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# Sustainable ferrate oxidation: Reaction chemistry, mechanisms and removal of pollutants in wastewater

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## ABSTRACT

This review is intended to evaluate the use of ferrate (Fe(VI)), being a green coagulant, sustainable and reactive oxidant, to remove micro pollutants especially pharmaceutical pollutants in contaminated water. After a brief description of advanced oxidation processes, fundamental dimensions regarding the nature, reactivity, and chemistry of this oxidant are summarized. The degradation of contaminants by Fe(VI) involves several mechanisms and reactive agents which are critically evaluated. The efficiency and chemistry of Fe(VI) oxidation differs according to the reaction conditions and activation agent, such as soluble Fe(VI) processes, which involve Fe(VI), UV light, and electro-Fe(VI) oxidation. Fe(VI) application methods (including single dose, multiple doses, chitosan coating etc), and Fe(VI) with activating agents (including sulfite, thiosulfate, and UV) are also described to degrade the micro pollutants. Besides, application of Fe(VI) to remove pharmaceuticals in wastewater are intensely studied. Electrochemical prepared Fe(VI) has more wide application than wet oxidation method. Meanwhile, we elaborated Fe(VI) performance, limitations, and proposed innovative aspects to improve its stability, such as the generation of Fe(III), synergetic effects, nanopores entrapment, and nanopores capsules. This study provides conclusive direction for synergetic oxidative technique to degrade the micro pollutants.

## 1. Introduction

Urban growth and industrial development have induced a sharp increase in commercial products to fulfil current market demands and, in turn, worldwide pollution (Bhavya et al., 2021; Chen et al., 2018; Satapute et al., 2019). Surface waters contain various micro pollutants including emerging organic contaminants, such as toxic hormonal chemicals, beauty products, and toxins (Gago-Ferrero et al., 2017; Klatter et al., 2017). These micro pollutants have detrimental effects on human health, marine ecosystem, and biodiversity (Jepson and Law, 2016; Yang et al., 2017; Ye et al., 2017). The continued release to the ecosystem of toxins, pharmaceuticals, flame retardants, and pesticides could have undesirable harmful effects on aquatic ecosystems (Kalliora et al., 2018). The long-term use of polluted water comprised with organic pollutant and heavy metals could present a severe danger to human health (Geetha et al., 2021; Shin et al., 2018).

Developing new techniques to remove organic contaminants, mainly pharmaceuticals, especially durable organic compounds, is highly demanding for water treatment (Paidí et al., 2021; Premnath et al., 2021). Different traditional methods, including filtration, adsorption, oxidation, and photocatalytic processes, are limited by comparatively high running costs and unsatisfactory performances. The focus of the current research is to develop renewable technologies that rely on eco-sustainable agents and are highly efficient (Huo et al., 2020; Sharma et al., 2013).

Advanced oxidation processes (AOPs) are distinguished by developing a potent oxidant called strong radical at sufficiently high concentrations to treat water. The target contaminant can be mineralized into CO<sub>2</sub> and H<sub>2</sub>O, which are the most stable conclusive end products of chemical oxidation under appropriate operating conditions, such as ample contact time and concentration. The exceptional concept of AOPs for chemical reactions is that they are thoroughly defined as

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“environmentally friendly” for this purpose (Azbar et al., 2005). It is possible to describe the primary treatment of AOPs in two steps: one is the generation of hydroxyl radicals (OH<sup>•</sup>), and the other is the oxidative reaction of pollutants with the generated radicals. The generation of (OH<sup>•</sup>) might be by using TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>, UV, UV/O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>, and one or two step processes (Pan et al., 2020b; Yonar, 2011).

Advanced oxidation techniques can easily and generally remove hormones, pharmaceuticals, and dyes (Mackul'ak et al., 2013; Yang et al., 2017). An advanced oxidation process comprised with different and unique advanced oxidation techniques for wastewater treatment. For example, the Fenton reaction and ozonation have been commonly useful to remove the toxic organic compounds (Chen et al., 2016; Liu et al., 2016; Liu et al., 2018; Usman and Ho, 2020; Wang and Xu, 2012). Besides, ozone produces additional toxic intermediate as compare to their parent compound (Dar et al., 2019). Permanganate and peroxydisulfate have contributed significantly to chemical reactions, but both oxidation mechanisms rely on pH (Hu and Xia, 2018). Peroxydisulfate, which requires in situ experiment analysis, is reasonably stable at ambient temperatures of ~20 °C (Luo et al., 2017; Luo et al., 2018; Xiao et al., 2017; Xiao et al., 2015). A significant risk of secondary exposure is posed by sulphate and its by-products. Oxidation of permanganate creates manganese oxides, which contributes to pore persevering and decreases the effectiveness of remediation (Li and Schwartz, 2005; Pan et al., 2019). The peroxone mechanism (coupling ozone with H<sub>2</sub>O<sub>2</sub>) is unreliable, leading to handling and storage issues (Fuerhacker et al., 2001; Zhu et al., 2015).

Use of advanced oxidation processes have received significant attention among the scientific community to remove organic micro pollutants. However, traditional advanced oxidation techniques (like Fenton oxidation, persulfate reagent) face certain limitations such as pH and temperature dependence, toxic intermediates, prolonged reaction time, high cost, handling, and storage issues. At the same time, Fe(VI) oxidation has been recognized as a green technology with non-toxic intermediates and quick treatment. There are several Fe(VI) application methods in reaction system (including single dose, multiple dose and encapsulation), which need to be addressed for more progressive implication. Even, Fe(VI) implication to degrade pollutant is inevitably complex. Our notion is to elucidate the fundamentals, reaction chemistry, reaction mechanism and to highlight emerging trends in Fe(VI) degradation.

Recently author reported the review article related to sewage sludge

treatment (SST) with Fe(VI), they highlighted the Fe(VI) contributions related to SST including (sludge minimization, dewatering, anaerobic fermentation and removal of pollutant. The authors conclude with these remarks that stability concern should be overcome and the in-situ preparation can reduce the manufacturing cost (Hu et al., 2020).

