed. The enhancement of photodegradation in D_2O further supports the conclusion that $^1\text{O}_2$ plays a critical role in photodegradation of MC-LR.

Table 4.1 Kinetics parameters of MC-LR degradation in presence of 500 μM RB

experimental condition	$k \text{ (min}^{-1}\text{)}$	R^2
argon-saturated in H_2O	0.012 ± 0.002	$\geq 96\%$
oxygen-saturated in H_2O	0.036 ± 0.007	$\geq 98\%$
oxygen-saturated in D_2O	0.073 ± 0.017	$\geq 97\%$

4.5.2 $^1\text{O}_2$ competition kinetic measurements

The singlet oxygen rate constant with MC-LR was determined using FFA as a competing probe based on the measurement of FFA concentration by HPLC monitoring absorption at 219 nm. FFA reacts with $^1\text{O}_2$ with the bimolecular rate constant of $k = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in water (Haag et al., 1986). The bimolecular reaction rate constant between MC-LR and $^1\text{O}_2$ is $3.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ by multiplying the slope of Fig.3 by k of FFA (Song et al., 2012). Since the MC-LR also can be degraded by RB^* via energy transfer, the actual bimolecular rate constant is $\sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

Figure 4.3 Competitive $^1\text{O}_2$ degradation of MC-LR with FFA

The dissolved organic matter is present in natural surface water, and $^1\text{O}_2$ and $\bullet\text{OH}$ are formed upon irradiation. Since the formation rate of $^1\text{O}_2$ is higher by two to three orders of magnitude than $\bullet\text{OH}$, the steady-state concentration of $^1\text{O}_2$ is ~ 50 -1,400 fold of $\bullet\text{OH}$ (Vione et al., 2010). The reported bimolecular rate constants of $^1\text{O}_2$ with organic

compounds in aqueous solution range from $\sim 10^6$ to $10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Czaplicka, 2006), whereas $\bullet\text{OH}$ is higher by one to three orders of magnitude than $^1\text{O}_2$ (Buxton et al., 1988). For MC-LR, the bimolecular rate constant for the reaction of $\bullet\text{OH}$ is $2.3 (\pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Song et al., 2009).

4.6 Conclusions

Our results demonstrate that MC-LR is rapidly photodegraded by RB, and the degradation of MC-LR follows the pseudo-first order kinetic model nicely under argon-saturated and oxygen-saturated conditions. The pseudo-first order kinetic rate constant of degradation increases three fold under oxygen-saturated condition compared to argon-saturated condition, demonstrating that $^1\text{O}_2$ process is the predominant degradation pathway and non- $^1\text{O}_2$ process (energy transfer) also plays an important role for the degradation of MC-LR. It is consistent with the increase of rate constant in D_2O . The measured bimolecular reaction rate constant between MC-LR and $^1\text{O}_2$ is $\sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$ from competition kinetics with furfuryl alcohol.

5 Chromium(VI) Removal by Maghemite Nanoparticles

5.1 Abstract

Maghemite nanoparticles were prepared by a co-precipitation method and characterized by Fourier transform infrared spectroscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, nitrogen adsorption and desorption isotherms. The Brunauer-Emmett-Teller surface area, average particle size, pore volume and porosity of maghemite were $73.8 \text{ m}^2 \text{ g}^{-1}$, $17.2 \pm 4.4 \text{ nm}$, $0.246 \text{ cm}^3 \text{ g}^{-1}$, and 56.3 %, respectively. Removal of Cr(VI) by the maghemite nanoparticles follows a pseudo-second-order kinetic process. Intraparticle diffusion kinetics implies the adsorption of Cr(VI) onto the maghemite occurs via two distinct phases: the diffusion controlled by external surface followed by an intra-particle diffusion. The equilibrium data was nicely fit to the Langmuir and Langmuir-Freundlich (L-F) models and indicates the adsorption of Cr(VI) is spontaneous and highly favorable. The heterogeneity index, 0.55, implies heterogeneous monolayer adsorption. The adsorption Cr(VI) is favorable under acidic and neutral conditions with maximum removal observed at pH 4. The adsorption of Cr(VI) is modestly inhibited by the presence of $\geq 5 \text{ ppm}$ humic acid. In summary, the adsorption of Cr(VI) by maghemite nanoparticles is rapid, can be accurately modeled, and is effective under a variety of conditions. Our results indicate these magnetic materials have promising potential to cleanup Cr(VI) contaminated waters to acceptable drinking water standards.

5.2 Keywords

Maghemite nanoparticles, chromate, adsorption isotherm, kinetic study, pH effect, humic acid

5.3 Introduction

Chromium is a common drinking water contaminant in the USA because of its wide spread use in industrial processes (Johnson et al., 2006). The use of chromium in wood preservatives, leather tanning, paint formulation, steel fabrication, and metal finishing are the main sources of chromium based pollution. The toxicity and mobility of chromium are strongly dependent on the oxidation state. In nature, chromium exists primarily in two oxidation states (III and VI). Cr(III), an essential trace element for human beings, may play a role in the metabolism of glucose (Mertz, 1993). Cr(VI) is a more toxic and soluble specie, compared to Cr(III) which is toxic only at a high concentrations. CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are the primary forms of Cr(VI) with $\text{Cr}_2\text{O}_7^{2-}$ being predominant under strongly acidic conditions and at high Cr(VI) concentrations in aqueous solutions (Pérez-Candela et al., 1995). Cr(VI) is a human carcinogen and poses a significant threat to the environment and human beings (Quievryn et al., 2002). The World Health Organization (WHO) recommends a maximum allowable level of 50 ppb total chromium for drinking water. The US Environmental Protection Agency established a guideline of 100 ppb maximum contaminant level for total chromium in drinking water (Thomas et al., 2002), while California's office of Environmental Health Hazard Assessment proposed in 1999 a public health goal of ≤ 2.5 ppb for total chromium (Pouran et al., 2008).

Unlike many organic pollutants, chromium species are not removed and/or degraded through typical environmental and biological processes, thus it is critical to develop and identify an effective method for the removal of chromium from industrial wastewater. Water purification technologies must be capable of reducing the level of

chromium considered safe for human consumption. A number of conventional methods have been employed for the removal of Cr(VI) from wastewater (Owlad et al., 2009). Adsorption processes can offer significant advantages including availability, profitability, ease of operation and efficiency, in comparison with many conventional methods. A variety of natural and synthetic materials have been used as Cr (VI) sorbents, including activated carbons, biological materials, zeolites, chitosan, and industrial wastes. Unfortunately, these sorbents can also suffer from a number of disadvantages, including high cost, low adsorption capacity and/or difficulties associated with separation and removal following treatment. The application of magnetic nanoparticles for adsorption is attractive because of their high surface area, easy separation and recovery (Banerjee et al., 2007; Hu et al., 2007). Iron based materials are especially attractive because they are inexpensive and environmentally friendly (Hu et al., 2004; Yavuz et al., 2006). The magnetite form of iron can be oxidized to maghemite under aerated conditions (Chowdhury et al., 2010). Maghemite, a common magnetic material, is a promising adsorbent for heavy metals removal because it is inexpensive, readily available and can be easily separated and recovered (Lin et al., 2012; Roy et al., 2012). While maghemite nanomaterials appear to be promising for Cr(VI) removal, detailed kinetic and adsorption studies have yet to be reported. Herein we report the synthesis of maghemite nanoparticles by a co-precipitation method. The observed adsorption of Cr(VI) by maghemite nanoparticles is rapid, accurately model and effective under a variety of conditions. Our results demonstrate these maghemite nanoparticles with high adsorption capacity and magnetic properties are promising materials for the Cr(VI) removal from aqueous solution.

5.4 Materials and methods

5.4.1 Materials

Trace metal grade nitric acid, sodium hydroxide, ferric chloride hexahydrate, ferrous chloride tetrahydrate, 29 % ammonium hydroxide and ethanol were purchased from Fisher. Potassium chromate was obtained from Mallinckrodt. Humic acid was obtained from Fluka. All the chemicals were used without further purification. All the solutions were prepared with Millipore filtered water ($18 \text{ M}\Omega \cdot \text{cm}$).

