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Enhanced Oxidation of Organic Contaminants by Ferrate: Acid-activated and Silica gel-enhanced Ferrate(VI) Oxidation Processes

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Abstract

Recently, the tetraoxy high-valent iron(VI), known as ferrate(VI) (Fe(VI); $\mathrm{Fe^{VI}O_4^{2}}$), received a great attention as a water-treatment chemical, because of its unique oxidation, disinfection, and coagulation properties. Though Fe(VI) has shown remarkable efficiency in oxidizing several pollutants in water, it has sluggish reactivity with some emerging organic contaminants, especially at basic pH conditions. Thus, the main objective of this PhD thesis was to activate or catalyze Fe(VI) oxidation reactions, at mild alkaline pH conditions, to enhance the oxidative transformation of organic pollutants and reduce the required dosage of Fe(VI) and contact time.

The activation of Fe(VI) by adding simple acids (HCl, HNO_3, and CH_3COOH) to the Fe(VI)-contaminant mixed solution in deionized water under slightly alkaline pH conditions was demonstrated for the first time. Acid activation of Fe(VI) resulted in increased oxidative transformation of caffeine (psychostimulant, CAF), acesulfame potassium (artificial sweetener), and atenolol (β-blocker) by ~30% within seconds to minutes (versus minutes to hours with non-activated Fe(VI)). A possible reason for the augmentation of the oxidative transformation of organics may be the increasing formation of reactive intermediate species, $\mathrm{Fe^{V}/Fe^{IV}}$, in the Fe(VI)-contaminant-acid mixture.

Further experiments demonstrated that acid-activated Fe(VI) oxidizes CAF in water at three times lower molar ratio of Fe(VI) to CAF than oxidative transformation observed by non-activated Fe(VI) (8.0 versus 25.0). CAF oxidation by acid-activated Fe(VI) was not negatively affected by anions such as Cl^-, HCO_3^-, and SO_4^{2-}, and cations such as Na^+ and Mg^{2+}. Natural organic matter (NOM) and secondary effluent (SE) wastewater organics decreased the efficiency of CAF transformation. However, acid-activated Fe(VI) could mineralize other organics present in both NOM and SE as indicated by the dissolved organic carbon removal. Comparatively, no mineralization was seen without activation of Fe(VI). Four oxidized products of CAF were identified by the liquid chromatography high resolution mass spectrometry technique. The reaction pathways of the oxidation of CAF by activated Fe(VI) have been proposed.

Moreover, the employment of simple solid silica gel (SiO_2) to remarkably enhance the oxidative transformation of CAF by Fe(VI) in water at mild alkaline pH conditions has also been demonstrated for the first time. Complete removal of CAF was achieved at Fe(VI) to CAF molar ratio of 6.0 in the presence of 4 g SiO_2/L. In the presence of SiO_2 gel, Na^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^-, and SO_4^{2-} ions had no significant effect on the removal of CAF by Fe(VI). NOM decreased the removal of CAF by Fe(VI) in the presence of SiO_2 gel. However, the influence of NOM on removal efficiency of CAF by Fe(VI) diminished by increasing the amount of SiO_2 gel in water. Identification of three products of CAF by Fe(VI)-SiO_2 system suggests a reaction pathway initiated by the attack on the C_4=C_5 double bond of CAF, which is supported by the frontier molecular orbitals calculations of CAF.

The findings of this work may spur further research on the impact of different activation methods and solid materials on the oxidation of a range of pollutants by Fe(VI).

Keywords

ferrate(VI), high-valent iron, acid activation, silica gel, enhanced oxidation, remediation, emerging organic contaminants, micropollutants, caffeine, oxidized products, ions, natural organic matter, water and wastewater treatment.

Co-Authorship Statement

This PhD thesis contains materials that are published or "under review" for publication in peer reviewed journals as listed below.

Chapter 2

Title of the Book Chapter: A Review on Ferrate(VI) and Photocatalysis as Oxidation Processes for the Removal of Organic Pollutants in Water and Wastewater

Authors: Kyriakos Manoli, Malini Ghosh, George Nakhla, Ajay K. Ray

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Chapter 3

Title of the Paper: Enhanced Oxidative Transformation of Organic Contaminants by Activation of Ferrate(VI): Possible Involvement of Fe^{V}/Fe^{IV} species.

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Reference: K. Manoli, G. Nakhla, A.K. Ray, V.K. Sharma, Enhanced oxidative transformation of organic contaminants by activation of ferrate(VI): Possible involvement of Fe^{V}/Fe^{IV} species, Chem. Eng. J. 307 (2017) 513–517

Chapter 4

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Reference: K. Manoli, G. Nakhla, A.K. Ray, V.K. Sharma, Oxidation of Caffeine by Acid-activated Ferrate(VI): Effect of Ions and Natural Organic Matter, AIChE J. (2017). doi:10.1002/aic.15878.

Chapter 5

Title of the Paper: Silica gel-enhanced Oxidation of Caffeine by Ferrate(VI)
Authors: Kyriakos Manoli, George Nakhla, Mingbao Feng, Virender K. Sharma, Ajay K. Ray
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Individual Contributions: The experimental plan was developed by Manoli in collaboration with Drs. Ray, Nakhla, and Sharma while the execution of the plan, data analysis, and writing of the manuscript predominantly completed by Manoli under the supervision of Drs. Ray, Nakhla, and Sharma. Frontier electron densities (FEDs) calculations were carried out by Dr. Feng.
Reference: K. Manoli, G. Nakhla, M. Feng, V.K. Sharma, A.K. Ray, Silica gel-enhanced oxidation of caffeine by ferrate(VI), Chem. Eng. J. (2017). doi:10.1016/j.cej.2017.08.036.

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“The roots of education are bitter, but the fruit is sweet.”

Aristotle (384-322 BC)

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List of Acronyms

AAP	acetaminophen
ABTS	2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonate)
ACE	acesulfame potassium
ATL	atenolol
CAF	caffeine
CBPs	chlorinated by-products
CSO	combined sewer overflows
DBPs	disinfection by-products
DCF	diclofenac
DOC	dissolved organic carbon
ENR	enrofloxacin
EDCs	endocrine disrupting compounds
EOCs	emerging organic contaminants
Fe(VI)	ferrate(VI)
FEDs	frontier electron densities
FLU	flumequine
HOMO	highest occupied molecular orbital
MAR	marbofloxacin
NHE	normal hydrogen electrode

NOM	natural organic matter
OFL	ofloxacin
OP	oxidized product
OTC	oxytetracycline
PMS	peroxymonosulfate
PPCPs	pharmaceuticals and personal care products
RMSE	root of the mean square error
SE	secondary effluent
USEPA	United States environmental protection agency
WWTP	wastewater treatment plant

Chapter 1

1 Introduction

Leonardo da Vinci (1452-1519), one of the brightest minds in human history with unparalleled artistic, philosophical, and scientific talents, defined water in one sentence: "*Water is the driving force of all nature*". Water is invaluable. Without it, there is no life. Ideally, all human beings should have easy access to clean water. Thus, there is a "diachronically urgent" need for the development of sustainable water and wastewater treatment technologies to meet the needs of current and future generations.

1.1 Motivation & Background

Access to clean water is a global challenge. Around 1.2 billion people do not have access to safe drinking water and 2.6 billion people have unacceptable water or no sanitation [1]. More than 2 million people die annually due to diseases related to unsafe water [1,2]. Among them, more than 1.5 million children die each year because of diarrheal disease [3]. Many more people are sickened by waterborne bacteria and enteric viruses [1]. In developing countries, the surface waters such as lakes and rivers, drastically increase the risk of waterborne diseases, which millions of people are infected by [3].

Population growth and industrialization resulted in the use of many synthetic and natural compounds to meet the needs of the modern society. For example, 300 million tons of synthetic compounds are used in consumer and industrial products, and several million tons of pesticides and fertilizers are used annually for agriculture needs [2]. These flows of chemicals that potentially end up in surface waters include a wide range of pollutants from traditional contaminants (e.g. heavy metals) to emerging organic contaminants (EOCs) such as endocrine disrupting compounds (EDCs), pharmaceuticals, and personal care products (PPCPs). Thus, not only researchers but also regulatory agencies focused on the quality of the surface waters such as lakes and rivers [4].

Most of the EOCs, also called organic micropollutants, persist in the environment and may accumulate in food web, with unanswered short- and long-term effects on human health, aquatic life and wildlife [5–7]. For example, pharmaceuticals are designed to biologically interact with human's and animal's organisms. These molecules are produced to target different mechanisms of an organism such as enzymatic and cell-signaling, at low doses [8]. Higher concentrations have immediate and/or chronic negative effects on human's and animal's organism. Considering that toxicity is a matter of both quality and quantity, the much smaller organisms present in aquatic systems are possibly affected by EOCs at much lower concentrations than humans. Many EOCs are not easily removed by conventional wastewater treatment plants that are based on biological treatment, due to their physicochemical properties (e.g. high solubility and negligible volatility), as indicated by their presence in drinking water [8]. Thus, different technologies such as filtration, adsorption, and oxidation processes are investigated as alternatives or additions to the existing treatment processes to remove EOCs.

Among the various treatment technologies that are being studied, oxidation processes are receiving a great attention because of their ability to degrade organics in water. In the last three decades, selective oxidants such as chlorine, chlorine dioxide, ozone etc., and non-selective hydroxyl radical which is a primary oxidant in advanced oxidation processes (AOPs) such as photocatalysis, UV/H_2O_2, UV/O_3, UV/H_2O_2/O_3, H_2O_2/Fe^{3+}, H_2O_2/Fe^{2+}, UV/H_2O_2/Fe^{3+}, UV/H_2O_2/Fe^{2+} etc., have been investigated for the degradation of EOCs in water [9–21]. Hydroxyl radical has higher reactivity than selective oxidants. However, the combination of chemicals and energy in the form of light (e.g. ultraviolet (UV)) are required for the generation of hydroxyl radicals. The design of reactors to enhance the light distribution as well as materials that utilize visible light, thus enabling the use of solar light, are under investigation. Moreover, hydroxyl radicals may be easily consumed by other water matrix components [22], rather than the target EOCs, due to their high reactivity.

Chlorine is the most commonly used oxidant/disinfectant worldwide [11]. Chlorine dioxide was suggested to reduce the formation of toxic chlorinated byproducts during the disinfection of wastewater by chlorine [9]. However, the accumulation of chlorite and chlorate as byproducts of chlorine dioxide, resulted in regulations to minimize the dose of the oxidant applied for wastewater treatment [14]. Ozone, which also reacts with the same moieties (electron-rich) as other selective oxidants, has been also used to oxidize contaminants in water [17]. Ozone reacts with bromide (Br^-) to form carcinogenic bromate ion [14,22]. Chlorine also reacts with Br^- to form HOBr, which can generate toxic halogenated byproducts [22].

There has been an increasing interest in the activation of oxidants to enhance the oxidative transformation of contaminants. For example, manganese oxidants can be activated by bisulfite to enhance the oxidation of organics [23]. It is well known that Fe(III) and Fe(II) activate hydrogen peroxide in the Fenton process [24]. Moreover, the enhanced transformation of sulfamethoxazole by benzoquinone-activated peroxymonosulfate was also reported [25]. UV light has been also used to activate chlorine and hydrogen peroxide [11,12,26]. Furthermore, solid materials were employed to enhance the oxidation of contaminants by oxidants. For example, the heterogeneous catalytic effect of iron-based materials, metal oxides, minerals and activated carbon on the degradation of various organic contaminants by ozone has been thoroughly studied [27–31]. The catalytic effect of solids such as manganese dioxide and ruthenium nanoparticles supported on ceria or titanium dioxide has been also demonstrated for enhanced oxidation of organics by permanganate [32–34].

This PhD thesis deals with ferrate(VI) (Fe(VI)), an iron-based chemical oxidant, that leaves a nontoxic Fe(III) as a byproduct after its application. Importantly, Fe(VI) does not form brominated and chlorinated by-products (CBPs). Contrary to the many studies on activation of other oxidants, very limited work has been done so far on the activation of Fe(VI) and on the effect of solid materials on the Fe(VI)-pollutant reaction in aqueous solution. It is well known that the oxidation power of Fe(VI) depends on the pH (Fe(VI)’s reactivity is higher at low pH than at high pH) [35]. Fe(VI)’s stability in water is also a function of the pH. Fe(VI) reacts with water and this undesired reaction is favored by low pH conditions. Moreover, in wastewater treatment, the required effluent pH is typically from 6 to 9 [36], and hence very high or low pH conditions are generally avoided. Interestingly, Fe(VI) is most stable at slightly basic pH values albeit less reactive [35,37].

Thus, activating or catalyzing Fe(VI) oxidation reactions at slightly basic pH conditions is becoming a necessity to enhance the oxidative transformation of pollutants by Fe(VI).

1.2 Thesis Objectives

The main objective of this research is to find simple methods for activating or catalyzing the Fe(VI) oxidation reactions, at slightly basic pH conditions, to enhance the oxidative transformation of organic contaminants, and decrease the Fe(VI) to organic molar ratio and reaction time required. The demonstration of the activation and catalysis of Fe(VI) reaction has been carried out using caffeine, an organic molecule with high environmental relevance, as a model pharmaceutical. The specific research objectives are to:

i) demonstrate the enhanced oxidation of caffeine, acesulfame K, and atenolol, by activating Fe(VI) using simple acid

ii) explore the possible reactive species responsible for the observed enhancement

iii) demonstrate the enhanced oxidation of caffeine by Fe(VI) in the presence of a simple solid silica gel (SiO_2)

iv) investigate the effect of inorganic ions and natural organic matter usually present in wastewater, on the oxidation of caffeine by Fe(VI), acid-activated Fe(VI) and silica gel-enhanced Fe(VI)

v) identify the oxidized products of caffeine by Fe(VI), acid-activated Fe(VI) and silica gel-enhanced Fe(VI)

vi) propose reaction pathways of the oxidation of caffeine by Fe(VI), acid-activated Fe(VI) and silica gel-enhanced Fe(VI)

1.3 Thesis Structure

This PhD thesis is written in the article-integrated format specified by the School of Graduate and Postdoctoral Studies of The University of Western Ontario. The contents of the six chapters included in this thesis are presented below.

Chapter 1 provides a brief introduction related to the background and motivation for developing oxidation technologies to oxidize emerging organic pollutants in water and wastewater. The research objectives of the thesis are also included in Chapter 1.

Chapter 2 is a part of a book chapter that provides a literature review on ferrate(VI). The research progress related to the oxidation of organics by ferrate(VI) (FeO_4^{2-}, Fe(VI)) is presented, including synthesis and characterization of Fe(VI), stoichiometry of the reactions (Fe(VI) to organic molar ratios), kinetic studies (second-order reaction rate constants) and pH dependency. The effects of ions on Fe(VI) oxidation of organic contaminants and the activation of Fe(VI) by different methods are also discussed. A brief review on caffeine as a model emerging organic contaminant including oxidation of caffeine by different oxidation processes is also presented.

Chapter 3 is a research article entitled “Enhanced Oxidative Transformation of Organic Contaminants by Activation of Ferrate(VI): Possible Involvement of Fe^{V}/Fe^{IV} species”. In this study, the activation of ferrate(VI) by acid (i.e. HCl, HNO_3 and acetic) was demonstrated for the first time. Acid-activation of ferrate(VI) resulted in a significant enhancement of the oxidative transformation of organics (i.e. caffeine, acesulfame potassium and atenolol) at slightly basic pH conditions, probably because of the increased formation of Fe(V)/Fe(IV) species.

Chapter 4 is a research article entitled “Oxidation of Caffeine by Acid-activated Ferrate(VI): Effect of Ions and Natural Organic Matter”. In this study, the effect of inorganic ions (Cl^-, SO_4^{2-}, HCO_3^-, Na^+, Mg^{2+} and Ca^{2+}), natural organic matter, and secondary effluent wastewater, on the oxidative transformation of caffeine by ferrate(VI) (non-activated ferrate(VI)) and acid-activated ferrate(VI) has been investigated. This article also includes the identification of the oxidized products of caffeine and proposed reaction pathways of the oxidation of caffeine by acid-activated ferrate(VI).

Chapter 5 is a research article entitled "Silica gel-enhanced Oxidation of Caffeine by Ferrate(VI)". In this study, the enhanced oxidation of a model pharmaceutical (caffeine) by ferrate(VI) in the presence of simple solid silica gel (SiO_2), in aqueous solution under mild alkaline conditions, has been demonstrated for the first time. The effect of SiO_2 gel properties (i.e. particle size and pore volume/surface area), inorganic ions (Cl^-, SO_4^{2-}, HCO_3^-, Na^+, Mg^{2+} and Ca^{2+}), and natural organic matter (5-30 mg/L) on the oxidation of caffeine by ferrate(VI) in the presence of SiO_2 gel was investigated. Moreover, the reaction pathway of the oxidation of caffeine by ferrate(VI) in the presence and absence of SiO_2 gel was proposed. Theoretical calculations of frontier electron densities (FEDs) of caffeine molecule support the initial reaction step of oxidation of caffeine by Fe(VI).

Chapter 6 includes the main conclusions of the thesis along with scientific contribution, study limitations, and recommendations for future work.

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Chapter 2

2 Literature Review

Chapter 2 provides a literature review of ferrate(VI) (Fe(VI)) including the methods used to synthesize Fe(VI) salts as well as analytical techniques used to characterize solid and liquid Fe(VI). Also, the methodology usually used for the kinetic investigation of oxidation of organics by Fe(VI) is discussed. Moreover, a comprehensive literature review of the kinetics of oxidation of PPCPs and EDCs by Fe(VI) and stoichiometry of the Fe(VI)-organic reactions (Fe(VI) to organic molar ratio) as a function of pH is presented. The effect of ions on Fe(VI) oxidation of organic contaminants and the activation of Fe(VI) by different methods are also discussed. A brief review on caffeine as a model emerging organic contaminant including oxidation of caffeine by different oxidation processes is also presented.

2.1 Introduction

Iron is one of the most abundant metals on earth, offering valence states of from 0 to VI, thus playing an important role in a wide range of areas from physiology to (bio)chemical and industrial processes [1]. In the past few decades, there has been an increasing interest in the tetraoxy high-valent iron(VI), known as ferrate(VI) (Fe(VI), FeO_4^{2-}), as a potential green molecule for organic synthesis, iron batteries, disinfection of viruses and bacteria, and water and wastewater treatment [1–7]. Fe(VI) is a powerful oxidant, leaving Fe(III) after its application, initiating the process of coagulation. As a result, Fe(VI) is a multipurpose water treatment chemical [5], acting as an oxidant, disinfectant and coagulant with a single dose and mixing unit process. The redox potentials of Fe(VI) compared to common oxidants used in water and wastewater treatment is given in Table 2.1. Fe(VI) has the highest redox potential of +2.20 V under acidic conditions (Table 2.1).

Table 2.1: Redox potentials for oxidants/disinfectants used in water and wastewater treatment [8–11].

Oxidant/Disinfectant	Reaction	E^o, V (vs NHE)
Chlorine	$Cl_2(g)+2e^- \leftrightarrow 2Cl^-$	1.36
Hypochlorite	$HClO+H^++2e^- \leftrightarrow Cl^-+H_2O$	1.48
	$ClO^-+H_2O+2e^- \leftrightarrow Cl^-+2OH^-$	0.84
Chlorine dioxide	$ClO_2(aq)+e^- \leftrightarrow ClO_2^-$	0.95
Perchlorate	$ClO_4^-+8H^++8e^- \leftrightarrow Cl^-+4H_2O$	1.39
Ozone	$O_3+2H^++2e^- \leftrightarrow O_2+H_2O$	2.08
	$O_3+H_2O+2e^- \leftrightarrow O_2+2OH^-$	1.24
Hydrogen peroxide	$H_2O_2+2H^++2e^- \leftrightarrow 2H_2O$	1.78
	$H_2O_2+2e^- \leftrightarrow 2OH^-$	0.88
Dissolved oxygen	$O_2+4H^++4e^- \leftrightarrow 2H_2O$	1.23
	$O_2+2H_2O+4e^- \leftrightarrow 4OH^-$	0.40
Permanganate	$MnO_4^-+4H^++3e^- \leftrightarrow MnO_2+2H_2O$	1.68
	$MnO_4^-+8H^++5e^- \leftrightarrow Mn^{2+}+4H_2O$	1.51
Ferrate(VI)	$FeO_4^{2-}+8H^++3e^- \leftrightarrow Fe^{3+}+4H_2O$	**2.20**
	$FeO_4^{2-}+4H_2O+3e^- \leftrightarrow Fe(OH)_3+5OH^-$	0.72

Fe(VI) is unstable in aqueous solutions. In other words, Fe(VI) reacts with water to form molecular oxygen (Eq. 2.1) [5]. It was recently shown that hydrogen peroxide (H_2O_2) is also formed from the self-decay of Fe(VI) in phosphate buffered solutions [12]. The rate of Fe(VI) self-decomposition depends on the pH, temperature, initial Fe(VI) concentration, water constituents, and the physical properties of the Fe(III) oxides/hydroxides formed during the Fe(VI) degradation [1].

$$2Fe^{VI}O_4^{2-} + 5H_2O \rightarrow 2Fe^{III} + 1.5O_2 + 10OH^- \quad (2.1)$$

Several reactions may occur during the oxidation of an organic compound (X) by Fe(VI) [5,13]:

i) $1\text{-}e^-/2\text{-}e^-$ transfer to form Fe^{V}/Fe^{IV} and ultimately Fe^{III}/Fe^{II} as final products (e.g. $Fe^{VI} \rightarrow Fe^{V} \rightarrow Fe^{III}$ and $Fe^{VI} \rightarrow Fe^{IV} \rightarrow Fe^{II}$).

ii) Further reaction of Fe(V) and/or Fe(IV) with X.

iii) Fe(VI), Fe(V) and Fe(IV) self-decompositions.

iv) Reactions between iron species $Fe^{II}/Fe^{III}/Fe^{IV}/Fe^{V}/Fe^{VI}$ and/or oxygen species (i.e. H_2O_2) formed from self-decompositions (e.g. $Fe^{VI} + Fe^{II} \rightarrow Fe^{V} + Fe^{III}$ and $Fe^{II}/Fe^{III} + O_2/H_2O_2 \rightarrow Fe^{IV}/Fe^{V}$).

It is known that Fe(V) is 2-4 orders of magnitude more reactive than Fe(VI) probably because of its partial free radical character [9].

2.2 Synthesis

Different approaches were investigated to produce Fe(VI) salts (e.g. $Na_2Fe^{VI}O_4$ and $K_2Fe^{VI}O_4$). The main methods used for the synthesis of sodium and potassium Fe(VI) i.e. the electrochemical, wet chemical, and dry thermal methods are discussed below.

2.2.1 Electrochemical Synthesis

In this method, highly concentrated NaOH or KOH or their combination is used as the electrolyte [14]. Cast iron is used as the anode (iron source) and it is dissolved and then it is oxidized to form K_2FeO_4 [8]. The reactions that take place are presented below (Eqs. 2.2-2.5) [8,11,14].

Anode reaction:

$$Fe + 8OH^- \rightarrow FeO_4^{2-} + 4H_2O + 6e^- \tag{2.2}$$

Cathode reaction:

$$2H_2O \rightarrow H_2 + 2OH^- - 2e^- \tag{2.3}$$

Overall reactions:

$$Fe + 2OH^- + 2H_2O \rightarrow FeO_4^{2-} + 3H_2 \tag{2.4}$$

$$FeO_4^{2-} + 2K^+ \rightarrow K_2FeO_4 \tag{2.5}$$

Other iron-based anodes such as steels are also used for the production of Fe(VI) [11]. The main advantage of the electrochemical method is the use of electrons as reactants to produce Fe(VI), while the main drawback of this method is the challenging separation of the product in solid form [9]. Moreover, the addition of the produced Fe(VI) solution to water results in high pH (>11) [11,15]. The Fe(VI) production efficiency mainly depends on the composition of anode, concentration of electrolyte, and current density [8,14]. In Table 2.2, the efficiencies (ratio of the experimentally produced Fe(VI) to the theoretical amount of Fe(VI) calculated by Faraday's law [16]) and the operational conditions of typical electrochemical production of Fe(VI) reported in different studies, are presented.

Table 2.2: Efficiency and operational conditions of electrochemical production of ferrate(VI).

Efficiency (%)	Operational Conditions	Reference
15	Raw iron current density=10 A/m^2 [NaOH]=16.5 M	[17]
27	Steel current density=10 A/m^2 [NaOH]=16.5 M	[17]
50	Cast iron current density=10 A/m^2 [NaOH]=16.5 M	[17]
35	Steel (0.1%C) current density=36 A/m^2 [NaOH]=16 M	[18]
38	Steel (0.3%C) current density=46.19 mA/cm^2 [NaOH]=12 M	[19]

2.2.2 Wet Chemical Method

In the presence of sodium hydroxide, Fe(III) salt (e.g. $FeCl_3$) reacts with sodium hypochlorite producing sodium Fe(VI) (Na_2FeO_4) [19]. Because of the high solubility of Na_2FeO_4 in NaOH solutions, it is difficult to obtain solid Na_2FeO_4 [11]. A much less soluble potassium Fe(VI) (K_2FeO_4) is precipitated by adding KOH to the Na_2FeO_4 solution [1,5]. The reactions that take place are presented below (Eqs. 2.6 and 2.7) [9]:

$$2FeCl_3 + 3NaOCl + 10NaOH \rightarrow 2Na_2FeO_4 + 9NaCl + 5H_2O \tag{2.6}$$

$$Na_2FeO_4 + 2KOH \rightarrow K_2FeO_4 + 2NaOH \tag{2.7}$$

The yield (in terms of potassium Fe(VI)-K_2FeO_4) of this procedure is 10%-15% and numerous separation steps are needed to obtain a solid potassium Fe(VI) of high purity (98%). A yield of potassium Fe(VI) up to 75% was achieved by replacing the sodium hydroxide with the potassium hydroxide [11,20]. In that case the formation of Na_2FeO_4 was avoided. Ozone instead of hypochlorite can be also used to prepare Fe(VI) [21].

2.2.3 Dry Thermal Method

Potassium Fe(VI) can be produced by calcination of ferric oxide-potassium peroxide mixture at 350-370 °C or by oxidizing the iron oxide using sodium peroxide at 370 °C, under dry oxygen conditions [8,9,11]. Moreover, galvanizing wastes were used to produce sodium Fe(VI), by mixing them with ferric oxide at 800°C. Then, the mixture was cooled down, stirred with solid sodium peroxide, and heated gradually for few minutes [8,11]. The yield of the dry thermal method is usually less than 50% [9]. The dry synthesis is considered as an old and expensive method due to the required high temperatures [11]. Solid sodium Fe(VI) was produced using caustic soda (instead of potassium hydroxide) and sodium hypochlorite (instead of calcium hypochlorite), which are cheaper [22].

2.3 Characterization

Different analytical techniques were investigated to characterize solid and liquid Fe(VI). Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction, X-ray absorption near edge structure (XANES) and Mössbauer spectroscopy are used to characterized solids salts of Fe(VI) [5,13]. The reactions of Fe(VI) with chromium(III) and arsenic(III) to form chromate(VI) and arsenate respectively, can be used to quantify $Na_2Fe^{VI}O_4$ and $K_2Fe^{VI}O_4$ in solutions (volumetric methods) [21]. The formed chromate is titrated with ferrous salt solution using sodium diphenylamine sulphonate as an indicator (in acidic medium) [8]. In the case of arsenic(III) method, the unreacted arsenite (after the addition of a weighted ferrate sample to the arsenite alkaline solution) is titrated with bromate or cerate solution [8]. Furthermore, electrochemical techniques including cyclic voltammetry and potentiometry are also available methods for Fe(VI) quantification in solutions [23,24]. In addition, a fluorescence method by means of Fe(VI) reaction with scopoletin (fluorescence agent) is also used to determine Fe(VI) in acidic solutions [25].

Among the various analytical techniques, three colorimetric methods (Iodide, ABTS and Direct) are mainly used for the quantification of Fe(VI) in solutions related to water treatment. Fe(VI) solutions have a characteristic purple color with a maximum absorbance at 510 nm and a molar absorptivity (ε) of 1150 M^{-1} cm^{-1} [21]. Thus, the direct colorimetric method is widely used for quantification of Fe(VI) in alkaline solutions where Fe(VI) is more stable, to investigate the kinetics of the reaction of Fe(VI) with organic molecules. A typical spectra of potassium Fe(VI) in Milli-Q water is shown in Figure 2.1. The interference with water constituents and the dependency on the pH and Fe(VI) stability are the main limitations of the direct colorimetric method [21].

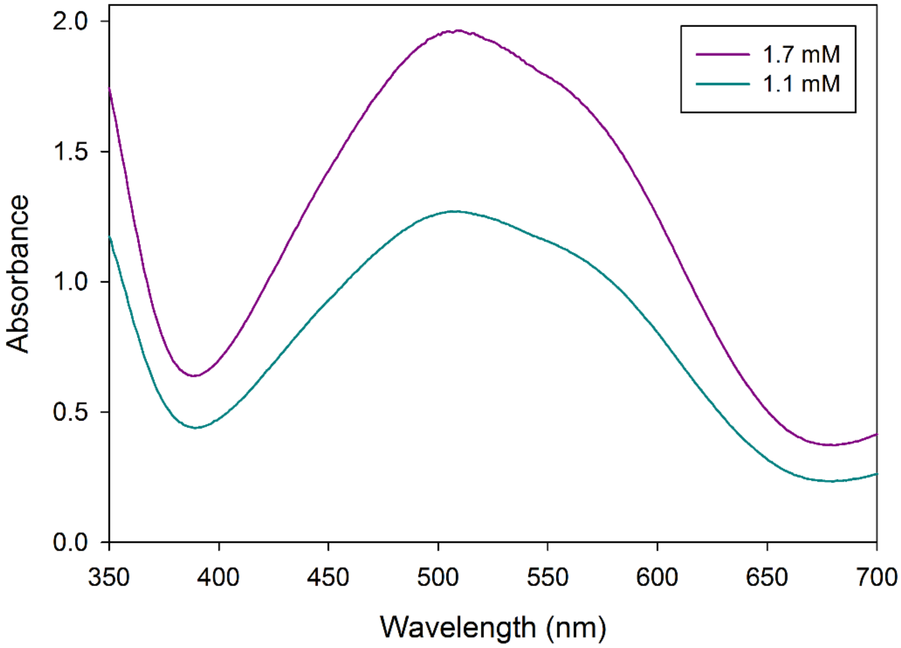


Figure 2.1: Spectra of ferrate(VI) in Milli-Q water.

The ABTS colorimetric method is based on the reaction of Fe(VI) with the 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS). A stable radical cation ($ABTS^{\bullet+}$) is formed showing peak absorbance at 415 nm [26]. The reaction of ABTS with Fe(VI) is very fast making the method suitable for determining Fe(VI) also in natural waters at a concentration range of 0.03-35 µM [26]. The Iodide colorimetric method is based on the reaction of Fe(VI) with sodium iodide, to produce I_3^- that shows peak absorbance at 351 nm [21]. The minimum detection limit of this method is 0.25 µM Fe(VI) and the method is also suitable for determining Fe(VI) in tap water [21]. A comparison of the three commonly used colorimetric methods is given in Table 2.3.

Table 2.3: Spectrophotometric methods for ferrate(VI) determination in water [11,22,27].

Method	**Reaction**	**Wavelength, λ (nm)**	**Molar absorptivity, ε (M^{-1} cm^{-1})**	**pH**
Direct	-	510	1150	9.1
ABTS	Fe(VI) + 2ABTS → Fe(III) + $ABTS^{\bullet +}$ + $ABTS_{oxidized}$	415	34000	4.3
Iodide	Fe(VI) + $3I^-$ → Fe(III) + I_3^-	351	29700	5.5-9.3

2.4 Oxidation

2.4.1 Kinetics of the Oxidation of Organics by Ferrate(VI)

Kinetic studies on the oxidation of a broad range of inorganic and organic compounds have been carried out to understand different reactions and the Fe(VI)-related chemistry [13,27–30]. Nowadays, there is an increasing interest in oxidation of emerging organic pollutants such as PPCPs and EDCs by Fe(VI), because of the increasing concerns related to their negative effects on the aquatic environment [1,11,31].

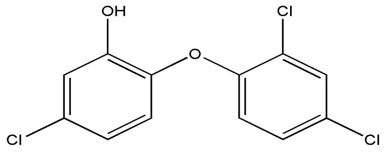
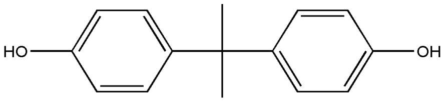
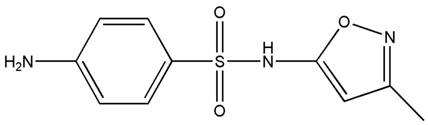
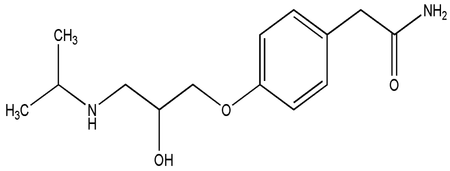
Most of the kinetic studies of oxidation of organic compounds (X) by Fe(VI) have been carried out using a stopped-flow spectrometry technique. The reactions of Fe(VI) with X follow overall second order kinetics i.e. first order with respect to each reactant, Fe(VI) and X (Eq. 2.8) [13]:

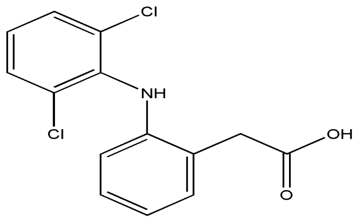
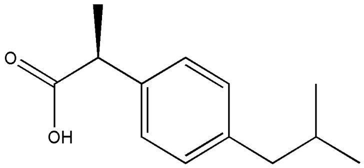
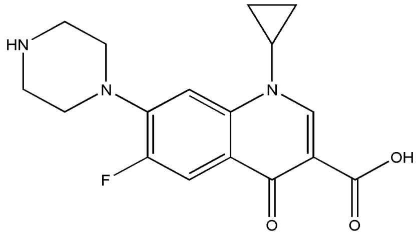
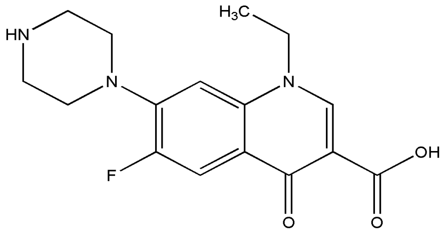
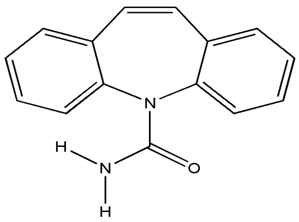
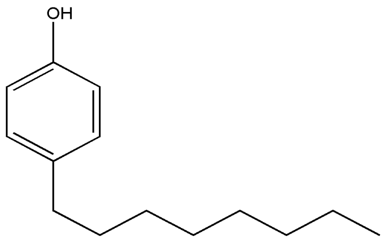
$$-\frac{d[Fe(VI)]}{dt} = k_{app} \times [Fe(VI)] \times [X] \tag{2.8}$$

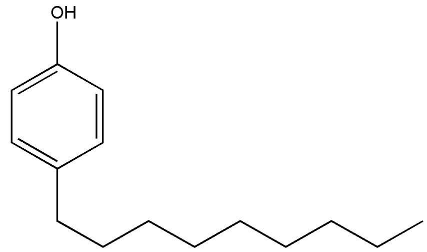
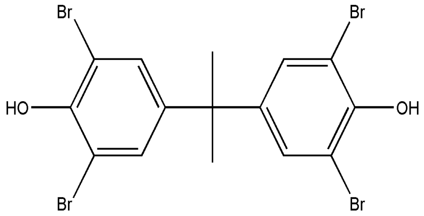
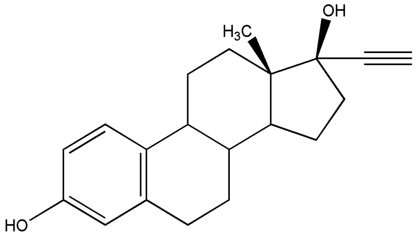
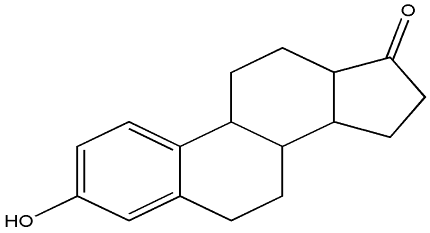
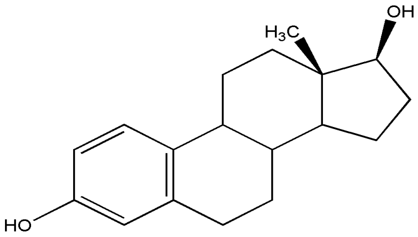
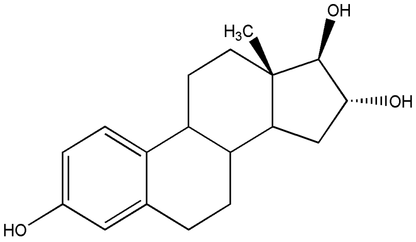
Where $\frac{d[Fe(VI)]}{dt}$ is the rate of the loss of Fe(VI), *[Fe(VI)]* and *[X]* are the concentrations of Fe(VI) and X respectively, and k_{app} is the apparent reaction rate constant. The reactivity of Fe(VI) with X is mostly investigated under pseudo first-order conditions, with X in excess ([Fe(VI)]<<[X]), by following the Fe(VI) concentration with time [5]. The rate constants are mostly calculated as a function of pH.