Topics covered in this review are the basic dimensions of Fe(VI), reaction mechanism, Fe(VI) implications, and Fe(VI) involvement to remediate various drugs. We briefly described the Fe(VI) efficacy by using different implication methods, such as single dose, multiple-dose, and encapsulation. Also, we highlighted the advancement in Fe(VI) oxidation and engraved various activation agents coupled with Fe(VI). Basic queries include: how to stabilize Fe(VI) for complete degradation? How to coupled Fe(III) radical, which are more reactive than Fe(VI)? Which activation agent is more reactive and productive? How photo generated electron contributes synergetic effect to Fe(VI)?

## 2. Advanced oxidation processes

The explanation of advanced oxidation techniques comprising their specific characteristics, generated radical, redox potential and their limitation has been provided in Table 1. According to these finding, Fenton having more redox potential as compared to other techniques with pH-based limitations. Besides, KMnO<sub>4</sub> having the least redox potential with the limitation of acid content enhancement.

Fe(VI) is, therefore, an efficient and attractive agent for treating different organic compounds in water (Sharma et al., 2011). Fe(VI) is the principal ingredient to degrade the organic pollutant. This is a thoughtful approach since there is a significant consistency of compounds (high valent iron) in aqueous solution. It is a well-known fact, from the other side, that Fe(V) is more sensitive as compare to Fe(VI) (Sharma et al., 2013).

### 2.1. Basic dimensions of Fe(VI)

Fe(VI) is the inorganic anion with the chemical formula [FeO<sub>4</sub>]<sup>2-</sup>. It is sensitive to light, gives light violet colour to a solution, and is one of the most effective water-stable oxygen species (Yang et al., 2017). Fe(VI) can be castoff as an environmental treatment for drinking water and wastewater (Evgenidou et al., 2015). Fe(VI) electrochemical procedure can be called a “natural” and simple solution since it usually requires a one-step reaction to convert of Fe (0) into Fe(VI) for the oxidation,

**Table 1**

Elucidation of advanced oxidation techniques with their specific characteristics, including generated radical, redox potential, and limitations.

Reagent	Active species	Redox potential	Reaction mechanism	Limitation	Reference
Fenton	•OH.	•OH/H <sub>2</sub> O = 2.73 V	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-}$ $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+}$ $\equiv Fe(III) + H_2O_2 \rightarrow \equiv Fe(II) + HO_2^{\bullet} + H^{+}$ $\equiv Fe(II) + H_2O_2 \rightarrow \equiv Fe(III) + HO^{\bullet} + OH^{-}$	<ul style="list-style-type: none"> <li>pH dependence (pH = 3.0)</li> <li>The generation of Fe(OH)<sub>2</sub> increases the pH till pH = 4.0.</li> <li>Ferric hydroxide residual sludge</li> </ul>	(Zhu et al., 2020; Zhu et al., 2019)
Ozone	•OH	2.07 V	$PhOH (PBP) + O_3 \rightarrow PhOH + O_3^{\bullet-}$ $O_3^{\bullet-} \rightarrow O_2 + O^{\bullet}$ $OH^{\bullet} \rightarrow O^{\bullet-} + H^{+}$ Or $O_3 + H_2O \rightarrow OH^{\bullet} + O_2$	<ul style="list-style-type: none"> <li>It produces more toxic intermediate than the mother compound.</li> <li>Highly toxic</li> <li>Handling precaution</li> <li>Handling issue</li> <li>Use with UV and Ozone</li> <li>Simplified process</li> <li>Increase the acid content and temperature</li> </ul>	(Wu et al., 2020a) (Dar et al., 2019)
Hydrogen peroxide	2H <sup>+</sup> , 2e <sup>-</sup>	1.77 V	$H_2O_2 \rightarrow O_2 + H_2O$ $H_2O_2 + 2e^{-} \rightarrow 2H_2O$	<ul style="list-style-type: none"> <li>Use with UV and Ozone</li> <li>Simplified process</li> </ul>	Grote (2012)
KMnO <sub>4</sub>	OH <sup>-</sup> , Mn <sup>2+</sup> , MnO <sub>4</sub> <sup>-</sup>	1.55 V (acidic), 0.58 V (neutral/ slight alkaline), 0.56 (alkaline)	$Phenol + 2MnO_4^{-} + 6 H^{+} \rightarrow Phenol + 2Mn^{2+} + 8H$ $Phenol + 12MnO_4^{-} + 36 H^{+} \rightarrow Intermediate + 12 Mn^{2+} + 23H_2O + CO_2 + Complex$		Shi et al. (2015)
Persulfate	SO <sub>4</sub> <sup>•-</sup> , •OH.	2.01 V	$S_2O_8^{2-} + activators \rightarrow 2SO_4^{\bullet-}$ $SO_4^{\bullet-} + H_2O \rightarrow HO^{\bullet} + SO_4^{2-} + H^{+}$ $S_2O_8^{2-} + H_2O \rightarrow HSO_5^{-} + HSO_4^{-} HSO_5^{-} + H_2O$ $\rightarrow H_2O_2 + HSO_4^{-} H_2O_2 + 2HO^{\bullet}$ $2 HO^{\bullet} \rightarrow 1/2 O_2 + H_2O$	Activation agent required	Cai et al. (2018)
Chlorine	•OH, •Cl, HOCl	1.36 V	$Cl_2 + H_2O \rightarrow HCl + HOCl$ $HCl + HOCl \rightarrow 2H^{+} + Cl^{-} + ClO-2HClO \rightarrow 2HCl + O_2$	By-product formation	Grote (2012)

without dangerous or costly chemicals (Evgenidou et al., 2015).

Molecular Fe(VI) and its water treatment mechanisms: Fe(VI) is usually a dark red powder crystal with a slight metallic luster, which is very soluble in water from a deep purple to violet colour solution. Fe(VI) can be used at the same time as an oxidant, disinfectant, adsorbent, flocculant, coagulant aid, and bactericide, flocculation, sterilization, adsorption as one of the multi-functional high-efficiency water treatment oxidants (Jiang and Lloyd, 2002). Fe(VI) has many applications in water treatment as a highly efficient multifunctional water treatment agent. (Jiang et al., 2016).