5.4.2 Preparation of maghemite

All solutions were purged with argon for 15 min to remove oxygen prior and during reaction. Iron solutions of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2.0 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.4 g) were diluted to 30 mL with water. The iron mixture was stirred magnetically, gently purged with argon and heated to 80°C and then 40 mL of 15 % diluted ammonium hydroxide solution added dropwise into the mixture over a 20 min time interval. The mixture was aged at 80°C for an additional 40 min. The product was rinsed with water then ethanol three times. The samples were separated using a magnet and dried in a vacuum oven at 50°C to a constant weight (Darezereshki et al., 2010).

5.4.3 Characterization

The dried maghemite samples from a single batch were used for adsorption experiments and characterization using XPS, FTIR and TEM. TEM was used for measurement of the average size. The Fourier transform infrared spectroscopy (FTIR) spectra were collected using a Perkin-Elmer spectrum 100 FTIR spectrometer. Transmission electron microscopy (TEM) was carried out using a Philips CM20 with field emission gun at 200 kV and energy dispersive analysis X-ray (EDAX). X-ray

photoelectron spectroscopy (XPS) was determined using a PHI 5000 VersaProbe with Al K α radiation (1486.6 eV) at a takeoff angle at 45°. The binding energies were referenced to the C1s core level at 284.8 eV. Nitrogen adsorption and desorption isotherms were performed on a Tristar 300 (Micromeritics) porosimeter analyzer. The sample was prepared by purging with nitrogen gas at 150 °C for 2.0 h using a Flow Prep 060 (Micromeritics) before analysis.

5.4.4 Adsorption tests

Volumetric glassware was used in the preparation and transfer of all Cr(VI) solutions. Maghemite particles were added to 200 mL Cr(VI) solutions at the desired concentration in a 250 mL Erlenmeyer flask. The experiments were carried out on an orbit shaker (Lab-line instrument Inc., model 3520) with continual mixing at 300 RPM at ~ 25 °C in a temperature controlled laboratory. Five mL of sample were taken at the specific time intervals and filtered through a 0.45 μ m PTFE filter immediately to remove the suspended particles. To the filtrates, nitric acid was added to yield a nitric acid concentration of 0.2 % prior to analysis. The concentration of chromium was measured using a Perkin-Elmer AA600 atomic absorption spectrophotometer. The current was 25.0 mA, with the wavelength of detection set at 357.9 nm and slit bandwidth of 0.7 nm as recommended by the manufacturer. Sample concentrations were determined based on a calibration of the instrument in the range from 1 to 50 ppb of chromium. The reproducibility based on representative triplicate runs was $\pm$ 5 %.

5.5 Results and discussion

5.5.1 Characterization

FTIR analysis was employed to determine specific functional groups of the nanoparticles. The most abundant functional group observed in our samples of maghemite was the hydroxyl group with a broad band at 3300 cm^{-1} (OH stretching mode), and bands at 1625.3 and 1428.2 cm^{-1} (OH bending modes). The Fe-O stretching bands appear at 539.2 and 526.8 cm^{-1} (Cornell et al., 2003). The TEM image of maghemite shows the average size of synthesized maghemite particle is $17.2 \pm 4.4\text{ nm}$ (**Figure. 5.1**). The EDAX analysis showed the particles contained 31.28 % O, 1.75 % C and 66.97 % Fe (Wt %).

Figure 5.1 TEM image of maghemite

The Brunauer-Emmett-Teller (BET) surface area, pore volume, porosity, Barret-Joyner- Halenda (BJH) pore size and distribution were obtained from nitrogen adsorption

and desorption isotherms. The nitrogen adsorption and desorption isotherms are showed in **Figure. 5.2** with a characteristic type H3 hysteresis loop. The BJH pore size distribution was inserted in **Figure. 5.2**, and a sharp peak appears at 13.28 nm. The BET surface area, pore volume and porosity are $73.8 \text{ m}^2 \text{ g}^{-1}$, $0.246 \text{ cm}^3 \text{ g}^{-1}$, 56.3 %, respectively. The chemical composition was further characterized using XPS. The XPS spectrum is shown in **Figure. 5.3**. The predominant elements are Fe and O, and small amounts of residual Cl and C are also present. The peaks at binding energy of 56, 198.3, 284.8 and 530.4 eV were designated for $\text{Fe}3\text{p}_{3/2}$, $\text{Cl}2\text{p}$, $\text{C}1\text{s}$ and $\text{O}1\text{s}$, respectively. High resolution XPS of $\text{Fe}2\text{p}$ is inserted in **Figure. 5.3**. Binding energy of $\text{Fe}2\text{p}_{1/2}$ is 724.8 eV and binding energy of $\text{Fe}2\text{p}_{3/2}$ is 711.1 eV. The presence of satellite peak at 719 eV is characteristic for maghemite. These results agree with literature values of maghemite particle (Gota et al., 1999; Li et al., 2011). A multiplet analysis of the $\text{Fe}2\text{p}_{3/2}$ peak indicates again the sample is maghemite (Grosvenor et al., 2004).

Figure 5.2 Nitrogen adsorption and desorption isotherms. The insert is pore size distribution of maghemite particles

Figure 5.3 XPS of maghemite particles and high resolution XPS of Fe2p core level (the insert)

5.5.2 Effect of the concentration of maghemite on Cr(VI) adsorption

The Cr(VI) adsorption by maghemite was performed with continuous mixing on an orbit shaker at room temperature and 300 RPM. The Cr(VI) remaining in solution was monitored as a function of maghemite concentration and contact time.

Experiments were run with the initial concentration of Cr(VI) at 500 ppb, while varying the contact time from 0 to 120 min, and initial concentration of maghemite from 0.1 to 1.5 g L⁻¹. The adsorption of Cr(VI) by maghemite particle was rapid in the first 5 min followed by a slow Cr(VI) adsorption stage at longer contact times as illustrated in **Figure. 5.4**. At initial maghemite concentrations ≥ 0.3 g L⁻¹, the concentration of Cr(VI) in the aqueous phase was effectively reduced to 100 ppb within 60 min. Under these conditions the concentration of Cr in solution was reduced within the drinking water guidelines recommended by EPA. The residual Cr(VI) in solution increased as a function of decreasing concentration of maghemite. Based on the adsorption studies, a concentration of 0.3 g L⁻¹ maghemite was employed for studying the kinetics and equilibrium adsorption isotherms.

Figure 5.4 Effect of the concentration of maghemite particles on Cr (VI) adsorption

5.5.3 Effect of the initial Cr(VI) concentration and contact time on Cr(VI) adsorption

The concentration of Cr(VI) in the aqueous phase versus the adsorption time at various initial concentrations of Cr(VI) is illustrated in **Figure. 5.5**. The adsorption process is rapid for the first 20 min, followed by a slower uptake. The concentration of Cr(VI) in the aqueous phase at equilibrium gradually increases with increases in the initial concentration of Cr(VI). After 2 hours, the observed removal efficiency of Cr(VI) by maghemite at initial Cr(VI) concentration of 50, 100, 200, 300, 400, 450 and 500 ppb were 100 %, 99.4 %, 98.5 %, 97.3 %, 96.7 %, 92.8 % and 91.4 %, respectively. Under these experimental conditions, the removal efficiency of Cr(VI) modestly decreased as a function of the increase in initial concentrations of Cr(VI).

Figure 5.5 Effect of the initial concentration of Cr(VI) and contact time on Cr(VI) removal

5.5.4 Adsorption kinetic study

5.5.4.1 Pseudo-second-order model

To further investigate the adsorption of Cr(VI) by co-precipitation prepared maghemite, an adsorption kinetic study was carried out. Application of pseudo-first order kinetic model to experimental data yielded poor results. With this in mind, we applied the pseudo-second-order equation expressed below (Yuan et al., 2010):

$$dQ_t/dt = k_p (Q_e - Q_t)^2 \quad (5.1)$$

where k_p is the rate constant of pseudo-second-order model ($\text{g mg}^{-1} \text{min}^{-1}$), t is the reaction time (min), Q_t is the amount of adsorbate adsorbed per unit mass by maghemite at the specific time (mg g^{-1}), and Q_e is the adsorption capacity at adsorption equilibrium (mg g^{-1}), respectively.