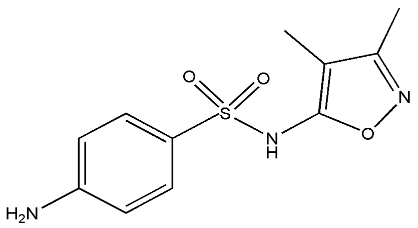
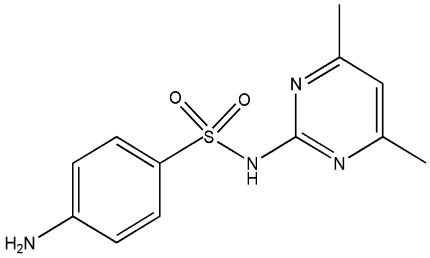
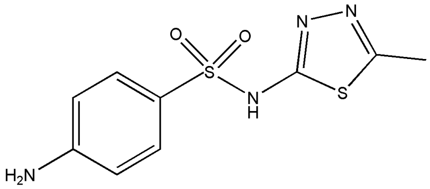
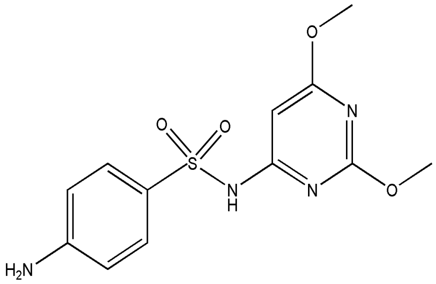
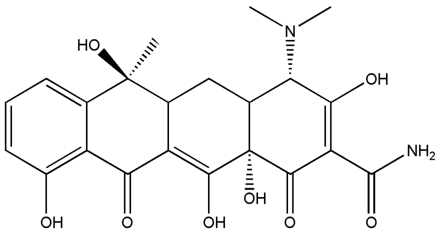
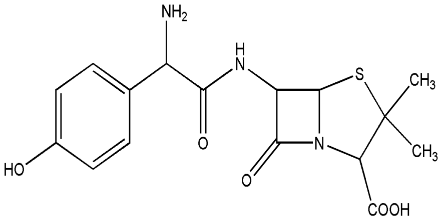
Apparent second-order reaction rate constants (k_{app}) of the reaction of Fe(VI) with selected PPCPs and EDCs at room temperature (23±2℃) are presented in Table 2.4. Kinetic studies were mostly carried out at neutral to slightly basic pH range of 7.0-9.0 which is relevant to water treatment processes and regulatory criteria. In addition, the instability of Fe(VI) in acidic conditions prevents kinetic investigations at low pH levels.

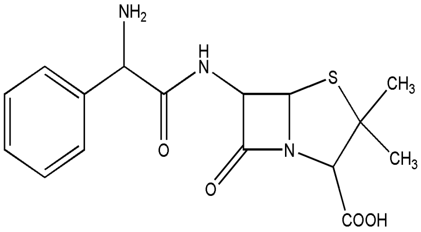
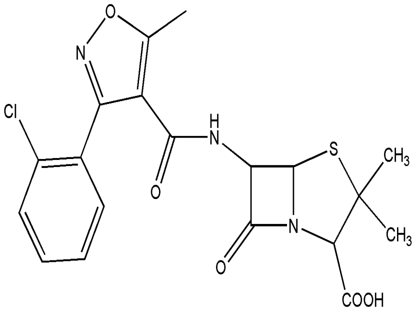
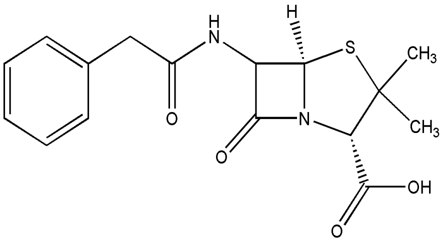
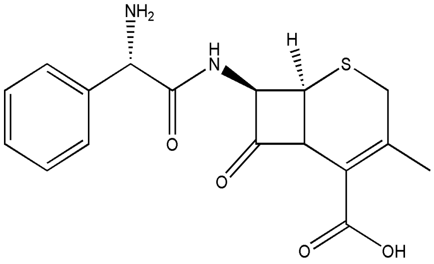
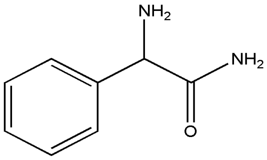
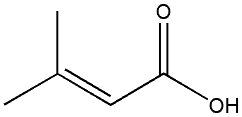
Table 2.4: Apparent second-order rate constants (k_{app}) of the oxidation of PPCPs and EDCs by Fe(VI) at room temperature.

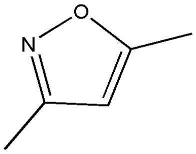
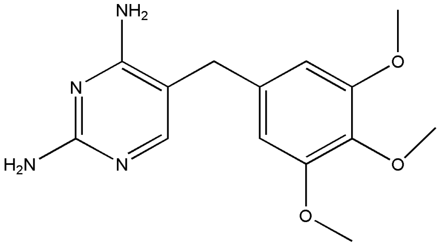
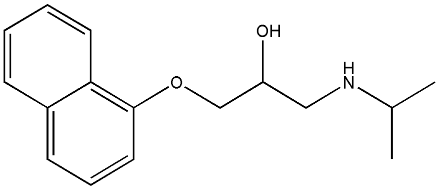
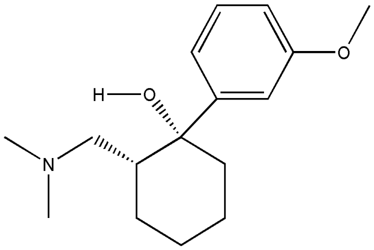
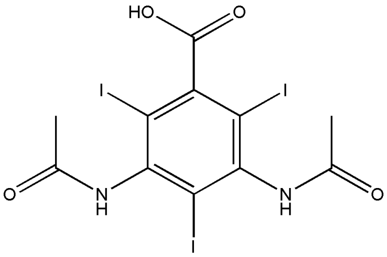
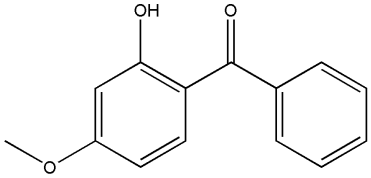
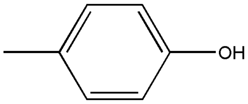
PPCP/EDC	Structure	pH	k_{app} (M^{-1} s^{-1})	Reference
Triclosan		7.0	1.1×10^{3}	[31]
			7.5×10^{2}	[32]
Bisphenol A		7.0	6.4×10^{2}	[31,33]
		8.0	4.1×10^{2}	[31]
Sulfamethoxazole		7.0	1.8×10^{3}	[31]
			1.3×10^{3}	[34]
		8.0	7.7×10^{1}	[31]
Atenolol		8.0	0.7×10^{1}	[35]

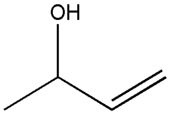
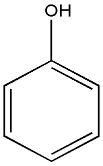
Diclofenac		7.0	1.3×10^{2}	[31]
			1.2×10^{1}	[36]
		8.0	3.2×10^{1}	[31]
		11.0	2.5×10^{0}	[36]
Ibuprofen		8.0	0.1×10^{0}	[37]
			$<0.1\times10^{0}$	[35]
			1.2×10^{-1}	[38]
		9.0	1.5×10^{-2}	[38]
Ciprofloxacin		7.0	4.7×10^{2}	[31]
		8.0	1.7×10^{2}	[31]
			1.1×10^{2}	[38]
		9.0	6.4×10^{1}	[38]
Enrofloxacin		7.0	4.6×10^{1}	[31]
		8.0	2.4×10^{1}	
Carbamazepine		7.0	6.7×10^{1}	[31]
		8.0	1.6×10^{1}	
Octylphenol		7.0	1.2×10^{3}	[39]
		8.0	0.3×10^{3}	

Nonylphenol		7.0	1.1×10^{3}	[40]
		8.0	2.7×10^{2}	
		9.0	1.0×10^{2}	
Tetrabromobisphenol A		7.0	7.9×10^{3}	[41]
		10.0	3.3×10^{1}	
17α-Ethinylestradiol		7.0	7.3×10^{2}	[31,33]
			8.1×10^{2}	[1,42]
		8.0	4.5×10^{2}	[31]
Estrone		7.0	1.0×10^{3}	[1,42]
17β-estradiol		7.0	7.6×10^{2}	[31]
			1.1×10^{3}	[1,42]
		8.0	4.6×10^{2}	[31]
Estriol		7.0	1.2×10^{3}	[1,42]

Sulphisoxazole		7.0	1.5×10^{3}	[1,34]
Sulfamethazine		7.0	1.0×10^{3}	[1,34]
Sulphamethizole		7.0	4.1×10^{2}	[1,34]
Sulfadimethoxine		7.0	0.8×10^{2}	[27,34]
Tetracycline		7.0	3.0×10^{2}	[1]
Amoxicillin		7.0	2.8×10^{3}	[43]
			7.7×10^{2}	[44]
		8.5	1.6×10^{2}	[44]

Ampicillin		7.0	1.1×10^{3}	[43]
			4.2×10^{2}	[44]
		8.5	5.0×10^{1}	[44]
Cloxacillin		7.0	1.2×10^{2}	[44]
		8.5	2.4×10^{1}	
Penicillin G		7.0	1.1×10^{2}	[44]
		8.5	1.8×10^{1}	
Cephalexin		7.0	6.9×10^{2}	[44]
		8.5	7.4×10^{1}	
2-amino-2-phenylacetamide		7.0	2.9×10^{2}	[44]
		8.5	3.4×10^{1}	
3-methylcrotonic acid		7.0	2.3×10^{0}	[44]
		8.5	0.5×10^{0}	

3,5-dimethylisoxazole		8.0	1.7×10^{-1}	[44]
Trimethoprim		7.0	4.0×10^{1}	[1,45]
Propranolol		8.0	2.0×10^{1}	[46]
Tramadol		7.0	1.4×10^{1}	[47]
		8.0	7.4×10^{0}	
Diatrizoic acid		7.0	5.5×10^{0}	[48]
Benzophenone-3		8.0	8.2×10^{1}	[49]
4-Methylphenol		7.0	6.9×10^{2}	[31]
		8.0	3.3×10^{2}	

Buten-3-ol		7.0	1.2×10^{1}	[31]
		8.0	3.0×10^{0}	
Phenol		7.0	7.7×10^{1}	[33]

Generally, the rate constants of Fe(VI) oxidation reactions increase with decreasing pH (Table 2.4). This pH dependency of k_{app} can be explained by the acid dissociation constants (K_a) expressed as pK_a (Eqs. 2.9-2.11) [13,50]:

$$H_3FeO_4^{+} \leftrightarrow H^{+} + H_2FeO_4 \qquad pK_{a1}=1.6 \tag{2.9}$$

$$H_2FeO_4 \leftrightarrow H^{+} + HFeO_4^{-} \qquad pK_{a2}=3.5 \tag{2.10}$$

$$HFeO_4^{-} \leftrightarrow H^{+} + FeO_4^{2-} \qquad pK_{a3}=7.3 \tag{2.11}$$

Fe(VI) has triprotonated ($H_3Fe^{VI}O_4^{+}$), diprotonated ($H_2Fe^{VI}O_4$), monoprotonated ($HFe^{VI}O_4^{-}$), and deprotonated ($Fe^{VI}O_4^{2-}$) species depending on pH (Eqs. 2.9-2.11). The speciation of Fe(VI) at different pH values is given in Figure 2.2. Species (acid-base) of ionizable compounds are also used to explain the trend of increasing reaction rates by decreasing the pH [31].

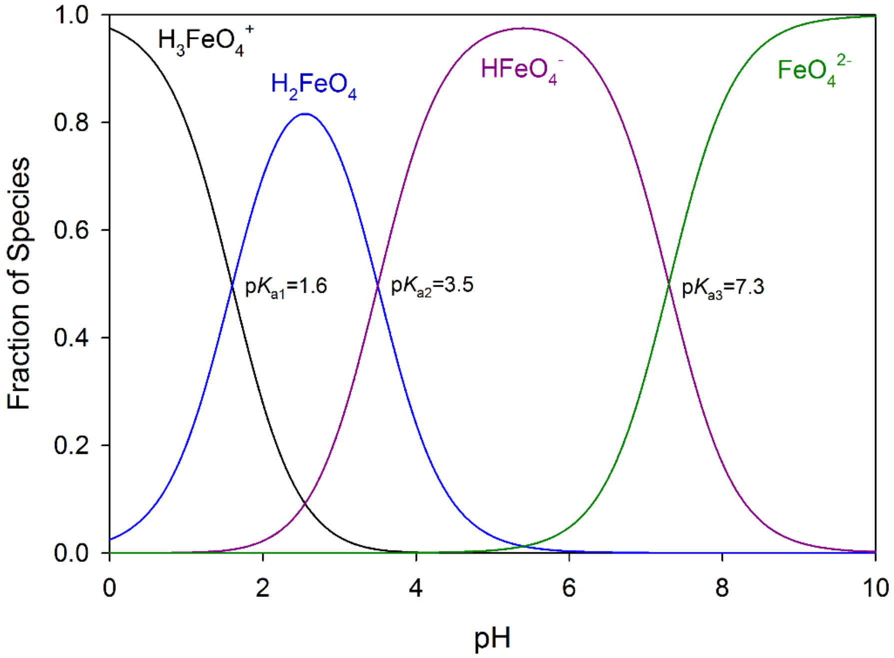


Figure 2.2: Speciation of ferrate(VI).

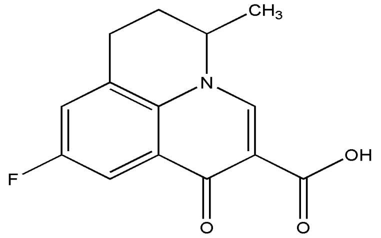
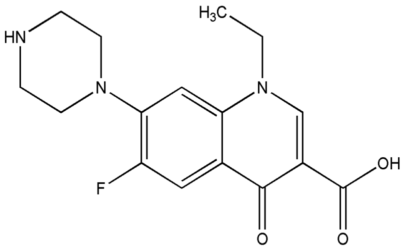
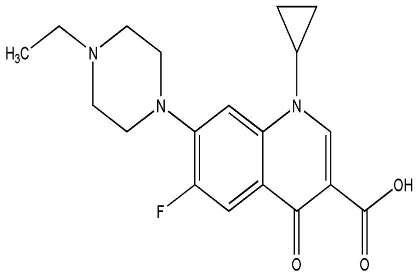
The second-order reaction rate constants show that Fe(VI) (selective oxidant) reacts preferably with electron-rich organic moieties such as phenolic, organosulfur and polycyclic aromatic compounds [35]. The k_{app} of the oxidation of PPCPs and EDCs range from 0.1×10^0 (ibuprofen) to 7.9×10^3 (tetrabromobisphenol A) M^{-1} s^{-1} at a pH relevant to wastewater treatment process and room temperature (Table 2.4).

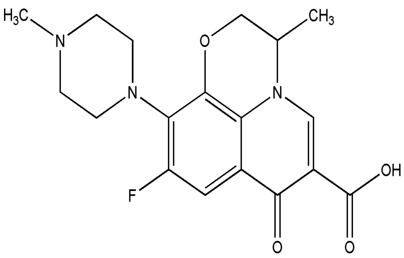
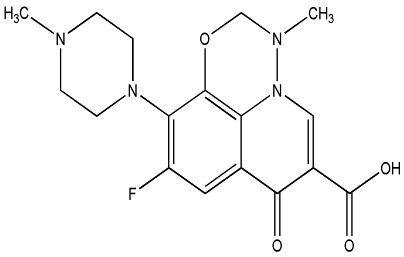
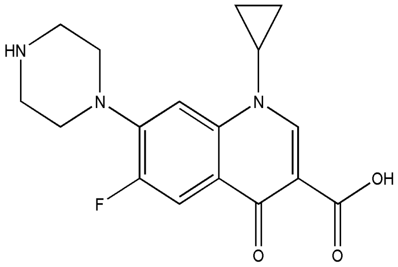
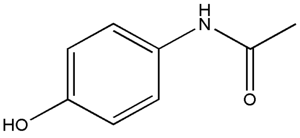
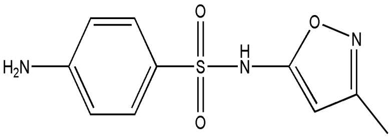
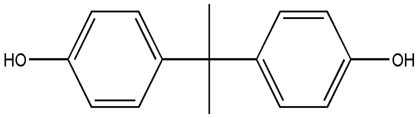
2.4.2 Stoichiometry

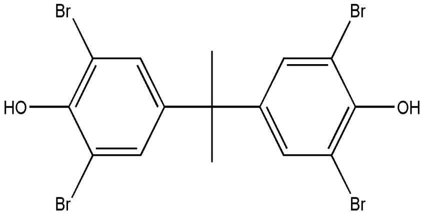
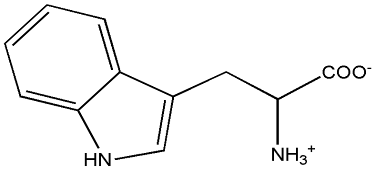
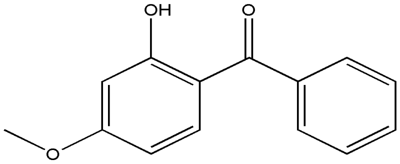
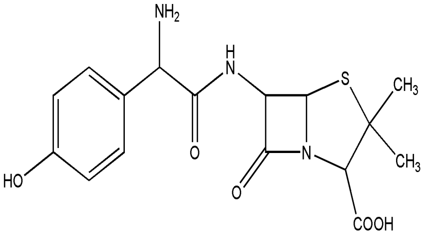
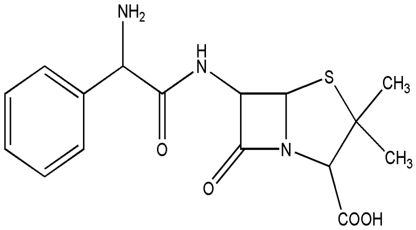
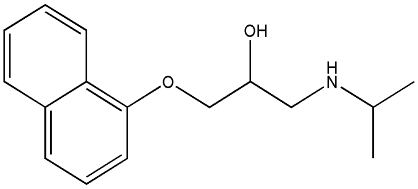
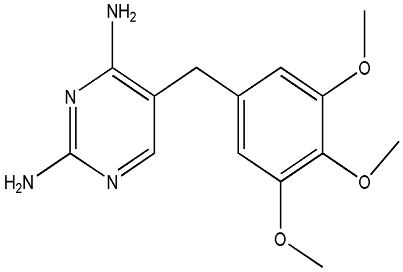
Information regarding the kinetics of oxidation of pollutants is useful to understand these reactions and compare the ability of different oxidants to oxidize pollutants in water. However, a higher k of an oxidant than a different one, does not necessarily mean higher oxidative transformation of the organic molecule, because of the competition for oxidants with target organic compound and wastewater matrix (i.e. ions and organic matter) [35].

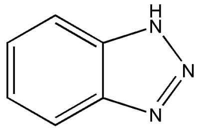
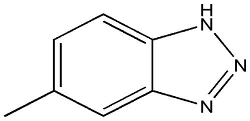
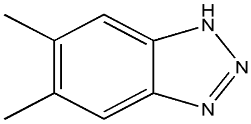
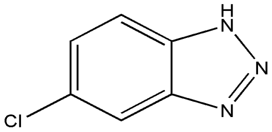
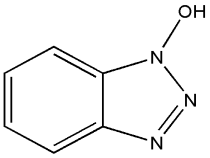
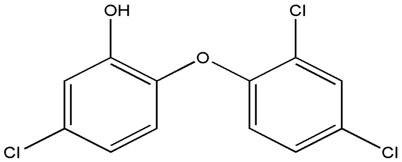
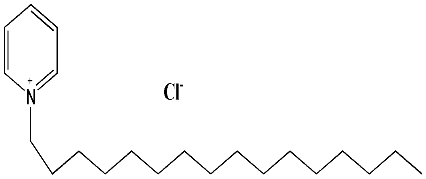
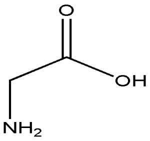
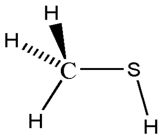
For example, the hydroxyl radical, a powerful non-selective oxidant, generally reacts much faster with organics than Fe(VI) ($k_{OH\bullet} > k_{Fe(VI)}$). However, the aforementioned competition is more obvious for hydroxyl radicals and this competition remains unchanged during the oxidation process because hydroxyl radicals react non-selectively with other water constituents [35]. Thus, the experimental investigation of the stoichiometry of the Fe(VI)-organic reactions is critical to optimize the required oxidant dose and to evaluate the ability of Fe(VI) to remove organics in water. Table 2.5 shows the required Fe(VI) to organic (X) molar ratios for complete removal of an organic in water, at a relevant to water treatment pH range and room temperature.

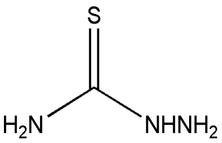
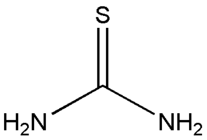
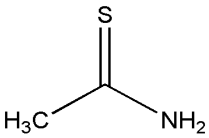
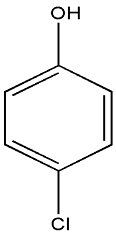
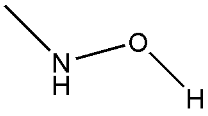
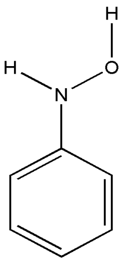
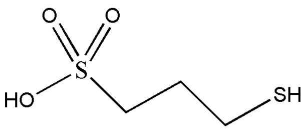
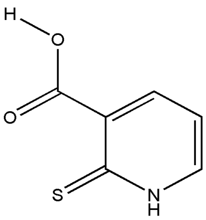
Table 2.5: Stoichiometry of oxidation of organic compounds by Fe(VI) at room temperature.

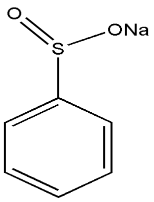
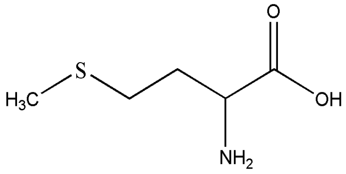
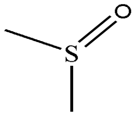
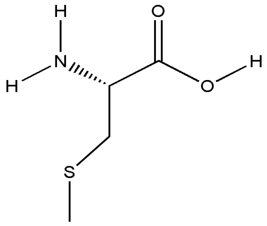
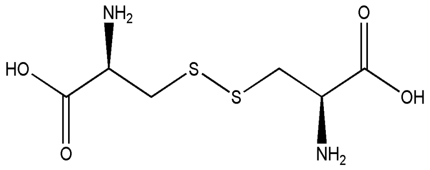
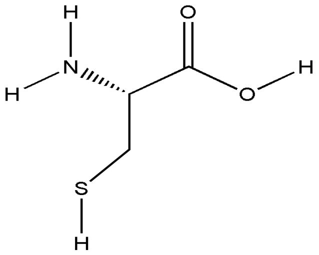
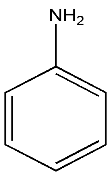
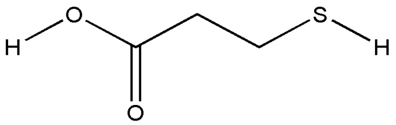
Compound (X)	**Structure**	**pH**	**[Fe(VI)]/[X] (mol/mol)**	**Reference**
Flumequine		7.0	>50	[51]
Enrofloxacin		7.0	15	[51]
		7.0	17	[52]
Norfloxacin		7.0	10	[51]

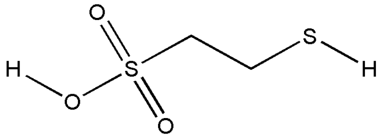
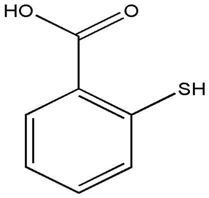
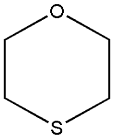
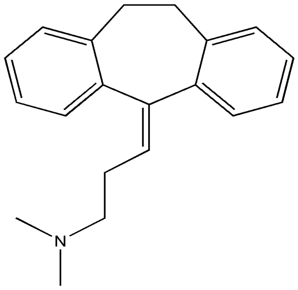
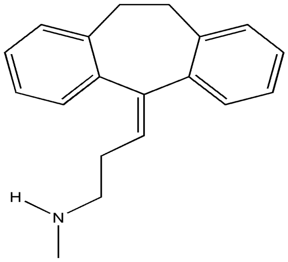
Ofloxacin		7.0	15	[51]
Marbofloxacin		7.0	20	[51]
Ciprofloxacin		7.0	13	[52]
Acetaminophen		6.0 – 9.0	25	[53]
Sulfamethoxazole		7.0 – 9.0	4	[54]
		9.0	4	[34]
Bisphenol A		7.0	8	[55]
		7.0	15	[41]
		8.0	10	
		9.4	5	[56]
		9.2	4	[42]

Tetrabromobisphenol A		7.0	6.3	[41]
		8.0	3.8	
Tryptophan		7.0 and 9.0	4	[57]
Benzophenone-3		8.0	25	[49]
Amoxicillin		7.0	4.5	[58]
Ampicillin		7.0	3.5	[58]
Propranolol		9.0	6	[46]
Trimethoprim		9.0	5	[45]

1H-benzotriazole		8.0	30	[59]
5-methyl-1H-benzotriazole		8.0	30	[59]
5,6-dimethyl-1H-benzotriazole hydrate		8.0	30	[59]
5-chloro-1H-benzotriazole		8.0	30	[59]
1-hydroxybenzotriazole		8.0	30	[59]
Triclosan		7.0	10	[32]
Cetylpyridinium chloride		9.2	1	[60]
Glycine		9.0	1	[61]
Methyl mercaptan		9.0	4.6	[62]

Thiosemicarbazide		9.0	2	[62]
Thiourea		9.0	2.7	[63]
Thioacetamide		9.0	2.7	[9,64]
4-Chlorophenol		9.2	5	[65]
N-methylhydroxylamine		8.0-11.0	0.5	[66]
N-phenylhydroxylamine		8.0-11.0	0.5	[66]
3-Mercapto-l-propane sulfonic acid		8.4-10.2	1	[67]
2-Mercaptonicotinic acid		8.4-10.2	0.5	[67]

Benzenesulfinate		9.0	0.7	[68]
Methionine		9.0	0.7	[68]
Dimethyl sulfoxide		9.0	0.7	[68]
Methyl cysteine		9.2- 10.4	0.7	[69]
Cystine		8.4-9.9	1.3	[69]
Cysteine		8.9- 10.2	1	[69]
Aniline		9.0- 10.0	0.5	[70]
3-Mercaptopropionic acid		9.0- 11.0	1.5	[71]

2-Mercaptoethanesulfonic acid		8.7-10.0	2	[71]
2-Mercaptobenzoic acid		9.6-10.4	0.7	[71]
1,4-Thioxane		9.0-9.8	1	[72]
Amitriptyline		9.0	20	[73]
Nortriptyline		9.0	15	[73]

Although the effect of the pH on the kinetics of Fe(VI) reaction with contaminants is clear (the higher the pH the lower the rate constant due to the fact that Fe(VI) is a stronger oxidant upon protonation; Figure 2.2 and Table 2.4), the oxidative transformation of contaminants by Fe(VI) does not significantly differ in the pH range of 7.0-9.0. However, three explanations have been reported in the literature so far to explain any observed effect of the pH on the removal of pollutants by Fe(VI): (i) when the removal is high at the high pH (e.g. pH 9), this is due to the fact that Fe(VI) is more stable at pH 9, and the Fe(VI)'s self-decomposition is diminished leading to higher Fe(VI) concentration, (ii) when the removal is high at low pH (e.g. 7.0), this is due to the fact that Fe(VI) is a stronger oxidant upon protonation and this is consistent with the effect of the pH on the rate constants, and (iii) when the effect of the pH on the removal of the contaminant is not significant, this is probably due to the high reactivity of Fe(VI) with the contaminant [38], that makes the effect of the pH, usually at the pH range 7.0-9.0, negligible. The effect of the pH on the removal of contaminants by Fe(VI) can be seen in recently reported studies that show different or negligible effect of the pH on the oxidative transformation of organics by Fe(VI). Yang et al. [41] studied the oxidation of tetrabromobisphenol A and bisphenol A by Fe(VI). In both cases, around 10% higher removal had been obtained at pH 8 compared to pH 7, and that was explained with the higher stability of Fe(VI) at pH 8 resulting in higher Fe(VI) concentration [41]. Casbeer et al. [57] investigated the oxidation of tryptophan by Fe(VI) at pH 7 and 9 and around 10% higher removal was observed at pH 9 compared to pH 7. The oxidation of bisphenol A by Fe(VI) has been also investigated by Han et al. [74] at various pHs and around 10% higher removal was reported at pH 7 compared to pH 9, which is in contrary to the aforementioned study of Yang et al. [41] on bisphenol A. The authors stated that this is due to the fact that Fe(VI) is a stronger oxidant upon protonation [74]. The aforementioned differences in oxidative transformation of organics at the pH range of 7.0-9.0 are very small (<10%) and within experimental and analytical errors. On the other hand, in all the cases mentioned above, the determined rate constants were higher at lower pH [41,57,74], as was expected. Zhou and Jiang [38] have recently investigated the degradation of ciprofloxacin by Fe(VI) at the pH range 6-9, and reported that the effect of the pH on the removal of ciprofloxacin is not significant due to the high reactivity of Fe(VI) with ciprofloxacin.

2.5 Discussion of Application of Fe(VI)

With one dose of Fe(VI), oxidation, disinfection, and coagulation take place, which makes Fe(VI) very attractive for wastewater treatment. Fe(VI) can be applied in primary treatment (replacing typical coagulants such as Fe^{3+} and Al^{3+} salts), in sludge treatment (e.g. disinfection of coliforms and oxidation of odor-causing compounds), drinking water treatment, etc. [8,75]. Recently, the application of Fe(VI) to disinfect secondary effluent wastewater (SE) has received great attention, due to the increased concentration of EOCs in SE. Chlorination, the most common disinfection technology worldwide, results in the formation of toxic disinfection by-products (DBPs) such as chlorinated by-products (CBPs) with potential negative health effects, because of the reaction of chlorine with organics present in SE [8,75]. Alternative disinfectants such chlorine dioxide and ozone also form DBPs such as brominated by-products (ozone), and chlorite and chlorate (chlorine dioxide) which are also considered to be toxic to aquatic environment. Importantly, Fe(VI) can be an alternative disinfectant without the formation of chlorinated and brominated by-products. Table 2.6 shows the disinfection performance of Fe(VI).

Table 2.6: Typical disinfection performance of Fe(VI)

Contaminant	Experimental Conditions	%Removal	Reference
E.coli	Dose: 6 mg Fe(VI)/L contact time = 7 min pH = 8.2	~100	[8]
Virus (f2 Coliphage)	Dose: 1 mg Fe(VI)/L contact time = 6 min pH = 6.9	99	[4]

Interestingly, Fe(VI) could inactivate aerobic spore-formers and sulfite-reducing *clostridia* both of which are chlorine resistant bacteria [5]. Fe(VI) at 2 mg/L reduced aerobic spore-formers count by 3-log units compared to 1-log unit by chlorine (3.5 mg/L) during the disinfection of river water [5]. Complete inactivation of sulfite-reducing clostridia has been achieved by Fe(VI) while these species were resistant to chlorination [5].

The removal of EOCs from SE or river water has been also investigated. Table 2.7 shows the ability of Fe(VI) in removing EOCs from real wastewater.

Table 2.7: Removal of PPCPs and EDCs spiked in real wastewater by Fe(VI).

Contaminant (X)	Experimental Conditions	%Removal	Reference
17α-ethinylestradiol, β-estradiol and bisphenol-A in Lake Zurich water (DOC=1.6 mg/L)	Dose: 0.5 mg Fe(VI)/L contact time = 30 min pH = 8 $[X]_0$ = 0.15 μM	99	[33]
17α-ethinylestradiol, β-estradiol and bisphenol-A in Kloten wastewater (DOC=5.3 mg/L)	Dose: 2 mg Fe(VI)/L contact time = 30 min pH = 8 $[X]_0$ = 0.15 μM	99	[33]
naproxen, paracetamol, diclofenac, carbamazepine and triclosan in wastewater (DOC=5 mg/L)	Dose: 10 mg Fe(VI)/L contact time = 1 - 5 min pH = 7 $[X]_0$ = 100 μg/L	~100	[76]
sulfamethoxazole, diclofenac, and carbamazepine in wastewater (DOC=5.1 mg/L)	Dose: 5 mgFe(VI)/L contact time = 3-5 h pH = 7 $[X]_0$ = 0.2-1 μM	>85	[31]

Interestingly, the simultaneous EOCs oxidation and phosphate (initial concentration of 3.5 mg PO_4-P/L) removal from SE wastewater (DOC=5.1 mg/L) by Fe(VI) has been also reported [31]. Fe(VI) (7.5 mg/L) achieved ~80% phosphate removal while almost complete removal of sulfamethoxazole, diclofenac, and carbamazepine (initial concentration of 0.5-1.0 μM) has also been observed [31]. Limited work has been done on the simultaneous oxidation, disinfection, and coagulation of SE wastewater to inactivate viruses and bacteria, oxidize EOCs, and remove particulate contaminants using Fe(VI) as a multipurpose water treatment chemical. The treatment of SE wastewater is probably the most promising application for Fe(VI), and more studies are needed to assess the performance of Fe(VI).

2.6 Effect of Ions on Oxidation of EOCs by Fe(VI)

The effect of water constituents on the removal of target pollutants is critical for the development of any water treatment technology. Zeng et al. [77] studied the effect of ions on the oxidation of oxytetracycline (OTC) by Fe(VI). The removal of OTC decreased from 95% to 79%, 29%, and 29% in the presence of 5 mM of calcium (Ca^{2+}), carbonate (CO_3^{2-}), and phosphate (PO_4^{3-}) ions respectively [77]. No obvious effect on the removal of OTC was observed in the presence of 5 mM of magnesium (Mg^{2+}), sodium (Na^+), chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), and bicarbonate (HCO_3^-) ions [77]. Similarly, no apparent effect of Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, Na^+, and K^+ on the oxidation of flumequine (FLU) by Fe(VI), at similar concentration of 5 mM has been observed [51]. The removal efficiency of FLU decreased from 51% to 40%, 35%, 42%, and 33% in the presence of 5 mM of Mg^{2+}, Ca^{2+}, Cu^{2+}, and Fe^{3+} respectively [51]. On the other hand, enhancement of the oxidation of acetaminophen (AAP) by Fe(VI) in the presence of Na^+, K^+, Mg^{2+}, Ca^{2+}, and SO_4^{2-}, at a concentration range of 0.2-5 mM has been reported [53]. However, the removal of AAP was negatively affected by Al^{3+}, CO_3^{2-}, and PO_4^{3-} ions [53]. Negative effects of ions on Fe(VI) reactions may be due to the enhanced self-decomposition of Fe(VI) in the presence of ions. Positive effects of ions may be due to catalytic effect. Limited work has been done so far on the effect of ions thus it is difficult to draw solid conclusions. Detailed investigation of the effect of ions on the oxidation of pollutants by Fe(VI) is needed, including control experiments to rule out possible interactions between the ions and the organic contaminant. In Table 2.8, the effects of ions (negative (-), positive (+) or no effect) on the oxidation of emerging organic contaminants by Fe(VI) are summarized.

Table 2.8: Effect of ions on oxidation of EOCs by Fe(VI).

Compound	***OTC***	***FLU***	***AAP***
[Ion]≤5mM	Fe(VI)	Fe(VI)	Fe(VI)
Cl^-	No effect	No effect	N/A
NO_3^-	No effect	No effect	N/A
HCO_3^-	No effect	No effect	N/A
CO_3^{2-}	-	N/A	-
SO_4^{2-}	No effect	No effect	+
PO_4^{3-}	-	N/A	-
Na^+	No effect	No effect	+
K^+	N/A	No effect	+
Mg^{2+}	No effect	-	+
Ca^{2+}	-	-	+
Cu^{2+}	N/A	-	N/A
Fe^{3+}	N/A	-	N/A
Al^{3+}	+	N/A	-
References	**[77]**	**[51]**	**[53]**

2.7 Activation of Ferrate(VI) in Aqueous Solution

Limited work has been done so far on the activation of Fe(VI) to enhance the oxidative transformation of contaminants. Feng et al. [78] demonstrated the activation of Fe(VI) by ammonia to enhance the oxidative transformation of flumequine (FLU) by ~25% at pH 8. It was postulated that the observed enhancement is due to the formation of ammonia complexes of Fe^V and/or Fe^{IV} [78]. The activation of Fe(VI) by ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonate) resulted in enhanced oxidative transformation of diclofenac (DCF) by ~65% at pH 8 and 9 [79]. It was reported that the observed enhancement is probably due to the oxidation of diclofenac by the $ABTS^{\bullet+}$ (stable radical cation), which is formed via the oxidation of ABTS by Fe(VI) [79,80]. Addition of peroxymonosulfate (PMS) to Fe(VI) was also able to activate the oxidant to degrade fluoroquinolone antibiotics [81]. The oxidative transformation of enrofloxacin (ENR), marbofloxacin (MAR), ofloxacin (OFL), and FLU was enhanced by 15%, 24%, 28% and 42% respectively due to the synergistic effect of PMS and Fe(VI) [81]. It was proposed that the possible formation of reactive sulfur species (e.g., $SO_4^{-\bullet}$), reactive oxygen species (e.g., $O_2^{-\bullet}$ and $^{\bullet}OH$), and high-valent iron species (e.g., Fe^{V} and Fe^{IV}) caused the observed enhancement [81]. The enhancement and experimental conditions of studies related to the activation of Fe(VI) are summarized in Table 2.9.

Table 2.9: Activation of ferrate(VI) by different methods

System	[Fe(VI)], µM	[X]*, µM	Concentration of activator	pH	Enhancement, %X removal	Reference
Fe(VI)-ammonia	600	30 (FLU)	10 mM	8.0	25 (FLU)	[78]
Fe(VI)-ABTS	150	30 (DCF)	5 µM	8.0 and 9.0	65 (DCF)	[79]
Fe(VI)-PMS	30 (ENR) 30 (MAR) 30 (OFL) 150 (FLU)	30 (ENR) 30 (MAR) 30 (OFL) 30 (FLU)	30 µM (ENR) 30 µM (MAR) 30 µM (OFL) 6 mM (FLU)	7.0	15 (ENR) 24 (MAR) 28 (OFL) 42 (FLU)	[81]

*X: model organic contaminant

2.8 Caffeine as a Model Emerging Organic Contaminant

CAF (1,3,7-Trimethylpurine-2,6-dione; $C_8H_{10}N_4O_2$) is the most consumed alkaloid worldwide and it is found in many plant species such as coffee, cacao, and tea leaves, as well as in many beverages (coffee, tea, energy drinks, soft drinks etc.) and foods (chocolates, pastries etc.) [82–84]. CAF is also a basic compound in the pharmaceutical industry as a wide variety of medicines contain CAF because it enhances the analgesic effect on headache, cough, cold, and acts as a central nervous system, cardiac, cerebral, and respiratory stimulant in the human's organism, enhancing the alertness, exercise performance, and learning capacity [82,85,86]. Because of the wide range of CAF's uses, large quantities of CAF are produced to meet the beverage, food, and medicinal needs and as a result CAF is included in the U.S. EPA list of High Production Volume Chemicals [82]. Thus, CAF is probably the most widely consumed legal drug [82,87–89], and one of the two most widely used psychostimulants worldwide [85,90], with a global average consumption of 70 mg/person/day [82,84].