At acidic or neutral pH values, the Fe(VI) anion is fragile, decomposing to iron (Fe(IV)). The decrease passes through degradation products, in which iron has Fe(V) and Fe(IV) oxidation states, which are extra responsive as compare to Fe(VI) (Sharma, 2013). In alkaline conditions, Fe(VI) is soluble, and stays reactive at a pH 8.0 or 9.0 for around 8–9 h (Sharma, 2012). Fe(VI) under an acidic environment has a typical reducing potential of 2.20 V and is substantially more than that of ozone (2.08 V) (Sharma, 2012). Fe(VI) is susceptible to reactions of degradation, which leave no substitute in treated water. Fe(VI) has been used for multipurpose purification (Jiang, 2014) like a wide variety of microorganisms (e.g. pathogen MS2 and *Escherichia coli*) (Prucek et al., 2013), micropollutants (e.g., endocrine disruptors and antimicrobials) (Casbeer et al., 2013), poisonous metals (e.g. cadmium and arsenic) and phosphates (Jiang, 2014; Sharma et al., 2013). Fe(VI) is also able to provide a high degree of fecal coliform inhibition at very low doses through a reasonable disinfection rate of >99.9% (Jiang and Lloyd, 2002; Jiang et al., 2006). Fe(VI) are wonderful antibiotic salts that can remove viruses (Lee et al., 2014). Fe(VI) has also established promising potential for treating N-nitrosodimethylamine (NDMA) catalysts, thus reducing the risk for NDMA formation (Lee et al., 2008). One of Fe(VI) 's vital benefits is that if the water sample produces bromide ions, it can reduce possible carcinogenic bromate ions (Sharma et al., 2011).

Although chemicals like chlorine (Cl<sub>2</sub>) may kill certain microorganisms such as anthrax, it can also contain disinfectant waste materials (DBPs), which may pose a danger to human health (Sharma, 2004). Therefore, over chlorine, various antiseptics (e.g., ozone) were given preference. However, it is understood that these substitutes shape multiple other waste material products, which also harmed individuals and aquatic animals to some point (Jiang et al., 2007). Over the previous two decades, considerable effort has been made to develop Fe(VI) approaches to degrade microorganisms, dyes, inorganic contaminants, and aquatic entertainment to address these problems (Jiang et al., 2013; Sharma, 2004). Water clean-up is susceptible to coagulation and oxidation/decontamination (Jiang et al., 2006). The Fe(VI) ion has become an excellent disinfectant because of its oxidising force (Gilbert et al., 1976). The abridged *Escherichia coli* (*E. coli*) levels were studied after addition of Fe(VI). It has a high oxidising ability relative to traditional disinfectants at 4.2–6.0 mgL<sup>-1</sup> concentrations, with a disinfectant potential as strong as mono-chloro amine. There was a 99 % reduction in coliforms among the effects of this analysis. Fe(VI) is a composition, which can act for heavy metals and suspended materials as an oxidant, biocide, and flocculant. In addition to molecular oxygen, no harmful residues are left in the treated water (Licht et al., 2008).

In contrast to other advanced oxidation techniques, Fe(VI) crops a small amount of sludge, which removes other toxins and makes additional sludge treatment convenient for use (Diak and Örmeci, 2016; Zhang et al., 2016). Fe(VI) oddly exhibit coagulating features as toxins are oxidised simultaneously. For coagulation, pH: 7.0 could be optimal as the oxidation rate decreases more as the pH value increases, as shown in a study (Sharma, 2004). Some researchers tried to boost the behaviour of Fe(VI) at a limited/acidic pH (Manoli et al., 2017a; Manoli et al., 2017b). Fe(VI) was mixed with ferric chloride in a new analysis to handle 12 different natural water forms (Jiang et al., 2016). This Fe(VI), employing the coagulation process, it was a rational system in which organic matter was removed from the water sources, which showed that Fe(VI) operated as the coagulant for wastewater and water treatment.

There are some other favourable properties for Fe(VI), including the production of a few waste products, a lack of microbial or toxin by-products, the capacity to generate stable salts, and a high oxidising strength across the entire pH spectrum. In various climate applications, these properties make it a “greener” tool. Mutagenic and carcinogenic compounds can occur with traditional and less eco-sustainable chemicals along with significant human health consequences. As discussed, the amputation of antibiotics or drugs using Fe(VI) is still in remediation's highlight, and additional research in this field is required. The usage of Fe(VI) as a solid oxidant for the elimination of bio-contaminants is also essential for the following purposes (Jiang et al., 2006; Norcross et al., 1997), coagulant for disabling infectious microorganisms (Jiang et al., 2003; Jiang et al., 2006), and as a way of removing inorganic contaminants, colloidal and metals particles in particular (Jiang et al., 2003).

## 2.2. Ferrate application methods

There are numbers of methods to add/use Fe(VI) in the reaction system, such as single dose (once in a reaction system), multiple-dose (step by step addition), and encapsulation (coating by different agents) method. Single dose application leads to quick degradation, but it may skip the necessary information about reaction mechanism and intermediate. Besides, multiple doses help to generate more and conclusive information about reaction mechanism and intermediates. While slow and conclusive release of Fe(VI) can also be achieved by encapsulation. By following these concerns, Table 2 provides the details, including their method, targeted compound, degradation rate, and limitations.

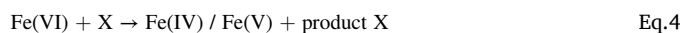
## 2.3. Reaction mechanism of Fe(VI)

Fe(VI) is an environment friendly, water-processing oxidant and chemical capable of performing a twofold oxidation and disinfection role. Although, Fe(VI) is relatively stable, Fe(IV) & Fe(V) species decline in seconds, depending on the reaction system (physical and chemical conditions) (Lee et al., 2014). Fe(VI) interacts with organic contaminants by  $\pi$ - $\pi$  interaction, while Fe (IV) or Fe (V) were the main oxidative agents during the reaction, as they have more redox potential than Fe (VI). It is a well-known fact, from the other side, that Fe(V) is more sensitive as compare to Fe(VI) (Sharma et al., 2013).