The pseudo-second-order kinetics model nicely simulates the adsorption of Cr(VI) by maghemite and the resulting kinetic parameters are summarized in **Table 5.1**. The data indicate the adsorption of Cr(VI) at each specific initial Cr(VI) concentration nicely fits the pseudo-second-order model based on the coefficient of determination (R^2). The mathematical expressions of initial Cr(VI) concentration (C_0 in ppb) versus k_p and Q_e , and both of with k_p and Q_e are a function of initial Cr(VI) concentration, are expressed in **Eqs. 5.2** and **5.3**. The k_p decreased as the increase of initial Cr(VI) concentration, while Q_e increased linearly. Substituting **Eqs. 5.2** and **5.3** into **Eq. 5.1** yields **Eq. 5.4**, an empirical adsorption kinetics equation. The adsorption rate is a function of C_0 . For a typical second-order kinetic reaction, the rate constants are temperature dependent, and it usually follows the Arrhenius equation. However the rate constants decreased with an increase in the initial Cr(VI) concentration. Ofomaja suggested that a chemical activation mechanism occurred during the adsorption process for an analogous behavior for adsorption of methylene blue onto palm kernel fibre (Ofomaja, 2007). The adsorption is accurately modeled by pseudo-second-order model at a fixed initial Cr(VI) concentration under these experimental conditions.

$$k_p = 22,142 C_o^{-1.838} \quad (5.2)$$

$$Q_e = 0.0031 C_o + 0.0294 \quad (5.3)$$

$$dQ_t/dt = 22,142 \times C_o^{-1.838} \times (0.0031 C_o + 0.0294 - Q_t)^2 \quad (5.4)$$

Table 5.1 Kinetic parameters of pseudo-second-order model for adsorption of Cr(VI) as a function of initial concentration of Cr(VI)

C_0	k_p	Q_e
(ppb)	(g mg ⁻¹ min ⁻¹)	(mg g ⁻¹)
50	17.22	0.166
100	4.01	0.333
200	1.58	0.661
300	0.62	0.984
400	0.38	1.304
450	0.28	1.409
500	0.23	1.551
$R^2 \geq 0.999$		

5.5.4.2 Intraparticle diffusion kinetic model

The intraparticle diffusion kinetic model has also been employed to investigate the adsorption processes (Mall et al., 2006). The model is expressed as:

$$Q_t = k_{id} t^{1/2} + C \quad (5.5)$$

where k_{id} is the intraparticle diffusion rate constant (mg g⁻¹ min^{-1/2}) and C , the intercept represents the thickness of boundary layer effect. There is a positive relationship between the value of C and the boundary layer effect that implies the contribution of surface sorption in the rate-controlling step. The intraparticle diffusion plot is given in **Figure. 5.6**. If the regression of Q_t against $t^{1/2}$ is linear and the intercept is 0, the adsorption rate was exclusively controlled by intraparticle diffusion. As shown in **Figure. 5.6**, the intercepts were not zero, indicating surface sorption and intraparticle

diffusion are rate controlling processes (Hameed et al., 2009). The plot suggests that the sorption followed two phases. The first phase is the diffusion controlled by external surface; and the second phase has been assigned to intra-particle diffusion (S. K. Singh et al., 2012).

Figure 5.6 Intraparticle diffusion plots for removal of Cr(VI) by maghemite particles

5.5.5 Adsorption isotherms

The adsorption of Cr(VI) onto maghemite was evaluated using the Freundlich, Langmuir, L-F and Temkin adsorption isotherms. Each of these models involves variations in the extent and different types of adsorption modes. The details of each model are provided in the following section and plots of the experimental data for models are illustrated in **Figure. 5.7-5.10**.

Freundlich isotherm assumes that the binding sites on the surface of adsorbent are heterogeneous, the adsorption is more difficult as more and more binding sites are occupied by adsorbates and multilayer adsorption can occur. The Freundlich isotherm (Reed et al., 1993) can be represented in the following form:

$$Q_e = KC_e^{1/n} \quad (5.6)$$

where C_e is the equilibrium chromium concentration in solution (mg g^{-1}). K indicates the relative adsorption capacity of the adsorbent and n represents the adsorption intensity. In order to linearize it, the Freundlich isotherm is expressed as:

$$\text{Log}Q_e = \log K + 1/n \log C_e \quad (5.7)$$

Figure 5.7 Freundlich isotherm illustrating the linear dependence of $\text{Log}Q_e$ on $\log C_e$

The K and n were derived from **Figure 5.7**. The value of K is 5.20 mg g^{-1} , while n is 2.77. The Freundlich constant, n , can be used to predict the adsorption characteristics. For $n < 1$ the adsorption is consider poor, n between a value of 1 and 2 adsorption is defined as moderately difficult with n values between 2 and 10 is considered good adsorption (Treybal, 1980). The value of $n = 2.77$ determined in our studies represents good adsorption. Our results indicate the removal of chromium with small dosages of maghemite is practical.

Langmuir isotherm equation is derived from the assumption that the adsorbent surface has a fixed number of equivalent binding sites, and the monolayer adsorption occurs without transmigration of adsorbate on the surface of adsorbent isotherm (Reed et al., 1993). The data were modeled with Langmuir adsorption isotherm.

$$C_e/Q_e = 1/bQ_m + C_e/Q_m \quad (5.8)$$

where b and Q_m are the Langmuir adsorption constant ($L\ mg^{-1}$) and maximum capacity of adsorbent ($mg\ g^{-1}$), respectively. The values of b and Q_m are determined from the plot of C_e/Q_e versus C_e (**Figure. 5.8**). Q_m is $1.62\ mg\ g^{-1}$, and b is $257.2\ L\ mg^{-1}$.

Figure 5.8 Langmuir isotherm illustrating the linear dependence of C_e/Q_e on C_e

A dimensionless constant separation factor, r , is proposed to predict whether a Langmuir adsorption system is favorable or not. The type of favorability of the absorption isotherm is defined for specific r values as follows, for $r > 1$ unfavorable, $r = 1$ is linear, r between 0 and 1 is favorable and $r = 0$ irreversible (Wan Ngah et al., 2002).

The separation factor, r , is defined as follow:

$$r = 1 / (1 + bC_0) \quad (5.9)$$

where C_0 is the initial concentration of chromium and b is the Langmuir adsorption constant (L mg^{-1}). Since both b and C_0 are greater than 0 in this study, the value of r lies within the range 0 to 1. This indicates the adsorption of Cr(VI) on maghemite particle is highly favorable under the experimental condition used in this study.

Standard Gibbs free energy (ΔG_0 , J mol^{-1}) can be used to evaluate the spontaneity of an adsorption process. A negative ΔG_0 indicates the adsorption occurs spontaneous and is thermodynamically stable, whereas the positive ΔG_0 means this process is a disfavored nonspontaneous reaction. The standard Gibbs free energy equation is expressed as following (Ho et al., 2005):

$$\ln(1/b) = \Delta G_0 / RT \quad (5.10)$$

where R is the ideal gas constant ($8.314 \text{ J K}^{-1}\text{mol}^{-1}$) and T is absolute temperature (K). Since b is 257.2 L mg^{-1} , ΔG_0 is negative in this study. The result indicates that the adsorption process is spontaneous.