CAF is among the compounds that are most frequently detected at the highest concentrations in the influents and effluents of wastewater treatment plants (WWTP) as well as in surface waters and groundwater worldwide, despite the appreciable CAF removal efficiencies (75%–99%) achieved in conventional WWTP [82,84,86,90–96], and the fact that it is almost completely metabolized (≥94%) in the human liver [86,97]. Moreover, many reported studies has proposed CAF as an anthropogenic marker for wastewater and combined sewer overflows (CSO) contamination of surface waters [82,84,93]. CAF concentrations in many surface streams and WWTP effluents can be as high as 230 µg/L [95].

The oxidation of CAF in aqueous solution using different oxidation processes such as photocatalysis [89,98], ozone [99], and chlorine [100], has been already investigated by different research groups. Table 2.10 shows the kinetic rate constants of oxidation of CAF by different oxidation processes. It was reported that the reaction of ozone with CAF was fast in the first 15 s of reaction time followed by a much lower reaction rate [99]. The chlorination of caffeine was reported to be a slow reaction (hours) [100,101]. Dalmazio et al. [89] reported ~90% CAF removal after 150 min of photocatalytic oxidation (UV/TiO_2) of CAF (160 µM).

Table 2.10: Kinetic rate constants of the oxidation of caffeine by different oxidation processes, at room temperature.

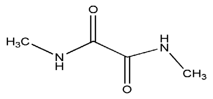
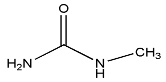
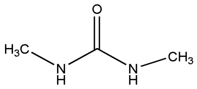
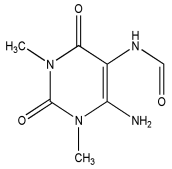
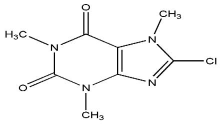
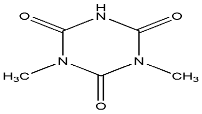
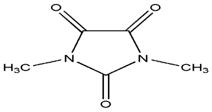
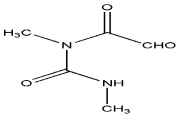
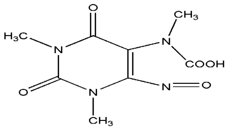
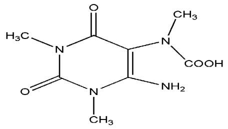
Oxidation process	pH	Order of reaction	Rate constant (k_{app})	Reference
Ozone* _(O_3)_	10	2nd	1.1 M^{-1} s^{-1}	[99]
	8		0.8 M^{-1} s^{-1}	
Hypochlorous acid _(HOCl)_	7	3rd	162 M^{-2} s^{-1}	[100]
Hydroxyl Radical	-	2nd	5.9×10^{9} M^{-1} s^{-1}	[102]
Photolysis	-	1st	6×10^{-6} s^{-1}	[98]

*rate constants obtained during the first 15 s of reaction time

Interestingly, insignificant reaction of peroxymonosulfate (PMS) with CAF at PMS to CAF molar ratio of 4 has been reported, and activation of PMS with catalyst was required to degrade CAF in water [103]. Lin and Chen [104] also reported low reactivity of oxone (peroxymonosulfate salt) with CAF (i.e. less than 40% CAF removal after 2 hours of reaction time), and catalyst required to enhance the CAF oxidation. Permanganate also exhibited low reactivity with CAF compared to other pharmaceuticals [105].

The oxidized products (OPs) of CAF by ozone and hypochlorite are presented in Table 2.11. Further discussion on the OPs of CAF and reaction pathways is presented in Chapters 4 and 5 of this thesis.

Table 2.11: OPs of CAF by hypochlorite and ozone.

Structure of products	Hypochlorite	Ozone
	+	+[a]
	+	
	+	
		+
	+	
	+	
	+	
		+
		+
		+
References	[101]	[99]

[a] [106]

CAF has been selected as the model emerging organic contaminant to demonstrate the acid-activated and silica gel-enhanced Fe(VI) oxidation processes because of the following reasons that make CAF an ideal model compound:

- CAF is a pharmaceutical of high environmental relevance that is found in surface waters and wastewaters worldwide
- The oxidation of CAF by Fe(VI) has not been investigated before
- Fe(VI) has sluggish reactivity with CAF, thus activation can be demonstrated
- CAF cannot be removed from water by SiO_2 gel alone

2.9 Synopsis of Literature Reviewed

In the last three decades, Fe(VI) received a great attention as a multi-purpose water treatment chemical. Researchers put a lot of efforts on (i) the synthesis of Fe(VI), (ii) the characterization of Fe(VI), (iii) the kinetic investigation of Fe(VI)-contaminant reactions, and (iv) the investigation of the stoichiometry of the reactions to determine required Fe(VI) to pollutant molar ratios, resulting in appreciable progress and better understanding of the Fe(VI) chemistry.

Nowadays, there is an increasing interest in the investigation of the oxidation of EOCs by Fe(VI), due to the increased discharge of EOCs in surface waters. Most of the studies related to Fe(VI) oxidation of EOCs focused on the kinetics of the reactions. Limited work has been done so far on the effect of water constituents i.e. inorganic ions and organic matter, on the oxidation of EOCs by Fe(VI). Moreover, further studies on identification of OPs of EOCs by Fe(VI) are needed to better understand the Fe(VI) chemistry and reactivity.

Furthermore, many of these EOCs are persistent to oxidation and activation of the oxidant is required for their efficient degradation in water. In addition, the instability of Fe(VI) at acidic pH conditions and the decreased reactivity of Fe(VI) at basic pH conditions remain a big challenge. Thus, activation of Fe(VI) at mild alkaline pH conditions to enhance the oxidative transformation of EOCs and reduce the required dose of Fe(VI) and reaction time becomes a necessity. The performance of the activation method should be evaluated under water treatment conditions e.g. presence of ions and organic matter, and pH range of 6-9.

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Chapter 3

3 Enhanced Oxidative Transformation of Organic Contaminants by Activation of Ferrate(VI): Possible Involvement of Fe^{V}/Fe^{IV} Species

3.1 Introduction

There has been increasing interest in the activation of oxidants in order to understand the potential for enhanced reactions of relevance to industrial, biological, energy, and environmental schemes [1-5]. This chapter deals with a simple high-valent iron(VI)-oxo species ($Fe^{VI}O_4^{2-}$, Fe(VI)) in aqueous solution because of its potential use as a green molecule in oxygen evolution, organic transformations, water treatment, and disinfection of viruses and bacteria [3, 6-16]. The oxidation power of Fe(VI) strongly depends on the pH, which has been shown in the oxidation of a number of inorganic and organic compounds [17-20]. Under acidic and neutral pH conditions, Fe(VI) has high reactivity, but it generally reacts with water at a faster rate than the target compound. This undesired reaction with water diminishes the capability of Fe(VI) in oxidative transformations of contaminants. Interestingly, at pH 9.0-10.5, Fe(VI) does not react significantly with water (e.g. 2 % in 1h at pH 9.0), but there is decreasing reactivity of Fe(VI) in this pH range [10, 21, 22]. Moreover, numerous reactions do not occur efficiently in alkaline medium. Additionally, Fe(VI) does not react with certain organic compounds in the aforementioned pH range. These drawbacks restrict applications of Fe(VI) in water remediation. This chapter demonstrates a discovery that overcomes the limitations by activating Fe(VI) to enhance its oxidation capacity.

The activation of Fe(VI) was demonstrated by selecting organic compounds that have sluggish reactivity with Fe(VI) at pH 9.0. These chosen molecules were caffeine (1,3,7-trimethylpurine-2,6-dione, CAF), acesulfame potassium (6-methyl-1,2,3-oxathiazine-4(3H)-one 2,2-dioxide, ACE) and atenolol ((RS)-2-{4-[2-hydroxy-3-(propan-2-ylamino)propoxy]-phenyl}acetamide, ATL), which have different structures (Figure S3.1 of Appendix A). Significantly, these compounds exist in a variety of water systems [23].

CAF is one of the two most widely used psychostimulants worldwide, with a global average consumption of 70 mg/person/day [24]. ACE is an artificial sweetener with wide application and ubiquitous occurrence in the environment due to its resistance to biodegradation and hydrolysis [25]. ATL is among the β-blockers of greatest concern due to its high toxicity to aquatic organisms [26]. CAF, ATL and ACE have been detected in surface waters, groundwater and influents and effluents of wastewater treatment plants [23, 27, 28]. It is imperative to remove these contaminants from water. Fe(VI) in the activated form is proposed herein to cause enhancement of oxidative transformation of the target organics.

3.2 Experimental

Details related to the reagent grade chemicals and Fe(VI) (>98% purity) used are presented in Text S3.1 of Appendix A. All experiments (Figures 3.2 and 3.4; Tables S3.1, S3.4 and S3.5 of Appendix A) were conducted in a 600-mL beaker under dark conditions at room temperature (24 ± 1 ℃). A 250 mL CAF solution was prepared in Milli-Q water and a certain volume of the Fe(VI) solution, also prepared in water, was added. The mixture was under rapid mixing using a magnetic stirrer. When the pH stabilized within 2 minutes (initial pH), selected amount of acid was added directly to the Fe(VI)-CAF solution. After completion of the reaction as evidenced by the disappearance of the characteristic purple color of Fe(VI) (Time (Fe(VI) Decay), the particulate Fe(III) was removed by filtration (Filtration Time). The filtered samples were subjected to analyses. The target compounds (CAF, ACE, and ATL) were analyzed using a UV-VIS spectrophotometer (UV-3600, Shimadzu Scientific Instruments, Columbia, MD, USA) and high performance liquid chromatography (HPLC) techniques (Text S3.2 of Appendix A). Details related to the control and nitrogen-purged experiments are presented in Texts S3.3 and S3.4 of Appendix A respectively.

3.3 Results and Discussion

In the initial set of experiments, Fe(VI) and CAF in water were mixed and the concentration of Fe(VI) in the mixed solution was monitored (inset Figure 3.1). The mixed solution had an initial pH of 8.5. The concentration of Fe(VI) without CAF was also followed (inset Figure 3.1). At the beginning of the reactions, there was no significant difference between the Fe(VI) concentration with and without CAF. After a longer period of time, the difference in the concentration of Fe(VI) in the two mixed solutions became apparent (inset Figure 3.1). The results showed that Fe(VI) not only reacted with water, but also reacted with CAF. However, the reaction between Fe(VI) and CAF was very slow.

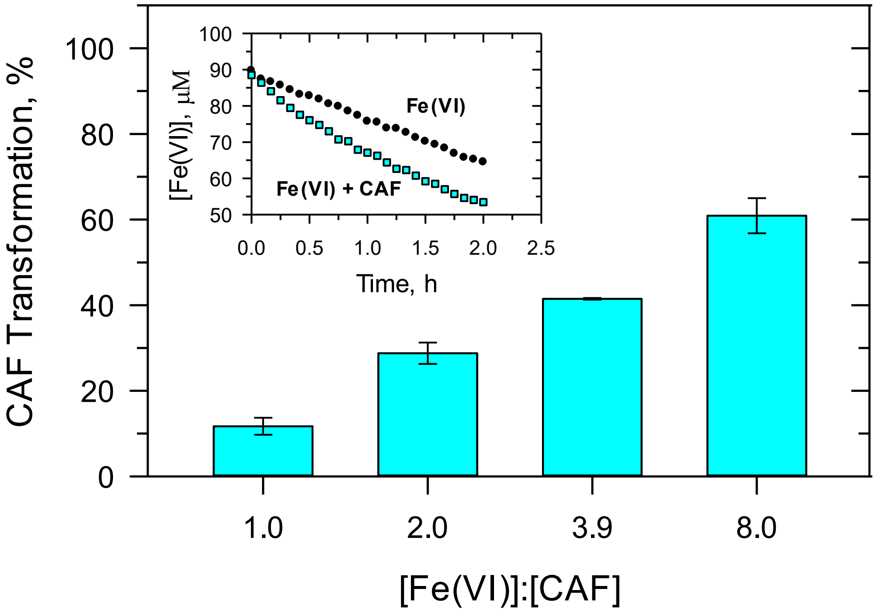

Figure 3.1: Oxidative transformation of CAF by Fe(VI) at different molar ratios of Fe(VI) to CAF at final pH 7.5 (Experimental conditions: [Fe(VI)]=88.5-634.5 µM; [CAF]=78.7-95.3 µM). Inset: Decay of Fe(VI) with and without CAF in solution at pH 8.5 ([CAF]=89.1 µM).

The oxidative transformation of CAF in mixed solutions at different molar ratios of Fe(VI) to CAF ([Fe(VI)]:[CAF] = 1.0 – 8.0) was also determined (Figure 3.1). The experimental conditions are given in Table S3.1 of Appendix A. The time taken for the disappearance of the color of Fe(VI) increased with the molar ratio of Fe(VI) to CAF. After the Fe(VI) was converted to Fe(III), the sample was filtered and CAF was analyzed. The final pH of the reaction solution before filtration was similar in all samples (~7.5) (Table S3.1 of Appendix A). The oxidative transformation of CAF increased from 12% to 61% with the increase in the molar ratio of Fe(VI) to CAF (Figure 3.1). This was expected due to the higher amount of oxidant available to react and oxidize the target compound (CAF).

Because of the longer contact time under the conditions used and also the incomplete transformation of CAF, a second set of experiments was conducted by adding a small amount of HCl acid (0.1-0.5 mL of 0.5 M HCl) in the Fe(VI)-CAF solution. It was expected that lowering pH would increase the redox potential (E^0(acidic) = +2.2 V versus E^0(basic) = +0.72 V [29]) hence the oxidation of CAF. To our surprise, the pH decreased by only 0.4-1.0 pH unit, depending on the concentration of HCl added, from an initial pH range of 8.8-9.5 (Table S3.1 of Appendix A). The enhancement of up to 30% of transformation of CAF (Figure 3.2) was also surprising because the addition of acid lowered the pH only by up to 1.0 unit. To rule out that the observed effect was related to simply reducing the pH by 1.0 pH unit, a third set of experiments was performed in which the pH of the mixed solution of Fe(VI) and CAF was varied by 1.0 pH unit (by increasing the Fe(VI) concentration at a constant Fe(VI) to CAF molar ratio) in the similar pH range of 8.0-9.0 without adding acid at a molar ratio of 2.0. Results showed no enhancement of the transformation of CAF when the pH decreased from 9.0 to 8.0 without acid addition to the reaction mixture (Table S3.2 of Appendix A). The expected pH range by adding acid into unbuffered Fe(VI)-CAF solution was supposed to be from 3.1 – 4.2 assuming both reactants had no buffering capacity. This suggested two processes that may have occurred by adding acid to the mixed solutions: (i) increase in reaction of Fe(VI) with water at lower pH, which releases OH^- ions ($2\ FeO_4^{2-} + 5\ H_2O \rightarrow 2\ Fe(OH)_3 + 3/2\ O_2 + 4\ OH^-$ [10]) and (ii) possible consumption of proton by the reaction between Fe(VI) and CAF. It is possible that both of these reactions ((i) and (ii)) simultaneously occurred in the mixture system.

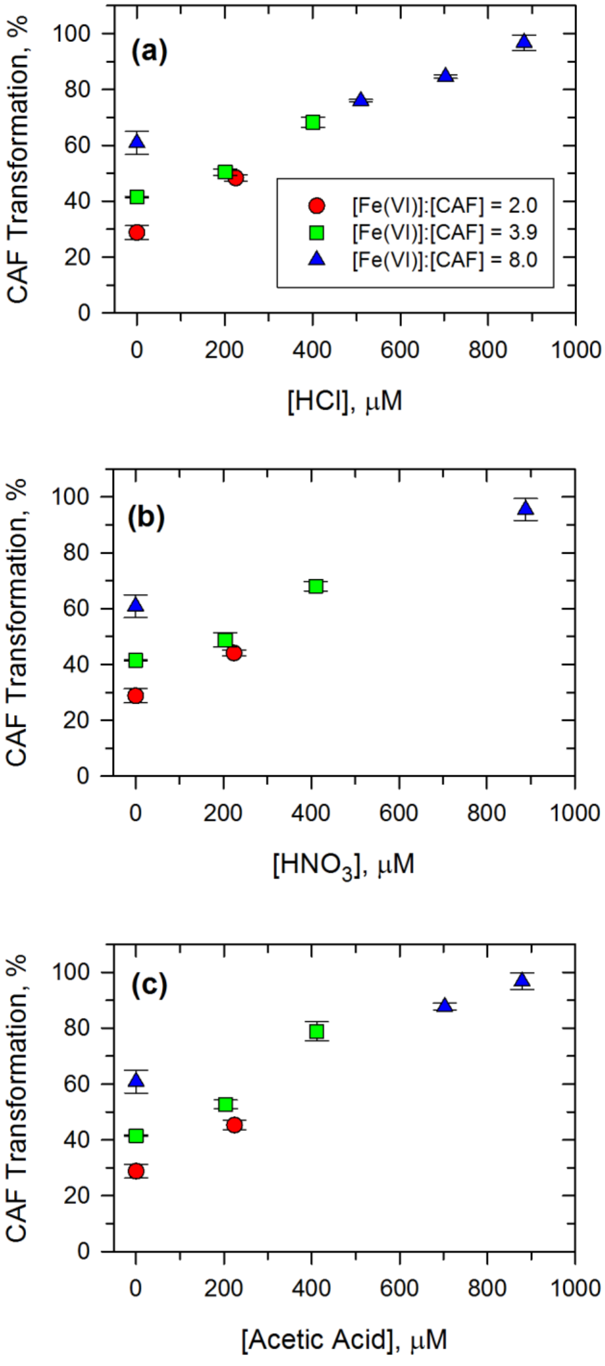

Figure 3.2: Effect of acids added to Fe(VI)-CAF mixed solution (a) HCl, (b) HNO_3 and (c) acetic acids (Experimental conditions: Fe(VI)]=177.5-634.5 µM; [CAF]=70.3-96.4 µM; final pH=7.5).

The role of the counter ion, Cl^- in the HCl, if any, was also explored by using other acids, nitric (HNO_3) and acetic (CH_3COOH) acids, in the oxidation of CAF by Fe(VI). As shown in Figures 3.2b and 3.2c, enhancement was observed using these two acids as well. In all three cases the complete transformation of CAF was seen (Figures 3.2a, 3.2b, and 3.2c). The control experiments ruled out the role of Fe(III), produced from Fe(VI), in the observed oxidation of CAF (Text S3.3 of Appendix A; Table S3.3 of Appendix A).

The possible species responsible for enhancing the oxidative transformation of organic compounds were explored by conducting experiments under nitrogen-purged conditions (Text S3.4 of Appendix A; Table S3.6 of Appendix A). The results of the conversion of CAF with and without purging with different acid solutions are presented in Figure 3.3.

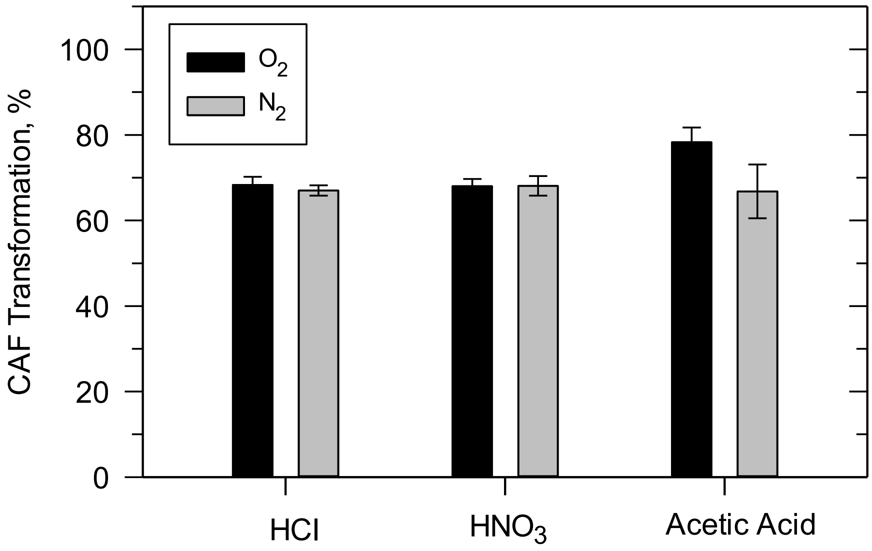

Figure 3.3: Oxidation of CAF by Fe(VI) under oxygenated and deoxygenated conditions using different acids. (Experimental conditions: [Fe(VI)]:[CAF]=3.9; [Acid]=393-431 μM; final pH(O_2)=7.5; final pH(N_2)=10.0).

In acidified solutions with HCl and HNO_3, the efficiency of oxidative transformation of CAF in the deoxygenated and oxygen-containing environments was similar (Figure 3.3).

The results indicate that the dissolved oxygen, present initially, played no role in the enhancement of oxidation of CAF by the activation of Fe(VI) by acids in these cases. Considering that pH (or protonated Fe(VI)) do not cause the enhancement, the possible species responsible for the increased removal of CAF, may be iron-based intermediate species, Fe^{V} and Fe^{IV}.

The formation of intermediate Fe^{V}/Fe^{IV} species may occur by the following reactions: (i) direct reduction of Fe(VI) by H^+ to final Fe(II)/Fe(III) species through 1-e^-/2-e^- transfer steps (e.g., $Fe^{VI} \rightarrow Fe^{IV} \rightarrow Fe^{II}$ and $Fe^{VI} \rightarrow Fe^{V} \rightarrow Fe^{III}$ [30, 31] and (ii) reduction of Fe(VI) by organics yields intermediate high-valent iron species. Formation of Fe^{V} and Fe^{IV} species during the decomposition of Fe(VI) has been recently demonstrated [32]. Participation of the Fe^{V}/Fe^{IV} species would increase the oxidation capacity of Fe(VI) (i.e. more electron-equivalents are available per mole of Fe(VI)). Both intermediates, i.e. Fe(V) and Fe(IV) species, are known to oxidize compounds at faster rates than Fe(VI). It is well known that Fe^{V}/Fe^{IV} species are about 2-4 orders of magnitude more reactive than Fe(VI) [33] thus causing enhanced transformation of organics by adding acid to the Fe(VI)-organic mixtures (Figure 3.2).

Another possibility for the formation of Fe^{V}/Fe^{IV} species is from the reactions: (a) $Fe^{VI} + Fe^{II} \rightarrow Fe^{V} + Fe^{III}$) and (b) Fe^{II}-org/Fe^{III}-org + $O_2/H_2O_2 \rightarrow Fe^{IV}$-org/$Fe^{V}$-org) [1, 34-36]. Fe^{II} and Fe^{III} are final reduced iron species from Fe(VI) and the generation of O_2/H_2O_2 is likely from the decomposition of Fe(VI) by acid [22]. Acetic acid could facilitate the generation of Fe^{V} species which were able to carry out selective oxidation of organics in oxygenated systems [34]. Interestingly, our observation of 10% higher transformation of CAF by acetic acid in the oxygenated solution than that in the deoxygenated condition (under N_2 environment) is consistent with findings of other researchers [1, 34, 37] (see Figure 3.3). This experimental observation further indicates the participation of the intermediate Fe^{V}/Fe^{IV} species in the activation of Fe(VI).

Experiments on the activation of Fe(VI) by HCl addition were also tested on other organic contaminants, ACE and ATL. As shown in Figure 3.4, enhancement of the oxidation power of Fe(VI) by H^+ was observed for ACE, with more than 90% transformation achieved. In the case of ATL, the enhancement due to H^+ ions, was also seen at a molar ratio of 10:1 ([Fe(VI):[ATL]), but the transformation was not that high i.e. 28% (Figure 3.4). Significantly, ATL could not be oxidized by Fe(VI) without acid at the studied Fe(VI) to ATL molar ratios. Interestingly, the enhancement in oxidative transformation due to H^+ ion was ~30%, which is similar to the increase from 64% to 95% in the transformation of ACE due to acid addition (Figure 3.4). Similar enhancement has been observed for both ATL and ACE in the case of acetic acid (Tables S3.4 and S3.5 of Appendix A).

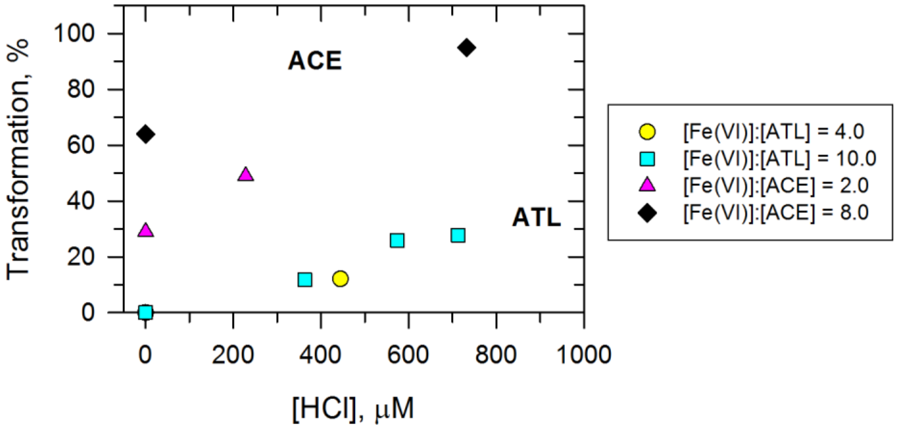

Figure 3.4: Effect of concentration of HCl on the transformation of acesulfame potassium (ACE) and atenolol (ATL) by Fe(VI). (Experimental conditions: [ACE]=49.0-81.4 µM; [ATL]=41.6-56.9 µM; [Fe(VI)]=161.9-569.2 µM; final pH=6.5-7.5).

3.4 Summary and Conclusions

This chapter reports the unexpected enhancement of the transformation of the studied organic molecules (CAF, ACE, and ATL) by ~30%, at slightly basic pH conditions (pH range of 8.0-9.0), by activating the Fe(VI) in aqueous solution with an addition of a small amount of simple acid (HCl, HNO_3, and CH_3COOH). The specific results are:

- Almost complete removal (≥95%) of CAF by activated Fe(VI) has been achieved, at a Fe(VI) to CAF molar ratio of 8.0 and ~885 μM HCl or HNO_3 or CH_3COOH, compared to ~60% CAF removal achieved by Fe(VI) (non-activated Fe(VI)).

- Similar removal efficiency of 95% was also achieved by adding 732 μM HCl to the Fe(VI)-ACE mixed solution at Fe(VI) to ACE molar ratio of 8.0, compared to ~65% ACE removal achieved without activation.

- In the case of ATL, which had no reactivity with Fe(VI), the enhancement by activated Fe(VI) was also seen (~30% ATL removal) at Fe(VI) to ATL molar ratio of 10.0 and 713 μM HCl.

- The added amounts of acids did not result in sharp decrease in pH and the final pH of the water was near to neutral pH (6.5-7.5).

- Significantly, activated Fe(VI) could transform these molecules over much shorter times (seconds to minutes) than non-activated Fe(VI) (hours).

- Similar removal efficiency of CAF by activated Fe(VI) has been observed under oxygenated and deoxygenated conditions. These results suggest that the possible species responsible for the increased oxidative transformation of organic contaminants may be high-valent iron-based intermediate species, Fe^{V} and Fe^{IV}.

The results presented in this chapter are the first report on the activation of Fe(VI) in aqueous solution and have implications for applications of the iron-based oxidant, including purification of polluted water. By adding a small amount of acid, Fe(VI) technology may be more efficient and faster for treating water. These results may initiate the investigation of the effect of different acids on a range of compounds having different functional groups and structures.

3.5 References

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Chapter 4

4 Oxidation of Caffeine by Acid-activated Ferrate(VI): Effect of Ions and Natural Organic Matter

4.1 Introduction

Global access to clean water is a diachronic challenge for humanity. Nowadays, the removal of pharmaceuticals from water to protect the aquatic environment and drinking water resources is of great importance [1]. These harmful compounds have negative effects on the freshwater fish and invertebrates, and contribute to the development of antibiotic resistant bacteria [1–4]. Among the various processes that are investigated, oxidation processes receive a great attention as alternative or as addition to conventional biological treatment technologies to remove organics from water [5–7]. Iron-based Fenton and Fenton-like processes have been receiving increasing interest in the oxidation of pollutants [8]. Studies in recent years have shown the activation of oxidants to enhance oxidation processes. For example, Fe-containing zeolite was used to catalyze Fenton processes for the removal of paracetamol from water [8]. High-valent iron species (Fe^{IV} and Fe^{V}) have also been suggested in the activation of iron(II)- and iron(III)-organo complexes with H_2O_2 in order to oxidize different pollutants in the environment [9–12].

This chapter deals with the high-valent tetraoxy iron(VI), also known as ferrate(VI) ($Fe^{VI}O_4^{2-}$; Fe(VI)), because of its potential use as a green chemical in organic synthesis, super-iron batteries, inactivation of viruses and water and wastewater treatment [13–18]. The fact that Fe(VI) is a powerful oxidant/disinfectant (Eqs. 4.1 and 4.2) [19], that leaves a non-toxic magnetically-separable coagulant i.e., Fe(III) after its application (Eq. 4.3) [20], makes it a multi-purpose water treatment chemical [21,22].

$$Fe^{VI}O_4^{2-} + 8\ H^+ + 3\ e^- \rightarrow Fe^{III} + 4\ H_2O,\ E^0 = +2.2\ V\ (vs\ NHE) \tag{4.1}$$

$$Fe^{VI}O_4^{2-} + 4\ H_2O + 3\ e^- \rightarrow Fe^{III}(OH)_3 + 5\ OH^-,\ E^0 = +0.7\ V\ (vs\ NHE) \tag{4.2}$$

$$2\ Fe^{VI}O_4^{2-} + 5\ H_2O \rightarrow 2\ Fe^{III}(OH)_3 + 1.5\ O_2 + 4\ OH^- \tag{4.3}$$

Though Fe(VI) has shown remarkable efficiency in oxidizing several pollutants in water [23,24], it has sluggish reactivity with some emerging contaminants. It is well known that Fe(VI) is more reactive at low pH conditions (Eqs. 4.1 and 4.2). However, the self-decay of Fe(VI) is also enhanced by acidic conditions (Eq. 4.3) [25]. Interestingly, Fe(VI) is more stable under basic conditions (pH 9.0-10.5), but the reactivity of Fe(VI) decreases in this pH range (Eqs. 4.1 and 4.2). Recently, we demonstrated that the activation of Fe(VI) by simple acids (HCl, HNO_3, and CH_3COOH) significantly enhanced the oxidative transformation of recalcitrant organics in water under slightly basic pH conditions, overcoming the aforementioned drawback [26]. This chapter explores for the first time the impact of ions and natural organic matter (NOM) on the acid-activated Fe(VI) oxidation of caffeine (CAF), in water. Furthermore, no study on the products of the oxidation of CAF by Fe(VI) has been performed.

CAF, an organic contaminant, has been found in the influent and effluent of wastewater treatment plants (WWTP) as well as in surface waters and groundwater worldwide [27–30]. For example, CAF was one of the most frequently detected emerging contaminants in the influent and effluent of a WWTP employing activated-sludge-based secondary treatment, at average concentrations of 17.7 µg/L and 5.8 µg/L, respectively [31]. CAF concentrations of as high as 230 µg/L have been reported in many surface streams and WWTP effluents [32,33]. Recent studies reported the detection of CAF in groundwater at concentrations up to 4.5 µg/L [34–36]. Furthermore, CAF may be the most widely consumed legal drug worldwide. Importantly, CAF is included in the U.S. EPA list of High Production Volume Chemicals [37], and the oxidation of CAF by different oxidation processes has been investigated [38–41]. CAF has low reactivity with Fe(VI) alone and requires activation of the oxidant to be oxidized efficiently in water [26].

Limited work has been done so far on the activation of Fe(VI) to lower Fe(VI) dose and shorten contact times [42,43]. In addition, most of the studies on the oxidation of organics by Fe(VI) focused on the kinetic investigations, and limited studies related to the effect of ions and organic matter usually present in wastewater on the Fe(VI) oxidation reactions have been conducted. The objectives of this chapter are to: (i) study the effect of Fe(VI) to CAF molar ratio on the oxidation of CAF by Fe(VI) (non-activated Fe(VI)) and acid-activated Fe(VI), (ii) develop an empirical model that predicts reasonably well the oxidative transformation of CAF at different Fe(VI) to CAF and HCl to Fe(VI) molar ratios, (iii) evaluate the effect of anions (Cl^-, SO_4^{2-} and HCO_3^-), monovalent cation (Na^+), divalent cations (Ca^{2+} and Mg^{2+}), natural organic matter (NOM) and secondary effluent wastewater on the CAF oxidation by Fe(VI) and activated Fe(VI), and (iv) identify the oxidized products (OPs) of the degradation of CAF by activated Fe(VI) and propose reaction pathways.

4.2 Materials and Methods

4.2.1 Chemicals

ReagentPlus grade caffeine powder (≥ 99.0% purity), magnesium chloride hexahydrate powder (≥ 99.0% purity) and sodium chloride powder (≥ 99.5% purity) were purchased from Sigma-Aldrich, Canada. Hydrochloric acid (36.5%-38.0%) and reagent grade calcium chloride, sodium sulfate and sodium bicarbonate were acquired from Caledon Laboratory Chemicals (Georgetown, Ontario, Canada). Ultrapure HPLC grade methanol (≥ 99.8% purity) and 0.45 μm polypropylene filters were bought from VWR International (Mississauga, Ontario, Canada). Suwannee River Natural Organic Matter (2R101N; NOM) in solid form was obtained from the International Humic Substances Society (IHSS, St. Paul, MN, USA). The secondary effluent wastewater (SE) was collected from the Adelaide Wastewater Treatment Plant, London, Ontario, Canada. The basic water quality parameters are presented in Table 4.1. All the chemicals mentioned above have been used without further purification. All solutions were prepared in doubly distilled water that was passed through 18.2 MΩ water purification system (Thermo Scientific, Barnstead^{TM} Easypure^{TM} RODi) (Milli-Q water). Fe(VI) was a salt of potassium (K_2FeO_4, 98% purity), which was prepared using the wet chemical method [20]. Fe(VI) solutions were prepared in Milli-Q water followed by centrifugation (Thermo Scietific, Sorvall Legend Centrifuge) at 3700 rpm for 2 min at 24 ºC. The concentrations of Fe(VI) in the filtered water were determined spectroscopically using molar absorptivity ($\varepsilon_{510nm} = 1150\ M^{-1}cm^{-1}$) [44]. Fresh solutions of Fe(VI) were prepared before each experiment.

Table 4.1: Basic water quality parameters of the secondary effluent wastewater (SE) used in the study.

Parameter	Value
pH	7.6 ± 0.2
Turbidity (NTU)	12.7 ± 0.4
Dissolved Organic Carbon, DOC (mg/L)	27.3 ± 1.3
Chemical Oxygen Demand, COD (mg/L)	29.3 ± 2.6
UV_{254} (cm^{-1})	0.135 ± 0.008
Total Phosphorus, TP (mg P/L)	0.23 ± 0.07
Total Nitrogen, TN (mg N/L)	19.9 ± 0.1
Soluble Nitrogen, SN (mg N/L)	19.8 ± 0.6
NO_3^- - N (mg N/L)	19.8 ± 0.2
NO_2^- - N (mg N/L)	0.217 ± 0.013
Ammonia (mg N/L)	0.03 ± 0.01
Total Solids, TS (mg/L)	567 ± 14
Total Suspended Solids, TSS (mg/L)	15 ± 3
Total Dissolved Solids, TDS (mg/L)	552 ± 14
Volatile Suspended Solids, VSS (mg/L)	9 ± 1

4.2.2 Experimental Procedures

All experiments were conducted in Milli-Q water under dark conditions. Solutions were rapidly mixed using a magnetic stirrer at room temperature (24±1 ℃). For all experiments, the desired amount of CAF was diluted by 250 mL of Milli-Q water and a sample was taken. Then, the desired amount of ion or NOM as dry matter was added to the CAF solution. The CAF-ion/NOM solution was mixed for one hour, using a magnetic stirrer, prior to the addition of Fe(VI) solution. After one hour, a sample was also taken. Both samples were analyzed for CAF. There was no difference in CAF concentration between the 2 samples. Hence, we ensured that the observed CAF removal is not related to any interaction between CAF and ion/NOM. The reaction was initiated by adding a certain volume of Fe(VI) solution to CAF or CAF-ion/NOM solution. For the SE wastewater experiments, a certain amount of CAF was diluted by 250 mL of SE instead of Milli-Q water. The pH of the Fe(VI)-CAF-ion/NOM/SE solution stabilized within 2 minutes (initial pH). After 2 minutes, the desired amount of HCl was added directly to the mixed solution.

In the cases of Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-} and SO_4^{2-}, where the pH of the reaction solution was more sensitive, the HCl was added drop by drop within 30 s to avoid a pH decrease below 8.0. The two methods of adding the acid (directly versus drop by drop within 30 s) have been confirmed experimentally to yield the same CAF removal. After completion of the reaction, the sample was filtered to remove Fe(III) particulate and analyzed for CAF. The experiments were conducted in triplicate, and the mean values with standard deviations were reported.

4.2.3 Analytical Methods

The CAF concentration was measured using an Agilent Technologies (1200 series) high performance liquid chromatography (HPLC), equipped with a diode array detector (set up at 272 nm) and a ZORBAX Eclipse XDB-C18 column (4.6 × 150 mm, particle size 5 µm) at 25 ℃. A mixture of methanol and Milli-Q water (70:30 v/v) was used as a mobile phase at a flow rate of 0.800 mL/min. The injection volume was 20 µL. UV-VIS spectrophotometer (UV-3600, Shimadzu Scientific Instruments, Columbia, MD, USA) was also applied to quantify CAF by measuring absorbance at 272 nm. A TOC analyzer (ASI-V_{CPN} Shimadzu), equipped with an ASI-V auto-sampler (Shimadzu), was applied to measure dissolved organic carbon (DOC). Solids-related parameters (Table 4.1) of the SE wastewater were measured according to standard methods [45]. Hach methods and testing kits (Hach Odyssey DR/2500; Hach, Loveland, Colorado) were performed to measure levels of chemical oxygen demand, nitrogen and phosphorous in SE wastewater (Table 4.1). The turbidity of the SE wastewater was measured using a Thermo Orion AQUAfast II AQ2010 Turbidity Meter (Beverly, MA, USA) (Table 4.1). The pH of the reaction solution was measured throughout the experiments using a Metrohm 780 pH Meter. Data were processed in Minitab 16 using response surface methodology to develop the model.