Different pathways may explain the reactivity of Fe(VI) for the deprivation of contaminants (X). The first option is the reduction of Fe (VI) to Fe(V) by radical-forming electron transfer mechanism (Eq. 1). Another direction is that the transition of two electrons produces radicals (Eq. 2) or dimers (Eq. 3). The radical species formed during reaction may further react with Fe(VI) (Eq. 4). Lastly, it is possible to detect oxygen atom transfer (Eq. 5) (Sharma, 2002). For example, this process has been reported for Fe(IV) and phenylhydroxylamine-forming aniline (Lee et al., 2005). Reactions concerning the pollutant (X) mentioned in Eqs. 1–5. In addition, Fe(VI) self-decomposition can occur, proceeding to the generation of species of Fe(V), Fe(IV), and reactive oxygen including O<sub>2</sub><sup>-</sup>, H<sub>2</sub>O<sub>2</sub> as well. Reactive oxygen species may be intricately in the pollutant degradation.



or



Fe(VI) responds hastily with organic medieties (electron rich)

**Table 2**

The methodology of ferrate application with their reaction conditions, including the type of pollutant, degradation rate/time, and limitations.

Method	Pollutant	pH	Degradation rate	Molar ratio (Fe (VI)/Pollutant)	Degradation time	Limitation/remarks	Reference
Single Dose	Bisphenol F	6.0–10.0	$2.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ to $1.2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$	10:1	5 min	<ul style="list-style-type: none"> <li>Quick degradation can be observed in few early seconds (30 s); this may skip the necessary information regarding reaction intermediate.</li> <li>More the Fe(VI) dose more the degradation, more residual as well.</li> </ul>	Yang et al. (2020)
Multiple Dose	Fluoroquinolone antibiotics	7.0		single addition multiple addition Fe(VI): FLU	40:1 5:1 10 min (85 % removal) 80 min (complete removal)	<ul style="list-style-type: none"> <li>Complicated reaction setup.</li> <li>Time-consuming</li> </ul>	Feng et al. (2016)
Encapsulation/ material Chitosan	Methyl orange	6.5		5 mg L <sup>-1</sup>	80 %	<ul style="list-style-type: none"> <li>Acidic medium required to engulf the encapsulated pallet/Fe(VI).</li> <li>High concentration of chitosan required to maximize the efficiency (2 % chitosan).</li> <li>Buffering agent required (petrochemical) which may enhance pollution.</li> <li>Characterization tools required for assessment.</li> <li>Time consuming</li> </ul>	Chen et al. (2019)
Ethyl cellulose and paraffin	2-sec-butyly-4,6 dinitrophenol	6.5		93 %	80 min	<ul style="list-style-type: none"> <li>Paraffins are saturated hydrocarbon, and categorically not in green material.</li> <li>Characterization tool required.</li> <li>Degradation influencing by coating to ferrate ratio.</li> <li>Time consuming and complex methodology.</li> </ul>	Wang et al. (2009)

including amines, anilines, phenols, olefins, etc (Shi et al., 2015). Besides, adsorption may occur on Fe(VI)'s precipitating reaction items. Besides, not only basic hydrocarbons, chlorinated ethylene, phenol, and also multifaceted organic contaminants with a more complex composition were examined for the reactivity of Fe(VI) (Yang et al., 2020).

The main reaction between organic pollutants and Fe(VI) is electron transfer between pollutants and Fe(VI). As Fig. 1 revealing, the reaction mechanism of Fe(VI) with organic pollutants mainly includes 1-e-or 2-e<sup>-</sup> transfer mechanism/processes. 1-e-transfer of Fe (VI) to Fe (V), 2-e-Fe (IV) was formed by the transformation. The intermediate valence Fe (V) & Fe (IV) can also continue to undergo 1-e- & 2-e-transfer to generate a lower valence. However, dissolved oxygen often exists in water, so the end product of Fe(VI) reaction is Fe(OH)<sub>3</sub>. The mechanism of Fe(VI) oxidation is explained from three aspects: (1) the second-order reaction rate constant: fitting the kinetic experimental results; (2) stoichiometric method: reasoning according to the stoichiometric ratio of Fe (VI) to X and the number of electron gains and losses; (3) the reaction products were identified by modern precise analytical instruments (Sharma et al., 2015).

Fe(VI) degradation of organic compounds mainly involve nitrogen-containing and sulfur-containing compounds, amines, phenols, and alcohols. The second order reaction rate constants of several substituted phenols, 17β-estradiol, 17α-ethinylestradiol, and bisphenol-A were determined with the change of pH (6.0–11.0). The results showed that the *k* of three endocrine disruptors fluctuated from  $6.4 \times 10^2$  to  $7.7 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  with pH 7.0. (Lee et al., 2004), (Sharma et al., 2015). Some phenolic substances are between  $6.6$  and  $3.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , which fully shows the capacity of Fe(VI) oxidation of phenolic endocrine disruptors. Yang et al. (2014) studied the reaction kinetics, mechanism and toxicity evaluation, and assessed the potential of Fe (VI) to degrade tetrabromobisphenol A (TBA). The results show that the second order reaction rate constant among Fe(VI) and tetrabromobisphenol A is  $7.9 (\pm 0.3) \times 10^3$  to  $3.3 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$ , with half-life of 1.7 s–419.3 s in the

range of pH 7.0–10.0. Compared with BPA, Fe(VI) is easier to oxidize TBBPA. Fe(VI) can abolish, and convert TBBPA molecules by β-fracture reaction, and produce low brominated products (Yang et al., 2014).

According to the product analysis (Fig. 2), Fe(VI) oxidizes the phenol part of tetrabromobisphenol-A through an electron transfer mechanism. In the first step, a phenoxy radical and Fe (V) is generated. The phenoxy is immobilized by the electron resonance effect and forms the free radical R1, and then the self-made radical R-1 forms a new free radical R-2, R-2 through β-cleavage (cleavage between the benzene ring and the isopropyl). Free radicals react with H<sub>2</sub>O and CH<sub>3</sub>OH to generate corresponding products A & B (Yang et al., 2014).

Zhou and Jiang (2015a) studied the kinetics of diclofenac (DCF), sulfamethoxazole (SMX), bezafibrate and carbamazepine oxidation by Fe(VI) with varying pH from 6.0 to 9.0 and Fe(VI) dose from 1 to 5 mg L<sup>-1</sup>. The results revealed that bezafibrate (BZF) degeneration was less than 25 %, with the second order reaction kinetics. The outcome of pH on the degradation efficiency of four substances was different. The second order reaction rate constants at pH 8.0 and 9.0 are  $360 \pm 17$  and  $1.26 \pm 0.02 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. Meanwhile, the second order reaction rate constant with bezafibrate is less than  $0.5 \text{ M}^{-1} \text{ s}^{-1}$  at pH = 8.0 & 9.0 (Zhou and Jiang, 2015b).