L-F isotherm is the combination of Langmuir and Freundlich isotherms (Umpleby et al., 2001). The experimental data were also modeled with L-F adsorption isotherm.

$$Q_e = Q_m k C_e^m / (1 + k C_e^m) \quad (5.11)$$

where Q_m is the total amount of binding sites on the adsorbent surface, k is related to the mean association constant (K_0), $K_0 = k^{1/m}$, and m represents the heterogeneity index of the binding site energy, which varies from 0 to 1. As m approaches to 1, the adsorbent is homogeneous and the L-F equation is reduced to Langmuir. For a heterogeneous material, $m < 1$, and when either m or k is 0, the L-F equation can be reduced to

Freundlich. Therefore, L-F isotherm is able to model both of homogeneous and heterogeneous adsorption systems. The maximum of R^2 is obtained from the plot of $1/Q_e$ vs $1/C_e^m$ (**Figure. 5.9**) by solver function of Microsoft Excel 2007, where $m = 0.55$. Therefore, the value of Q_m is 2.62 mg g^{-1} , and k is equal to 8.42 mg^{-1} . The mean association constant is 48.3 mg^{-1} .

Figure 5.9 L-F isotherm illustrating the linear dependence of $1/Q_e$ on $1/C_e^m$

The Temkin isotherm equation is given as (Özacar et al., 2005):

$$Q_e = (RT/b_i) \ln K_t + (RT/b_i) \ln C_e \quad (5.12)$$

where K_t is the Temkin isotherm constant (L g^{-1}), b_i is the Temkin constant related to heat of sorption (J mol^{-1}), R is the ideal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the Kelvin temperature (K). The value of K_t and b_i were obtained by the plotting of Q_e vs $\ln C_e$ (**Figure. 5.10**). K_t is 4.39 L g^{-1} , while b_i is 8.64 kJ mol^{-1} .

Figure 5.10 Temkin isotherm illustrating the linear dependence of Q_e on $\ln C_e$

A comparison of R^2 was made among four adsorption isotherms. Compared to Langmuir, Freundlich and Temkin adsorption isotherms, L-F isotherm has the highest value of R^2 , indicating the adsorption of chromium by maghemite fits better with L-F isotherm. The heterogeneity index of L-F isotherm is 0.55, which is between 0 and 1. The adsorption has partial adsorption characteristics of Langmuir and Freundlich models. The adsorption fits also the Langmuir model nicely, and it may be due to monolayer adsorption. Therefore, adsorption isotherm studies imply that it is a heterogeneous monolayer adsorption (Lee et al., 1995).

5.5.6 The effect of pH on Cr(VI) adsorption

The pH effect on Cr(VI) adsorption was evaluated over a pH range from 2 to 10. HNO_3 and NaOH solutions were used to adjust solution pH. **Figure. 5.11** shows the Cr(VI) removal as a function of pH. Electrostatic interactions can have a pronounced impact on adsorption processes. The pK_{a1} and pK_{a2} of chromic acid are 0.74 and 6.50,

respectively. The zero point of charge (ZPC) of maghemite is 6.6 (Cornell et al., 2003). Below the pH of the ZPC the particle surface becomes positively charged, while Cr(VI) exists predominantly in dianionic (CrO_4^{2-}) and mono-anionic (HCrO_4^-) forms between pH ~2 and 6.5. Thus under mildly acidic conditions, attractive electrostatic interactions between negatively charged Cr(VI) species and the positive surface lead to favorable adsorption. We observed the removal efficiency of Cr(VI) increases with the decrease of pH to 4. However under strongly acidic conditions the adsorption decreases modestly as the Cr(VI) speciation becomes dominated by the neutral form (H_2CrO_4) eliminating the strong electrostatic attraction of negatively charged chromate species and positively charged surface. Above the pH of ZPC, the particle surface processes an overall negative charge while the dominant species of Cr(VI) is CrO_4^{2-} (Tandon et al., 1984) and thus under basic conditions electrostatic repulsion exists and poor adsorption is observed. While pH can have a pronounced influence on the adsorption, effective removal can be achieved over a significant pH range from 2 to 8.

Figure 5.11 Effect of pH on Cr(VI) adsorption. $[\text{Cr(VI)}]_0 = 500 \text{ ppb}$, $[\text{maghemite}] = 0.3 \text{ g/L}$

5.5.7 Effect of humic acid

The presence of humic acids in surface waters can have a pronounced effect on iron based water treatment processes (Gu et al., 1994). Humic acids contain carboxylic acid and phenolic functional groups which can engage in ligand exchange and complexation of metal ions (Vermeer et al., 1999). The adsorption of Cr(VI) by nanoparticles as a function of humic acid concentration is illustrated in **Figure. 5.12**. The interaction of humic acid with iron oxides can alter the surface property of maghemite nanoparticles and the subsequent adsorption of Cr(VI). In the presence of 1 ppm humic acid we observed minimal change in the overall adsorption of Cr(VI). Under such conditions stabilization of the suspension leading to inhibition of particle aggregation, reduction of Cr(VI) (Wittbrodt et al., 1995), and humic acid complexation of chromate species can contribute to the removal of Cr(VI) (Uyguner et al., 2004). At intermediate humic acid concentrations the observed Cr(VI) adsorption also does not change significantly. However as the concentration of humic acid increases the Cr(VI) adsorption decreases under our experimental conditions. The coating of maghemite nanoparticles with humic acid will increase with humic acid blocking potential adsorption sites for Cr(VI) and increasing the presence of negatively charged carboxylic groups at the surface essentially decreasing the ZPC of the particles (Illés et al., 2003). Under these conditions repulsion will increase between negatively charged Cr(VI) and negatively charged humic acid modified surface. At high humic acid concentrations Cr(VI) adsorption decreased significantly possibly due to humic acid coating the iron oxide particle (Hu et al., 2010). The removal of Cr(VI) can be achieved in the presence of significant levels of humic acid.

Figure 5.12 Effect of humic acid on Cr(VI) adsorption. $[\text{Cr(VI)}]_0 = 500$ ppb, $[\text{maghemite}] = 0.3$ g/L

5.6 Conclusion

Magnetic maghemite nanoparticles were synthesized by a co-precipitation method, characterized and employed for Cr(VI) removal. The adsorption kinetics for Cr(VI) are accurately modeled by a pseudo-second-order model. The intraparticle diffusion model implies that the adsorption was controlled by surface sorption and intraparticle diffusion, followed by a redox reaction. The adsorption isotherm fits the L-F and Langmuir equations well implying heterogeneous monolayer adsorption. The standard Gibbs free energy, adsorption characteristics and effect of separation factor on isotherm shape indicate that adsorption of Cr(VI) is spontaneous, favorable and practical. The adsorption under basic condition is weak, but strong under the mildly acidic and neutral conditions often associated with contaminated surface waters. The presence of low concentrations of humic acid does not have a significant impact on the adsorption of Cr(VI) however at relatively high humic acid concentration (20 ppm) the adsorption of Cr(VI) can be

partially inhibited. The maghemite nanoparticles are low-cost, easily prepared, magnetic, and good adsorbents for Cr(VI) making them a promising material for removal of Cr(VI) from aqueous solution.

6 Cr(VI) Adsorption and Reduction by Humic Acid Coated Magnetite

6.1 Abstract

We report the effective adsorption and reduction of toxic Cr(VI) to non-toxic Cr(III) by easily separable humic acid coated magnetite (HA-Fe₃O₄) nanoparticles. The adsorption fits the Langmuir isotherm model nicely and the extraction of Cr(VI) from aqueous media by HA-Fe₃O₄ particles follows pseudo-second-order kinetics. The extraction and reduction of Cr(VI) is effective under acidic, neutral, and basic conditions. Characterization of the Cr loaded HA-Fe₃O₄ materials by X-ray absorption near edge structure spectroscopy (XANES) demonstrates Cr(VI) was reduced to Cr(III) while the valence state of iron core is unchanged. Fe K-edge EXAFS and X-ray diffraction measurements also indicate no detectable transformation of Fe₃O₄ core occurs during Cr(VI) adsorption and reduction. We propose HA on the surface of HA-Fe₃O₄ is responsible for the reduction of Cr(VI) to Cr(III) and not the Fe₃O₄ core. The functional groups associated with HA act as ligands leading the Cr(III) complex via a coupled reduction-complexation mechanism. Extended X-ray absorption fine structure spectroscopy (EXAFS) demonstrates the Cr(III) in the chromium loaded HA-Fe₃O₄ materials has six neighboring oxygen atoms in an octahedral geometry with average bond lengths of 1.98 Å. These results demonstrate easily separable HA-Fe₃O₄ particles have promising potential for removal and detoxification of Cr(VI) in aqueous media.