Oxidized products identification. All MS data were obtained using a Q-Exactive Quadrupole Orbitrap mass spectrometer (Thermo Fisher Scientific), coupled to an Agilent 1290 high-performance liquid chromatography (HPLC) system with a Zorbax Eclipse Plus RRHD C18 column (2.1 × 50 mm, 1.8 µm; Agilent) maintained at 35 °C. The mobile phase was comprised of water with 0.1% formic acid (A), and acetonitrile with 0.1% formic acid (B) (Optima grade, Fisher Scientific, Lawn, NJ, USA). The gradient begins with 100% A for 30 seconds before increasing B to 100% over 3 minutes. B was held at 100% for 2 minutes prior to returning to 0% over 30 s. Injection volume was 2 μL. The flow rate was 0.3 mL/min. The following conditions were used for positive HESI: capillary voltage, 4.0 kV; capillary temperature, 400 °C; sheath gas, 17.00 units; auxiliary gas, 8.00 units; probe heater temperature, 450 °C; S-Lens RF level, 45.00. A top-5 data dependent acquisition (DDA) method involved a full MS scan at 35,000 resolution over a 50-500 *m/z*; automatic gain control (AGC) target and maximum injection time (max IT) was 3e6 and 120 ms respectively. The five highest intensity ions from the full scan were sequentially selected using a 1.2 *m/z* isolation window and analyzed at resolution of 17,500; AGC target, 1e5; max IT, 60 ms; normalized collision energy (NCE) 25; threshold intensity 1.0e5; and dynamic exclusion of 8 s. Full MS spectra were screened for OPs with the Xcalibur software, whereupon MS/MS spectra of putative OPs were analyzed manually.

4.3 Results and Discussion

4.3.1 Oxidation of CAF by Fe(VI) and activated Fe(VI)

Figure 4.1 shows the oxidation of CAF by Fe(VI) (i.e., non-activated Fe(VI)) and activated Fe(VI) at different molar ratios of Fe(VI) to CAF. At a molar ratio of 8.0, almost complete transformation of CAF by activated Fe(VI) was observed. Comparatively, 39.1% CAF remained when Fe(VI) was used at the same molar ratio of 8.0 (Figure 4.1). Non-activated Fe(VI) needed a molar ratio of 25.0 to achieve complete transformation of CAF (Figure 4.1). This enhanced oxidation of CAF is similar to the observation seen in oxidation of organic contaminants including CAF previously [26]. Details of the experiments are provided in Table 4.2, and Tables S4.1 and S4.2 of Appendix B. Importantly, the time of the complete decay of Fe(VI) and filtration time before analyzing CAF were much shorter for activated Fe(VI) than non-activated Fe(VI) (seconds and minutes versus hours) (Table 4.2, and Table S4.2 of Appendix B).

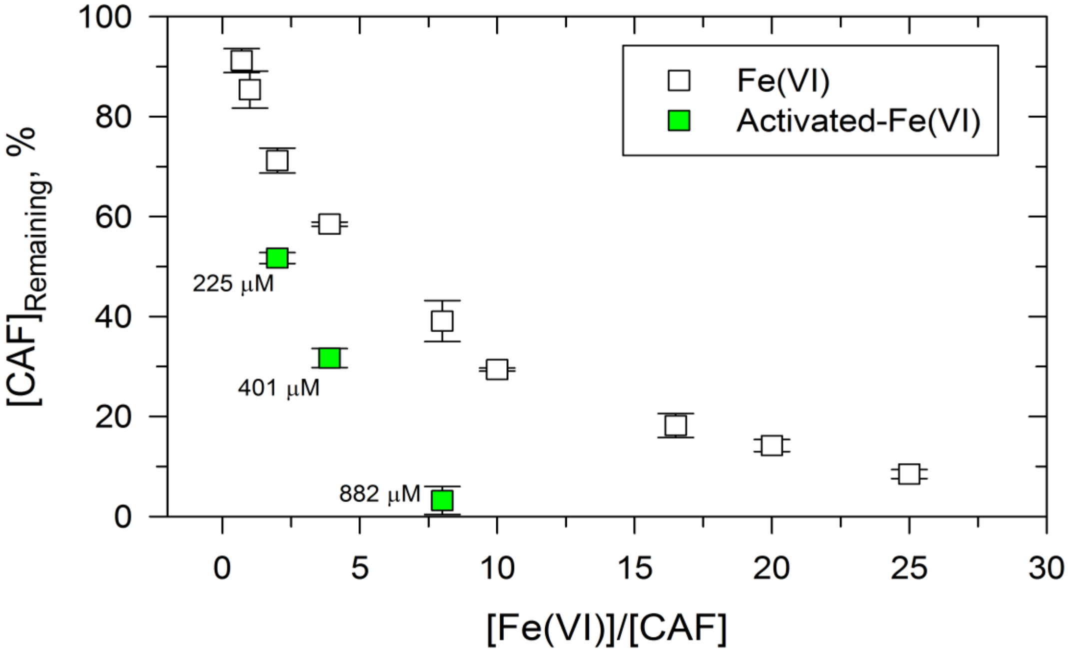

Figure 4.1: Effect of Fe(VI) to CAF molar ratio on the oxidation of CAF by Fe(VI) and acid-activated Fe(VI). (Experimental conditions: [Fe(VI)] = 41.7-1314.8 µM; [CAF] = 51.4-95.3 µM; [HCl] = 225-882 µM; final pH (acid-activated Fe(VI)) = 7.5; final pH (Fe(VI)) = 7.3-8.6).

Variation of pH. As evident from Table 4.2, the final pH (pH (4)) of the reaction solution is lower than the initial pH (pH (1)). It is noted that no buffer was used and the initial pH could be only manipulated by changing the Fe(VI) concentration (the higher the Fe(VI) concentration the higher the initial pH). The consumption of proton initially causes a slight decrease of the pH (pH (2)). Then, the pH increased because of the formation of hydroxide ions (OH^-) (pH (3)) (Eq. 4.3), as expected. Hydroxide ions are then most probably consumed by: (i) the reaction of Fe(VI) with CAF and/or (ii) by Fe(III) produced as a product of the Fe(VI) reduction (formation of Fe(III) hydroxide), resulting in lower final pH than initial pH. Moreover, Fe(VI) is a more basic species than Fe(III), hence a decrease of the pH is expected as observed in our experimental studies. Moreover, the addition of acid would apparently cause a decrease in the pH.

Table 4.2: Variation of pH and oxidative transformation of CAF with and without acid for typical experiments.

[Fe(VI)]/[CAF] (mol/mol)	[HCl] (μM)	pH (1)	pH (2)	pH (3)	pH (4)	Time (Fe(VI) Decay)	Filtration Time (h)	CAF Remaining (%)
3.9	No Acid	9.0	-	9.3	7.5	3 h	6.0	58.5 ± 0.4
3.9	401	9.3	8.9	9.5	7.5	10 min	1.0	31.7 ± 1.9
8.0	No Acid	9.6	-	10.3	7.5	4 h	8.0	39.1 ± 4.1
8.0	882	9.5	8.8	9.1	7.5	10 s	0.5	3.2 ± 2.8

pH(1) - Initial pH of Fe(VI)-CAF mixture; pH(2) - Immediate pH after the addition of acid; pH(3) - Highest pH reached during the reaction; pH(4) - Final pH before filtration;

4.3.2 Activation Mechanism

The possible species responsible for the observed enhancement of the oxidative transformation of CAF could be iron-based and/or reactive oxygen-related species. The activation mechanism of acid (HCl and HNO_3) on Fe(VI) was discussed in our previous study when experiments under oxic (dissolved oxygen present initially in the solution) and anoxic (nitrogen purging) conditions were conducted [26]. The same transformation of CAF was achieved under oxygenated and deoxygenated conditions suggesting less likely involvement of oxygen-related species [26]. The effect of Fe(III) has been also ruled out experimentally [26], and the effect of Fe(VI) alone is shown in the Figure 4.1, Table 4.2, and Table S4.2 of Appendix B. As a result, Fe(V) and Fe(IV) (iron oxidation states between III and VI) are most likely responsible for the observed enhancement since is known that Fe(V)/Fe(IV) species are more reactive than Fe(VI) [46–48].

A possible participation of Fe(V)/Fe(IV) species in the oxidation process would cause enhanced oxidation of CAF because more electron-equivalents would be available per mole of Fe(VI) (increased oxidation capacity of Fe(VI)) (Figure 4.1). The reduction of Fe(VI) by CAF and/or H^+ to the final Fe(II)/Fe(III) species through 1-e^-/2-e^- transfer steps may yield Fe(V)/Fe(IV) species (e.g. $Fe^{VI} \rightarrow Fe^{V} \rightarrow Fe^{IV} \rightarrow Fe^{III} \rightarrow Fe^{II}$, $Fe^{VI} \rightarrow Fe^{IV} \rightarrow Fe^{II}$ and $Fe^{VI} \rightarrow Fe^{V} \rightarrow Fe^{III}$) [26,49,50]. Interestingly, the formation of Fe(V) and Fe(IV) species during the decomposition of Fe(VI) has been recently demonstrated [51]. Possible reactions between iron species $Fe^{II}/Fe^{III}/Fe^{IV}/Fe^{V}/Fe^{VI}$ may also contribute to the formation of reactive species (e.g. $Fe^{VI} + Fe^{II} \rightarrow Fe^{V} + Fe^{III}$) [20,26].

4.3.3 Empirical Model

Figure 4.1 suggests that the transformation of CAF by activated Fe(VI) depends on the acid concentration and molar ratio of Fe(VI) to CAF. A model was developed by considering the molar ratios of Fe(VI) to CAF and HCl to Fe(VI). Molar ratios of Fe(VI) to CAF ranged from 2.0-8.0 while corresponding HCl to Fe(VI) molar ratios were in the range of 0.00-1.74. The removal of CAF as percentage was the response of the model. More details regarding the data used for the model development and the analysis of variance for the response are given in Tables S4.3 and S4.4 of Appendix B, respectively. A 2-factor linear model ($R^2 = 0.981$, $R^2(adj) = 0.977$ and R^2 (pred) = 0.961) was developed using response surface methodology in Minitab 16. The square root of the mean square error (RMSE) was equal to 3.6% CAF removal. The normality of the data, which is a basic assumption for the statistical analysis [52], was checked and confirmed by the normal probability plot of standardized residuals (Figure S4.1 of Appendix B).

The model predicts reasonably well the removal of CAF in the Fe(VI)-CAF system at a molar ratio range of 2.0-10.0, which achieved ~70% CAF removal (Figure 4.2). The prediction at higher molar ratios than 10.0 is not good (Figure S4.2 of Appendix B). The ability of different models to predict the CAF removal efficiency at high Fe(VI) to CAF molar ratios of the Fe(VI)-CAF system (non-activated Fe(VI)) is discussed in Text S4.1 of Appendix B. In the HCl-activated Fe(VI) system, the prediction of the model is good over the entire range of molar ratio of Fe(VI) to CAF (2.0-8.0) and molar ratio of HCl to Fe(VI) (0.64-1.74) (Figure 4.2). Importantly, the model also predicts reasonably well the removal of CAF in the Fe(VI)-CAF-Acid system when nitric instead of hydrochloric acid was used (Figure 4.2). An attempt to include an interaction term to the model (e.g. {[F(VI)]/[CAF]}×{[HCl]/[Fe(VI)]}) did not result in significantly different model prediction ability. This is due to the much lower coefficient (in coded units) of the interaction factor compared to the other 2 factors. Also, the high P-value of 0.296 is greater than that the alpha level (0.05), indicating that the interaction factor is not statistically significant (Table S4.5 of Appendix B). Details regarding the model prediction are given in Tables S4.6-S4.8 of Appendix B.

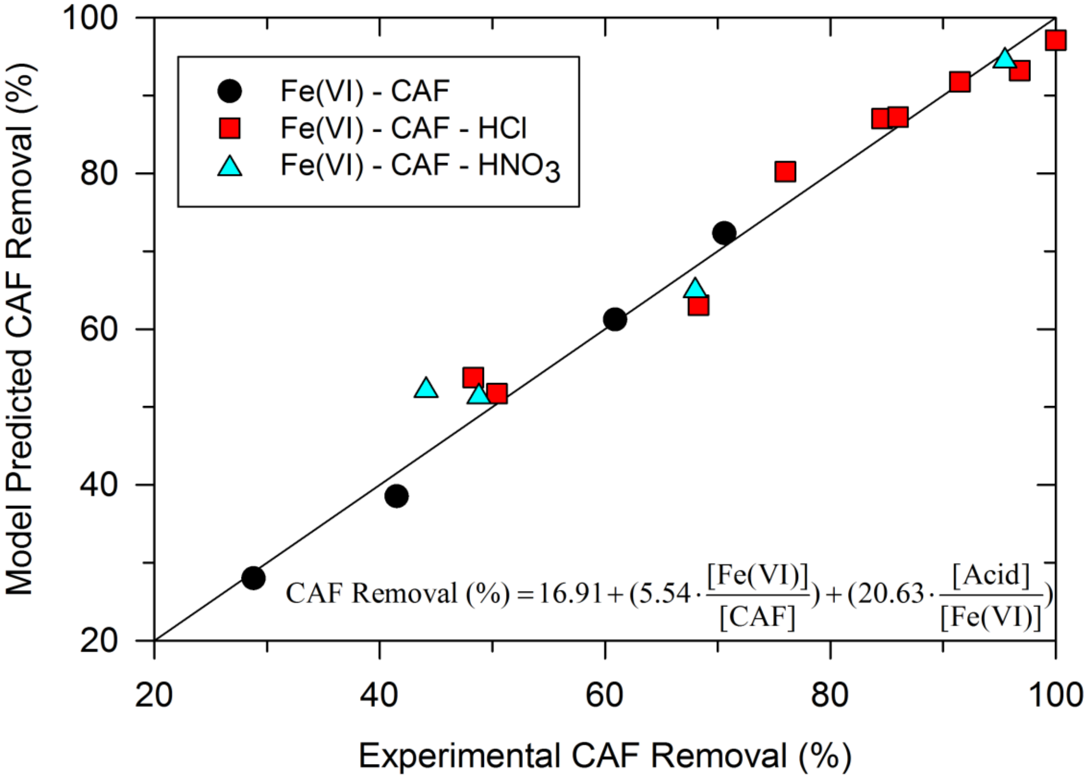

Figure 4.2: Linear model equation and prediction: The model is valid at Fe(VI) to CAF molar ratio range of 2.0-10.0 for Fe(VI) and from 2.0 to 8.0 for acid-activated Fe(VI), acid to Fe(VI) molar ratio range of 0.00-1.74, immediate pH after the addition of acid of 8.0 or higher and room temperature. R^2 = 0.981, R^2(adj) = 0.977 and R^2(pred) = 0.961. Note: Nitric acid data taken from our previous study [26].

The goal for the development of this empirical model was to point out the effect of the acid. Thus, the molar ratio of HCl to Fe(VI) was introduced. The presence of Fe(VI) in the system is crucial to demonstrate the activation by acid. In other words, if the Fe(VI) to CAF molar ratio is zero, the activation by acid could not be demonstrated. Hence, the proposed empirical model is restricted by this variable (Fe(VI) to CAF molar ratio should not be zero) (Figure 4.2). As shown experimentally, there was no effect of the initial pH in a pH range of 8-9 (Table S4.1 of Appendix B). Increased concentration of acid (compared to Fe(VI) concentration), resulted in low pH values complicating the differentiation between pH and acid-activation effects. Hence, in all the experiments used for the development of the empirical model, the immediate pH after the addition of acid was 8.0 or higher, to minimize pH effects.

4.3.4 Effect of Ions on Oxidation of CAF by Fe(VI) and Activated Fe(VI)

The effect of water constituents on the removal of target pollutants is critical for the development of any water treatment technology. The effects of anions (Cl^-, SO_4^{2-} and HCO_3^-), monovalent cation (Na^+) and divalent cations (Ca^{2+} and Mg^{2+}), which are usually present in raw wastewater and surface waters, on the oxidation of CAF by Fe(VI) and acid-activated Fe(VI) were investigated at a molar ratio of Fe(VI) to CAF of 2.0. The concentrations of ions were chosen to be relevant to the concentrations normally encountered in wastewater [53–55]. The initial pH was between 8.0 and 9.0, where there was no effect of pH (Table S4.1 and S4.9 of Appendix B). Blank experiments ruled out the effect of ions and acid alone in the observed removal of CAF (Table S4.10 of Appendix B). In all cases, t-test comparisons with a 95% confidence interval were performed when comparing each experiment with the control experiment (Tables S4.11 and S4.12 of Appendix B). In the case of Fe(VI) (non-activated Fe(VI)), no apparent effect was observed by adding HCO_3^-, Cl^- and Na^+ in the reaction solution (Figure 4.3a; Table S4.11 of Appendix B). The removal of CAF by the Fe(VI)-CAF system was negatively affected by the SO_4^{2-}, Mg^{2+} and Ca^{2+} ions (Figure 4.3a). The CAF removal decreased from 28.8% to 24.5%, 20.7% and 17.0%, respectively (differences between with and without ions of 4.3%, 8.1% and 11.8% CAF removal efficiencies respectively) (Figure 4.3a; Table S4.11 of Appendix B). In order to exclude the possibility of consumption of Fe(VI) by the aforementioned ions, an axially configured Vista-Pro inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to determine the concentrations of the ions in the treated samples. Results showed no effect on the ions concentrations (Table S4.13 of Appendix B). Similar effects of calcium and magnesium ions on the oxidation of flumequine by Fe(VI) have been reported [23].

A possible reason for the decrease in oxidative transformation of CAF in the presence of these ions is the enhanced self-decay of Fe(VI) [56]. In other words, Fe(VI)'s reaction with water is enhanced by these ions. This phenomenon resulted in less oxidation of CAF by Fe(VI) in the presence of ions than it would otherwise be in the absence of ions. Interestingly, no such effect of sulfate and magnesium was seen when acid-activated Fe(VI) was used (Figure 4.3a; Table S4.12 of Appendix B). Acid-activated Fe(VI) reaction with CAF was only negatively affected by calcium ions. However, the effect of calcium ions on CAF oxidation by acid-activated Fe(VI) was not as significant (4.6% CAF removal) as by non-activated Fe(VI) (11.8% CAF removal) (Figure 4.3a; Tables S4.11-S4.12 of Appendix B). Interestingly, the CAF removal increased slightly from 48.3% to 53.0% (difference of 4.7% CAF removal) in the presence of bicarbonate ion in the Fe(VI)-CAF-HCl system.

Calcium showed the highest negative effect on CAF oxidation by both Fe(VI) and activated Fe(VI). In order to diminish the effect of calcium, more experiments were carried out at higher Fe(VI) to CAF molar ratio of 3.9. The concentration of calcium was the same like the previous experiments i.e. 2 mM Ca^{2+} (Fe(VI) to CAF molar ratio of 2.0). The HCl to Fe(VI) molar ratio was also similar (~1.2). Interestingly, no effect of calcium was seen by increasing the Fe(VI) to CAF molar ratio when acid-activated Fe(VI) was used (Figure 4.3b; Table S4.12 of Appendix B). In the case of non-activated Fe(VI), although the negative effect of calcium decreased from 11.8% (Fe(VI) to CAF molar ratio of 2.0) to 9.0% CAF removal efficiency (Fe(VI) to CAF molar ratio of 3.9), it did not disappear (Figure 4.3b; Table S4.11 of Appendix B). It is shown for the first time here that the oxidation of organics by acid-activated Fe(VI) is not significantly affected by ions usually present in water (except for Ca^{2+}). Hence, the empirical model (Figure 4.2) can be also used to predict the oxidative transformation of CAF by acid-activated Fe(VI) in the presence of the studied ions.

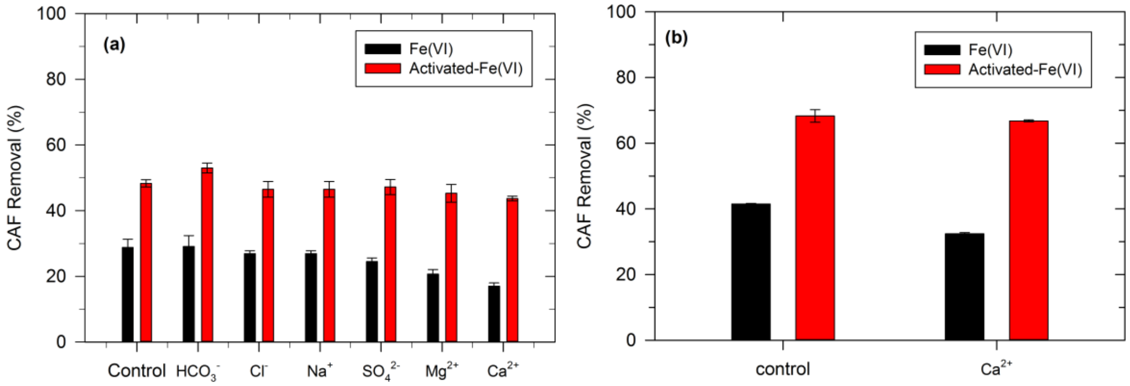

Figure 4.3: (a) Effect of bicarbonate (HCO_3^-; $NaHCO_3$), chloride (Cl^-; NaCl), sodium (Na^+; NaCl), sulfate (SO_4^{2-}; Na_2SO_4), magnesium (Mg^{2+}; $MgCl_2.6H_2O$) and calcium (Ca^{2+}; $CaCl_2$), on CAF oxidation by Fe(VI) and acid-activated Fe(VI). (Experimental conditions: [Fe(VI)]/[CAF] = 2 mol/mol; $[HCO_3^-]$ = 1.2 mM; $[Cl^-] = [Na^+]$ = 4 mM; $[Mg^{2+}]$ = 1 mM; $[Ca^{2+}] = [SO_4^{2-}]$ = 2 mM; [HCl] = 211-225 µM). (b) Effect of calcium at [Fe(VI)]/[CAF] = 3.9 mol/mol; $[Ca^{2+}]$ = 2 mM; [HCl] = 401-410 µM. Initial pH = 8.0-9.0 and final pH = 7.0-8.3.

4.3.5 Effect of NOM and SE on Oxidation of CAF by Fe(VI) and Activated Fe(VI)

The effects of NOM in water and SE wastewater were also investigated (Tables S4.14 and S4.15 of Appendix B). Figure 4.4a shows that the transformation of CAF in water decreased from 28.8% to 20.7% and from 48.3% to 36.2% for Fe(VI) and acid-activated Fe(VI), respectively, in the presence of NOM (5 mg DOC/L). In the case of SE wastewater (27 mg DOC/L), the transformation of CAF decreased from 28.8% to 13.8% and from 48.3% to 16.9 % for Fe(VI) and acid-activated Fe(VI), respectively. This decrease in the removal of CAF in the presence of NOM was expected because Fe(VI) could react with organic components present in NOM (Figure 4.4b). Moreover, the further reduction of CAF removal efficiency from NOM to SE, is due to the higher DOC concentration of SE (27 mg/L) than NOM (5 mg/L). Ions present in SE wastewater may also contribute to the decrease of CAF removal efficiency. Importantly, 22.3% and 8.9% DOC removal was achieved by acid-activated Fe(VI), compared to no mineralization without activation, confirming the increased oxidative capacity of acid-activated Fe(VI) (Figure 4.4b). It is noted that no mineralization of CAF (no DOC removal) was observed in the Fe(VI)-CAF-HCl system (in the absence of NOM/SE). The results show that the activation of Fe(VI) by simple acid is beneficial in terms of oxidizing organics in a real wastewater matrix. Acid-activated Fe(VI) also reacted with less recalcitrant organics than CAF, resulting in their mineralization as indicated by the DOC removal.

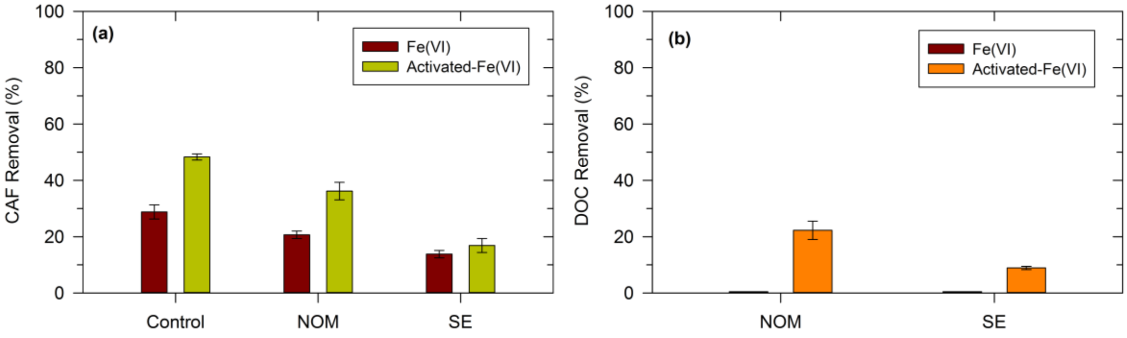

Figure 4.4: Effect of Suwannee River Natural Organic Matter (NOM) and secondary effluent (SE) wastewater on CAF oxidation by Fe(VI) and acid-activated Fe(VI): (a) CAF removal; (b) DOC removal. (Experimental conditions: [Fe(VI)]/[CAF] = 2 mol/mol; [NOM] = 5.1 mg/L; [HCl] = 216-228 µM; initial pH = 8.6; DOC(NOM) = 5 mg/L; DOC(SE) = 27 mg/L; final pH(NOM)=6.8-7.3; final pH(SE)=8.2-8.3).

4.3.6 Proposed Reaction Pathways of Oxidation of CAF by Acid-activated Fe(VI)

4.3.6.1 Products Identification

The DOC measurements carried out after the oxidation of CAF by HCl-activated Fe(VI) indicated no mineralization of CAF at the studied Fe(VI) to CAF molar ratios even when complete removal of CAF was achieved, suggesting the formation of persistent OPs. Four OPs were identified: (i) N,N'-Dimethyloxamide (OP1), (ii) N-Methylurea (OP2), (iii) N,N'-Dimethylurea (OP3) and (iv) 6-amino-5-(N-formylmethylamino)-1,3-dimethyluracil (OP4). The proposed fragments of OPs, measured by LC-HRMS are presented in Figure S4.3 of Appendix B. The protonated molecular ion $[M+H]^+$ was chosen as the parent ion. Accurate mass measurements of the four OPs allowed us to propose their molecular formulae (Table S4.16 of Appendix B). The structures of OP1, OP2 and OP3 (protonated form at m/z 117.0664, 75.0562 and 89.0717 respectively) were supported by the product ion at m/z 58.0298 that corresponds to losses of fragments as C_2H_5NO, NH_3 and CH_5N for OP1, OP2 and OP3 respectively (Figure S4.3 and Table S4.16 of Appendix B). The formulae ($[M+H]^+$) that best match the experimental masses are $C_4H_9N_2O_2$, $C_2H_7N_2O$ and $C_3H_9N_2O$, with errors of 4.67 ppm, 12.40 ppm and 8.65 ppm for OP1, OP2 and OP3 respectively (Table S4.16 of Appendix B). The structures of OP1, OP2 and OP3 have been also confirmed by standard samples. The structure of OP4 (protonated form at m/z 199.0830) was supported by the product ions at m/z 142.0615 and 125.0031 corresponding to the individual losses of fragments as C_2H_3NO and NH_3 (Figure S4.3 and Table S4.16 of Appendix B). The formula ($[M+H]^+$) that best matches the experimental mass is $C_7H_{11}N_4O_3$ with an error of 2.28 ppm (Table S4.16 of Appendix B). The reduction of DBE (double bond equivalent) from 6 (CAF) to 2, 1, 1 and 5 for OP1, OP2, OP3 and OP4 respectively also supports the proposed structures (Table S4.16 of Appendix B). These OPs have been seen in the oxidation of CAF by oxidants. OP1, OP2 and OP3 have been identified as products of the degradation of CAF by hypochlorite [41]. OP1 has been also reported as a product of the reaction of CAF with ozone [57]. OP4, a biological metabolite of CAF [58], has been identified as a product of the degradation of CAF by activated oxone [59], ozone [39], electrochemical oxidation [60], and activated peroxymonosulfate [61].

4.3.6.2 Proposed Reaction Pathways

OP1, OP2 and OP3 could be formed through pathway I (Figure 4.5). An initial attack of Fe(VI) to C_4=C_5 double bond of CAF results in C1 (nine-membered ring structure). The intermediacy of C1 has also been suggested for the degradation of CAF by ozone [57], advanced oxidation [62], and hypochlorite [41,63]. Degradation of C1 could lead to C2 as suggested for oxidation of CAF by hypochlorite (see Figure 4.5) [41]. Kolonko et al. [57] also suggested that the degradation of C1 leads to C2 during ozonation of CAF. Finally, hydrolysis A, B and C of C2 leads to OP1, OP2 and OP3 respectively (Figure 4.5) [41].

OP4 could be formed via pathway II (Figure 4.5). Pathway II was individually initiated by the addition of hydroxyl to the C_8 position of CAF, that leads to C3 (Figure 4.5). Interestingly, the hydroxylation reaction during oxidation of different pharmaceuticals such as flumequine and sulfamethoxazole by Fe(VI) has been recently suggested by other research groups [23,64]. The hydroxyl addition to the C_8 position of CAF as an initial step of the oxidation reaction pathway has also been reported for the oxidation of CAF by ozone, activated oxone, advanced and electrochemical oxidation [39,59,60,62]. An attack by high-valent iron species on the carbon-nitrogen bond of the five-membered ring, resulting in a ring-opening reaction, would lead to the formation of C4 (Figure 4.5) [59]. Finally, degradation of C4 through demethylation reaction generates OP4 (Figure 4.5). Overall, pathways proposed for the oxidation of CAF by activated Fe(VI) are in agreement with the identified OPs.

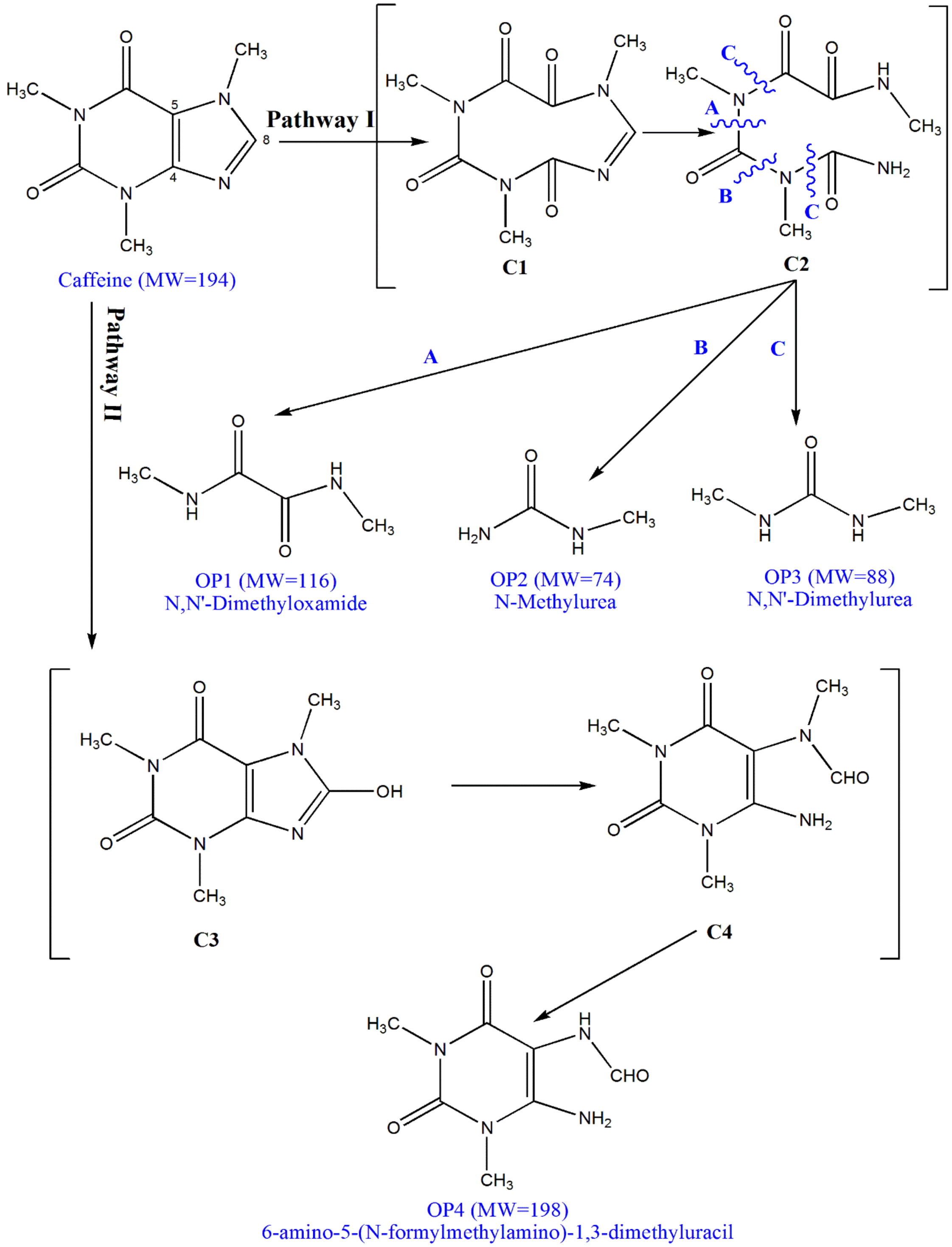

Figure 4.5: Proposed reaction pathways of degradation of CAF by acid-activated Fe(VI). (Experimental conditions: [Fe(VI)] = 662.7 μM; [Fe(VI)]/[CAF] = 8.0 mol/mol; [HCl]/[Fe(VI)] = 1.74; immediate pH after the addition of acid = 8.8; final pH = 7.2).

4.4 Summary and Conclusions

By adding acid, Fe(VI) technology is not only more efficient and faster, but also not negatively affected by common inorganic ions (Cl^-, SO_4^{2-}, HCO_3^-, Na^+, and Mg^{2+}) present in wastewater and surface waters. The specific results are:

- CAF could be oxidized by acid-activated Fe(VI) at a 3-times lower Fe(VI) to CAF molar ratio than Fe(VI) (non-activated Fe(VI)) (8.0 versus 25.0).

- The acid-activated Fe(VI) reaction with CAF was faster (seconds to minutes) than Fe(VI) (hours).

- A linear model was developed using response surface methodology ($R^2 = 0.981$, R^2(adj) = 0.977, and R^2(pred) = 0.961). The model predicts well the percentage removal of CAF by Fe(VI)-CAF, Fe(VI)-CAF-HCl and Fe(VI)-CAF-HNO_3 systems. The model is valid at Fe(VI) to CAF molar ratio range of 2.0-10.0 for Fe(VI), and from 2.0 to 8.0 for acid-activated Fe(VI), acid to Fe(VI) molar ratio of 0.00-1.74, immediate pH after the addition of acid of 8.0 or higher, and room temperature.

- The oxidative transformation of CAF by acid-activated Fe(VI) slightly decreased from 48.3% to 43.7% in the presence of Ca^{2+} ions (2 mM), at Fe(VI) to CAF molar ratio of 2.0 and HCl to Fe(VI) molar ratio of ~1.2. This effect of Ca^{2+} ions could be overcome by increasing the molar ratio of Fe(VI) to CAF from 2.0 to 3.9, at the same Ca^{2+} concentration (2 mM) and HCl to Fe(VI) molar ratio (~1.2).

- In the case of Fe(VI) (non-activated Fe(VI)), no apparent effect was observed by adding HCO_3^-, Cl^- and Na^+ in the reaction solution.

- The removal of CAF by Fe(VI) (non-activated Fe(VI)) decreased from 28.8% to 24.5%, 20.7% and 17.0%, in the presence of 2 mM SO_4^{2-}, 1 mM Mg^{2+} and 2 mM Ca^{2+} ions respectively, at Fe(VI) to CAF molar ratio of 2.0.

- The transformation of CAF in water decreased from 28.8% to 20.7% and from 48.3% to 36.2% for Fe(VI) and acid-activated Fe(VI), respectively, at Fe(VI) to CAF molar ratio of 2.0, in the presence of 5.1 mg NOM/L (DOC=5 mg/L).

- In case of SE wastewater (DOC=27 mg/L), the transformation of CAF decreased from 28.8% to 13.8% and from 48.3% to 16.9 % for Fe(VI) and acid-activated Fe(VI), respectively.

- Importantly, the acid-activated Fe(VI) was able to mineralize other organics present in NOM and SE, confirming higher oxidative capacity upon acid activation, compared to Fe(VI) where no mineralization was observed.

- A total of four OPs of CAF, i.e. N,N'-Dimethyloxamide, N-Methylurea, N,N'-Dimethylurea, and 6-amino-5-(N-formylmethylamino)-1,3-dimethyluracil were identified for the first time, and the reaction pathways of the oxidation of CAF by activated Fe(VI) were postulated according to the experimental results.

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Chapter 5

5 Silica gel-enhanced Oxidation of Caffeine by Ferrate(VI)

5.1 Introduction

There is a growing environmental concern related to the contamination of surface waters with emerging organic pollutants [1–5]. For example, pharmaceuticals are considered as emerging contaminants because of their persistent presence in hospital effluents, soil, ground water, and drinking water resources [6–9]. The released pharmaceuticals are either mobilized in their original structures or transformed into other active (or inactive) organic compounds in aquatic environments. The concentrations of pharmaceuticals range from parts-per-billion (ng/L) to parts-per-million (μg/L). This paper deals with caffeine (1,3,7-trimethylpurine-2,6-dione, CAF, Figure S5.1 of Appendix C) in water.

CAF is one of the most widely consumed psychostimulants with a global average consumption of 70 mg/person/day [10–13]. CAF is included in the United States Environmental Protection Agency (USEPA) list of High Production Volume Chemicals [11]. It is one of the most frequently detected emerging organic pollutants in surface waters and influents and effluents of wastewater treatment plants worldwide [1,14,15]. CAF has been found in influents of wastewater treatment plants globally at concentrations of as high as 1.5 μM [11]. The release of CAF individually and in a mixture with other pharmaceuticals in water may induce toxic effects to aquatic organisms [16,17]. It is of utmost importance that CAF is treated before its release to the aquatic environment. Chemical oxidation processes have been investigated to remove CAF from water [18–22]. The focus of this chapter is on the chemical oxidation of CAF by ferrate(VI) ($Fe^{VI}O_4^{2-}$, Fe(VI)).