Besides, the oxidation intermediates of sulfamethoxazole and diclofenac were recognized, and the possible conversion path was speculated, but the products of bezafibrate were not noticed. In the reaction process, Fe(VI) attacks the amino nitrogen of sulfamethoxazole, leading to the hydrogen extraction reaction and oxygen insertion reaction, and the hydroxylation reaction. At the same time, through oxygen transfer, the attack amino acid part leads to the formation of nitrobenzene derivatives (Fig. 3). When Fe(VI) attacks the amino part of diclofenac, it lead to mono aromatic ring products, decarboxylation can also occur, leading to the formation of amino quinone derivatives. Besides, hydroxyl substitution reactions occur in aromatic ring and side-chain to generate dihydroxylated products (Fig. 4) (Zhou and Jiang, 2015a).

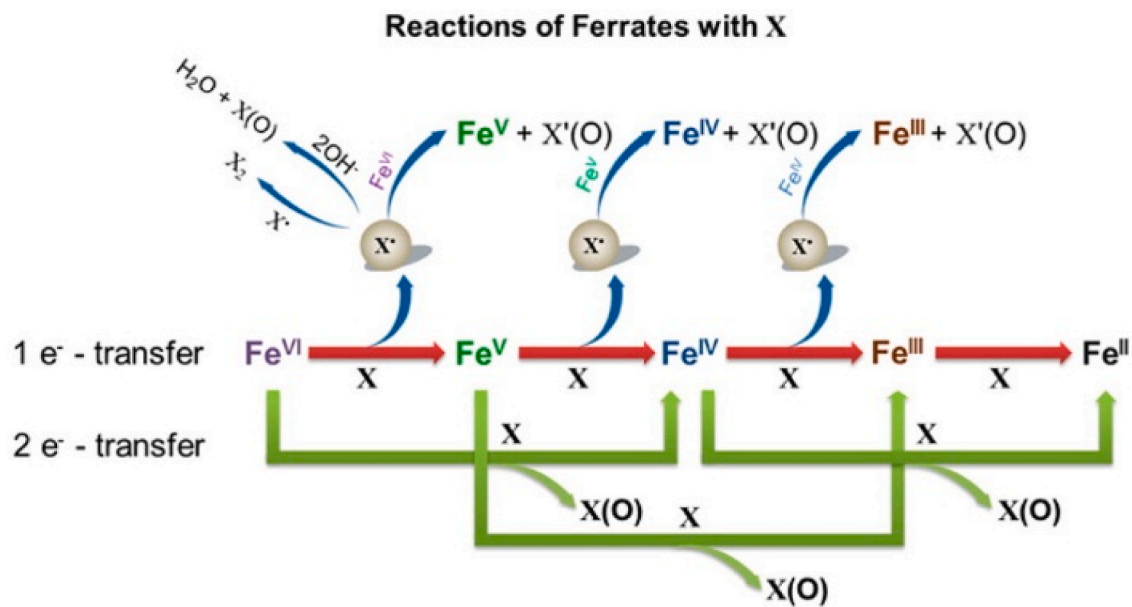


Fig. 1. Possible reaction steps of Ferrate oxidation compound (x) (Lee et al., 2004).

Fe(VI) can react with organic contaminants as follows:

- (i) Fe(V) & Fe(IV) leads additional reactions to organic pollutants.
- (ii) Fe(VI), Fe(V) and Fe(IV) self-decomposition of organisms.
- (iii) Reactive oxygen species including ( $\cdot\text{O}_2^-$ , and  $\text{H}_2\text{O}_2$  generated from self-degradation/decompositions (e.g.,  $\text{Fe(VI)} + \text{Fe(II)} \rightarrow \text{Fe(V)} + \text{Fe(III)}$  and  $\text{Fe(II)/Fe(III)} + \text{O}_2/\text{H}_2\text{O}_2 \rightarrow \text{Fe(IV)/Fe(V)}$ ) (Sharma et al., 2015).

### 3. Recent advancement of ferrate

There are number of methods elucidated in the last forty-five years. Some of them belong to sustained-release (single and multiple-dose), in-situ activation (encapsulated, activation by reagent and UV); detail of these is given in Fig. 5. The mentioned data in Fig. 5, is extracted from

the web of science on 06-June-2021.

#### 3.1. Catalytic activation of Fe(VI)

The oxidative capability of Fe(VI) was extremely reliant on pH, water nature/constituents, and contamination level (Feng et al., 2016). Fe(VI) amplification or catalysis has recently been put forward to improve the oxidation of organic contaminants (Feng and Sharma, 2018) (Manoli et al., 2017a) (Sun et al., 2019). For example, acid activation of Fe(VI) (e.g. HCl) may facilitate the oxidative transition to the development of the intermediate iron species (Fe(V)/Fe(IV)) of micropollutants (Ghosh et al., 2019; Manoli et al., 2017b). The radical sulphate and hydroxy radical were the major oxidants in a detailed analysis during the Fe(VI)/per-oxymonosulfate reaction (Wu et al., 2018). The agents that inhibit one and two electrons showed accelerated ferrate (VI) toxin