6.2 Introduction

The presence of chromium (Cr) in many aquatic systems and sources of drinking water supply is a serious threat to the environment and human health. The US EPA and World Health Organization have set maximum contaminant limits for total chromium in drinking water of 100 and 50 µg/L, respectively (Thomas et al., 2002). Exposure to Cr

has detrimental health consequences on humans and has been linked to carcinomas of the respiratory organs, mutations, chromosomal aberrations, and DNA damage (Nordberg et al., 2007). The introduction of chromium into aquatic environments occurs from both natural sources and anthropogenic activities. The world-wide production of chromite is 12.8 million tons in 1999, and estimated 1068 thousand metric tons of chromium are introduced into biosphere annually (Bishnoi et al., 1993). The toxicity, solubility, and mobility of Cr are highly dependent on the oxidation state. Speciation of Cr in aqueous media occurs predominately between Cr(VI) and Cr(III). Although Cr(III) is an essential micronutrient in the human body, Cr(VI) is highly soluble in aqueous media, acutely toxic, mutagenic, and carcinogenic (O'Brien et al., 1995). Reduction of the Cr(VI) to Cr(III) is critical in the detoxification of Cr(VI)-contaminated media and effective treatment processes. Treatment strategies and current removal methods typically involve reduction of Cr(VI) to Cr (III) followed by adsorption and subsequent separation of the Cr laden absorbent by filtration or other methods (Idris et al., 2010; Owlad et al., 2009).

Iron based materials have received significant attention for environmental applications and treatment of a variety of pollutants and toxins from aqueous solutions (Niu et al., 2011; Yavuz et al., 2006). Iron magnetic nanoparticles (MNPs) are attractive for remediation applications as they possess high surface areas, are inexpensive, and easily separated and recovered by simply applying an external magnetic field. Magnetite, the most magnetic of naturally occurring minerals, is a mixture of Fe(II) and Fe(III) and exists in sediments in natural aquatic systems (King et al., 1982). Bare magnetite, Fe_3O_4 nanoparticles have been successfully applied for remediation of Cr(VI)-contaminated waters (Hu et al., 2004). The Fe(II) in magnetite can initiate the reduction of Cr(VI) to

Cr(III), and the Cr(III) can subsequently be chelated by OH groups at the surface of iron oxide to form an inner-sphere surface complex (Grossl et al., 1997; Kendelewicz et al., 2000). In addition Cr(III) can form precipitates such as Cr(OH)_3 and $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3$ in aqueous solutions (Rai et al., 1987; Sass et al., 1987). However the Fe(II) present in magnetite is highly susceptible to auto-oxidation forming Fe(III) materials which can dramatically reduce the associated magnetic properties (Chowdhury et al., 2010). Thus the reduction of Cr(VI) by Fe(II) based MNP will lead to the decrease in the magnetic properties of the materials which in turn could make their separation by simple application of a magnetic field not very effective.

Surface modification of MNP iron materials can inhibit their auto-oxidation and increase the adsorption selectivity and capacity. A number of naturally occurring and synthetic organic materials have been employed as coating materials (shells) for magnetite. Humic acid MNPs (HA- Fe_3O_4) have been synthesized and are promising materials for the removal of metals and organic contaminants (J.-f. Liu et al., 2008; Niu et al., 2011). The HA- Fe_3O_4 materials are remarkably stable under ambient conditions, resistant to auto-oxidation and maintain their magnetic properties (J.-f. Liu et al., 2008).

Humic acids are derived from plants and microbial residues, and present ubiquitous in aquatic environments. Humic acid has a high affinity to magnetite (Korshin et al., 1997) and the iron core HA shell MNPs are readily synthesized through surface complexation-ligand exchange reactions between HA and iron oxide. Humic acid materials possess a variety of functional groups, notably carbonyl groups, carboxylic acids, phenolic and hydroxyl groups. Humic acids have high adsorption capacity for metal ions because of the different and large numbers of functional groups which are

capable of complexing metal ions. Another consequence of coating of magnetite with HA is a reduction in the aggregation of iron oxide particles. The adsorption of HA can insulate the aggregation of magnetite, and the negatively charged functional groups associated with HA can neutralize magnetite particle. Magnetite particles which are completely covered by HA exhibit the characteristic of HA (Hu et al., 2010), low pH of point of zero charge and negatively charged under solution pH > 3.

Chromium(VI) removal and reduction by bare Fe based MNPs unfortunately leads to deterioration of the magnetic properties required for simple separation following treatment. HA-Fe₃O₄ hybridized materials have shown tremendous potential for water purification; however, their application for the removal of Cr has not yet been reported. The Fe(II) core and HA can in theory function as reductants for Cr(VI) under environmental conditions (Buerge et al., 1997; Wittbrodt et al., 1996). We report herein the application of HA-Fe₃O₄ nanoparticles for the removal Cr(VI) from aqueous solution. Characterization of the Cr loaded HA-Fe₃O₄ materials show Cr(VI) is reduced to Cr(III) by HA on the surface of HA-Fe₃O₄, and the functional groups associated with HA act as ligands for Cr(III) via a coupled reduction-complexation mechanism. Cr(III) has six neighboring oxygen atoms arranged in an octahedral geometry. Our results provide a fundamental understanding of the chemistry of the HA-Fe₃O₄ in the reductive complexation and immobilization of Cr(VI) from aqueous media. The HA insulates the iron core from auto-oxidation and electron transfer with Cr(VI), preserving the magnetic properties of these materials with the HA mediated conversion of carcinogenic Cr(VI) to non-toxic Cr(III). The HA-Fe₃O₄ particles are easily separated following treatment by

application of a magnetic field. Our results demonstrate their tremendous potential for removal and detoxification of Cr(VI) in aqueous media.

6.3 Materials and methods

6.3.1 Materials

Potassium chromate (99.8 %), sodium hydroxide (99.4 %), trace metal grade nitric acid (67-70 %), ammonium hydroxide (29.15 %), and ferric chloride tetrahydrate (100.8 %) were purchased from Fisher. Ferrous chloride tetrahydrate (≥ 99.0 %) and HA (sodium salt, CAS no. 68131-04-4) were obtained from Sigma. All solutions were prepared with Millipore filtered water ($18 \text{ M}\Omega \cdot \text{cm}$) produced from a nanopure diamond lab water system (Barnstead Thermolyne Corporation, Dubuque, IA).

6.3.2 Preparation of bare Fe_3O_4 , HA- Fe_3O_4 and Cr-loaded HA- Fe_3O_4

The bare Fe_3O_4 and HA- Fe_3O_4 materials were prepared according to a published method (J.-f. Liu et al., 2008). Iron solutions of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (3.0 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (6.1 g) were dissolved in 100 mL of water. The iron mixture was heated to 90°C in a 250 mL round bottom flask equipped with a reflux condenser. The reaction solution was magnetically stirred throughout the reaction process. Ten mL of 25 % ammonium hydroxide and 50 mL of 1.0 % HA solution (for HA- Fe_3O_4 synthesis) were added to the mixture rapidly and sequentially. The mixture was aged at $90 \pm 5^\circ\text{C}$ for an additional 30 min. The solid products were washed with water and dried to constant weight in a vacuum oven at $\sim 40^\circ\text{C}$. The vacuum-dried particles were stored in a vacuum desiccator.