Fe(VI) received a remarkable attention in the last two decades because of its potential use as a green molecule in disinfection of viruses, organic transformations, and water and wastewater treatment [23–32]. Its oxidation, disinfection and coagulation properties, with a single dose and mixing unit process, promote it as a multipurpose molecule for water and wastewater treatment [33,34]. The Fe(VI)'s treatment capability has been investigated for the removal of a wide range of contaminants such as organosulfur, nitrogen-containing, metals, viruses and bacteria [35–39]. Recent studies emphasized the oxidation of emerging organic pollutants such as endocrine disrupting compounds, pharmaceuticals and personal care products [40–42]. Despite the model compounds of different moieties, most of the reported studies focused on the kinetic investigation of the Fe(VI)-contaminant oxidation reaction, and limited work has been done on the effect of ions and natural organic matter (NOM) usually present in water and wastewater [32].

It is well known that the oxidation power of Fe(VI) depends on the pH (Fe(VI)'s reactivity is higher at low pH than at high pH) [38]. Fe(VI)'s stability in water is also a function of the pH. Fe(VI) reacts with water to form molecular oxygen ($2\ FeO_4^{2-} + 5\ H_2O \rightarrow 2\ Fe(OH)_3 + 3/2\ O_2 + 4\ OH^-$ [23,38]) and this undesired reaction is also favored at low pH conditions. Moreover, the relevant pH for water treatment is 6.0 to 9.0 [26], hence very high or low pH conditions are generally avoided to meet discharge criteria set by the regulatory agencies. Interestingly, Fe(VI) is most stable at slightly basic pH values despite reduced reactivity. Thus, activating or catalyzing Fe(VI) oxidation reactions at slightly basic pH conditions is required to enhance the oxidative transformation of pollutants. With this aim, we have recently activated Fe(VI) in water by adding simple acids (i.e. HCl, HNO_3 and CH_3COOH) that showed enhanced removal of recalcitrant pollutants in water [43]. Additions of peroxymonosulfate and ammonia to Fe(VI) were also able to activate the oxidant to degrade fluoroquinolone antibiotics [44,45]. This chapter showed for the first time the activation of Fe(VI) by the addition of a solid material, silica gel (SiO_2), to enhance the removal of CAF in water under mild alkaline conditions.

Numerous investigations that show the use of SiO_2 gel to accelerate the reactions of organic compounds have been reported [46–48]. For example, it was shown that SiO_2 gel fixed-bed catalyzes the acetyl migration reactions to synthesize thiol compounds [47]. The alkylation of phenols and heterocyclic aromatic compounds (e.g., thiophene and furan) is also catalyzed by SiO_2 gel [48]. Addition of solid material to Fe(VI) to enhance oxidation of organic compounds has rarely been reported [49,50]. Earlier studies were conducted either in strong alkaline solution or in nonaqueous environment (acetonitrile-water)

[49,50]. These studies have almost no use in real water treatment conditions where regulatory pH requirements specify a pH range of 6-9. Other studies explored only the influence of montmorillonite K10 (up to 40 mg/L) as a constituent of water to oxidize tetrabromobisphenol A and bisphenol A by Fe(VI), and reported no effect on removal efficiency by Fe(VI) [51]. Significantly, in this chapter, we have shown the catalytic effect of SiO_2 gel on Fe(VI) oxidation of CAF in water at slightly basic pH range of 8.0-9.0. Importantly, a significantly lower Fe(VI) dose was needed for complete removal of CAF compared to the absence of SiO_2 gel.

The objectives of this chapter are to: (i) investigate the effect of Fe(VI) to CAF molar ratio and concentration of SiO_2 gel on the removal efficiency of CAF, (ii) evaluate the effect of particle size and pore volume of SiO_2 gel on CAF oxidation by Fe(VI), (iii) assess the effect of anions (Cl^-, HCO_3^- and SO_4^{2-}), cations (Na^+, Ca^{2+} and Mg^{2+}) and NOM usually present in wastewater on the oxidative transformation of CAF by Fe(VI) in the presence of SiO_2 gel (iv) identify the oxidized products (OPs) of CAF oxidation by Fe(VI)-SiO_2 in order to propose a possible reaction pathway, and (v) apply density functional theory calculations to support the proposed reaction pathway.

5.2 Materials and Methods

5.2.1 Chemicals

ReagentPlus grade CAF powder (≥99.0% purity), high-purity grade SiO_2 gels powder (≥99.0% purity), magnesium chloride hexahydrate powder (≥99.0% purity) and sodium chloride powder (≥99.5% purity) were purchased from Sigma-Aldrich, Canada. The characteristics of the SiO_2 gels used in the study are presented in Table 5.1. The choice of SiO_2 gels was made to facilitate the delineation of the impact of particle size and pore volume/surface area. Reagent grade calcium chloride, sodium sulfate and sodium bicarbonate were acquired from Caledon Laboratory Chemicals (Georgetown, Ontario, Canada). Ultrapure HPLC grade methanol (≥99.8% purity) and 0.45 μm polypropylene filters were bought from VWR International (Mississauga, Ontario, Canada). Suwannee River Natural Organic Matter (2R101N; NOM) in solid form was obtained from the

International Humic Substances Society (IHSS, St. Paul, MN, USA) and characterized in terms of dissolved organic carbon (DOC) (DOC=0.80 NOM) (Appendix H). All chemicals were used without further purification. All solutions were prepared in doubly distilled water that was passed through 18.2 MΩ water purification system (Thermo Scientific, Barnstead™ Easypure™ RODi) (Milli-Q water). Solid potassium ferrate(VI) ($K_2Fe^{VI}O_4$; 98% purity) was synthesized using the wet chemical method [52]. Fe(VI) solutions were prepared by adding a desired amount of solid K_2FeO_4 to Milli-Q water followed by centrifugation (Thermo Scietific, Sorvall Legend Centrifuge) at 3700 rpm for 2 min at 24 ºC. The concentrations of Fe(VI) in Milli-Q water were determined spectroscopically using molar absorptivity (ε_{510nm} = 1150 M^{-1} cm^{-1}) [53]. Fresh solutions of Fe(VI) were prepared before each experiment to avoid its decomposition in water.

Table 5.1: Characteristics of silica gels (SiO_2) used in the study.

Silica gel	Surface area (m^2/g)	Particle size (μm)	Pore volume (cm^3/g)
SiO_2(1)	480	250-500	0.75
SiO_2(2)	480	35-75	0.75
SiO_2(3)	300	250-500	1.15

5.2.2 Oxidation of CAF by Fe(VI) in the Presence of SiO_2 gel

All experiments were conducted in a 600-mL beaker under dark conditions. The solutions were rapidly mixed using a magnetic stirrer at room temperature (24 ± 1 °C). A 250 mL CAF solution was prepared in Milli-Q water. Initially, the desired amount of SiO_2 gel was added to the 250-mL solution. The solution was mixed for 1 h before a 20-mL sample was withdrawn to analyze CAF in the mixed solution. These measurements were performed to ensure that any CAF adsorbed on the solid surfaces of SiO_2 gel is considered. The reaction was initiated by adding a certain volume of the fresh, centrifuged, and standardized Fe(VI) solution in water to the CAF-SiO_2 mixed solution. The pH stabilized within 2 minutes, defined as the initial pH. When the characteristic purple color of Fe(VI) fully disappeared, the time was defined as time of the decay of Fe(VI). The generated Fe(III) particulate was removed by filtration (i.e. classified as filtration time). This filtration time was longer than time of decay of Fe(VI), ensuring completion of the reaction. The reported pH was the final pH. The filtered samples were subjected to analysis of CAF.

In order to assess any possible removal of CAF due to Fe(III) particulate, separate experiments were performed. In this set of experiments, Fe(VI) in solution without CAF was first allowed to decompose to Fe(III) in the presence of SiO_2 gel. Then, the CAF solution was added. After filtration of Fe(III)-SiO_2, the concentration of CAF in filtered reaction solution was determined. Significantly, no removal of CAF was observed due to Fe(III)-SiO_2 system.

Experiments were also performed under anaerobic conditions to explore the role of the dissolved oxygen present initially in the reaction solution. A 100 mL CAF solution was transferred to a gas-tight Pyrex-glass reactor and nitrogen gas was purged to create anaerobic conditions. The CAF solution was purged by nitrogen gas for 60 min in the presence of SiO_2 gel to ensure anoxic conditions in the CAF-SiO_2 mixed solution. Then, the Fe(VI) solution was added and the mixture was allowed to react under continuous N_2 sparging.

To investigate the influence of ions and NOM usually present in natural waters and wastewaters on the oxidative transformation of CAF by Fe(VI) in the presence of SiO_2 gel, inorganic anions (Cl^-, HCO_3^- and SO_4^{2-}), cations (Na^+, Mg^{2+} and Ca^{2+}) and NOM (5-30 mg/L) were individually mixed with the CAF-SiO_2 solution prior to the addition of Fe(VI).

5.2.3 Analytical Methods

An Agilent Technologies (1200 series) high-performance liquid chromatography (HPLC), equipped with a ZORBAX Eclipse XDB-C18 column (4.6 × 150 mm, particle size 5 μm) and a diode array detector (set up at 272 nm) were used for quantifying CAF. The column temperature was set at 25 °C. A mixture of methanol and Milli-Q water (70:30 v/v) was used as a mobile phase at a flow rate of 0.800 mL/min. The injection volume was 20 µL. UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu Scientific Instruments, Columbia, MD, USA) was also used to quantify CAF (peak absorbance at 272 nm) and Fe(VI) in Milli-Q water. A TOC analyzer (ASI-V_{CPN} Shimadzu), equipped with an ASI-V auto-sampler (Shimadzu), was used to measure dissolved organic carbon (DOC). The pH of the reaction solution was measured throughout the experiments using a Metrohm 780 pH Meter.

All MS data were obtained using a Q-Exactive Quadrupole Orbitrap mass spectrometer (Thermo Fisher Scientific), coupled to an Agilent 1290 high-performance liquid chromatography (HPLC) system with a Zorbax Eclipse Plus RRHD C18 column (2.1 × 50 mm, 1.8 µm; Agilent) maintained at 35 °C. The mobile phase was comprised of water with 0.1% formic acid (A), and acetonitrile with 0.1% formic acid (B) (Optima grade, Fisher Scientific, Lawn, NJ, USA). The gradient begins with 100% A for 30 seconds before increasing B to 100% over 3 minutes. B was held at 100% for 2 minutes prior to returning to 0% over 30 s. Injection volume was 2 µL. The flow rate was 0.3 mL/min. The following conditions were used for positive HESI: capillary voltage, 4.0 kV; capillary temperature, 400 °C; sheath gas, 17.00 units; auxiliary gas, 8.00 units; probe heater temperature, 450 °C; S-Lens RF level, 45.00. A top-5 data dependent acquisition (DDA) method involved a full MS scan at 35,000 resolution over a 50-500 *m/*z; automatic gain control (AGC) target and maximum injection time (max IT) was 3e6 and 120 ms respectively. The five highest intensity ions from the full scan were sequentially selected using a 1.2 *m/z* isolation window and analyzed at resolution of 17,500; AGC target, 1e5; max IT, 60 ms; normalized collision energy (NCE) 25; threshold intensity 1.0e5; and dynamic exclusion of 8 s. Full MS spectra were screened for OPs with the Xcalibur software.

5.2.4 Calculation of Frontier Electron Densities (FEDs) of CAF Molecule

In this study, Gaussian 09 software package (Gaussian, Inc.) was applied to optimize the chemical structure of CAF molecule (see Table 5.2). The related calculations were performed using the hybrid density functional theory (DFT)/B3LYP/6-311G** method. Importantly, the effect of solvent (i.e., water) was considered in performing these calculations. Subsequently, orbital calculations were conducted using the keyword of "pop=reg". Generally, the electrophilic reaction prefers to take place at the atoms with higher values of the highest occupied molecular orbital (HOMO) [54,55]. Therefore, values of $2FED^2_{HOMO}$ were calculated to estimate the initial attack site of CAF by Fe(VI) for electron extraction.

Table 5.2: Frontier electron densities on the atoms of CAF molecule calculated by Gaussian 09 program at the B3LYP/6-311G level.**

Atom (number)	$2FED^2_{HOMO}$	Atom (number)	$2FED^2_{HOMO}$
C (1)	0.5545	O (11)	0.9982
N (2)	1.1493	O (12)	0.9820
C (3)	3.1748	C (13)	0.2918
C (4)	***4.4336***	N (17)	0.6438
C (5)	0.3075	N (18)	0.3016
N (6)	0.8631	C (19)	0.2408
C (7)	0.1764	C (20)	0.0261

5.3 Results and Discussion

5.3.1 Effect of Concentration of SiO_2 gel

In the initial set of experiments, Fe(VI) and CAF in Milli-Q water in the presence and absence of SiO_2 gel were mixed at a Fe(VI) to CAF molar ratio of 2.0. The details of the experimental conditions are given in Table S5.1 of Appendix C. The oxidative transformation of CAF increased from 29.9% to 44.5% by increasing the concentration of SiO_2 gel from 0 to 8 g/L (Figure 5.1). The control experiments suggest that Fe(III) (produced from Fe(VI) in the presence of SiO_2 gel) and SiO_2 gel alone had no role in the observed oxidation of CAF (Table S5.2 of Appendix C).

A second set of experiments was conducted at a higher Fe(VI) to CAF molar ratio of 6.0 in order to further enhance the oxidative transformation of CAF (see details in Table S5.1 of Appendix C). The oxidative transformation of CAF increased significantly from 53.0% to 90.3% when 1 g/L SiO_2 gel was added to mixed solution of Fe(VI) and CAF (Figure 5.1). Importantly, the time taken for the disappearance of the color of Fe(VI) (time (Fe(VI) decay)) has decreased from 4 h to 70 min, in the absence and in the presence of 1 g SiO_2/L, respectively (Table S5.1 of Appendix C). Further increase of the concentration of SiO_2 gel to 4 g/L, at the same Fe(VI) to CAF molar ratio of 6.0, resulted in complete removal of CAF (Figure 5.1). Higher concentrations of SiO_2 gel (up to 8 g/L) also resulted in complete removal of CAF (Figure 5.1). Further details related to the experimental conditions are given in Table S5.1 of Appendix C. Comparatively, only 53.0% CAF removal was achieved when no SiO_2 was present in the Fe(VI)-CAF mixed solution, at the same molar ratio of Fe(VI) to CAF (6.0) and similar pH conditions (Figure 5.1). Overall, the results clearly show a significant enhancement of the oxidative transformation of CAF by Fe(VI) in the presence of simple SiO_2 gel (Figure 5.1). Additions of 1 g/L of Ru/CeO_2 and Ru/TiO_2 also exhibited catalytic effects on the oxidation of emerging organic pollutants by permanganate [56,57]. The results of Figure 5.1 are in agreement with the oxidation of emerging contaminants by ozone in the presence of 1-5 g/L of iron-based catalysts [58].

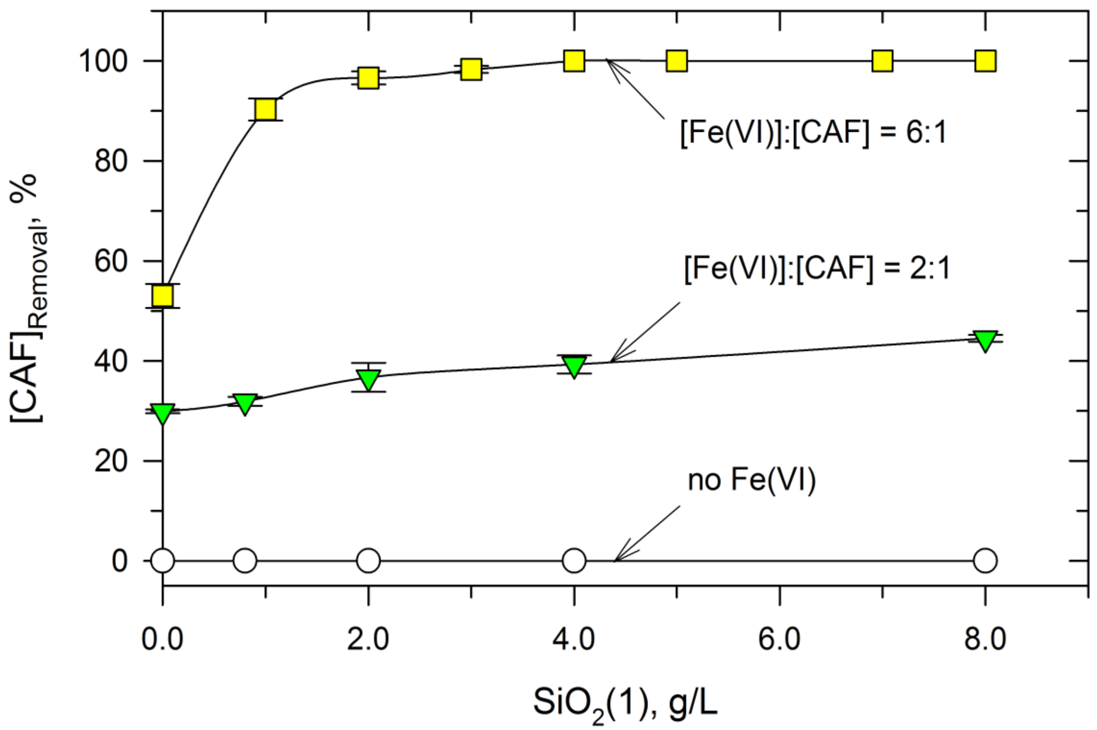

Figure 5.1: Effect of SiO_2 gel concentration on the oxidation of CAF by Fe(VI) at different molar ratios of Fe(VI) to CAF. (Experimental conditions for [Fe(VI)]:[CAF]=2:1: [Fe(VI)]=45.5-162.4 µM; [CAF]=23.0-80.0 µM; initial pH=7.7-8.3; final pH=7.3-7.7; and [Fe(VI)]:[CAF]=6:1: [Fe(VI)]=513.4-535.4 µM; [CAF]=85.6-89.1 µM; initial pH=8.2-9.3; final pH=7.9-8.0).

Figure 5.1 suggests that the transformation of CAF by Fe(VI) in the presence of SiO_2 gel mainly depends on the molar ratio of Fe(VI) to CAF. A third set of experiments was conducted at different Fe(VI) to CAF molar ratios (ranged from 2.0-8.0) in the presence and absence of 8 g SiO_2/L (details are in Table S5.3 of Appendix C). The oxidative transformation of CAF increased significantly from 44.5% to 83.2% and 94.3% by increasing the Fe(VI) to CAF molar ratio from 2.0 to 3.9 and 5.0, in the presence of 8 g SiO_2/L, respectively (Figure 5.2). Complete removal of CAF was achieved at a molar ratio of Fe(VI) to CAF of 6.0 or higher in the presence of SiO_2 gel (see Figures 5.1 and 5.2).

Interestingly, only 29.9%, 41.5%, 53.0%, and 60.9% removal of CAF was seen in the absence of SiO_2 gel at Fe(VI) to CAF molar ratios of 2.0, 3.9, 6.0, and 8.0 respectively (Figure 5.2). The results in Figures 5.1 and 5.2 show that a molar ratio of Fe(VI) to CAF of 6.0 and a concentration of SiO_2 gel of 4 g/L are the optimum conditions for complete removal of CAF, and therefore these conditions were applied to assess the effect of ions later in this study. Results show clearly that SiO_2 gel catalyse the Fe(VI)-CAF reaction resulting in a significant enhancement of up to ~50% of transformation of CAF under these optimum conditions.

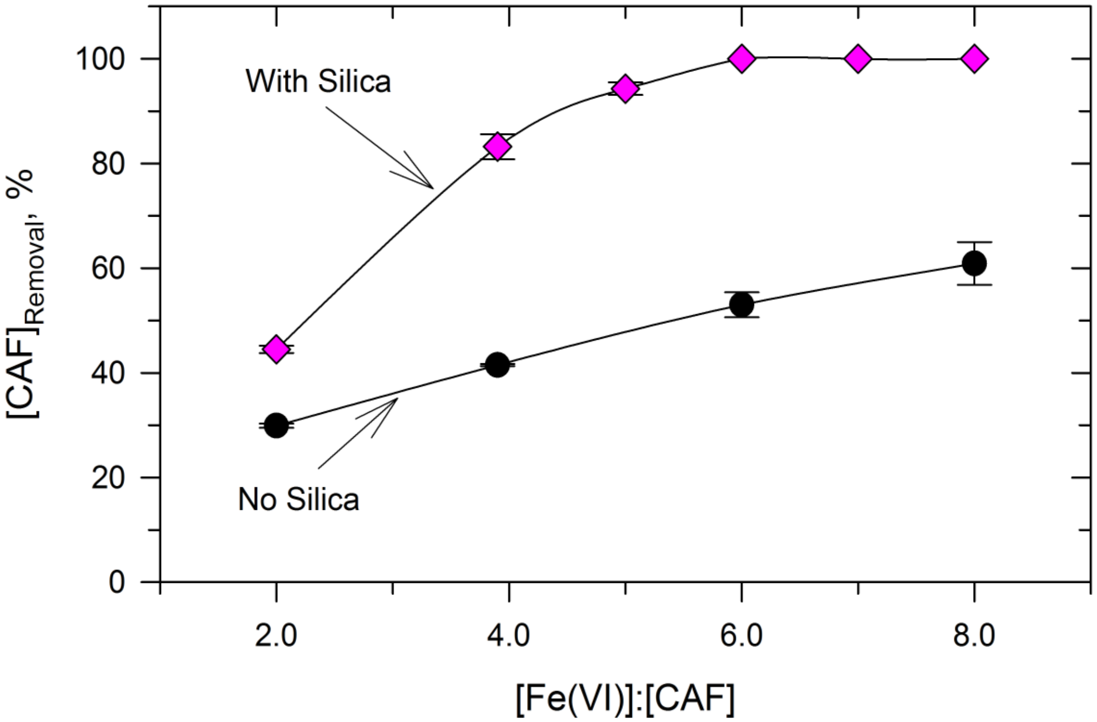

Figure 5.2: Effect of Fe(VI) to CAF molar ratio on the oxidation of CAF by Fe(VI) in the presence and absence of SiO_2 gel. (Experimental conditions in the presence of SiO_2 gel: [Fe(VI)]=146.8-662.5 µM; [CAF]=73.8-90.1 µM; [SiO_2(l)]=8 g/L; initial pH=7.7-8.4; final pH=7.5-8.0 and in the absence of SiO_2 gel: [Fe(VI)]=45.5-634.5 µM; [CAF]=23.0-89.1 µM; initial pH=8.0-9.6; final pH=7.3-8.0).

5.3.2 Effect of Particle Size and Pore Volume of SiO_2 gel

Considering the catalytic effect of SiO_2 gel on the oxidation of CAF by Fe(VI), further experiments were carried out to evaluate the effect of different properties i.e. particle size and pore volume of SiO_2 gel. Details of the experimental conditions are given in Tables S5.4 and S5.5 of Appendix C. Initially, $SiO_2(2)$ of smaller particle size of 35-75 µm than $SiO_2(1)$ (250-500 µm) was used at Fe(VI) to CAF molar ratios of 2.0 and 3.9 (Figure 5.3a and Table 5.1). No effect of the SiO_2 particle size on the CAF oxidation by Fe(VI) was observed (Figure 5.3a). Similar oxidative transformation of CAF by Fe(VI) in the presence of different particle size SiO_2 gel was observed at both Fe(VI) to CAF molar ratios of 2.0 and 3.9 (Figure 5.3a).

The effect of pore volume of SiO_2 gel on the oxidation of CAF by Fe(VI) was also investigated by using a $SiO_2(3)$ of higher pore volume than $SiO_2(1)$ of 1.15 cm^3/g and 0.75 cm^3/g respectively (Figure 5.3b and Table 5.1). The oxidative transformation of CAF decreased very slightly from 100% in the presence of 4 g $SiO_2(1)$/L to 96.9% in the presence of 4 g $SiO_2(3)$/L, at the same Fe(VI) to CAF molar ratio of 6.0 (Figure 5.3b). Higher concentrations of 5 g/L and 6 g/L of $SiO_2(3)$, which has lower surface area than $SiO_2(1)$, resulted in complete removal of CAF by Fe(VI) (Figure 5.3b and Table 5.1). The initial pH (8.3-8.4) and final pH (8.0) were similar in all experiments (Figure 5.3b, and Table S5.5 of Appendix C). Overall, the effect of pore volume of SiO_2 gel on the oxidation of CAF by Fe(VI) was essentially negligible at the studied Fe(VI) to CAF molar ratios and the SiO_2 gel concentrations. This is consistent with the results presented in Figures 5.1 and 5.2.

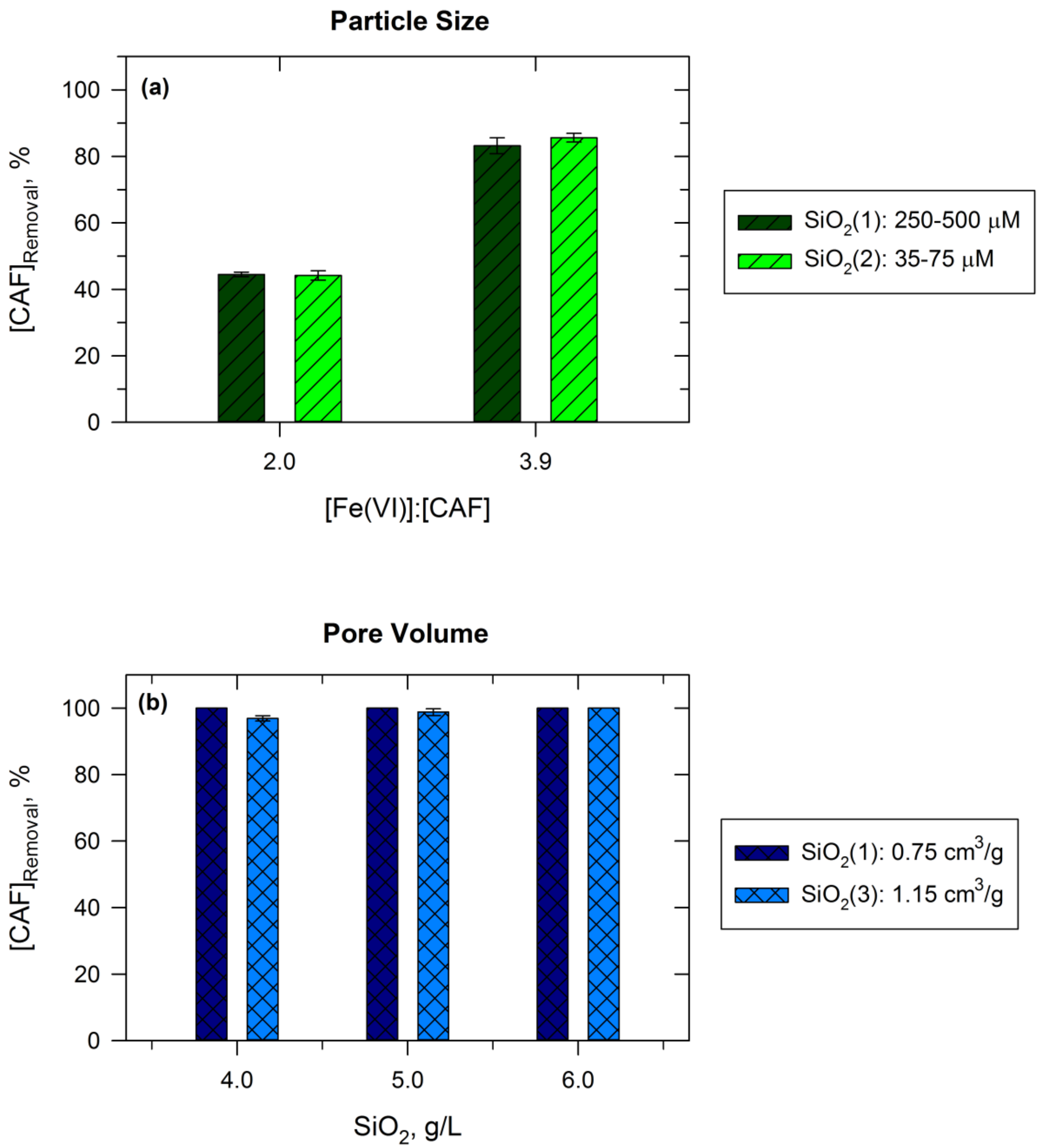

Figure 5.3: Oxidation of CAF by Fe(VI) in the presence of SiO_2 gel. (a) Effect of particle size of SiO_2 gel. (Experimental conditions: [Fe(VI)]=146.8-344.5 μM; [CAF]=73.9-87.8 μM; [SiO_2]=8 g/L; initial pH=7.7-8.1; final pH=7.5-7.8) and (b) Effect of pore volume of SiO_2 gel (Experimental conditions: [Fe(VI)]:[CAF]=6.0; [Fe(VI)]=513.4-532.1 μM; [CAF]=85.6-89.0 μM; initial pH=8.3-8.4; final pH=8.0). See Table 5.1 for SiO_2 gels characteristics.

Several reactions may be occurring during the oxidation of a pollutant by Fe(VI), which include (i) 1-e$^-$/2-e$^-$ transfer to form Fe^{V}/Fe^{IV} and ultimately Fe^{III}/Fe^{II} as final products (e.g. Fe^{VI} → Fe^{V} → Fe^{III} and Fe^{VI} → Fe^{IV} → Fe^{II}), (ii) further reaction of Fe^{V}/Fe^{IV} with the pollutant, (iii) Fe^{VI}, Fe^{V} and Fe^{IV} self-decompositions, and (iv) reactions between iron species Fe^{II}/Fe^{III}/Fe^{IV}/Fe^{V}/Fe^{VI} and/or oxygen species (i.e. H_2O_2) formed from self-decompositions (e.g. Fe^{VI} + Fe^{II} → Fe^{V} + Fe^{III} and Fe^{II}/Fe^{III} + O_2/H_2O_2 → Fe^{IV}/Fe^{V}) [38].

In order to assess the effect of oxygen related species on the enhanced oxidative transformation of CAF, experiments under nitrogen-purging conditions were carried out. Complete removal of CAF was also seen under nitrogen-purging conditions (deoxygenated environment). This indicates that the dissolved oxygen, present initially in the reaction solution, played no role in the enhancement of CAF removal by Fe(VI) in the presence of SiO_2 gel (Table S5.6 of Appendix C). Considering the lack of dissolved oxygen, the oxidation of Fe^{II}/Fe^{III} species, if any, may occur by high-valent iron species (Fe^{VI} and Fe^{V}) instead of oxygen-related species (see reaction (iv)), resulting in less exposure of Fe(VI). Interestingly, it was recently reported that dissolved silicate retarded the oxidation of Fe(II) to Fe(III) [59]. A possible retarded oxidation of Fe^{II}/Fe^{III} by Fe^{VI}/Fe^{V} in the presence of SiO_2 gel would result in higher Fe(VI) exposure (higher Fe(VI) concentration available to react with CAF) than in the absence of SiO_2 gel. Hence, enhanced oxidative transformation of CAF by Fe(VI) in the presence of SiO_2 gel could be observed.

The catalytic effect of SiO_2 gel is possible when one of the reactants or both reactants (Fe(VI) and CAF) are adsorbed on the surface of the catalyst [60]. Our experimental studies showed no adsorption of CAF on the SiO_2 gel surface (see Figure 5.1, and Table S5.2 of Appendix C). Thus, Fe(VI) is the reactant that is most probably adsorbed on the surface of SiO_2 gel. Interaction of Fe and Si would change the surface redox processes enhancing the oxidation of CAF [61]. It was reported that the interaction of Fe with Si favored the generation of strong oxidants including Fe(IV), during the activation of H_2O_2 by silica-supported iron oxide [61]. Our control experiments showed no removal of CAF due to Fe(III)-SiO_2 system (Table S5.2 of Appendix C). Hence, a possible interaction of high-valent iron species (Fe(VI)/Fe(V)) with Si caused the increase in the transformation of CAF. Moreover, adsorption of Fe(VI) on SiO_2 gel surface seems to diminish the self-decomposition of Fe(VI) (reaction (iii)), thus increasing the oxidant concentration available to react with CAF (increased oxidative capacity of Fe(VI) i.e., more electron-equivalents are available per mole of Fe(VI)).

Silica gel is one of the solid acids that have been used as catalysts in numerous reactions because of their higher reactivity and easier recovery than Lewis acids [47]. Interestingly, Fe(VI) could be activated by Lewis acids to enhance the oxidation of organic compounds in organic solvents [62]. It is possible that all the aforementioned mechanisms contribute to the enhanced oxidative transformation of CAF in the presence of SiO_2 gel. The role of SiO_2 gel needs to be further examined in future studies to better comprehend the mechanisms of the enhancement of the oxidation of CAF by the Fe(VI)-SiO_2 system.

5.3.3 Effect of Ions and NOM

The effect of individual anions (Cl^-, HCO_3^- and SO_4^{2-}) and cations (Na^+, Mg^{2+} and Ca^{2+}), usually present in wastewater, on the oxidation of CAF by Fe(VI) in the presence of SiO_2 gel was investigated. The optimum conditions of molar ratio of Fe(VI) to CAF as 6.0 and 4 g SiO_2/L were applied. Under these conditions, complete removal of CAF was observed without the ions present in solution (Table S5.7 of Appendix C). The concentrations of ions were chosen to be relevant to the concentrations normally encountered in wastewater [63–65]. Results presented in Figure 5.4 showed almost no effect of ions on the removal of CAF by Fe(VI)-SiO_2 system. Complete removal of CAF by Fe(VI) in the presence of SiO_2 gel was observed in both the presence and absence of Cl^-, SO_4^{2-}, Na^+, Mg^{2+}, and Ca^{2+} (Figure 5.4). The CAF removal efficiency slightly decreased from 100.0% to 92.4% in the presence of HCO_3^- (Figure 5.4). However, the negative effect of bicarbonate ions is negligible (less than 10.0% CAF removal efficiency). Overall, the oxidation of CAF in the presence of SiO_2 gel, is not significantly affected by the studied anions and cations. Furthermore, minimal pH changes were observed with the initial pHs ranging from 8.0 to 8.4 and final pH varying from 7.8 to 8.3.

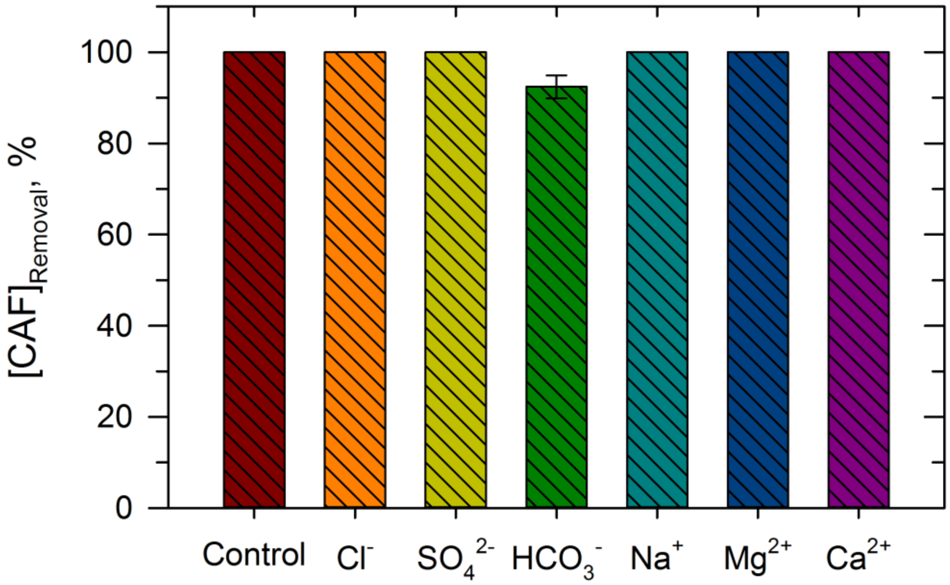

Figure 5.4: Effect of bicarbonate (HCO_3^-; $NaHCO_3$), chloride (Cl^-; $CaCl_2$), sodium (Na^+; Na_2SO_4), sulfate (SO_4^{2-}; Na_2SO_4), magnesium (Mg^{2+}; $MgCl_2•6H_2O$) and calcium (Ca^{2+}; $CaCl_2$), on CAF oxidation by Fe(VI) in the presence of SiO_2 gel (Experimental conditions: [Fe(VI)]:[CAF]=6.0; [Fe(VI)]=513.2-530.2 µM; [CAF]=85.7-88.2 µM; [SiO_2(1)]=4 g/L; [HCO_3^-]=[Mg^{2+}]=1 mM; [Ca^{2+}]=[SO_4^{2-}]=2 mM; [Cl^-]=[Na^+]=4 mM; initial pH=8.0-8.4; final pH=7.8-8.3).

The effect of NOM on the oxidation of CAF by Fe(VI) in the presence of SiO_2 gel was also investigated at a Fe(VI) to CAF molar ratio of 6.0 (Table S5.8 of Appendix C). The studied concentrations of NOM were 5, 15 and 30 mg/L, simulating a range of wastewaters. The oxidative transformation of CAF by Fe(VI) in the presence of 4 g SiO_2/L decreased from 100% to 88.1%, 68.0%, and 36.4% in the presence of 5, 15 and 30 mg NOM/L respectively (Figure 5.5). This was expected as Fe(VI) would react with other organic moieties present in NOM. Interestingly, the oxidative transformation of CAF by Fe(VI) in the presence of 30 mg NOM/L, increased from 36.4% (4 g SiO_2/L) to 46.4% and 67.7% in the presence of higher concentration of SiO_2 gel of 8 g/L and 16 g/L respectively (Figure 5.5). Similarly, the removal of CAF by Fe(VI) in the presence of 15 mg NOM/L, increased from 68.0% (4 g SiO_2/L) to 74.3% and 84.4% in the presence of 8 g SiO_2/L and 16 g SiO_2/L respectively (Figure 5.5). Importantly, the effect of NOM at a concentration of 5 mg/L almost disappeared when 8 g SiO_2/L (96.5% CAF removal) instead of 4 g SiO_2/L (88.1% CAF removal) were used (Figure 5.5). No DOC removal has been observed in the Fe(VI)-CAF-SiO_2-NOM system. Initial (8.0-8.4) and final pH (7.6-8.1) of the reaction solution were similar in all experiments (Table S5.8 of Appendix C). The results show that organic components of NOM decreased the removal of CAF by Fe(VI) in the presence of SiO_2 gel and higher CAF removal could be achieved by increasing the concentration of SiO_2 gel at the same Fe(VI) dose (i.e., same Fe(VI) to CAF molar ratio).