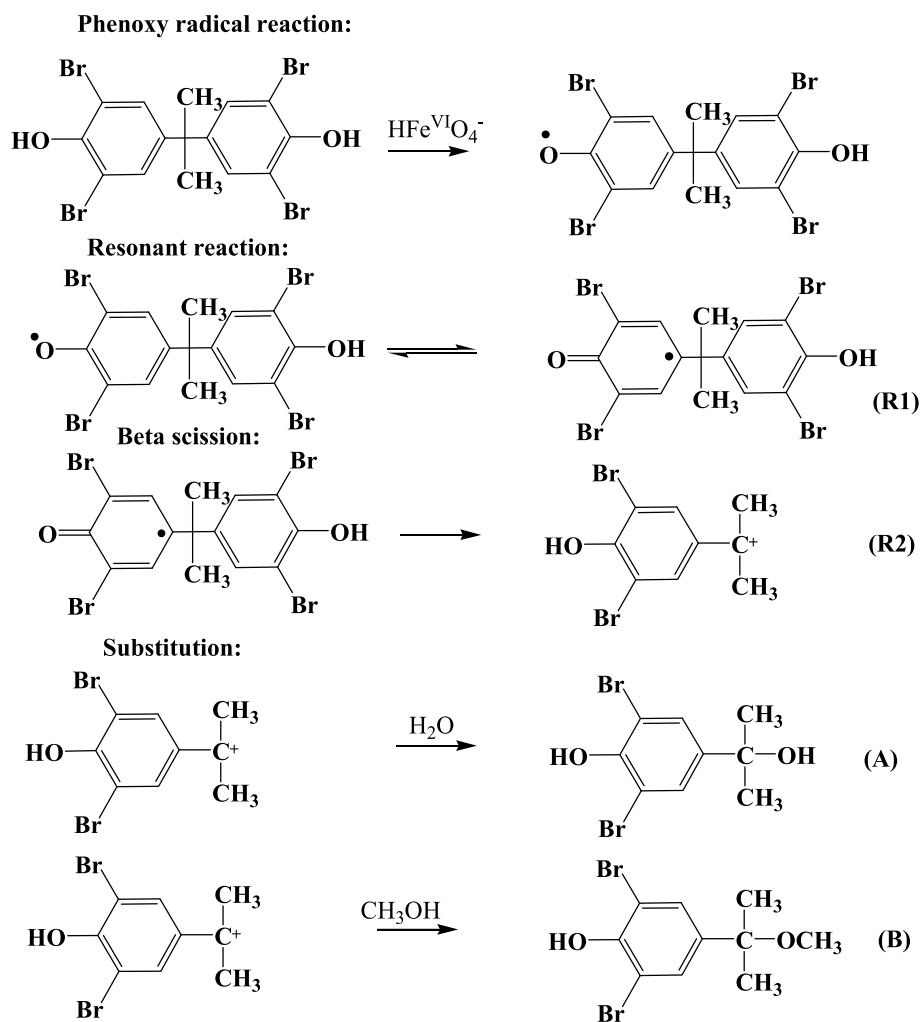


Fig. 2. Projected reaction pattern for oxidation of tetrabromobisphenol A by Fe (VI) (Yang et al., 2014).

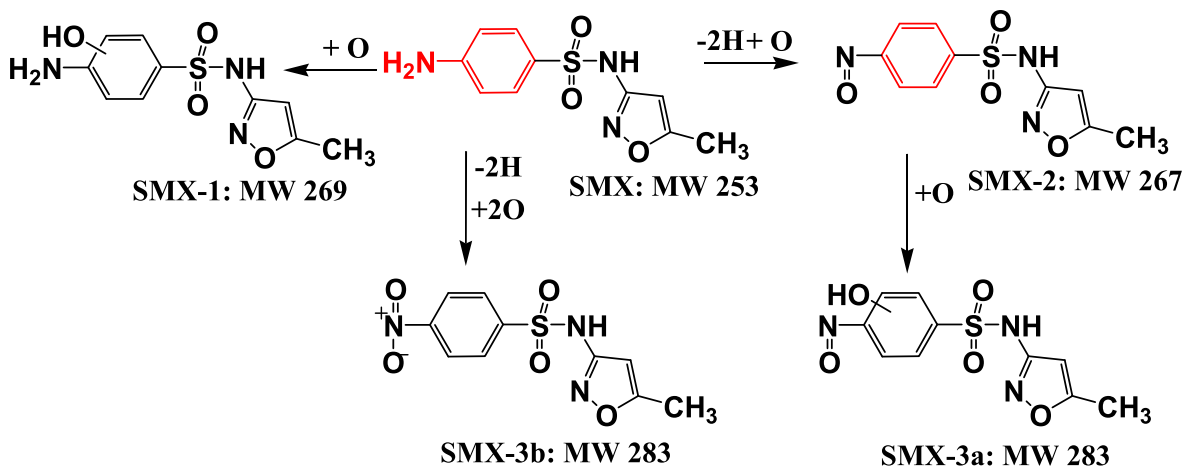


Fig. 3. Reaction degradation pathways of sulfamethoxazole by Fe (VI) (Zhou and Jiang, 2015b).

oxidation in the 30s. In general, there is limited information regarding activation by Fe(VI), yet efficient methods for growing Fe(VI) oxidation still need to be developed (Feng et al., 2018). Recent advancements elucidating the different activation agents to activate Fe(VI) are presented in Table 3. Carbonaceous materials act as emerging UV catalyst, which help Fe(VI) by generating electron, which couple with Fe(VI) and

produce synergistic effects. Besides, carbonaceous material act as absorber which may help to ferrate for greater stability (Ali et al., 2020; Wang and Hu, 2014). This is very obvious and reported that Fe(VI) generates one or two electron, these generated electron contribute with electron produced by UV, and synergistically they contribute for comprehensive degradation.