HA- Fe_3O_4 particles (0.5 g) were added to 50 mL of 1.0 mM potassium chromate solution in a 250 mL Erlenmeyer flask. The solution pH was adjusted using 5 % aqueous

solutions of NaOH and HNO₃. The experiments were carried out on an orbit shaker (Lab-line instrument Inc., model 3520) with continual mixing at 300 revolutions per minute (RPM) for 4 hrs in a temperature-controlled laboratory. Samples were separated from the suspension with a handheld permanent magnet, washed with ~ 10 mL water four times, and dried in a vacuum oven at ~ 40 °C to constant weight. The total Cr and dissolved organic carbon in the aqueous phase were measured using an atomic absorption spectrophotometer (AAS) (Perkin-Elmer AA600) (Jiang et al., 2013) and Shimadzu TOC-VCSH total organic carbon analyzer, respectively. For the effect of humic acid on Cr in aqueous solution, the samples were filterer through Macrosep advance centrifugal devices (3K molecular weight cut-off) at 5000 RPM to remove residual humic acid, and followed by an AAS measurement.

6.3.3 Characterizations

The FTIR spectra of HA-Fe₃O₄ and Cr-loaded HA-Fe₃O₄ were collected using a Perkin-Elmer 100 FTIR spectrometer. Transmission electron microscopy (TEM) measurements were run using a Phillips CM-200 (200 kV). Nitrogen adsorption and desorption isotherms were performed for Brunauer-Emmett-Teller (BET) surface area on a Micromeritics TriStar II 3020 system and HA-Fe₃O₄ was prepared by purging with nitrogen gas at 80 °C for 4.0 h before analyses. The total carbon of HA-Fe₃O₄ was measured using a Carlo Erba NA 1500 analyzer. The X-ray diffraction (XRD) analysis was carried out on beamline X14A at National Synchrotron Light Source, Brookhaven National Lab (NSLS, BNL). The storage ring was operated at 3.0 GeV with current ~ 280 mA. The wavelength of incident beam was set at 0.7785 Å by a sagittal-focusing monochromator (Chung et al., 2000). The spot size was ~ 1.5 × 1 mm (horizon vs

vertical). A sample filled capillary tube (0.7 mm diameter) was rotated by a spinner on a six-circle Huber diffractometer. The diffraction peaks in the range $4 - 46^\circ$ were collected using a Si strip position-sensitive detector mounted on the diffractometer. The zeta potential of bare Fe_3O_4 , $\text{HA-Fe}_3\text{O}_4$ and Cr-loaded $\text{HA-Fe}_3\text{O}_4$ were measured at different pH using Malvern zetasizer Nano ZS (Malvern Instruments, UK).

The X-ray absorption spectra (XAS) were obtained on vacuum-dried samples employing a beamline X19A at NSLS. The storage ring was operated under conditions described above for XRD measurements. The relative energy resolution of X19A was approximately 2×10^{-4} for Fe *K*-edge (7112 eV) and Cr *K*-edge (5989 eV) XAS measurements, and the harmonics were minimized by detuning double-crystal Si (111) monochromator to obtain a 30 % reduction in the intensity of the incident X-ray. The Fe *K*-edge spectra and Cr *K*-edge XAS spectra of reference Cr compounds were collected using a Canberra PIPS-detector in fluorescence mode. Given the relatively low Cr concentrations, the Cr *K*-edge XAS spectra at of Cr-loaded $\text{HA-Fe}_3\text{O}_4$ samples were measured using a 4-elements Si-drift Vortex detector in fluorescence mode. The incident beam was monitored by an ion chamber filled with nitrogen gas. The X-ray absorption spectra were divided into XANES and EXAFS regions. X-ray absorption near edge structure spectroscopy were analyzed by IFEFFIT and Demeter package (Ravel et al., 2005), while EXAFS were analyzed using WinXAS 3.1 (Ressler, 1998).

6.4 Results and discussion

6.4.1 The pH effect on adsorption and reduction of Cr(VI)

We chose to investigate the adsorption and reduction of Cr(VI) on $\text{HA-Fe}_3\text{O}_4$. The synthesized $\text{HA-Fe}_3\text{O}_4$ materials employed for removal of toxic Cr(VI) are

composed of particles with average diameters of ~ 15 nm and BET surface areas $104 \text{ m}^2/\text{g}$ (**Figure. 6.1**). HA-Fe₃O₄ (0.5 g) was added to Cr(VI) solution (50 mL of 1.0 mM), and the pH was adjusted and the suspension was agitated at 300 RPM. After 4 hrs of mixing, the HA-Fe₃O₄ MNP with adsorbed Cr were separated using a hand held magnet. The solution was retained for analyses of levels of total carbon (TC) and Cr. The released TC from HA-Fe₃O₄ is an indication of desorbed HA back into solution from the particles. Only $\leq 2\%$ TC was leached under acidic, basic, and neutral conditions. Our results are consistent with a number of reports indicating desorption of HA from such materials is highly unfavorable (J.-f. Liu et al., 2008; Yang et al., 2012). After ultrafiltration for the removal of HA, the concentration of Cr did not show any significant difference, indicating that the leaching HA does not have a critical effect on the chromium in the resulting solutions.

Figure 6.1 Nitrogen adsorption and desorption isotherms of humic acid coated magnetite

The capacity for the particles to adsorb Cr was measured under acidic (pH 4), neutral (pH 7) and alkaline (pH 10) conditions. The particles maintained high Cr removal efficiency, removing 80-90 % of the Cr from solutions under acidic, neutral and alkaline conditions as illustrated in **Figure. 6.2**. While there appears to be a slight decrease in the adsorption capacity moving from acidic to alkaline conditions, the overall differences are within the reproducibility of the experiments. The solution pH often influences the adsorption processes. While under extreme pH the humic acid materials may be hydrolyzed from the surface, under the typical range of solution pH (4-10) desorption was insignificant. The observation is consistent with the documented high affinity of HA for magnetite via a ligand exchange reactions (Gu et al., 1995). The surface properties of the HA-Fe₃O₄ particles are characteristic of the HA with respect to the surface charge and the presence of HA inhibits particle aggregation normally observed in the case of unmodified magnetite (Illés et al., 2006). The pH of zero point charge (pH_{PZC}) of bare magnetite is ~ 7.6, while the pH_{PZC} of the HA-Fe₃O₄ and Cr-loaded HA-Fe₃O₄ materials was reported to be ~ 3.3 (**Figure. 6.3**), indicating that the adsorption of Cr does not change the pH_{PZC} of HA-Fe₃O₄. The HA-Fe₃O₄ materials are negatively charged except under strong acidic conditions and effective for adsorption of positively charged ions by electrostatic attraction. The pK_{a1} and pK_{a2} of H₂CrO₄ are 0.74 and 6.50, respectively. The common chemical species of Cr(VI) in aqueous media, CrO₄²⁻, HCrO₄⁻, Cr₂O₇²⁻, are negatively charged. While adsorption is often governed by electrostatic repulsion and attraction between adsorbent and adsorbate, our results demonstrate that the repulsive electrostatic interaction between the HA-Fe₃O₄ and Cr species does not inhibit the removal (extraction) of Cr(VI) from the solution.

Figure 6.2 Effect of pH on removal efficiency of chromium by HA-Fe₃O₄. [Cr(VI)]₀ = 1 mM, [HA-Fe₃O₄] = 10 g/L

Figure 6.3 Zeta potential of bare HA-Fe₃O₄, HA-Fe₃O₄, and Cr-loaded HA-Fe₃O₄ at different pHs.

To better understand the adsorption and complexation involved in the extraction of Cr(VI) by HA-Fe₃O₄, the speciation of Cr and Fe in Cr-loaded HA-Fe₃O₄ were measured using XANES technique. Cr *K*-edge XANES spectra of Cr(III), Cr(VI) and Cr(0) are provided as references for comparison with Cr-loaded HA-Fe₃O₄ under acidic, neutral and alkaline pH in **Figure. 6.4**. The spectra of the Cr-loaded HA-Fe₃O₄ materials are unchanged over the range of pH, the presence of characteristic Cr(III) features and the absence of the strong pre-edge band for Cr(VI) and the broad feature of Cr(0) clearly indicate the predominant specie is Cr(III) in the Cr-loaded HA-Fe₃O₄. The results confirm that conversion of Cr(VI) to Cr(III) is facilitated by the particles. While bare magnetite has been employed for Cr(VI) reduction(White et al., 1996), the reduction is fast under acidic conditions but decreases significantly with increasing pH (Polizzotto et al., 2005). Chromium *K*-edge XANES spectra indicate that the change of pH under our experimental conditions has no significant effect on reduction of Cr(VI). While a strong pH dependence is observed for bare Fe₃O₄, the extraction and reduction of Cr(VI) by HA-Fe₃O₄ is minimally influenced by solution pH, suggesting the reduction of Cr(VI) by these iron substrates follows different mechanisms.