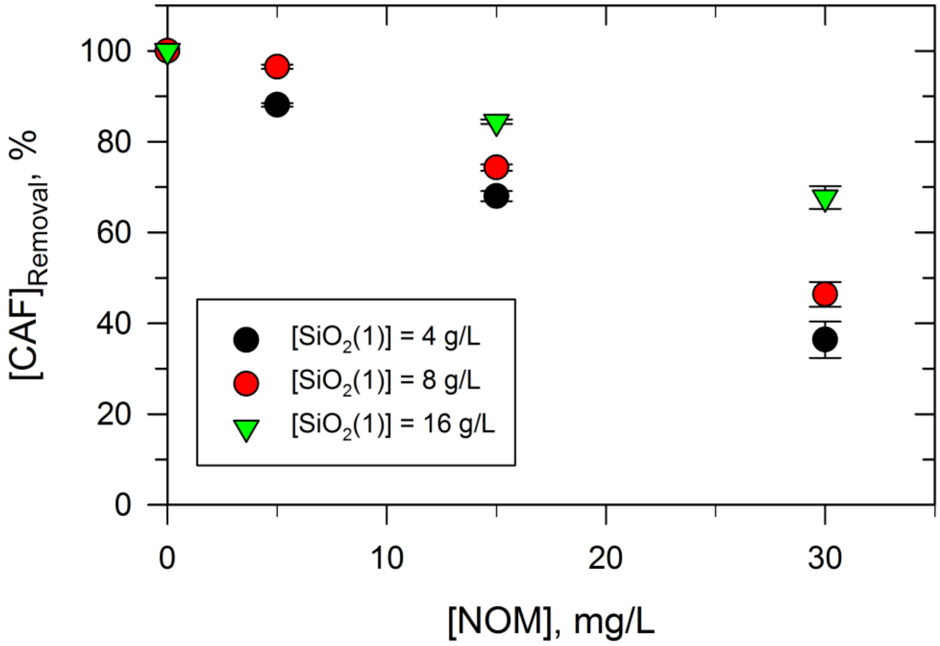

Figure 5.5: Effect of Suwannee River natural organic matter (NOM) on the oxidation of CAF by Fe(VI) in the presence of SiO_2 gel (Experimental conditions: [Fe(VI)]:[CAF]=6.0; [Fe(VI)]=503.6-559.6 µM; [CAF]=83.7-93.4 µM; initial pH=8.0-8.4; final pH=7.6-8.1); $DOC_{(mg\ C/L)}$=0.80 $NOM_{(mg\ NOM/L)}$).

5.3.4 Oxidized Products of CAF

5.3.4.1 Identification

The oxidation of CAF by Fe(VI) in the presence and absence of SiO_2 gel was first investigated by DOC measurement. The results showed no mineralization of CAF (no DOC removal) at the studied Fe(VI) to CAF molar ratios even when complete removal of CAF was achieved. Analysis of the oxidized products (OPs) showed the degradation of CAF to organic compounds. Three persistent OPs were identified as N,N'-Dimethyloxamide (OP1), N-Methylurea (OP2), and N,N'-Dimethylurea (OP3). The same OPs were also identified in the absence of SiO_2 (i.e., Fe(VI) only). The fragments of OPs, measured by LC-HRMS, are presented in Figure S5.2 of Appendix C. The protonated molecular ion $[M+H]^+$ was chosen as the parent ion. Accurate mass measurements of the three OPs allowed us to propose their molecular formulae (Table S5.9 of Appendix C). The molecular structures of OP1, OP2, and OP3 (protonated form at m/z 117.0664, 75.0562 and 89.0717 respectively) were supported by the product ion at m/z 58.0298 that corresponds to losses of fragments as C_2H_5NO, NH_3 and CH_5N for OP1, OP2 and OP3, respectively (Figure S5.2 and Table S5.9 of Appendix C). The formulae ($[M+H]^+$) that best match the experimental masses are $C_4H_9N_2O_2$, $C_2H_7N_2O$, and $C_3H_9N_2O$, with errors of 4.67 ppm, 12.40 ppm and 8.65 ppm for OP1, OP2 and OP3 respectively (Table S5.9 of Appendix C). The structures of OP1, OP2 and OP3 were also confirmed by their standard samples. The reduction of DBE (double bond equivalent) from 6 (CAF) to 2, 1, and 1 for OP1, OP2, and OP3, respectively, also supports the proposed structures (Table S5.9 of Appendix C). OP1, OP2 and OP3 have been identified as products of the degradation of CAF by hypochlorite [66]. OP1 was also reported as a product of the reaction of CAF with ozone [67].

5.3.4.2 Proposed Reaction Pathway

Based on the identified OP1, OP2 and OP3, the proposed pathway is given in Figure 5.6. An initial attack of Fe(VI) on $C_4=C_5$ double bond of CAF results in C1 (nine-membered ring structure). The generation of this intermediate was confirmed by the high $2FED^2_{HOMO}$ value (4.4336) of C_4 (Table 5.2) and high electron-cloud density of $C_4=C_5$ double bond

(Figure S5.3 of Appendix C), which makes the olefinic group as the electron-rich moiety. Theoretically, the value of HOMO describes the electron donating ability of the atoms in the molecule (e.g., CAF). The atoms or groups with higher HOMO values have higher electron clouds, which make them as the good electron donors, thus facilitating the electrophilic reactions by Fe(VI). This finding agreed well with the reported reactions of Fe(VI) with organic contaminants via electrophilic oxidation mechanism [38]. The intermediacy of C1 has also been suggested for the degradation of CAF by ozone [67], advanced oxidation (UV/TiO_2, UV/H_2O_2 and Fenton) [68], and hypochlorite [66]. Degradation of C1 could lead to the formation of C2 (similar to the degradation of CAF by hypochlorite) (see Figure 5.6) [66]. This has been also reported for ozonation of CAF [67]. Finally, hydrolysis A, B, and C of C2 result in the formation of OP1, OP2, and OP3, respectively [66]. Overall, the proposed reaction pathway for the oxidation of CAF by Fe(VI) and Fe(VI)-SiO_2, is in agreement with the identified OPs.

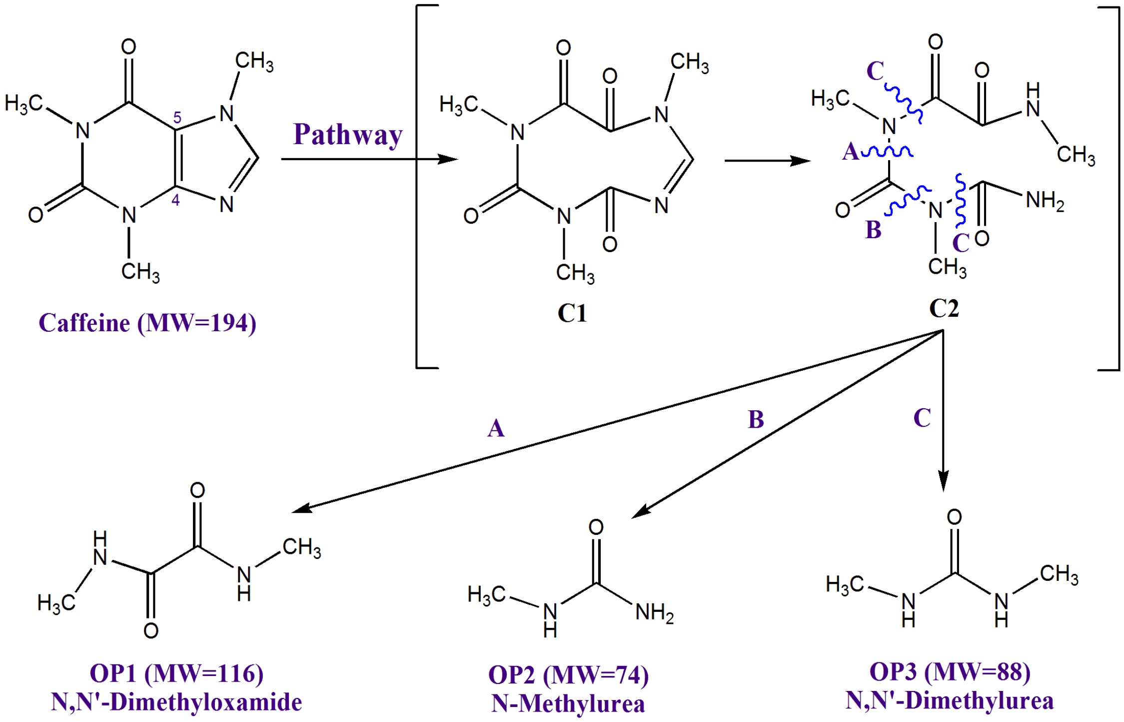

Figure 5.6: Proposed degradation pathway of CAF by Fe(VI) in the presence and absence of SiO_2 gel. (Experimental conditions in the presence of SiO_2 gel: [Fe(VI)]=513.4 µM; [CAF]=85.6 µM; [SiO_2]=4 g/L; initial pH=8.3; final pH=8.0 and in the absence of SiO_2 gel: [Fe(VI)]=535.4 µM; [CAF]=89.1 µM; initial pH=9.3; final pH=8.0).

5.4 Summary and Conclusions

A remarkable enhancement (up to ~50%) of the oxidative transformation of CAF by Fe(VI) in the presence of SiO_2 gel, in aqueous solution at slightly basic pH conditions (pH range of 8.0-9.0), was achieved for the first time. The specific results are:

- Complete removal of CAF was accomplished at a Fe(VI) to CAF molar ratio of 6.0 in the presence of 4 g SiO_2/L, compared to only 53.0% CAF removal seen in the absence of SiO_2 gel.

- No significant effect of the SiO_2 gel particle size and pore volume/surface area, and ions (Cl^-, HCO_3^-, SO_4^{2-}, Na^+, Mg^{2+}, and Ca^{2+}) on the oxidation of CAF by Fe(VI) in the presence of 4 g SiO_2/L, at a Fe(VI) to CAF molar ratio of 6.0, was observed.

- The removal of CAF by Fe(VI)-SiO_2 ([Fe(VI)]/[CAF]=6.0; 4 g SiO_2/L) decreased from 100% to 88.1%, 68.0%, and 36.4% in the presence of 5, 15 and 30 mg NOM/L respectively. Interestingly, the oxidative transformation of CAF by Fe(VI) in the presence of 30 mg NOM/L, increased from 36.4% (4 g SiO_2/L) to 46.4% and 67.7% in the presence of higher concentration of SiO_2 gel of 8 g/L and 16 g/L respectively. Importantly, the effect of NOM at a concentration of 5 mg/L almost disappeared when 8 g SiO_2/L (96.5% CAF removal) instead of 4 g SiO_2/L (88.1% CAF removal) were used.

- A total of three OPs i.e. N,N’-Dimethyloxamide, N-Methylurea, and N,N’-Dimethylurea of CAF by Fe(VI) in the presence and absence of SiO_2 gel were identified. Oxidation of CAF involved a reaction pathway initiated by an attack of Fe(VI) on the C_4=C_5 double bond of CAF, which is supported by FED calculations.

The findings of this study may initiate the investigation of the effect of different solid materials on the oxidation of a range of pollutants by ferrate(VI).

5.5 References

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Chapter 6

6 Conclusions and Recommendations

6.1 Major Conclusions

This PhD thesis reported the unexpected enhancement of the transformation of the studied organic contaminants (caffeine, acesulfame K and atenolol) by ~30%, at slightly basic pH conditions, by activating the Fe(VI) in aqueous solution with an addition of a small amount of simple acid (e.g. HCl). Transient species, Fe^V and Fe^{IV} which increased oxidation capacity of Fe(VI), are most probably responsible for the observed enhancement. Importantly, activated Fe(VI) reduced required dosages and reaction times for transformation.

A molar ratio of Fe(VI) to caffeine of 25.0 was required for the complete removal of caffeine (CAF) by Fe(VI) (non-activated Fe(VI)) compared to molar ratio of 8.0 by acid-activated Fe(VI). The oxidative transformation of CAF by acid-activated Fe(VI) slightly decreased by Ca^{2+} ions from 48.3% to 43.7%, at Fe(VI) to CAF molar ratio of 2.0. This effect of Ca^{2+} ions could be overcome by increasing the molar ratio of Fe(VI) to CAF from 2.0 to 3.9. On the other hand, Fe(VI) (without activation) reaction was negatively affected by divalent cations (Ca^{2+} and Mg^{2+}) and sulfate at similar molar ratio of Fe(VI) to CAF of 2.0. The CAF removal decreased from 28.8% to 24.5%, 20.7%, and 17.0%, in the presence of SO_4^{2-}, Mg^{2+}, and Ca^{2+} ions respectively. NOM and secondary effluent wastewater (SE) significantly influenced the oxidation of CAF by both Fe(VI) and acid-activated Fe(VI) and less caffeine removal was observed. However, the acid-activated Fe(VI) was able to mineralize other organics present in NOM and SE, as indicated by the dissolved organic carbon removal, confirming higher oxidative capacity upon acid activation, compared to Fe(VI) where no mineralization was observed.

Furthermore, SiO_2 gel significantly enhances the oxidation of caffeine by ferrate(VI). Complete removal of caffeine was accomplished at a Fe(VI) to caffeine molar ratio of 6.0 in the presence of 4 g SiO_2/L, at mild alkaline conditions. Importantly, inorganic ions (Cl^-, HCO_3^-, SO_4^{2-}, Na^+, Mg^{2+}, and Ca^{2+}) do not affect the oxidation of caffeine by silica gel-enhanced ferrate(VI) oxidation process. NOM decreases ferrate(VI) removal efficiency of CAF which could be overcome by increasing the concentration of SiO_2 gel at the same molar ratio of Fe(VI) to CAF.

The oxidized products of caffeine by Fe(VI), acid-activated Fe(VI) and silica gel-enhanced Fe(VI) were identified using liquid chromatography high resolution mass spectrometry. A total of three oxidized products of CAF by Fe(VI) were identified in the presence and absence of SiO_2 gel i.e. N,N'-Dimethyloxamide (OP1), N-Methylurea (OP2), and N,N'-Dimethylurea (OP3). An additional oxidized product was identified in the case of acid-activated Fe(VI) i.e. 6-amino-5-(N-formylmethylamino)-1,3-dimethyluracil (OP4). The reaction pathways of oxidation of CAF by Fe(VI), acid-activated Fe(VI) and silica gel-enhanced Fe(VI) were proposed. It is postulated that Fe(VI) attacks the C=C double bond of caffeine to form OP1, OP2 and OP3. Theoretical calculations support the initial reaction step of oxidation of caffeine. In the case of activated Fe(VI), OP4 could be formed via an additional reaction pathway that was individually initiated by the addition of hydroxyl to the C_8 position of caffeine.

6.2 Scientific Contribution

- The results presented in the thesis are the first report on the activation of the simple high-valent oxo species (ferrate) by acids in aqueous solution. Thus this study advances the chemistry of ferrate (or high-valent iron species) in aquatic systems.

- The first-time demonstration of significant enhancement of the oxidation of a recalcitrant organic pollutant (caffeine) by ferrate(VI) in the presence of silica gel under water treatment pH conditions.

- It was shown that the silica gel-enhanced ferrate(VI) oxidation process is not significantly affected by anions (Cl^-, HCO_3^-, and SO_4^{2-}) and cations (Na^+, Mg^{2+}, and Ca^{2+}) usually present in wastewater and surface waters. The HCl-activated ferrate(VI) oxidation process was only negatively affected by Ca^{2+} ions (no negative effect has been observed in the presence of Cl^-, HCO_3^-, SO_4^{2-}, Na^+, and Mg^{2+}).

- The identification of the oxidized products of caffeine and proposed reaction pathways of the oxidation of caffeine by Fe(VI), acid-activated Fe(VI) and silica gel-enhanced Fe(VI) were reported for the first time.

6.3 Study Limitations

Acid-activated and silica gel-enhanced Fe(VI) yielded increased oxidative transformation of organic contaminants. However, the nature of these reactions highlights the following limitations:

- The Fe(VI) reaction with organics is much faster in acidic conditions than basic conditions due to protonation of Fe(VI). In addition, Fe(VI) is much less stable in acidic environments than at basic (the self-decay of Fe(VI) is enhanced by low pH). It is not possible to differentiate between effect of the pH (protonated Fe(VI) species) and activation of Fe(VI), at neutral and acidic conditions. Thus, the acid-activation of Fe(VI) cannot be demonstrated at low pH conditions. However, the novelty and significance of the findings stem directly from the acid activation of Fe(VI) at slightly basic pH conditions which resulted in increased oxidation capacity.

- The enhanced oxidative transformation of organic contaminants by acid-activated and silica gel-enhanced Fe(VI) can be only demonstrated using model compounds that have sluggish reactivity with Fe(VI) alone.

- The employment of any solid material to enhance the oxidation of pollutants by Fe(VI) would preferably be demonstrated for pollutants that cannot be removed from water by the solid material alone.

- Acid-activated Fe(VI) oxidation reactions are very fast occurring within seconds, thus kinetic studies could not be performed using this experimental setup.

6.4 Recommendations

The findings of this PhD thesis have wider implications in purifying water from pollutants and in organic synthesis. The following recommendations for future work are made:

- The role of reactive Fe(V)/Fe(IV) needs to be examined in future studies to comprehend the mechanism of this extraordinary activation of Fe(VI) by the H^+ ions.

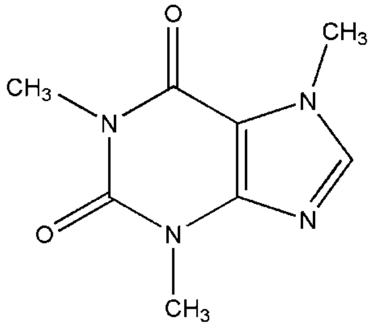
- Similarly, the role of SiO_2 gel also needs to be further examined to better understand the mechanisms of the enhancement of the oxidation of caffeine by the Fe(VI)-SiO_2 system.

- Different activation methods and the effect of different solid materials on the oxidation of a range of organic and inorganic pollutants particularly those present in secondary effluent wastewater by ferrate(VI) need to be explored.

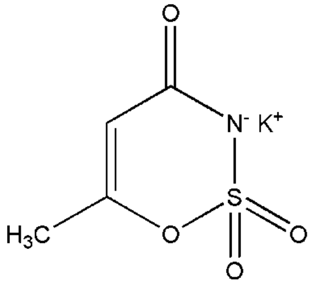
- Acid-activated and silica gel-enhanced Fe(VI) oxidation processes may be applicable for disinfection of wastewater

Appendices

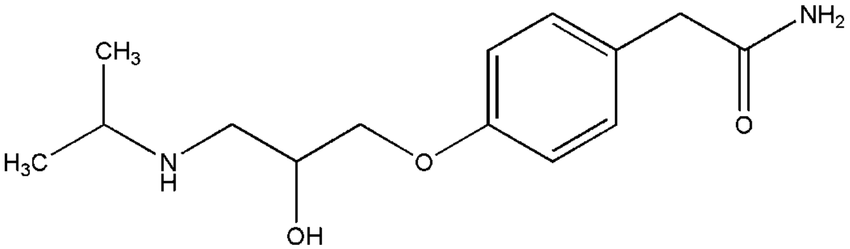
Appendix A: Supplementary material of Chapter 3



Caffeine (CAF)



Acesulfame potassium (ACE)



Atenolol (ATL)

Figure S3.1: Structures of selected organic compounds in the study.

Text S3.1: Chemicals and Fe(VI).

ReagentPlus grade caffeine powder (≥99.0 % purity), nitric acid (70 %) and acetic acid (>99.7 %) were purchased from Sigma-Aldrich, Canada. Ultrapure HPLC grade methanol (≥99.8 % purity) and 0.45 µm polypropylene filters were purchased from VWR International (Mississauga, Ontario, Canada). Hydrochloric acid (36.5-38.0 %) was purchased from Caledon Laboratory Chemicals (Georgetown, Ontario, Canada). All the chemicals mentioned above have been used without further purification. Fe(VI) was a salt of potassium (K_2FeO_4, 98% purity), which was prepared using the wet chemical method [1]. Fe(VI) solutions were prepared in doubly distilled water that was passed through 18.2 MΩ water purification system (Thermo Scientific, Barnstead^{TM} Easypure^{TM} RODi), followed by centrifugation (Thermo Scietific, Sorvall Legend Centrifuge) at 3700 rpm for 2 min at 24 °C. The concentrations of Fe(VI) in filtered water were determined spectroscopically using molar absorptivity (ε_{510nm} = 1150 $M^{-1}cm^{-1}$ [2]). Fresh solutions of Fe(VI) were prepared before the experiments in order to avoid its decomposition in water. All experiments were performed at room temperature (24±1 ℃).

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Text S3.2: Analytical methods.

An Agilent Technologies (1200 series) high-performance liquid chromatography (HPLC), equipped with a ZORBAX Eclipse XDB-C18 column (4.6 × 150 mm, 5 μm) and a diode array detector (set up at 272 nm), was used for the quantification of caffeine. A mixture of methanol and Milli-Q water (70:30 v/v) was used as a mobile phase at a flow rate of 0.800 mL/min. The injection volume was 20 μL. UV-VIS spectrophotometer (UV-3600, Shimadzu Scientific Instruments, Columbia, MD, USA) was also used for the quantification of caffeine (peak absorbance at 272 nm), atenolol (peak absorbance at 223 nm) and acesulfame potassium (peak absorbance at 226 nm).

Text S3.3: Control experiments.

Fe(VI) in solution without CAF was first allowed to decompose to Fe(III) (with and without acid), followed by addition of CAF. After filtration of Fe(III), the concentration of CAF in filtered reaction solution was determined.

Text S3.4: Experiments under nitrogen-purging conditions.

A 100 mL CAF solution was transferred to a gas-tight Pyrex-glass reactor that allowed us to purge gas during the reaction. The CAF solution was purged by nitrogen gas for 30 min. The Fe(VI) solution was added, followed by the addition of the acid. The mixture was allowed to react under continuous N_2 bubbling.

Table S3.1: Degradation of caffeine (CAF) by Fe(VI) at room temperature: Effect of acid.

#	[Fe(VI)] (µM)	[CAF] (µM)	[Fe(VI)]:[CAF] (mol/mol)	Acid Concentration	pH(1)	pH(2)	pH(3)	pH(4)	Time (Fe(VI) Decay)	Filtration Time	CAF Transformation (%)
1	88.5	89.1	1.0	No Acid	8.5	-	8.7	7.5	45 min	2.0 h****	11.7 ± 2.0
2	192.0	95.3	2.0	No Acid	8.7	-	8.9*	7.5	1 h	2.5 h	28.8 ± 2.5
3	339.0	86.0	3.9	No Acid	9.0	-	9.3**	7.5	3 h	6.0 h	41.5 ± 0.2
4	634.5	78.7	8.0	No Acid	9.6	-	10.3***	7.5	4 h	8.0 h	60.9 ± 4.1
5	179.3	91.3	2.0	225 µM HCl	8.8	8.3	9.0	7.5	10 s	0.5 h	48.3 ± 1.1
6	191.8	96.4	2.0	224 µM HNO_3	8.8	8.5	9.3	7.5	10 s	0.5 h	44.1 ± 1.0
7	177.5	90.9	2.0	224 µM $C_2H_4O_2$	8.8	8.4	9.2	7.5	10 s	0.5 h	45.3 ± 1.7
8	311.7	80.5	3.9	201 µM HCl	9.1	8.8	9.8	7.5	30 min	2.0 h	50.4 ± 1.1
9	328.5	83.4	3.9	204 µM HNO_3	9.1	8.7	9.8	7.3	30 min	2.0 h	48.8 ± 2.5
10	328.1	85.0	3.9	204 µM $C_2H_4O_2$	9.0	8.8	9.7	7.3	30 min	2.0 h	52.7 ± 1.6
11	335.6	87.1	3.9	401 µM HCl	9.3	8.9	9.5	7.5	10 min	1.0 h	68.3 ± 1.9
12	320.7	83.2	3.9	410 µM HNO_3	9.1	8.7	9.4	7.5	10 min	1.0 h	68.0 ± 1.7
13	284.9	73.6	3.9	411 µM $C_2H_4O_2$	9.0	8.4	9.3	7.5	10 min	1.0 h	78.9 ± 3.4
14	554.4	69.6	8.0	510 µM HCl	9.4	9.1	10.0	7.7	2 h	4.0 h	76.0 ± 0.4
15	563.4	70.9	8.0	703 µM HCl	9.5	8.7	9.5	7.5	30 min	2.0 h	84.6 ± 0.6
16	570.4	71.0	8.0	882 µM HCl	9.5	8.8	9.1	7.5	10 s	0.5 h	96.8 ± 2.8
17	550.4	68.9	8.0	888 µM HNO_3	9.4	8.7	9.3	7.5	10 s	0.5 h	95.5 ± 3.9
18	563.4	70.8	8.0	703 µM $C_2H_4O_2$	9.5	8.9	9.9	7.5	30 min	2.0 h	87.7 ± 1.2
19	559.7	70.3	8.0	879 µM $C_2H_4O_2$	9.5	8.5	9.6	7.5	10 min	1.0 h	96.8 ± 2.9

pH(1) - Initial pH of Fe(VI)-CAF mixture; pH(2) - Immediate pH after the addition of acid; pH(3) - pH after 10 min; pH(4) - Final pH before filtration; *after 0.5 h; **after 2 h; ***after 3 h; ****Note: Time in inset Fig. 1 of the manuscript, represents both Time (Fe(VI) Decay) and Filtration Time

Table S3.2: Effect of initial pH.

#	[Fe(VI)] (µM)	[CAF] (µM)	[Fe(VI)]:[CAF] (mol/mol)	Acid Concentration	pH(1)	pH(2)	pH(3)	pH(4)	Time (Fe(VI) Decay)	Filtration Time	CAF Transformation (%)
1	45.5	23.0	2.0	No Acid	8.0	-	8.5	7.3	30 min	1.0 h	31.7 ± 3.1
2	103.9	51.2	2.0	No Acid	8.5	-	8.8*	7.5	1 h	2.0 h	29.5 ± 6.2
3	195.0	96.3	2.0	No Acid	9.0	-	9.4**	7.8	2 h	3.0 h	30.4 ± 2.4

pH(1) - Initial pH of Fe(VI)-CAF mixture; pH(2) - Immediate pH after the addition of acid; pH(3) - pH after 10 min; pH(4) - Final pH before filtration; *after 0.5 h; **after 1 h

Table S3.3: Control experiments.

#	[Fe(VI)] (µM)	[CAF] (µM)	Acid Concentration	pH	Filtration Time	CAF Transformation (%)
Blank experiments						
1	-	105.3	6173 µM HCl	2.2	5.0 h	0.0
2	-	99.3	6173 µM HNO_3	2.3	5.0 h	0.0
3	-	106.0	6173 µM $C_2H_4O_2$	3.5	5.0 h	0.0
Effect of Fe(III)						
4	429.0 (degraded to Fe(III))	82.9	No Acid	7.5	2.0 h	0.0
5	334.7 (degraded to Fe(III))	104.0	416 µM HCl	7.0	3.0 h	0.0
6	275.5 (degraded to Fe(III))	72.0	337 µM $C_2H_4O_2$	7.3	15.0 h	0.0

Table S3.4: Degradation of atenolol (ATL) by Fe(VI) at room temperature: Effect of acid.

#	[Fe(VI)] (µM)	[ATL] (µM)	[Fe(VI)]:[ATL] (mol/mol)	Acid Concentration	pH(1)	pH(2)	pH(3)	pH(4)	Time (Fe(VI) Decay)	Filtration Time	ATL Transformation (%)
1	-	72.7	-	1085 µM HCl	-	2.7	-	2.7	-	3.0 h	0.0
2	192.6	47.7	4.0	No Acid	9.0	-	9.3	7.2	45 min	2.0 h	0.0
3	204.6	51.7	4.0	444 µM HCl	8.8	7.5	6.0	6.0	Immediately	1.0 h	12.1
4	569.1	56.9	10.0	No Acid	9.6	-	10.6*	7.5	3 h	15.0 h	0.0
5	490.5	49.0	10.0	363 µM HCl	9.5	9.1	9.9	7.5	30 min	2.0 h	11.8
6	415.8	41.6	10.0	574 µM HCl	9.4	8.8	9.2	7.7	10 s	0.5 h	26.0
7	487.3	48.6	10.0	713 µM HCl	9.5	6.7	8.8	7.0	Immediately	0.5 h	27.8
8	447.6	44.7	10.0	543 µM $C_2H_4O_2$	9.4	8.9	9.8	7.2	2 min	1.0 h	22.9

pH(1) - Initial pH of Fe(VI)-ATL mixture; pH(2) - Immediate pH after the addition of acid; pH(3) - pH after 10 min; pH(4) - Final pH before filtration; *after 1 h

Table S3.5: Degradation of acesulfame potassium (ACE) by Fe(VI) at room temperature: Effect of acid.

#	[Fe(VI)] (µM)	[ACE] (µM)	[Fe(VI)]:[ACE] (mol/mol)	Acid Concentration	pH(1)	pH(2)	pH(3)	pH(4)	Time (Fe(VI) Decay)	Filtration Time	ACE Transformation (%)
1	-	72.7	-	4975 µM HCl	-	2.4	-	2.4	-	5.0 h	0.0
2	164.4	81.4	2.0	No Acid	8.9	-	9.2	7.3	1 h	2.0 h	28.8
3	161.9	80.6	2.0	228 µM HCl	8.8	7.8	6.5	6.6	Immediately	0.5 h	48.9
4	155.4	77.6	2.0	228 µM $C_2H_4O_2$	8.8	7.9	6.5	6.5	Immediately	0.5 h	50.1
5	569.2	70.9	8.0	No Acid	9.5	-	9.7	7.5	6.0 h	8.0 h	63.5
6	502.7	63.0	8.0	732 µM HCl	9.4	7.1	8.4	7.1	10 s	0.5 h	94.9

pH(1) - Initial pH of Fe(VI)-ACE mixture; pH(2) - Immediate pH after the addition of acid; pH(3) - pH after 10 min; pH(4) - Final pH before filtration

Table S3.6: Effect of N_2 on the degradation of caffeine by Fe(VI) using acids.

#	[Fe(VI)] (μM)	[CAF] (μM)	[Fe(VI)]:[CAF] (mol/mol)	Acid Concentration	pH(1)	pH(4)	Filtration Time	CAF Transformation (%)
1	327.0	83.1	3.9	393 μM HCl + N_2 bubbling	9.1	9.9	4.0 h	67.0 ± 1.2
2	296.4	76.5	3.9	431 μM HNO_3 + N_2 bubbling	9.3	10.3	24.0 h	68.1 ± 2.3
3	339.3	87.1	3.9	416 μM $C_2H_4O_2$ + N_2 bubbling	9.2	10.0	9.0 h	66.8 ± 6.3

pH(1) - Initial pH of Fe(VI)-CAF mixture; pH(4) - Final pH before filtration

Appendix B: Supplementary material of Chapter 4

Table S4.1: Effect of initial pH on oxidation of CAF by Fe(VI).

#	[Fe(VI)] (μM)	[CAF] (μM)	[Fe(VI)]/[CAF] (mol/mol)	[HCl] (μM)	pH (1)	pH (2)	pH (3)	pH (4)	Time (Fe(VI) Decay)	Filtration Time (h)	CAF Removal (%)
1	45.5	23.0	2.0	No Acid	8.0	-	8.5	7.3	30 min	1.0	29.9 ± 0.4
2	103.9	51.2	2.0	No Acid	8.5	-	8.8	7.5	1 h	2.0	30.2 ± 1.2
3	195.0	96.3	2.0	No Acid	9.0	-	9.4	7.8	2 h	3.0	29.6 ± 2.2
4	571.0	281.2	2.0	No Acid	9.6	-	10.6	8.2	2 h	8.0	17.8 ± 0.3

pH(1) - Initial pH of Fe(VI)-CAF mixture; pH(2) - Immediate pH after the addition of acid; pH(3) - Highest pH reached during the reaction; pH(4) - Final pH before filtration;

Table S4.2: Oxidation of CAF by Fe(VI) and acid-activated Fe(VI).

#	[Fe(VI)] (μM)	[CAF] (μM)	[Fe(VI)]/[CAF] (mol/mol)	[HCl] (μM)	pH (1)	pH (2)	pH (3)	pH (4)	Time (Fe(VI) Decay)	Filtration Time (h)	CAF Remaining (%)
1	41.7	61.4	0.7	No Acid	8.0	-	8.4	7.3	30 min	1.0	91.2 ± 2.4
2	88.5	89.1	1.0	No Acid	8.5	-	8.7	7.5	45 min	2.0	85.4 ± 3.7
3	192.0	95.3	2.0	No Acid	8.7	-	8.9	7.5	1 h	2.5	71.2 ± 2.5
4	339.0	86.0	3.9	No Acid	9.0	-	9.3	7.5	3 h	6.0	58.5 ± 0.4
5	634.5	78.7	8.0	No Acid	9.6	-	10.3	7.5	4 h	8.0	39.1 ± 4.1
6	705.4	70.5	10.0	No Acid	9.7	-	10.4	7.6	4 h	11.0	29.4 ± 0.3
7	866.4	52.4	16.5	No Acid	9.7	-	10.6	7.8	>4 h	24.0	18.2 ± 2.4
8	1026.5	51.4	20.0	No Acid	9.9	-	10.8	7.9	>4 h	46.0	14.2 ± 4.4
9	1314.8	52.6	25.0	No Acid	10.3	-	11.1	8.6	>4 h	45.0	8.5 ± 0.9
10	179.3	91.3	2.0	225	8.8	8.3	9.0	7.5	10 s	0.5	51.7 ± 1.1
11	335.6	87.1	3.9	401	9.3	8.9	9.5	7.5	10 min	1.0	31.7 ± 1.9
12	570.4	71.0	8.0	882	9.5	8.8	9.1	7.5	10 s	0.5	3.2 ± 2.8

pH(1) - Initial pH of Fe(VI)-CAF mixture; pH(2) - Immediate pH after the addition of acid; pH(3) - Highest pH reached during the reaction; pH(4) - Final pH before filtration;

Table S4.3: Data used for the development of the model.

[Fe(VI)]/[CAF] (mol/mol)	[HCl]/[Fe(VI)] (mol/mol)	CAF Removal (%) Experimental
2.0	1.25	48.3
3.9	0.64	50.4
3.9	1.19	68.3
8.0	0.92	76.0
8.0	1.25	84.6
8.0	1.55	96.8
8.0	1.26	86.0
8.0	1.48	91.5
8.0	1.74	100.0
2.0	0.00	28.8
3.9	0.00	41.5
8.0	0.00	60.9

Table S4.4: Analysis of variance for response.

Source	**Sum of squares (SS)**	**F-value**	**P-value**
Model (linear)	5917	231.32	< 0.0005
[Fe(VI)]/[CAF]	4400	142.35	< 0.0005
[HCl]/[Fe(VI)]	1517	118.61	< 0.0005

$R^2 = 0.981$, $R^2(\text{adj}) = 0.977$ and $R^2(\text{pred}) = 0.961$

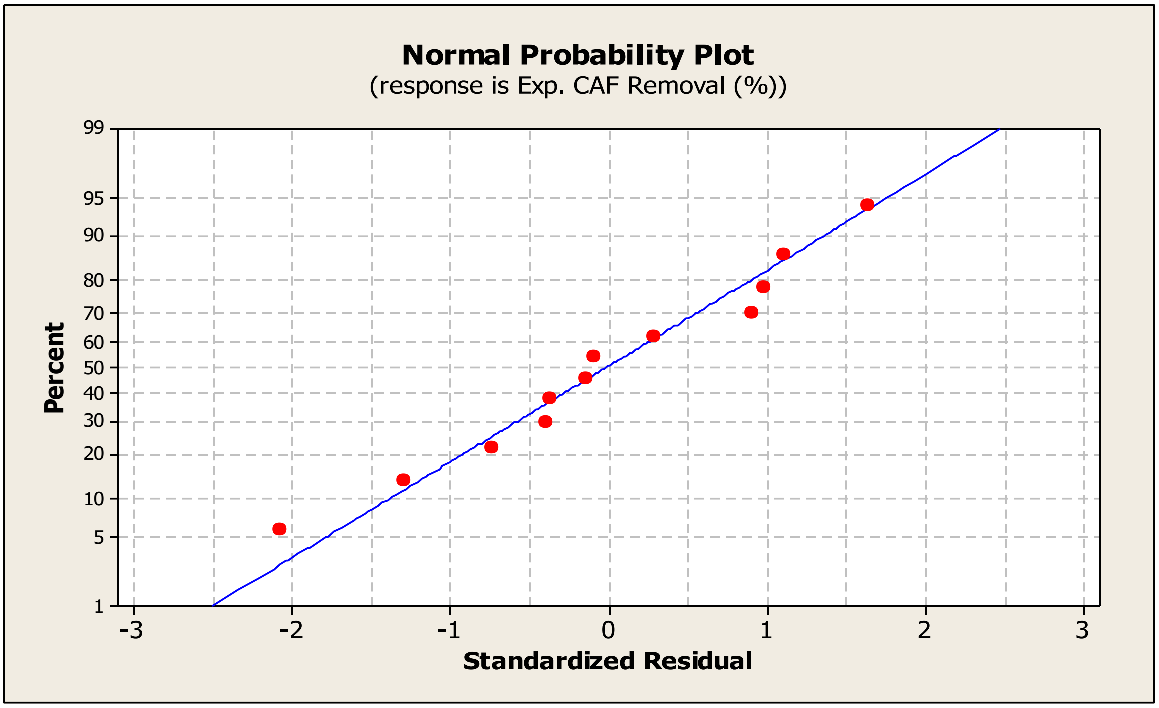


Figure S4.1: Normal probability plot of the standardized residuals for the linear model.