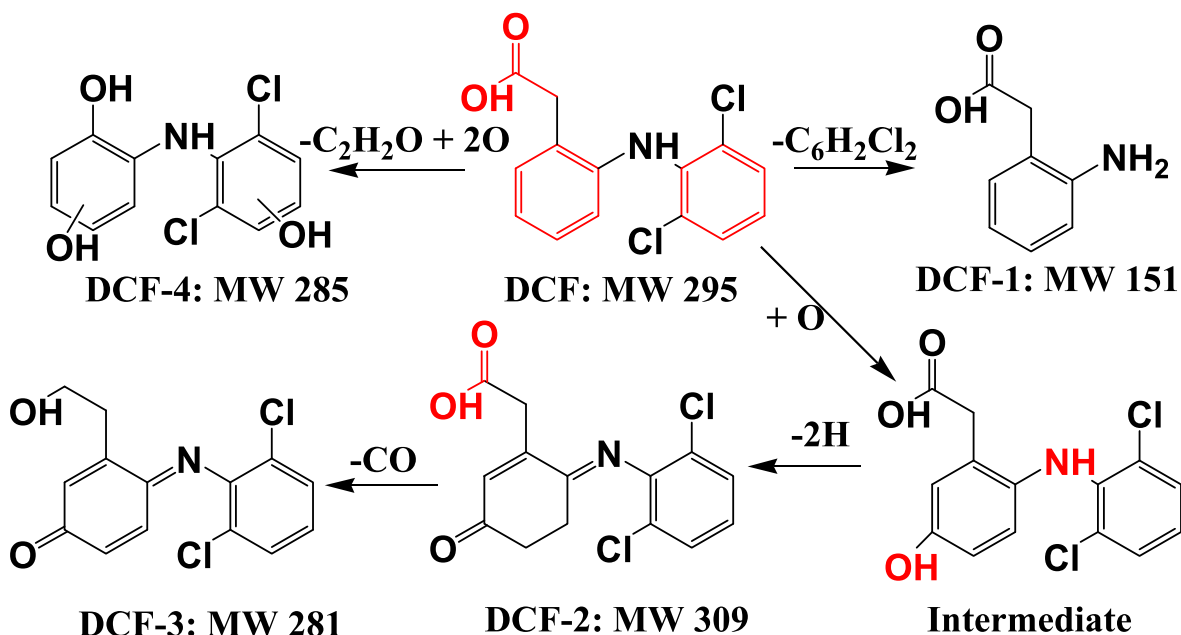


Fig. 4. Reaction degradation pathway of diclofenac by Fe (VI) (Zhou and Jiang, 2015b).

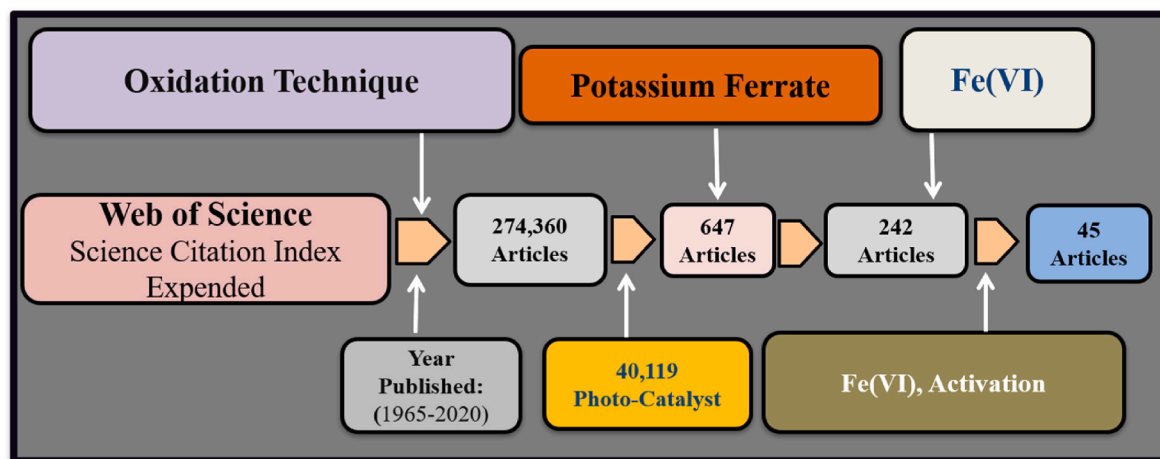


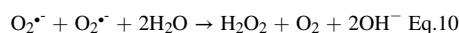
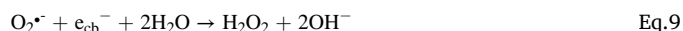
Fig. 5. Recent advancement in ferrate oxidation from 1965 to 2020.

### 3.1.1. Catalytic oxidation of ferrate by using ultraviolet light

Through UV light, Fe(VI) reduction was achieved with the consecutive formation of the single-electron transfer point, Fe(V), Fe(IV) and Fe(III). In comparison, the redox potential of Fe(III) and Fe(V) are more higher than Fe(VI) (Sharma et al., 2013). Photocatalysis was proposed as an eco-friendly and efficient process, to increase the oxidation capacity of Fe(VI) for organic pollutants (Chen et al., 2015) (Luo et al., 2019; Matafonova and Batoev, 2018) (Talaiekhosani et al., 2016). These studies suggested that Fe(V), a Fe(VI) reduction agent through ultraviolet light, may be the most reactive species. In addition to Fe(V), active UV/Fe(VI) oxidation species were also inferred from  $\cdot\text{OH}$  (Aslani et al., 2017).

The degradation pathways of UV oxidation have been in the following sequence: UV/Fe(VI) > UV/chlorinated > UV/H<sub>2</sub>O<sub>2</sub> > UV/PS > UV/TiO<sub>2</sub> > UV/PMS. The UV/PMS, UV/TiO<sub>2</sub> methods and UV/PS methods were poorly prepared for the degradation phase, and the UV/E2 (estradiol) phase displayed mild degradation, whereas the phase of degradation was greatly increased by UV/chlorine process (Chuang

et al., 2019; Mboula et al., 2015). The new technique for water purification can therefore be established UV/Fe (VI) oxidation. The general proposed reaction mechanism is given in Eq. 6 to Eq. 12. The generated radical in the below equations will facilitate the Fe(VI) process.





**Table 3**

Activated Fe(VI) treatment performance for the degradation of different organic pollutants, including pharmaceuticals.