Fe(II) and HA have similar reduction capacities and are capable of reducing Cr(VI) (Eary et al., 1991). To determine the involvement of Fe(II) in the core of the HA-Fe₃O₄ in the reduction of Cr(VI), iron XANES spectra were obtained **Figure. 6.5** demonstrates that no detectable change is observed in the valence states of iron during the reduction of Cr. The result indicates Fe(II) in HA-Fe₃O₄ is not responsible for Cr(VI) reduction. We employed a relatively high concentration of HA (31 g/L) for the synthesis of the HA-Fe₃O₄ particles. Complete surface coverage of magnetite can be obtained at

solution concentrations of 20 mg/L HA (Hu et al., 2010). Under our experimental conditions it appears the HA effectively insulates the iron core, prohibits the interaction of Cr(VI) and Fe(II), and thus Cr(VI) is reduced by HA (Wittbrodt et al., 1997). HA contains a variety of functional groups, including substituted phenols, α -hydroxyl carboxylic acids, oxalic acid, and α -carbonyl carboxylic acids, which are capable of initiating the reduction of Cr(VI) to Cr(III) (Deng et al., 1996; Elovitz et al., 1995). Chromium(III) can be chelated by the functional groups in HA (Nakayasu et al., 1999; Wittbrodt et al., 1995) and we propose a coupled reduction-complexation mechanism occurs between the functional groups in HA and Cr(VI).

Figure 6.4 Cr *K*-edge XANES spectra of chromium reference compounds and Cr-loaded HA-Fe₃O₄ at different pH conditions.

Figure 6.5 Fe K-edge XANES spectra of iron reference compounds and Cr-loaded $\text{HA-Fe}_3\text{O}_4$ at different pH conditions

6.4.2 The local coordination environment

EXAFS was carried out for determination of coordination number (N), bond length (R) and the Debye-Waller value (σ^2) of Cr in Cr-loaded $\text{HA-Fe}_3\text{O}_4$ (**Figure 6.6-A**, **6.7-A**, and **Table 6.1**). The typical bond lengths of Cr(III)-O and Cr(VI)-O are 1.98 ± 0.01 Å and 1.63 ± 0.03 Å (Peterson et al., 1996), respectively. The measured Cr-O bond links in the Cr loaded $\text{HA-Fe}_3\text{O}_4$ materials are identical to the literature values for Cr(III)-O bonds, summarized in **Table 6.1**. The bond length further demonstrates Cr(VI) is reduced to Cr(III) upon adsorption to $\text{HA-Fe}_3\text{O}_4$ materials. The local coordination environment of Cr(III) is the same at different solution pH under our experimental

conditions. The coordination number of Cr(III) is 6, likely an octahedral geometry (Lytle et al., 1998) as proposed in **Figure. 6.8**. Given the heterogeneous mixture of functional groups in HA, we anticipate a variety of ligands are involved in the complexation of Cr(III). The carboxylate, quinone and phenolic groups are abundant in HA and have an affinity to complex with a central Cr(III) atom.

Figure 6.6 k^3 -weighted Cr (A) and Fe (B) K-edge EXAFS spectra

Figure 6.7 Fourier-transform spectral of Cr (A) and Fe (B) resulting in a radial structure function

Table 6.1 Chromium K-edge EXAFS fitting parameters

sample	bond	N	R (Å)	σ^2 (Å ²)
K ₂ CrO ₄	Cr-O	4.0	1.65	0.0010
Cr-loaded HA-Fe ₃ O ₄ (pH 4)	Cr-O	6.4	1.98	0.0030
Cr-loaded HA-Fe ₃ O ₄ (pH 7)	Cr-O	6.2	1.98	0.0038
Cr-loaded HA-Fe ₃ O ₄ (pH 10)	Cr-O	6.3	1.98	0.0034

The coordination number (N), bond length (R) and the Debye-Waller value (σ^2) from the least-square fit of EXAFS spectra. N values were referenced against model compound K₂CrO₄. Estimated errors for N approximately 20 %, R 0.01 Å.

Figure 6.8 The proposed surface structure of adsorbed Cr on HA-Fe₃O₄

6.4.3 Crystal transformation

The FTIR analysis was employed to study the binding of HA on magnetite surface (**Figure. 6.9**). The free C=O stretching peak typically occurs $\sim 1700\text{ cm}^{-1}$, however upon complexation with Fe_3O_4 the $\text{C}=\text{O}_{\text{HA}}$ bond is weakened and the IR band shifts to the right. The observed peak at $\sim 1560\text{ cm}^{-1}$ is assigned to the $\text{C}=\text{O}_{\text{HA}}$ and is indicative of complexation of the $\text{C}=\text{O}_{\text{HA}}$ by the magnetite surface (J.-f. Liu et al., 2008). Humic acid has a high binding affinity to magnetite, and subsequent desorption is very difficult (Gu et al., 1994). The adsorption of Cr does not appear to affect the interaction between HA and Fe_3O_4 under acidic, neutral and alkaline pH conditions as indicated by the unchanged C=O band.

Figure 6.9 FTIR of $\text{HA-Fe}_3\text{O}_4$ and Cr-loaded $\text{HA-Fe}_3\text{O}_4$ particles: (a) $\text{HA-Fe}_3\text{O}_4$, (b) Cr-loaded $\text{HA-Fe}_3\text{O}_4$ (pH 4), (c) Cr-loaded $\text{HA-Fe}_3\text{O}_4$ (pH 7), and (d) Cr-loaded $\text{HA-Fe}_3\text{O}_4$ (pH 10)

X-ray diffraction was employed to assess the crystal lattice of Fe_3O_4 core in HA- Fe_3O_4 after loading with Cr(VI). The peak position and relative intensity match the literature well and demonstrate no change in lattice of iron core is observed (**Figure. 6.10**) (Sun et al., 2002). The XRD spectra show no detectable difference between the original HA- Fe_3O_4 and Cr-loaded HA- Fe_3O_4 , and iron XANES (**Figure. 6.5**), imply no transformation from magnetite to maghemite during extraction of Cr(VI). The dissolution of maghemite can lead to the formation of goethite (Polizzotto et al., 2005); however we did not detect goethite under our experimental conditions. Fe *K*-edge EXAFS (**Figure. 6.6-B, 6.7-B, and Table 6.2**) indicate there was no significant difference in the iron core of the original HA- Fe_3O_4 and Cr-loaded HA- Fe_3O_4 (Kobayashi et al., 1995). Therefore, the iron core of HA- Fe_3O_4 is unchanged during Cr adsorption and reduction processes.

Figure 6.10 XRD patterns of HA- Fe_3O_4 and Cr-loaded HA- Fe_3O_4 particles: (a) HA- Fe_3O_4 , (b) Cr-loaded HA- Fe_3O_4 (pH 4), (c) Cr-loaded HA- Fe_3O_4 (pH 7), and (d) Cr-loaded HA- Fe_3O_4 (pH 10).