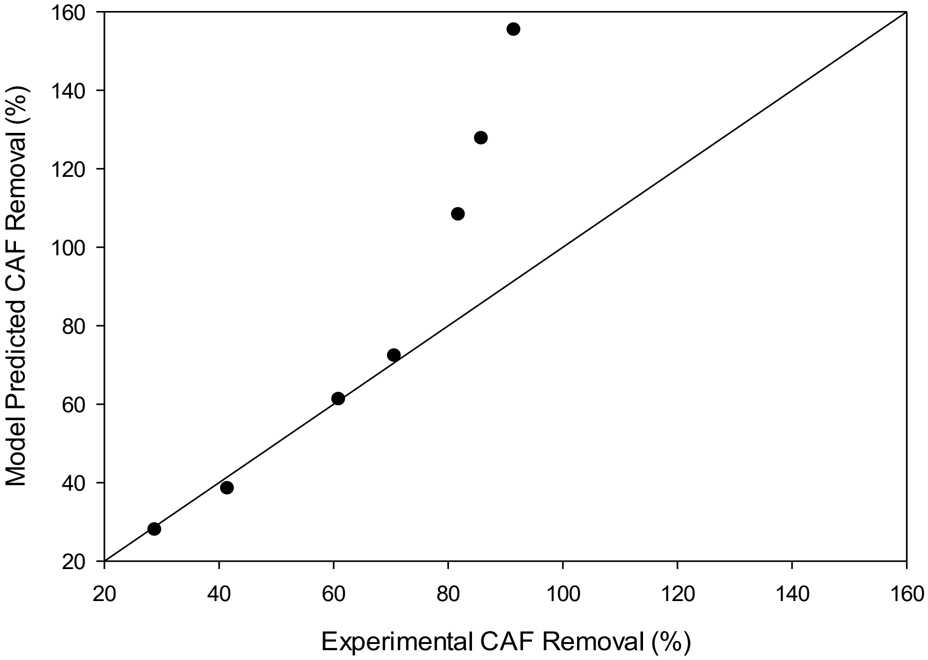


Figure S4.2: Model prediction of the removal of CAF in the Fe(VI)-CAF system.

Table S4.5: Coefficients in coded units, for the "linear + interaction" model (R^2 = 0.984 R^2(adj) = 0.977 R^2(pred) = 0.946).

Factor	Coefficient (coded units)	P-value
Constant	62.025	< 0.0005
[Fe(VI)]/[CAF]	16.680	< 0.0005
[HCl]/[Fe(VI)]	17.346	< 0.0005
{[Fe(VI)]/[CAF]}×{[HCl]/[Fe(VI)]}	2.109	0.296

$$\text{CAF Removal (\%)} = 20.39 + (4.86 \cdot \frac{[\text{Fe(VI)}]}{[\text{CAF}]}) + (15.90 \cdot \frac{[\text{HCl}]}{[\text{Fe(VI)}]}) + (0.81 \cdot \frac{[\text{Fe(VI)}]}{[\text{CAF}]} \cdot \frac{[\text{HCl}]}{[\text{Fe(VI)}]})$$

Table S4.6: Model prediction for Fe(VI)-CAF.

[Fe(VI)]/[CAF] (mol/mol)	[HCl]/[Fe(VI)] (mol/mol)	Experimental CAF Removal (%)	Model predicted CAF Removal (%) Linear model	Model predicted CAF Removal (%) Linear + Interaction
2.0	0.00	28.8	28.0	30.1
3.9	0.00	41.5	38.5	39.3
8.0	0.00	60.9	61.2	59.3
10.0	0.00	70.6	72.3	69.0
16.5	0.00	81.8	108.3	100.6
20.0	0.00	85.8	127.7	117.6
25.0	0.00	91.5	155.4	141.9

Table S4.7: Model prediction for Fe(VI)-CAF-HCl.

[Fe(VI)]/[CAF] (mol/mol)	[HCl]/[Fe(VI)] (mol/mol)	Experimental CAF Removal (%)	Model predicted CAF Removal (%) Linear model	Model predicted CAF Removal (%) Linear + Interaction
2.0	1.25	48.3	53.8	52.0
3.9	0.64	50.4	51.7	51.5
3.9	1.19	68.3	63.1	62.0
8.0	0.92	76.0	80.2	79.9
8.0	1.25	84.6	87.0	87.2
8.0	1.55	96.8	93.2	94.0
8.0	1.26	86.0	87.2	87.5
8.0	1.48	91.5	91.8	92.4
8.0	1.74	100.0	97.1	98.2

Table S4.8: Model prediction for Fe(VI)-CAF-HNO_3.

[Fe(VI)]/[CAF] (mol/mol)	[HNO_3]/[Fe(VI)] (mol/mol)	Experimental CAF Removal (%)	Model predicted CAF Removal (%) Linear model	Model predicted CAF Removal (%) Linear + Interaction
2.0	1.17	44.1	52.1	50.6
3.9	0.62	48.8	51.3	51.2
3.9	1.28	68.0	64.9	63.7
8.0	1.61	95.5	94.4	95.3

Text S4.1

The prediction (linear model) at higher molar ratios than 10.0 of the Fe(VI)-CAF system (non-activated Fe(VI)) is not good (Figure S4.2 of Appendix B). A full quadratic response surface model has been also developed using the same data (Table S4.3 of Appendix B) ($R^2 = 0.995$, $R^2(\text{adj}) = 0.991$ and $R^2(\text{pred}) = 0.930$):

$$\text{CAF Removal (\%)} = 4.92 + \left(12.54 \cdot \frac{[\text{Fe(VI)}]}{[\text{CAF}]}\right) + \left(8.08 \cdot \frac{[\text{HCl}]}{[\text{Fe(VI)}]}\right) - \left(0.70 \cdot \left(\frac{[\text{Fe(VI)}]}{[\text{CAF}]}\right)^2\right) + \left(7.60 \cdot \left(\frac{[\text{HCl}]}{[\text{Fe(VI)}]}\right)^2\right) + \left(0.29 \cdot \frac{[\text{Fe(VI)}]}{[\text{CAF}]} \cdot \frac{[\text{HCl}]}{[\text{Fe(VI)}]}\right)$$

The full quadratic response surface model does not predict well the %CAF removal in the Fe(VI)-CAF system (non-activated Fe(VI)) when high removal efficiencies were achieved (high Fe(VI) to CAF molar ratios of 16.5, 20.0, and 25.0). The full quadratic model predicts CAF removal efficiencies of 60.3%, 21.3%, -24.3%, and -119.1% for Fe(VI) to CAF molar ratios of 10.0, 16.5, 20.0, and 25.0 respectively (HCl to Fe(VI) molar ratio of zero). Experimental CAF removal efficiencies are 70.6%, 81.8%, 85.8%, and 91.5%, at the same molar ratios, respectively. The prediction of negative CAF removal efficiencies is due to the negative coefficient of the Fe(VI) to CAF molar ratio square factor (-0.70). This negative coefficient does not make any sense considering a positive coefficient of the Fe(VI) to CAF molar ratio (12.54). This inconsistency is due to the high Fe(VI) to CAF molar ratios required to remove CAF by non-activated Fe(VI). A molar ratio of Fe(VI) to CAF of 10.0 is required for ~70% CAF removal, but the remaining ~20% decrease in CAF was achieved using additional molar ratio of 15.0 (to reach a molar ratio of 25.0 for 92% CAF removal by non-activated Fe(VI)) (Table S4.2 of Appendix B).

Another full quadratic response surface model has been developed using the same data (Table S4.3 of Appendix B) plus the data of higher Fe(VI) to CAF molar ratios of non-activated Fe(VI) (molar ratios of 10.0, 16.5, 20.0, and 25.0 corresponding to 70.6%, 81.8%, 85.8%, and 91.5% CAF removal respectively). The quadratic model is shown below ($R^2 = 0.986$, $R^2(\text{adj}) = 0.979$ and $R^2(\text{pred}) = 0.926$):

$$\text{CAF Removal (\%)} = 18.90 + \left(6.19 \cdot \frac{[\text{Fe(VI)}]}{[\text{CAF}]}\right) + \left(8.91 \cdot \frac{[\text{HCl}]}{[\text{Fe(VI)}]}\right) - \left(0.135 \cdot \left(\frac{[\text{Fe(VI)}]}{[\text{CAF}]}\right)^2\right) + \left(5.57 \cdot \left(\frac{[\text{HCl}]}{[\text{Fe(VI)}]}\right)^2\right) + \left(0.62 \cdot \frac{[\text{Fe(VI)}]}{[\text{CAF}]} \cdot \frac{[\text{HCl}]}{[\text{Fe(VI)}]}\right)$$

The prediction of the CAF removal by non-activated Fe(VI) has been improved using this model. This model predicts 67.3%, 84.3%, 88.7%, and 89.3% CAF removal efficiencies for Fe(VI) to CAF molar ratios of 10.0, 16.5, 20.0, and 25.0 respectively (experimental CAF removal efficiencies at the same molar ratios are 70.6%, 81.8%, 85.8%, and 91.5% respectively). However, this model also includes a negative coefficient of the Fe(VI) to CAF molar ratio square factor (-0.135) which does not make any sense considering a positive coefficient of the Fe(VI) to CAF molar ratio (6.19). This inconsistency is due to the high Fe(VI) to CAF molar ratios required to remove CAF by non-activated Fe(VI), resulting in big numbers of the $\{[Fe(VI)]/[CAF]\}^2$.

Table S4.9: Effect of ions on the oxidation of CAF by Fe(VI) and acid-activated Fe(VI).

#	[Fe(VI)] (μM)	[CAF] (μM)	[Fe(VI)]/[CAF] (mol/mol)	[Ion] (mM)	[HCl] (μM)	pH (1)	pH (2)	pH (3)	pH (4)	Time (Fe(VI) Decay)	Filtration Time (h)	CAF Removal (%)
1	192.0	95.3	2.0	No ion	No Acid	8.7	-	8.9	7.5	1 h	2.5	28.8 ± 2.5
2	179.3	91.3	2.0	No ion	225	8.8	8.3	9.0	7.5	10 s	0.5	48.3 ± 1.1
3	151.4	74.4	2.0	1.2 HCO_3^-	No Acid	8.7	-	9.2	8.3	2 h	4.0	29.1 ± 3.3
4	158.5	79.9	2.0	1.2 HCO_3^-	216	8.6	8.0	8.4	8.2	5-10 min	0.5	53.0 ± 1.5
5	114.3	57.5	2.0	4.0 Cl^-	No Acid	8.2	-	8.6	7.5	45 min	1.5	26.9 ± 0.9
6	176.2	88.6	2.0	4.0 Cl^-	215	8.5	8.2	7.6*	7.0	10 s	0.5	46.5 ± 2.4
7	114.3	57.5	2.0	4.0 Na^+	No Acid	8.2	-	8.6	7.5	45 min	1.5	26.9 ± 0.9
8	176.2	88.6	2.0	4.0 Na^+	215	8.5	8.2	7.6*	7.0	10 s	0.5	46.5 ± 2.4
9	112.0	56.4	2.0	2.0 SO_4^{2-}	No Acid	8.2	-	8.7	7.5	1 h	2.0	24.5 ± 1.1
10	173.5	87.7	2.0	2.0 SO_4^{2-}	213	8.5	8.0	8.1	7.0	2 min	0.5	47.2 ± 2.3
11	103.4	51.9	2.0	1.0 Mg^{2+}	No Acid	8.2	-	9.0	7.5	105 min	2.5	20.7 ± 1.4
12	185.8	93.8	2.0	1.0 Mg^{2+}	211	8.8	8.3	8.7	7.5	2 min	0.5	45.3 ± 2.7
13	102.3	52.5	2.0	2.0 Ca^{2+}	No Acid	8.5	-	9.3	7.5	1.0 h	2.5	17.0 ± 1.0
14	184.8	93.3	2.0	2.0 Ca^{2+}	212	8.7	8.2	8.5	7.3	1 min	0.5	43.7 ± 0.7
15	339.0	86.0	3.9	No ion	No acid	9.0	-	9.3	7.5	3 h	6.0	41.5 ± 0.2
16	326.5	84.3	3.9	2.0 Ca^{2+}	No acid	9.1	-	10.0	8.0	1.5 h	6.0	32.4 ± 0.4
17	335.6	87.1	3.9	No ion	401	9.3	8.9	9.5	7.5	10 min	1.0	68.3 ± 1.9
18	338.3	86.0	3.9	2.0 Ca^{2+}	410	9.0	8.1	9.6	7.6	10 s	1.0	66.8 ± 0.3

pH(1) - Initial pH of Fe(VI)-CAF-Ion mixture; pH(2) – Lowest pH during the addition of acid; pH(3) - Highest pH reached after the addition of acid; pH(4) - Final pH before filtration; *pH after 10 min

Table S4.10: Blank experiments: Effect of ions.

#	[Fe(VI)] (μM)	[CAF] (μM)	[Ion] (mM)	[HCl] (μM)	Initial pH	Final pH	Filtration Time (h)	CAF Removal (%)
1	-	85.0	1.2 HCO_3^-	238	7.4	8.1	2.0	0.0
2	-	68.3	2.0 SO_4^{2-}	238	3.6	3.6	2.0	0.0
3	-	82.2	1.0 Mg^{2+}	238	3.5	3.5	2.0	0.0
4	-	89.5	2.0 Ca^{2+}	238	3.5	3.5	2.0	0.0

Table S4.11: Effect of ions on CAF oxidation by Fe(VI): Comparisons (t-test) with the control (Fe(VI)-CAF VS Fe(VI)-CAF-Ion) at Fe(VI) to CAF molar ratio of 2.0.

Ion	**95% confidence interval of difference**	**Estimate for difference (%CAF removal)**	**P-value**	**Comment on null hypothesis**	**Is there a statistically significant difference?**
Ca^{2+}	(7.5, 16.1)	11.8	0.003 < 0.05	Rejected	Yes
Ca^{2+} [Fe(VI)]/[CAF]=3.9	(8.2, 9.8)	9.0	0.000 < 0.05	Rejected	Yes
Mg^{2+}	(4.1, 12.1)	8.1	0.005 < 0.05	Rejected	Yes
SO_4^{2-}	(0.5, 8.1)	4.3	0.036 < 0.05	Rejected	Yes
Cl^-/Na^+ (NaCl)	(-2.4, 6.2)	-	0.258 > 0.05	Accepted	No
HCO_3^-	(-5.0, 4.5)	-	0.890 > 0.05	Accepted	No

Null Hypothesis: (Average %CAF Removal)$_{\text{(Fe(VI)-CAF; control)}}$ – (Average %CAF Removal)$_{\text{(Fe(VI)-CAF-Ion)]}}$ = 0

Table S4.12: Effect of ions on CAF oxidation by acid-activated Fe(VI): Comparisons (t-test) with the control (Fe(VI)-CAF-HCl VS Fe(VI)-CAF-HCl-Ion) at Fe(VI) to CAF molar ratio of 2.0.

Ion	**95% confidence interval of difference**	**Estimate for difference (%CAF removal)**	**P-value**	**Comment on null hypothesis**	**Is there a statistically significant difference?**
Ca^{2+}	(2.8, 6.4)	4.6	$0.002 < 0.05$	Rejected	Yes
Ca^{2+} [Fe(VI)]/[CAF]=3.9	(-1.6, 4.6)	-	$0.229 > 0.05$	Accepted	No
Mg^{2+}	(-1.7, 7.6)	-	$0.134 > 0.05$	Accepted	No
SO_4^{2-}	(-2.4, 4.6)	-	$0.434 > 0.05$	Accepted	No
Cl^-/Na^+ (NaCl)	(-1.9, 5.4)	-	$0.258 > 0.05$	Accepted	No
HCO_3^-	(-7.1, -2.4)	-4.7	$0.003 < 0.05$	Rejected	Yes

Null Hypothesis: (Average %CAF Removal)$_{\text{(Fe(VI)-CAF-HCl; control)}}$ – (Average %CAF Removal)$_{\text{(Fe(VI)-CAF-HCl-Ion)}}$ = 0

Table S4.13: ICP-EOS analysis of ions after the treatment.

	Fe(VI) (Fe(VI)-CAF-Ion)	**Activated Fe(VI)** (Fe(VI)-CAF-Ion-HCl)	**Blank** (CAF-Ion-HCl)
Ca^{2+} added (mM)	2.0	2.0	2.1
Ca^{2+} measured after treatment (mM)	1.9	1.9	2.0
Mg^{2+} added (mM)	1.0	1.0	1.0
Mg^{2+} measured after treatment (mM)	0.9	0.9	1.0
SO_4^{2-} added (mM)	2.0	2.0	2.0
SO_4^{2-} measured after treatment (mM)	2.1	2.1	2.2

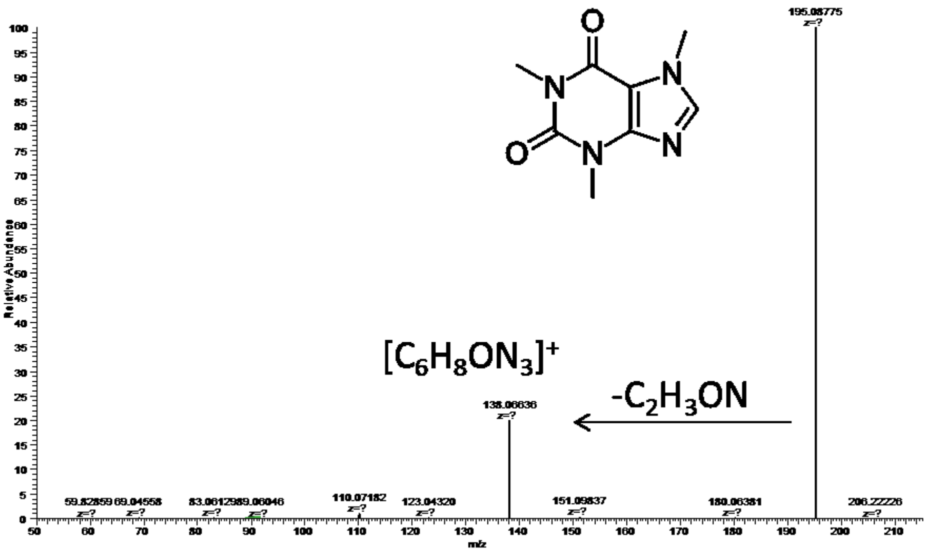
Table S4.14: Effects of NOM and SE on oxidation of CAF by Fe(VI) and acid-activated Fe(VI).

#	[Fe(VI)] (μM)	[CAF] (μM)	[Fe(VI)]/[CAF] (mol/mol)	NOM or SE	[HCl] (μM)	pH (1)	pH (2)	pH (3)	pH (4)	Time (Fe(VI) Decay)	Filtration Time (h)	CAF Removal (%)
1	173.3	86.9	2.0	5.1 mg NOM/L	No Acid	8.6	-	9.6	7.3	1 h	3.0	20.7 ± 1.3
2	161.9	81.4	2.0	5.1 mg NOM/L	216	8.6	8.2	7.2*	6.8	2 s	0.5	36.2 ± 3.1
3	163.0	81.6	2.0	SE	No Acid	8.6	-	9.0	8.3	30 min	3.0	13.8 ± 1.3
4	157.6	77.7	2.0	SE	228	8.6	8.1	8.5	8.2	10 min	1.0	16.9 ± 2.5

pH(1) - Initial pH of Fe(VI)-CAF-OM/SE mixture; pH(2) - Immediate pH after the addition of acid; pH(3) - Highest pH reached after the addition of acid; pH(4) - Final pH before filtration; *pH after 10 min

Table S4.15: Blank experiments: Effects of NOM and SE.

#	[Fe(VI)] (μM)	[CAF] (μM)	NOM or SE	[HCl] (μM)	Initial pH	Final pH	Filtration Time (h)	CAF Removal (%)
1	-	84.9	5.1 mg NOM/L	216	3.5	3.5	2.0 h	0.0
2	-	86.2	SE	238	7.4	8.2	2.0 h	0.0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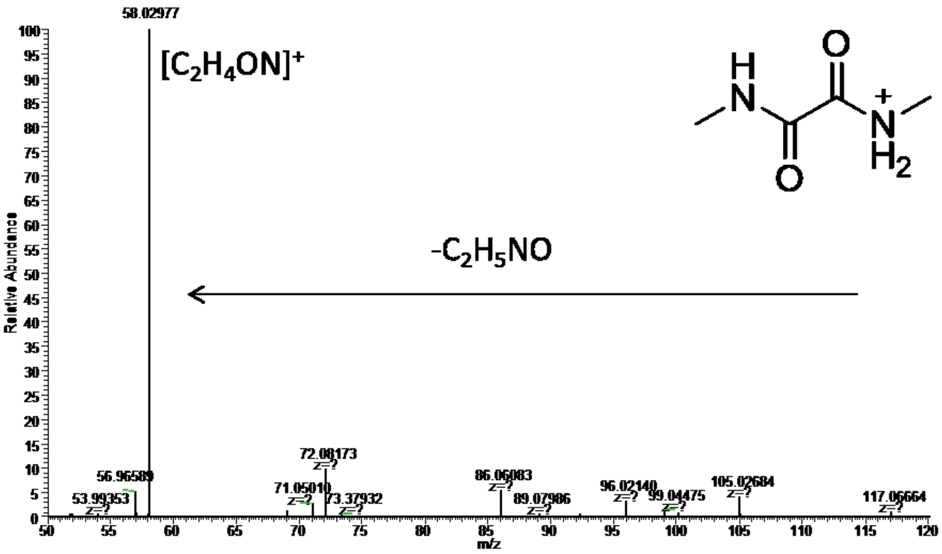
Relative Abundance
m/z

(CAF)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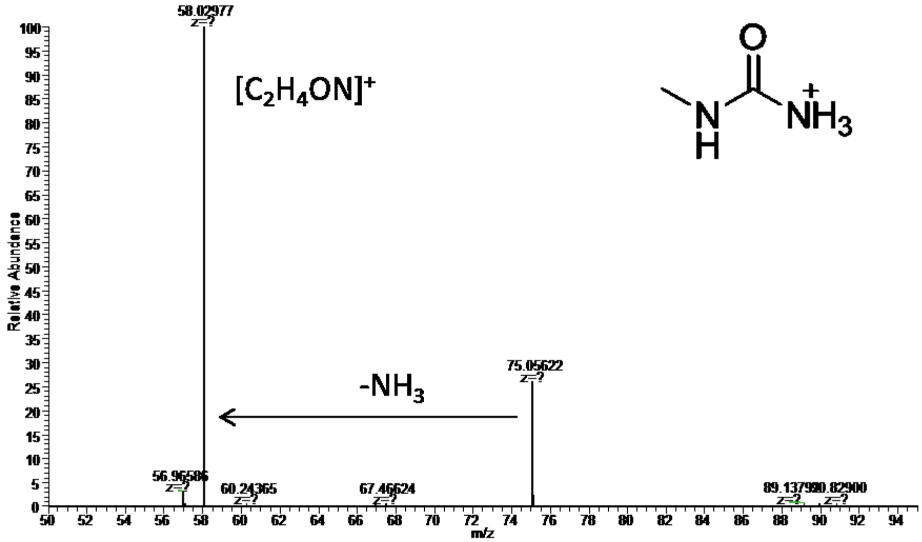
Relative Abundance
m/z

(OP1)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m/z
O
N
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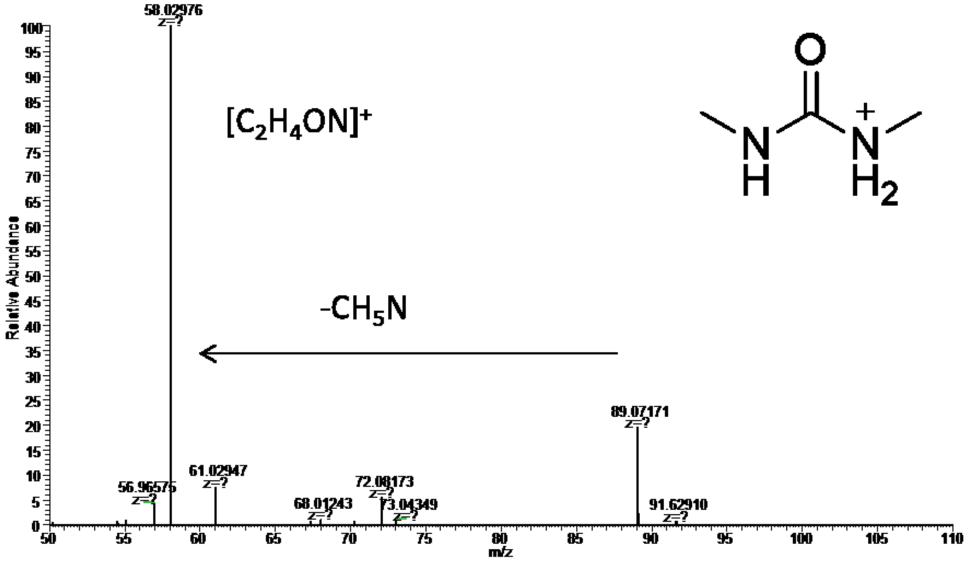
+

(OP2)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68.01243
z=?
73.04349
z=?
91.62910
z=?
Relative Abundance
m/z
O
N
H
N
H₂
+

(OP3)

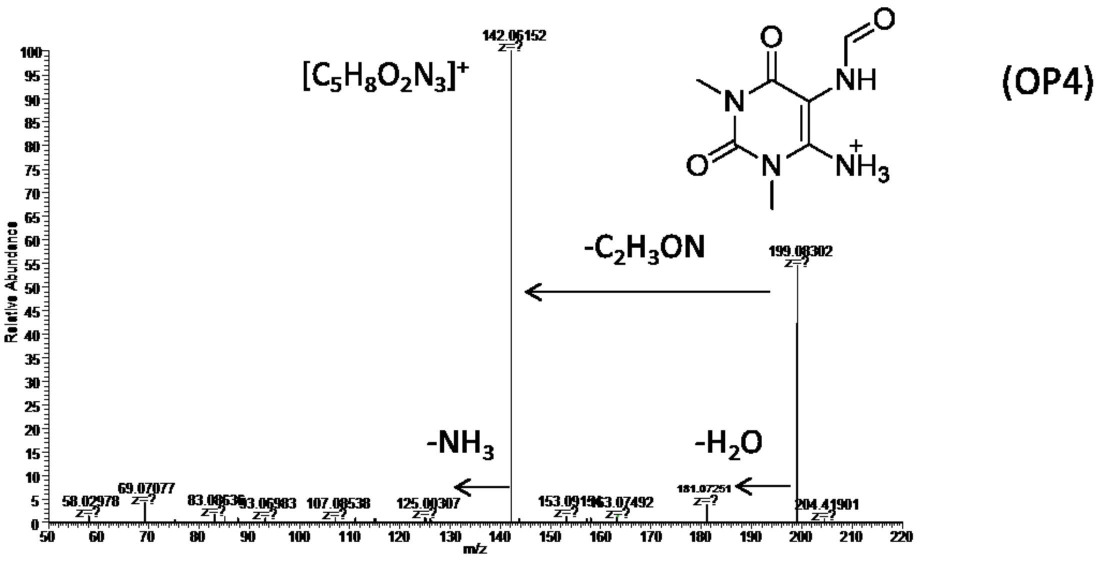


Figure S4.3: Product ion spectra of CAF and its degradation products (OP1, OP2, OP3 and OP4) by acid-activated Fe(VI), which were measured by LC-HRMS, and their proposed fragments. (Experimental conditions: [Fe(VI)] = 662.7 µM; [Fe(VI)]/[CAF] = 8.0 mol/mol; [HCl]/[Fe(VI)] = 1.74; immediate pH after the addition of acid = 8.8; final pH = 7.2).

Table S4.16: Accurate mass measurements of CAF and its transformation products determined by LC-HRMS.

Compound	R_t (min)	Formula $[M + H]^+$	Calculated mass (*m/z*)	Experimental mass (*m/z*)	Error (ppm)	DBE*
Caffeine	2.33	$C_8H_{11}N_4O_2$	195.0877	195.0877	0.25	6
OP1	1.34	$C_4H_9N_2O_2$	117.0659	117.0664	4.67	2
OP2	0.5	$C_2H_7N_2O$	75.0553	75.0562	12.40	1
OP3	0.7	$C_3H_9N_2O$	89.0709	89.0717	8.65	1
OP4	2.09	$C_7H_{11}N_4O_3$	199.0826	199.0830	2.28	5

* double bond equivalent

Appendix C: Supplementary material of Chapter 5

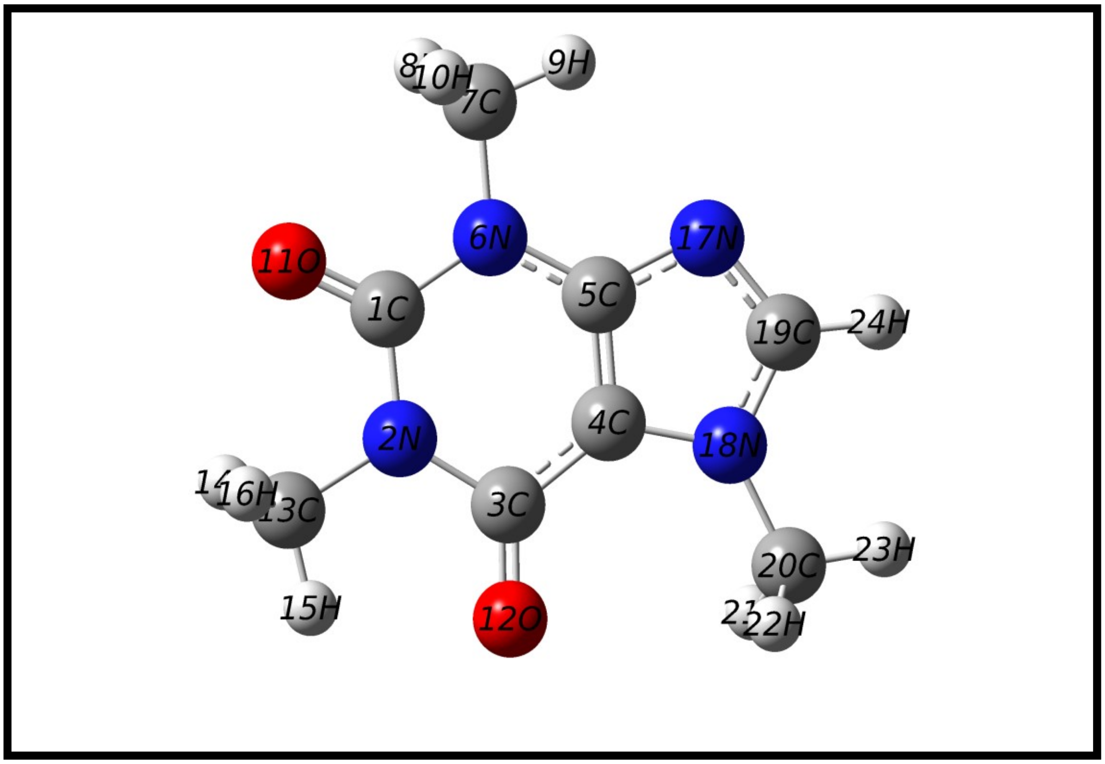
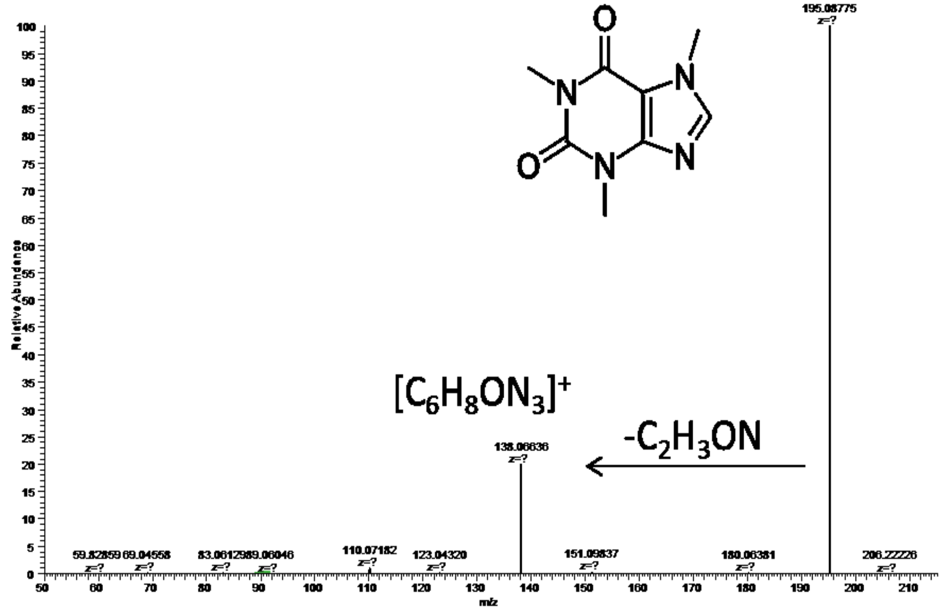


Figure S5.1: The optimized geometry of CAF molecule at the B3LYP/6-311G level.**
]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-C2H3ON
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z=?
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89.06046
110.07182
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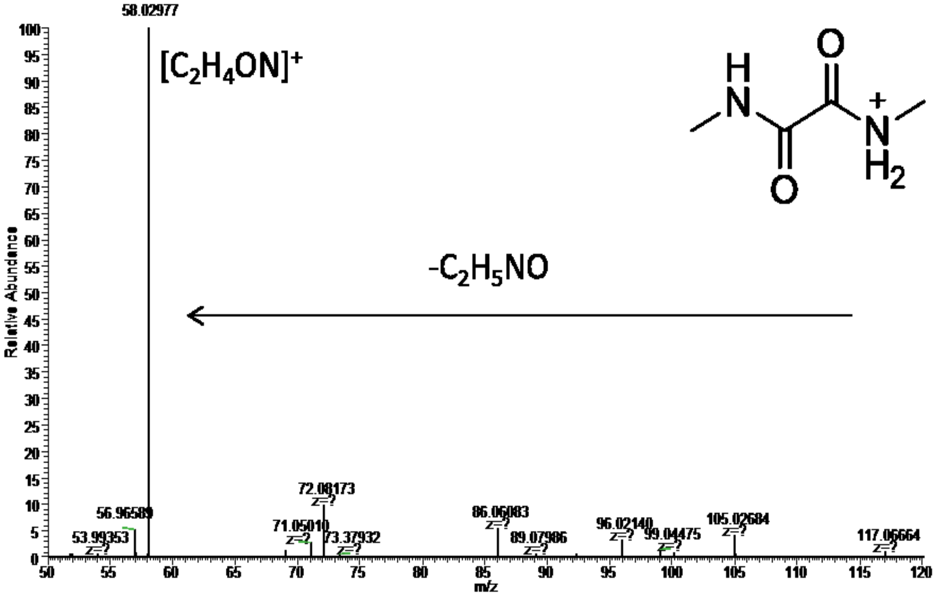
180.06381
206.22226
Relative Abundance
m/z

(CAF)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H
N
O
O
N
+
H2
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71.05010
73.37932
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z=?
Relative Abundance
m/z

(OP1)

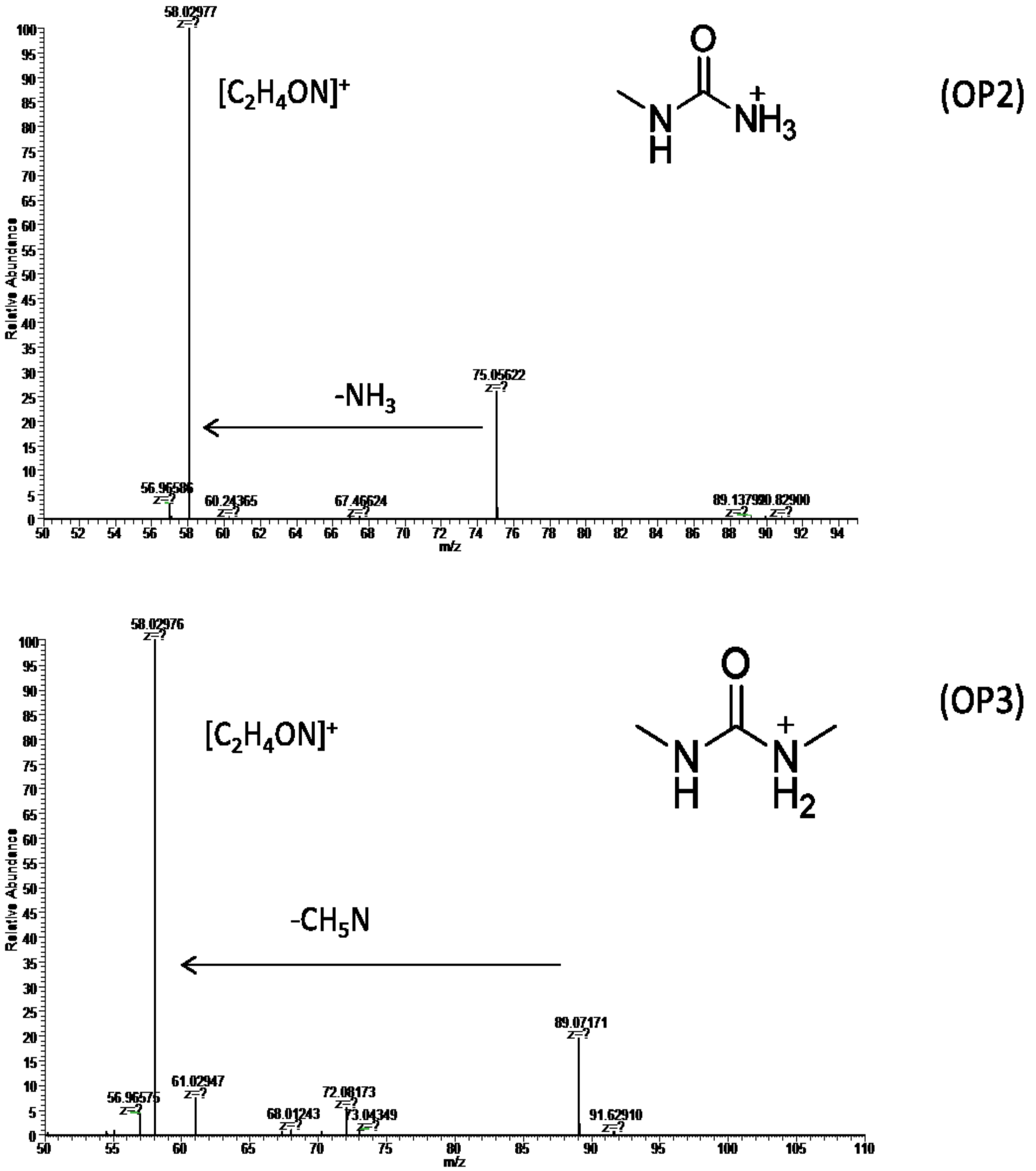


Figure S5.2: Product ion spectra of CAF and its degradation products (OP1, OP2, and OP3), which were measured by LC-HRMS, and their proposed fragments.

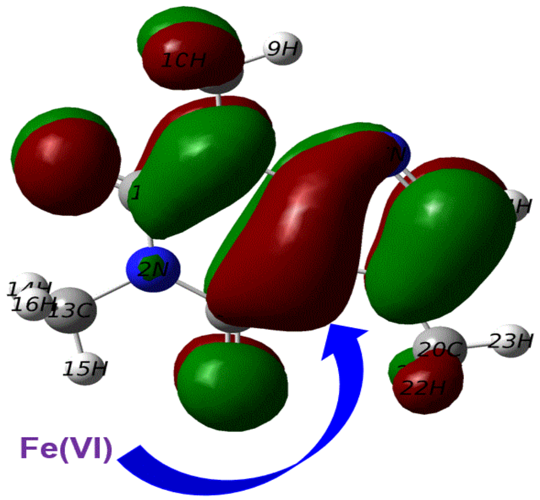


Figure S5.3: The atomic orbital composition of frontier molecular orbitals (HOMO) of CAF, which was calculated using Gaussian 09 program at the B3LYP/6-311G level. The blue arrow represents the possible attack site of CAF by Fe(VI).**

Table S5.1: Oxidation of CAF by Fe(VI) in the presence and absence of SiO_2 gel: Effect of concentration of SiO_2 gel.

#	[Fe(VI)] (µM)	[CAF] (µM)	[Fe(VI)]:[CAF] (mol/mol)	[SiO_2] (g/L)	pH(1)	pH(2)	pH(3)	Time (Fe(VI) Decay)	Filtration Time	CAF Transformation (%)
1	45.5	23.0	2.0	No SiO_2	8.0	8.5	7.3	30 min	1.0 h	29.9 ± 0.4
2	148.4	74.3	2.0	0.8	8.2	8.5	7.7	50 min	1.5 h	31.9 ± 0.9
3	162.4	80.0	2.0	2	8.3	8.5	7.7	45 min	2.0 h	36.7 ± 2.9
4	153.1	76.4	2.0	4	8.0	8.2	7.7	25 min	1.0 h	39.3 ± 1.8
5	152.2	75.1	2.0	8	7.7	7.9	7.5	10 min	45 min	44.5 ± 0.7
6	535.4	89.1	6.0	No SiO_2	9.3	10.3	8.0	4.0 h	6.0 h	53.0 ± 2.4
7	526.8	87.8	6.0	1	8.8	9.7	8.0	70 min	5.0 h	90.3 ± 2.2
8	524.7	87.4	6.0	2	8.6	9.4	8.0	50 min	5.0 h	96.6 ± 1.3
9	520.5	86.5	6.0	3	8.4	9.1	8.0	50 min	5.0 h	98.3 ± 0.7
10	513.4	85.6	6.0	4	8.3	8.9	8.0	45 min	4.0 h	100
11	522.8	87.2	6.0	5	8.3	8.9	8.0	40 min	4.0 h	100
12	517.0	86.1	6.0	7	8.3	8.7	8.0	40 min	4.0 h	100
13	520.3	87.0	6.0	8	8.2	8.6	7.9	35 min	4.0 h	100

pH(1) - Initial pH of Fe(VI)-CAF-SiO_2 mixture; pH(2) - Highest pH reached during the reaction; pH(3) - Final pH before filtration

Table S5.2: Control experiments: Fe(III)-CAF-SiO_2 and CAF-SiO_2.

#	[Fe(VI)] (µM)	[CAF] (µM)	[SiO_2] (g/L)	Initial pH	Final pH	Filtration Time	CAF Transformation (%)
1	152.1 µM Fe(VI) degraded to Fe(III) in the presence of SiO_2. Then, the CAF solution was added.	71.0	8	8.5	7.4	2 h	0.0
2	-	88.3	4	9.0 (adjusted using 0.5 mL of 0.2 M NaOH)	7.5	4 h	0.0

Table S5.3. Oxidation of CAF by Fe(VI) in the presence and absence of SiO_2 gel: Effect of Fe(VI) to CAF molar ratio.

#	[Fe(VI)] (µM)	[CAF] (µM)	[Fe(VI)]:[CAF] (mol/mol)	[SiO_2] (g/L)	pH(1)	pH(2)	pH(3)	Time (Fe(VI) Decay)	Filtration Time	CAF Transformation (%)
1	45.5	23.0	2.0	No SiO_2	8.0	8.5	7.3	30 min	1.0 h	29.9 ± 0.4
2	339.0	86.0	3.9	No SiO_2	9.0	9.3	7.5	3.0 h	6.0 h	41.5 ± 0.2
3	535.4	89.1	6.0	No SiO_2	9.3	10.3	8.0	4.0 h	6.0 h	53.0 ± 2.4
4	634.5	78.7	8.0	No SiO_2	9.6	10.3	7.5	4.0 h	8.0 h	60.9 ± 4.1
5	146.8	73.8	2.0	8.0	7.7	7.9	7.5	10 min	45 min	44.5 ± 0.7
6	344.5	87.8	3.9	8.0	8.1	8.3	7.8	30 min	2.0 h	83.2 ± 2.4
7	451.2	90.1	5.0	8.0	8.2	8.4	7.8	30 min	3.0 h	94.3 ± 1.2
8	520.3	87.0	6.0	8.0	8.2	8.6	7.9	35 min	4.0 h	100
9	573.6	82.1	7.0	8.0	8.2	8.7	8.0	40 min	4.0 h	100
10	662.5	82.6	8.0	8.0	8.4	8.8	8.0	45 min	6.0 h	100

pH(1) - Initial pH of Fe(VI)-CAF-SiO_2 mixture; pH(2) - Highest pH reached during the reaction; pH(3) - Final pH before filtration

Table S5.4: Oxidation of CAF by Fe(VI) in the presence of SiO_2 gel: Effect of particle size of SiO_2 gel.

#	[Fe(VI)] (µM)	[CAF] (µM)	[Fe(VI)]:[CAF] (mol/mol)	[SiO_2] (1) or (2) (g/L)	pH(1)	pH(2)	pH(3)	Time (Fe(VI) Decay)	Filtration Time	CAF Transformation (%)
1	152.2	75.1	2.0	8 (1)	7.7	7.9	7.5	10 min	45 min	44.5 ± 0.7
2	344.5	87.8	3.9	8 (1)	8.1	8.3	7.8	30 min	2.0 h	83.2 ± 2.4
3	146.8	73.9	2.0	8 (2)	7.6	7.8	7.5	10 min	45 min	44.2 ± 1.4
4	341.6	87.6	3.9	8 (2)	8.0	8.3	7.8	30 min	2.0 h	85.6 ± 1.3

pH(1) - Initial pH of Fe(VI)-CAF-SiO_2 mixture; pH(2) - Highest pH reached during the reaction; pH(3) - Final pH before filtration; Silica used (particle size (1): 250 – 500 µm; particle size (2): 35 – 75 µm; pore volume: 0.75 cm^3/g; surface area: 480 m^2/g)

Table S5.5: Oxidation of CAF by Fe(VI) in the presence of SiO_2 gel: Effect of pore volume of SiO_2 gel.

#	[Fe(VI)] (µM)	[CAF] (µM)	[Fe(VI)]:[CAF] (mol/mol)	[SiO_2] (1) or (3) (g/L)	pH(1)	pH(2)	pH(3)	Time (Fe(VI) Decay)	Filtration Time	CAF Transformation (%)
1	513.4	85.6	6.0	4 (1)	8.3	8.9	8.0	45 min	4.0 h	100
2	522.8	87.2	6.0	5 (1)	8.3	8.9	8.0	40 min	4.0 h	100
3	517.0	86.1	6.0	6 (1)	8.3	8.8	8.0	40 min	4.0 h	100
4	532.1	89.0	6.0	4 (3)	8.4	9.2	8.0	45 min	5.0 h	96.9 ± 0.8
5	519.2	86.5	6.0	5 (3)	8.3	9.1	8.0	40 min	5.0 h	98.8 ± 1.0
6	530.7	88.2	6.0	6 (3)	8.3	8.9	8.0	40 min	4.0 h	100

pH(1) - Initial pH of Fe(VI)-CAF-SiO_2 mixture; pH(2) - Highest pH reached during the reaction; pH(3) - Final pH before filtration; Silica used (surface area (1): 480 m^2/g; surface area (3): 300 m^2/g; pore volume (1): 0.75 cm^3/g; pore volume (3): 1.15 cm^3/g; particle size: 250 – 500 µm)

Table S5.6: Oxidation of CAF by Fe(VI) in the presence of SiO_2 gel: Effect of nitrogen.

#	[Fe(VI)] (μM)	[CAF] (μM)	[Fe(VI)]:[CAF] (mol/mol)	[SiO_2] (g/L)	pH(1)	pH(2)	pH(3)	Time (Fe(VI) Decay)	Filtration Time	CAF Transformation (%)
O_2	513.4	85.6	6.0	4	8.3	8.9	8.0	45 min	4.0 h	100
N_2	517.8	85.9	6.0	4	8.5	-	9.0	45 min	4.0 h	100

pH(1) - Initial pH of Fe(VI)-CAF-SiO_2 mixture; pH(2) - Highest pH reached during the reaction; pH(3) - Final pH before filtration

Table S5.7: Oxidation of CAF by Fe(VI) in the presence of SiO_2: Effect of ions.

#	[Fe(VI)] (μM)	[CAF] (μM)	[Fe(VI)]:[CAF] (mol/mol)	[SiO_2] (g/L)	[Ion]	pH(1)	pH(2)	pH(3)	Time (Fe(VI) Decay)	Filtration Time	CAF Transf. (%)
1	513.4	85.6	6.0	4	No ion	8.3	8.9	8.0	45 min	4.0 h	100
2	513.2	85.7	6.0	4	4 mM Cl^-	8.1	8.2	7.8	15 min	70 min	100
3	525.3	87.5	6.0	4	2 mM SO_4^{2-}	8.1	8.6	8.0	30 min	4.0 h	100
4	530.2	88.2	6.0	4	1 mM HCO_3^-	8.4	9.0	8.3	45 min	5.0 h	92.4 ± 2.5
5	525.3	87.5	6.0	4	4 mM Na^+	8.1	8.6	8.0	30 min	4.0 h	100
6	523.9	86.9	6.0	4	1 mM Mg^{2+}	8.0	8.2	7.9	15 min	70 min	100
7	513.2	85.7	6.0	4	2 mM Ca^{2+}	8.1	8.2	7.8	15 min	70 min	100

pH(1) - Initial pH of Fe(VI)-CAF-SiO_2-Ion mixture; pH(2) - Highest pH reached during the reaction; pH(3) - Final pH before filtration

Table S5.8: Oxidation of CAF by Fe(VI) in the presence of SiO_2: Effect of Suwannee River natural organic matter (NOM).

#	[Fe(VI)] (µM)	[CAF] (µM)	[Fe(VI)]:[CAF] (mol/mol)	[SiO_2] (g/L)	[NOM] (mg/L)	pH(1)	pH(2)	pH(3)	Time (Fe(VI) Decay)	Filtration Time	CAF Transf. (%)
1	513.4	85.6	6.0	4	No NOM	8.3	8.9	8.0	45 min	4.0 h	100
2	533.5	89.0	6.0	4	5	8.3	8.8	8.0	50 min	4.0 h	88.1 ± 0.4
3	516.1	85.9	6.0	4	15	8.3	8.7	8.0	60 min	4.0 h	68.0 ± 1.1
4	521.0	86.7	6.0	4	30	8.3	8.6	7.8	45 min	4.0 h	36.4 ± 4.0
5	521.9	86.8	6.0	8	30	8.2	8.3	7.7	20 min	4.0 h	46.4 ± 2.7
6	521.5	86.7	6.0	8	15	8.1	8.3	7.7	30 min	4.0 h	74.3 ± 0.7
7	559.6	93.4	6.0	8	5	8.4	8.7	8.1	30 min	4.0 h	96.5 ± 0.5
8	542.8	90.0	6.0	16	15	8.0	8.1	7.7	20 min	4.0 h	84.4 ± 0.5
9	503.6	83.7	6.0	16	30	8.0	8.1	7.6	15 min	4.0 h	67.7 ± 2.5

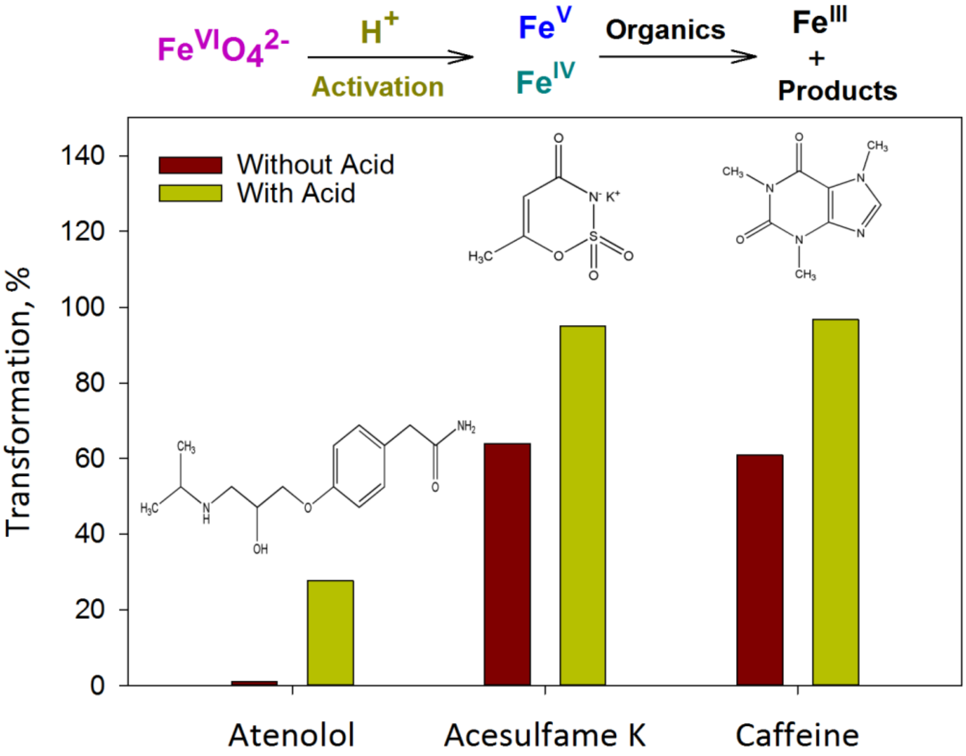
pH(1) - Initial pH of Fe(VI)-CAF-SiO_2-NOM mixture; pH(2) - Highest pH reached during the reaction; pH(3) - Final pH before filtration

Table S5.9: Accurate mass measurements of CAF and its transformation products determined by LC-HRMS.

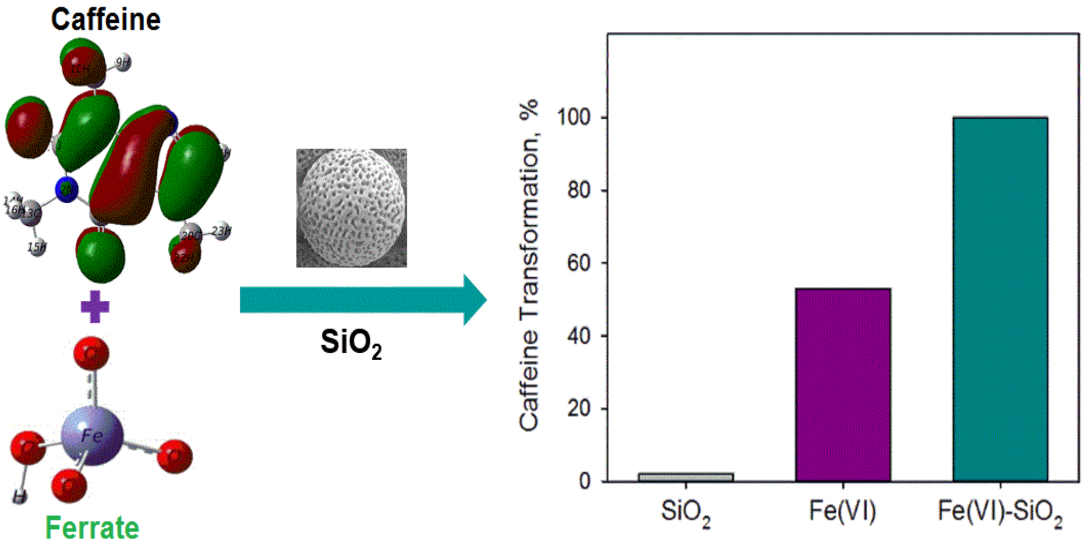
Compound	R_t (min)	Formula $[M + H]^+$	Calculated mass (*m/z*)	Experimental mass (*m/z*)	Error (ppm)	DBE*
Caffeine	2.33	$C_8H_{11}N_4O_2$	195.0877	195.0877	0.25	6
OP1	1.34	$C_4H_9N_2O_2$	117.0659	117.0664	4.67	2
OP2	0.5	$C_2H_7N_2O$	75.0553	75.0562	12.40	1
OP3	0.7	$C_3H_9N_2O$	89.0709	89.0717	8.65	1

* double bond equivalent

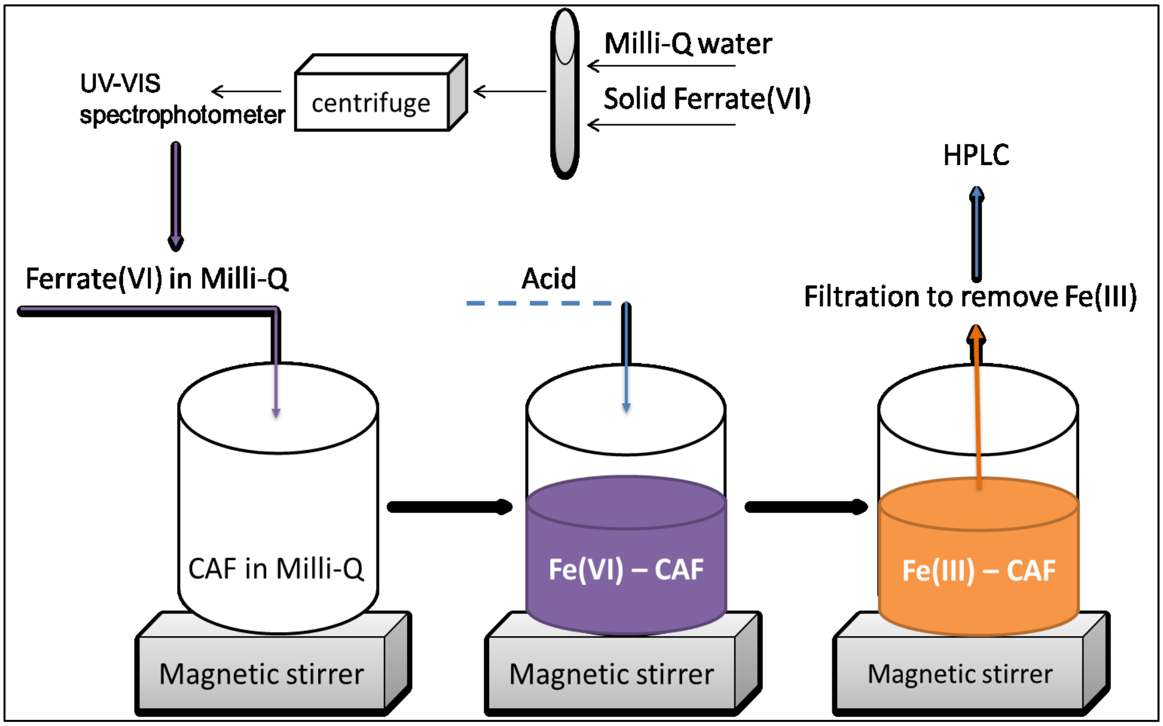
Appendix D: Graphical abstract of Chapter 3.



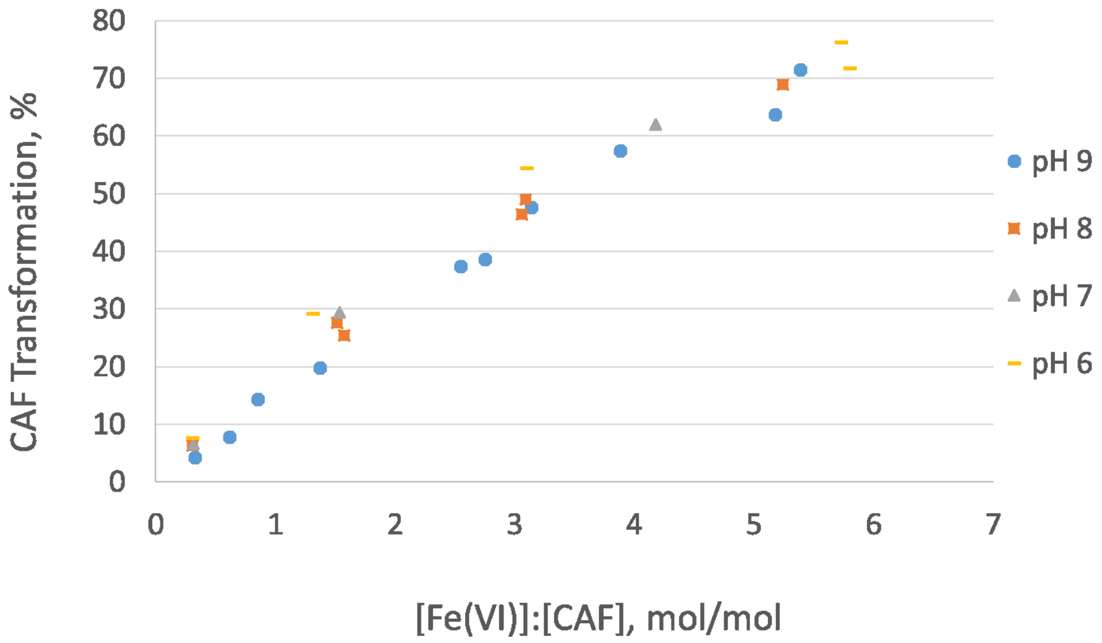
Appendix E: Graphical abstract of Chapter 5.



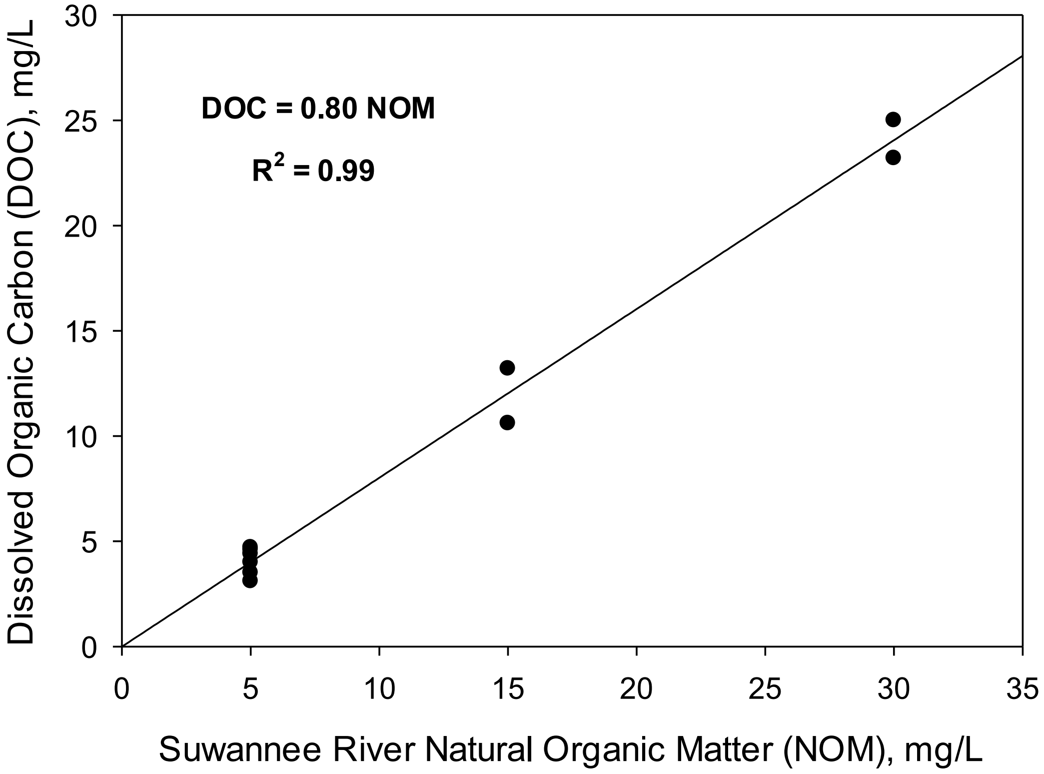
Appendix F: Experimental setup



Appendix G: Effect of Fe(VI) to caffeine molar ratio on the transformation of CAF, when the pH was manually maintained during the experiments using HCl



Appendix H: Correlation between DOC and NOM.



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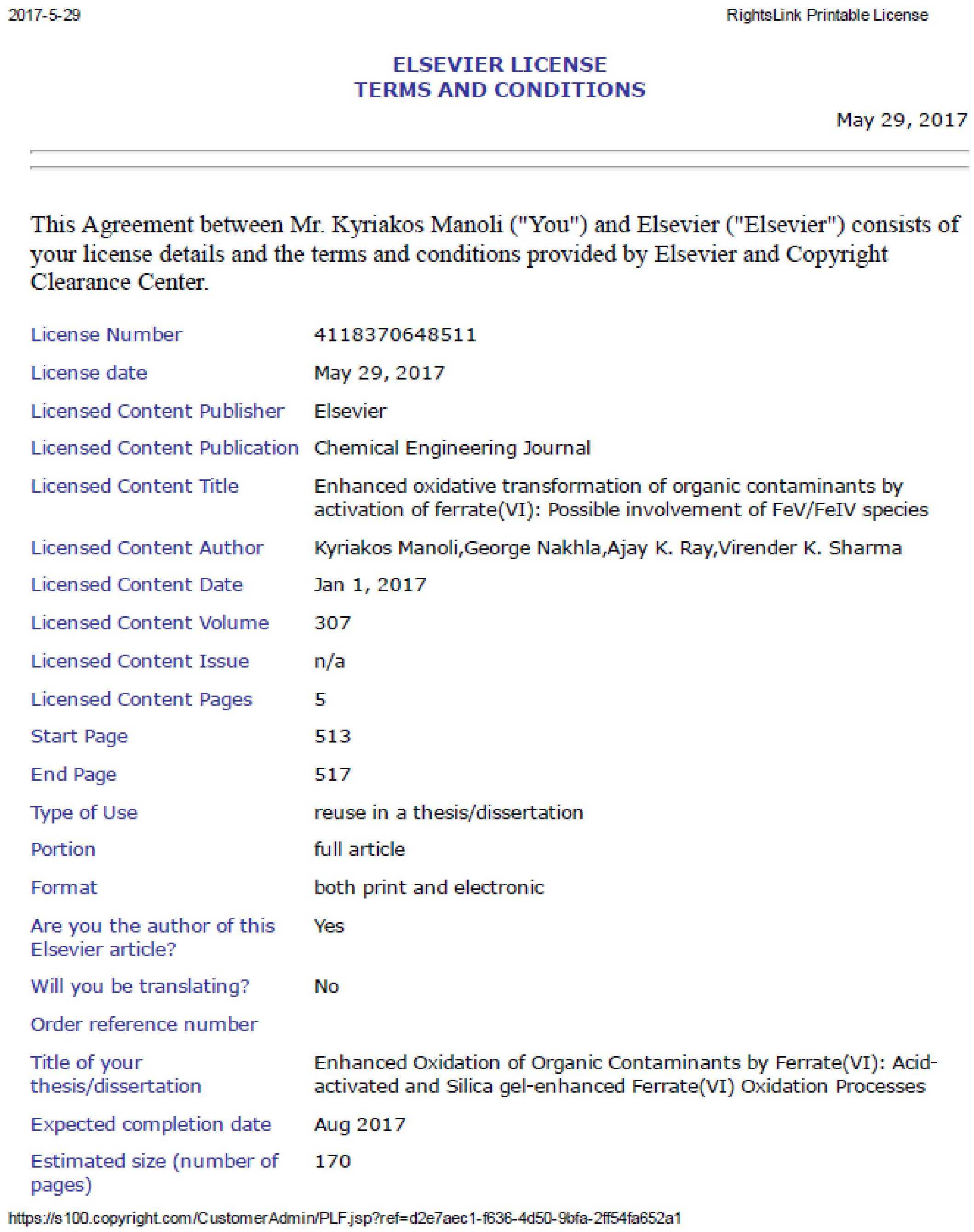

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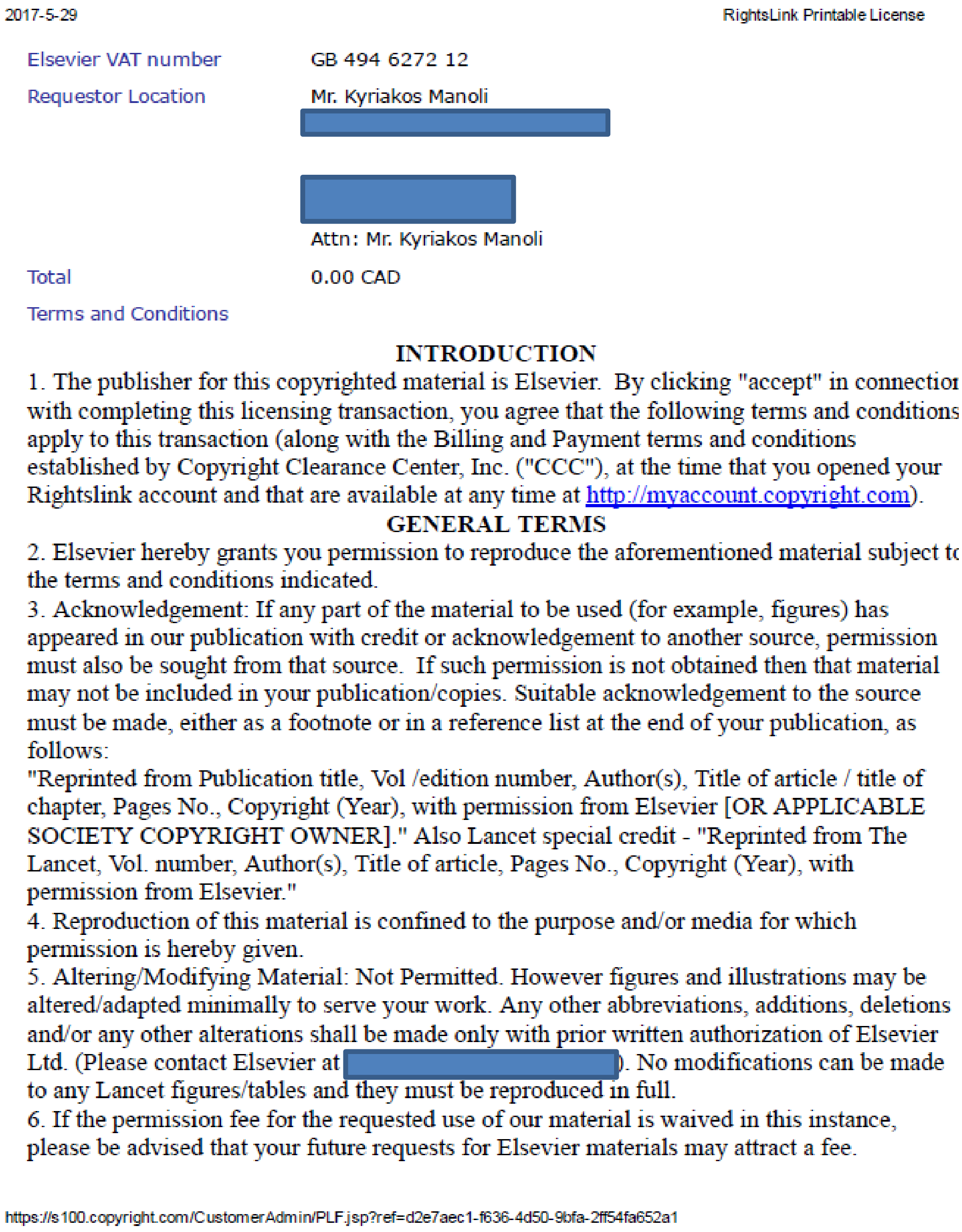

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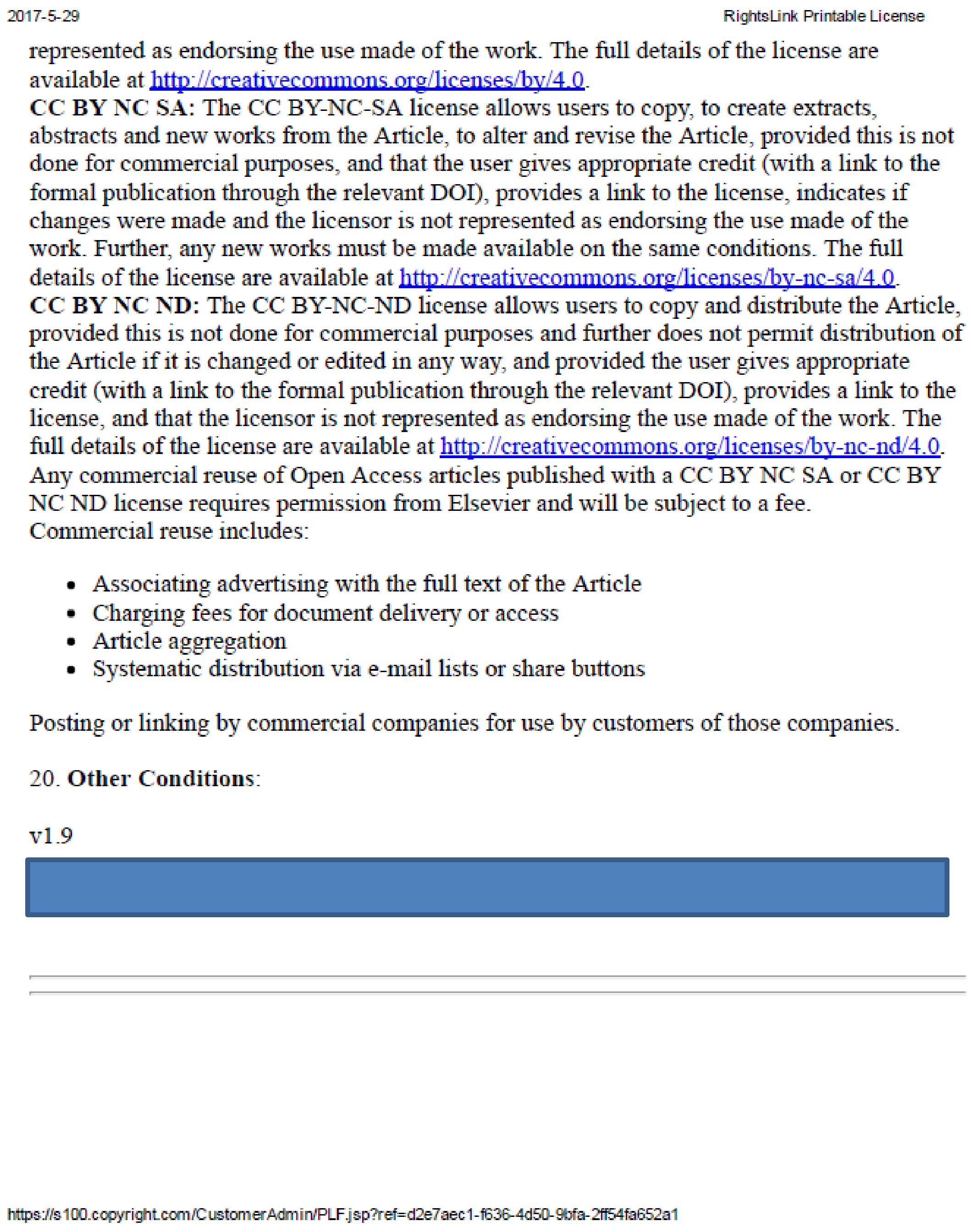

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Curriculum Vitae

Name: Kyriakos Manoli

Post-secondary Education and Degrees:

Aristotle University of Thessaloniki
Thessaloniki, Greece
2007-2012, Five-year diploma equivalent to MEng
Chemical Engineering

The University of Western Ontario
London, Ontario, Canada
2013-2017 PhD
Chemical and Biochemical Engineering

Honours and Awards:

Nominated for the Graduate Student Teaching Assistant Award
Tutorial instructor: i) Reaction Engineering
ii) Mass Transfer Operations
Graduate Student Teaching Assistant Awards Committee
The university of Western Ontario
2016-2017

Session's Best Paper/Presentation Award
2016 AIChE Annual Meeting
San Francisco, CA, USA
Session: Liquid phase reaction engineering
2016

Best Graduate Teaching Assistant Award
Tutorial instructor: Mass Transfer Operations
Awarded by Chem Club (undergraduate student chapter)
The university of Western Ontario
2015-2016

Second place award, Oral presentation
Research Bridges Symposium, Sarnia, Ontario, Canada
2015

The University of Western Ontario Graduate Research Scholarship
2013-2017

Scholarship by the Hellenic Republic,
Scholarships Foundation, Greece
First place among third-year undergraduate students for excellence in studies and ethics
Aristotle University of Thessaloniki
2009-2010

Related Work Experience

Visiting Researcher
City of Toronto, Toronto Water, Ashbridges Bay Treatment Plant
May-August, 2016

Graduate Teaching Assistant
The University of Western Ontario
2013-2017

Graduate Research Assistant
The University of Western Ontario
2013-2017

Chemical Engineer-Intern
Ambrosia Oils (1976) Ltd, Larnaka, Cyprus
Funded by European Union, European Social Fund
July-August, 2011

Conferences

100th Canadian Chemistry Conference and Exhibition
Toronto, ON, Canada
Oral presentation
May, 2017

46th Annual WEAO Technical Symposium & OPCEA Exhibition
Ottawa, ON, Canada
Oral presentation
April, 2017

2016 AIChE Annual Meeting
San Francisco, CA, USA
Oral presentation
November, 2016

Research Bridges Symposium
Sarnia, ON, Canada
Oral presentation
July, 2015

9th Panhellenic Scientific Chemical Engineering Congress
Athens, Greece
Poster
May, 2013

Publications:

K. Manoli, G. Nakhla, A.K. Ray, V.K. Sharma, Enhanced Oxidative Transformation of Organic Contaminants by Activation of Ferrate(VI): Possible Involvement of Fe^{V}/Fe^{IV} Species, Chem. Eng. J. 307 (2017) 513–517. (Paper: Published)

K. Manoli, G. Nakhla, A.K. Ray, V.K. Sharma, Oxidation of Caffeine by Acid-activated Ferrate(VI): Effect of Ions and Natural Organic Matter, AIChE J. (2017). doi:10.1002/aic.15878. (Paper: Published online)

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K. Manoli, M. Ghosh, G. Nakhla, A.K. Ray, A Review on Ferrate(VI) and Photocatalysis as Oxidation Processes for the Removal of Organic Pollutants in Water and Wastewater, Advanced Materials for Wastewater Treatment: John Wiley Scrivener USA. (2017). (Book Chapter: In Press)