Table 6.2 Iron K-edge EXAFS fitting parameters

sample	shell	bond	N	R(Å)	σ^2 (Å ²)
HA-Fe ₃ O ₄	1	Fe-O	4.4	1.95	0.011
	2	Fe-Fe	2.9	3.00	0.011
	3	Fe-Fe	7.1	3.46	0.011
	4	Fe-O	7.3	3.52	0.021
Cr-loaded HA-Fe ₃ O ₄ (pH 4)	1	Fe-O	4.8	1.95	0.010
	2	Fe-Fe	2.9	2.99	0.009
	3	Fe-Fe	8.4	3.47	0.011
	4	Fe-O	6.1	3.52	0.014
Cr-loaded HA-Fe ₃ O ₄ (pH 7)	1	Fe-O	4.8	1.95	0.010
	2	Fe-Fe	2.9	2.99	0.010
	3	Fe-Fe	7.9	3.46	0.010
	4	Fe-O	5.9	3.51	0.012
Cr-loaded HA-Fe ₃ O ₄ (pH 10)	1	Fe-O	4.2	1.95	0.011
	2	Fe-Fe	2.7	2.99	0.010
	3	Fe-Fe	6.9	3.47	0.011
	4	Fe-O	8.1	3.53	0.029

The coordination number (N), bond length (R) and the Debye-Waller value (σ^2) from the least-square fit of EXAFS spectra. Estimated errors for N approximately 20 %, R 0.01 Å.

6.4.4 Adsorption kinetics and adsorption isotherm

The adsorption kinetics and adsorption isotherm were conducted at a constant HA-Fe₃O₄ concentration (0.8 g/L) while varying initial Cr(VI) concentrations from 1-5 ppm without adjusting pH. The adsorption equilibrium was achieved by shaking the HA-Fe₃O₄ suspension at 300 RPM for 120 min, and experimental results followed a pseudo-second order kinetics nicely based on the coefficient of determinations (R^2) of the plots of t/Q_t versus t ($R^2 > 0.98$).

$$dQ_t/dt = k_p (Q_e - Q_t)^2 \quad (6.1)$$

where k_p is the rate constant of pseudo-second-order model (g/(mg · min)), t is the reaction time (min), Q_t is the amount of adsorbate adsorbed per unit mass by HA-Fe₃O₄ at the specific time (mg/g), and Q_e is the adsorption capacity at adsorption equilibrium (mg/g), respectively.

The kinetic results were analyzed using an intraparticle diffusion model, indicating that the adsorption of Cr(VI) occurs in two phases: the surface adsorption and intraparticle diffusion, followed by a redox reaction (**Figure. 6.11**).

$$Q_t = k_{id}t^{1/2} + C \quad (6.2)$$

where C is the intercept and k_{id} is the intraparticle diffusion rate constant.

Figure 6.11 Intraparticle diffusion plots

Langmuir adsorption model was employed to assess the adsorption capacity of HA-Fe₃O₄ for Cr. Langmuir adsorption isotherm assumes that the adsorbent surface has a specific number of equivalent sorption sites, and the monolayer adsorption occurs without interaction between sorption sites. The data were modeled with Langmuir adsorption isotherm (Jiang et al., 2013).

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right) C_e \quad (6.3)$$

where b and Q_m are the Langmuir adsorption constant (L/mg) and maximum capacity of adsorbent (mg g^{-1}), respectively. The values of b and Q_m are determined from the plot of C_e/Q_e versus C_e . The plot exhibits a good coefficient of correlation ($R^2 = 99\%$). In the current study, $Q_m = 3.37 \text{ mg/g}$, and $b = 23146 \text{ L/mg}$, indicating a high chromium bonding strength on HA-Fe₃O₄ that is likely due to the formation of octahedral complex.

6.5 Implications for Cr(VI) detoxification in natural aquatic systems.

Since Cr(VI) is toxic and carcinogenic, the reduction of Cr(VI) to non-toxic Cr(III) is highly desirable for treatment of Cr(VI)-contaminated water. Magnetite (Fe₃O₄) and HA are capable of reducing Cr(VI). Magnetite effectively reduces Cr(VI) but the process diminishes the associated magnetic properties. HA alone may be effective for extraction of Cr(VI) from aqueous media, however recovery of the toxin loaded HA materials is difficult. The HA-Fe₃O₄ materials are robust and easily separable. We have demonstrated the effective adsorption and extraction of Cr(VI) from aqueous media by HA-Fe₃O₄ materials. The Cr loaded HA-Fe₃O₄ materials maintain magnetic properties and are easily separated by applying a magnetic field. The extraction of Cr(VI) is effective under acidic, neutral and basic conditions. Characterization of Cr loaded HA-Fe₃O₄ materials demonstrate Cr(VI) is reduced to non-toxic Cr(III) by HA to form an octahedral complex within the HA-Fe₃O₄ materials. These easily separable materials have a high capacity for Cr(VI) adsorption and initiate reductive-complexation leading to an immobilized Cr(III) complex. HA-Fe₃O₄ appear to have remarkable potential for the treatment of Cr(VI)-contaminated water.

7 General Summary

Photocatalytic processes and magnetic iron oxide materials were employed for water treatment. The reactive oxygen species, which are generated by photoexcited TiO_2 materials and rose bengal, effectively degrades a variety of contaminants in aqueous solution. The reactive oxygen species include hydroxyl radical, singlet oxygen, superoxide anion radical and hydrogen peroxide. The magnetic iron oxide materials are used for removal of chromium(VI).

The rates of formations, steady-state concentrations, and kinetic parameters of hydroxyl radical and singlet oxygen produced by various TiO_2 photocatalysts under UV or Vis irradiations were measured using selective chemical probes. Due to the extremely high reaction rate of $\bullet\text{OH}$, its steady-state concentration is lower by 3-4 orders of magnitude than singlet oxygen. Hydroxyl radical is a predominant reactive oxygen species, and its generation is highly dependent on experimental conditions. The generation of hydroxyl radical by hollow glass microspheres coated with photocatalytic TiO_2 (HGM- TiO_2) is optimized using response surface methodology. The 3D response surface graphs of hydroxyl radical yield and average hydroxyl radical generation rate indicated that optimum conditions of loading of HGM- TiO_2 , concentration of terephthalate acid and irradiation time were 8.0 g/L, 4.0 mM, and 20 min, respectively. The optimal conditions were applied for the degradation of dimethyl phthalate (DMP). HGM- TiO_2 photocatalysis leads to the rapid destruction of DMP and there is a linear correlation between the DMP destruction and hydroxyl radical production. Conventional water treatment methods are often not effective or not practical for the removal of MC-LR. Fortunately, advanced oxidation processes have exhibited an attractive performance. $^1\text{O}_2$ can play an important role in the environmental fate and detoxification of MC-LR, so

we employed rose bengal (RB), a singlet oxygen ($^1\text{O}_2$) sensitizer, to study the photo-oxidative destruction of microcystin-LR (MC-LR). The degradation of MC-LR in presence of 500 μM RB follows the pseudo-first order kinetic model nicely, and rate constant of degradation increase three fold under oxygen-saturated condition compared to argon-saturated condition, demonstrating that photo-oxidation is the predominant degradation process. The measured bimolecular reaction rate constant between MC-LR and $^1\text{O}_2$ is $\sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$ based on competition kinetics with furfuryl alcohol.

Chromium(VI) is one common heavy metal in waste water, and the classic adsorbent need a time consuming separation process after treatment. Magnetic iron oxide materials are promising for chromium(VI) removal, since it can be easily separated by a magnetic field. Two magnetic materials, maghemite and humic acid coated magnetite, were synthesized, characterized and applied for the treatment of chromium(VI) contaminated water. The adsorption of chromium(VI) by maghemite and humic acid coated magnetite follow a pseudo-second-order kinetic process, and the adsorption of chromium(VI) is accurate modeling using adsorption isotherms. The solution pH and presence of humic acid influence adsorption behavior of maghemite, but there is a little effect of solution pH on adsorption by humic acid coated magnetite. Humic acid coated magnetite can adsorb and reduce chromium(VI) to non-toxic chromium (III). The functional groups associated with humic acid act as ligands leading the Cr(III) complex via a coupled reduction-complexation mechanism. Extended X-ray absorption fine structure spectroscopy (EXAFS) demonstrates the Cr(III) in the chromium loaded HA- Fe_3O_4 materials has six neighboring oxygen atoms in an octahedral geometry with average bond lengths of 1.98 Å.

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