Sr No.	Compound name	Activation agent	Incubation time	Optimal pH and reaction temperature	Reaction condition	Results	Reference
1	Carbamazepine (CBZ)	K <sub>2</sub> FeO <sub>4</sub> with carbonaceous materials	30 min	pH: 9.0, time: 25 ± 1 °C	Fe <sup>VI</sup> O <sub>4</sub> <sup>2-</sup> in the presence of five carbonaceous materials (C.M.s) (i.e., G.O., hydrochar, rGO, graphite, and fullerene)	Removal efficiency; 30 %	Pan et al. (2020a)
2	DCF (2,6- dichlorophenyl)	Hydrochar and graphene oxide	30 min	pH: 9.0, time: 25 ± 1 °C	Fe <sup>VI</sup> O <sub>4</sub> <sup>2-</sup> in the presence of G. O. and hydrochar	N.A	Pan et al. (2020a)
3	TMP [2,4-diamino-5-(3',4',5'-trimethoxybenzyl) pyrimidine]	Hydrochar and graphene oxide	30 min	pH: 9.0, time: 25 ± 1 °C	Fe <sup>VI</sup> O <sub>4</sub> <sup>2-</sup> in the presence of G. O. and hydrochar	N.A	Pan et al. (2020a)
4	Roxarsone	Hematite/sulfite/ light system and PMSO as a probe compound	10 min	pH: 10 ± 0.05	Fe(IV/V) oxidizes PMSO, Xenon lamp with the irradiation intensity of 28.5 mWcm <sup>-2</sup>	Removal efficiency >80 %	Zhu et al. (2020)
5	Cyanotoxin, microcystin-LR (MC-LR)	Fe(VI) UV/H <sub>2</sub> O <sub>2</sub>		pH: 7.5 to 8.1 at 20 °C	[MC-LR] = 3.33 μM; [Fe(VI)] = 66.6 μM;	Degradation efficiency >95 %	Jiang et al. (2014)
6	ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate)	Fe(VI)-ABTS System with H <sub>2</sub> O <sub>2</sub>		pH: 7	ABTS (80 μM) with Fe(VI) (2–24 μM), Applied Photophysics SX–17 MV stopped–flow spectrophotometer	It was observed that degradation efficiency of Fe(VI) is less than the computed value.	Lee et al. (2014)
7	Trimethoprim (TMP), naproxen (NAP), and sulfonamide antibiotics (SAs)	Fe(VI) and S.A.s, UV–vis		pH: 6.93–9.50, temp:25 °C	Fe(VI) 300 μM, UV–vis spectrophotometer at 390 nm	Fe(VI) is a capable oxidant for the degradation of pharmaceuticals in hydrolyzed urine.	Luo et al. (2019)
8	Carbamazepine	Fe(VI) oxidation by gamma radiation source	240 min	Temp: 25 °C.	Co source was used to conduct the experiments at the dose rate of 103 Gy/min.	Decrease the adsorbed dose, and enhance the mineralization of carbamazepine by radiation	Wilde et al. (2013)
9	2,4-dichlorophenol (2,4-DCP)	Fe(VI), UV/PS	60 min	pH: 3.0–6.0, temp: 25 ± 0.2 °C	UV lamps linked with 15 W tubes (185 nm, each light intensity = 0.136 mW/cm <sup>2</sup> )	A innovative method for pollutant degradation using UV/Fe(VI) oxidation and give new insights into the oxidation mechanisms and the degradation efficiency reached 73.0 %	Wu et al. (2020b)
10	Organic pollutants (DCF, SMX, CIP, CBZ, and DEET)	Fe(VI) activation by biochar	20 min	pH:7–8, at temp: 25 °C	Fe(VI) (50 μM) magnetic stirrer (500 r/min)	Removal efficiency 75 % of SMX, 70 % of CBZ, 97 % of CIP, and 65 % of DCF.	Tian et al. (2020)
11	Oxygen-evolution reaction (OER)	K <sub>2</sub> FeO <sub>4</sub> and Ni <sub>2</sub> O <sub>3</sub>	20 min	pH:13.0	Ni foam was operated at 10.0 V	The experiments showed that K <sub>2</sub> FeO <sub>4</sub> , compared to Ni <sub>2</sub> O <sub>3</sub> , is more active toward OER. K <sub>2</sub> FeO <sub>4</sub> is not stable in the presence of Ni (II) oxide	Akbari et al. (2020).
12	Sulfamethoxazole, coliforms and E.coli	Fe(VI) and ferric salts		pH: 7.83	Spectrophotometrically measured using the ABTS method, UV <sub>254</sub> abs	Fe(VI) in the presence of Fe (III) was described to hasten the degradation.	Zheng et al., 2020
13	Bypass wastewaters	Fe(VI)– iron electrocoagulation system	45 min	pH: 7.0–9.3	iron electrocoagulation system used in the experiments	The experimental results demonstrated the synergetic effect of the coupled processes for the removal of COD from bypass wastewater.	Elnakar and Buchanan (2020)
14	selenium pollution [Se(IV)]	K <sub>2</sub> FeO <sub>4</sub> , ex-situ and in-situ adsorption,	30–120 min	pH: 2.5–6.5, temp: 25 °C	K <sub>2</sub> FeO <sub>4</sub> (0.05 g) with 100 mL Se(IV) solutions shaken at 200 rpm	Removal efficiency >97 %	Xu and Fu (2020).
15	Ethynl-estradiol Estradiol Bisphenol A	FeO <sub>4</sub> <sup>-2</sup>	30 min	pH:8, temp: 25 °C	Ferrate (VI) 10 and 20 mgL <sup>-1</sup> , fast mixing at 400 rpm for 1 min after dosing,	Removal efficiency >99 %	Lee et al. (2005).
16	Benzophenone-3			pH:8.0 temp: 24 ± 1 °C		Removal efficiency >95 %	(Yang and Ying, 2013)
17	Triclosan (TCS)			pH: 7.0 temp: 24 ± 1 °C		Removal efficiency >95 %	(Yang and Ying, 2013)
18	Bisphenol A	Fe(VI)	10 min	pH:7.0, temp:25 °C	Fe(VI) to BPA (0.1–8.0 M), TUV detector set at 280 nm	Removal efficiency >97.5 %	Han et al. (2015)
19	Carbamazepine	Mn(VII); KMnO <sub>4</sub> And Fe(VI); K <sub>2</sub> FeO <sub>4</sub>		pH: 7.0 temp: 25 °C	3 × 10 <sup>2</sup> M <sup>-1</sup> s <sup>-1</sup> for Mn(VII) and 70 M <sup>-1</sup> s <sup>-1</sup> for Fe(VI)	N/A	Hu et al. (2009)
20	Ciprofloxacin (CIP)	K <sub>2</sub> FeO <sub>4</sub>		temp: 25 °C	Ferrate (VI) dose of 1–5 mg L <sup>-1</sup>	Removal efficiency >70 %	Zhou and Jiang (2015a)

(continued on next page)

**Table 3** (continued)

Sr No.	Compound name	Activation agent	Incubation time	Optimal pH and reaction temperature	Reaction condition	Results	Reference
21	Diclofenac			pH:8.0, temp: 20 ± 2 °C		Removal efficiency >99 %	Chiu et al. (2016)
22	Naproxen			pH:7.0, temp:23 ± 2 °C		Removal efficiency >99.9 %	Chiu et al. (2016)
23	Flurbiprofen	Fe(VI): UV	20 min.	pH:4.0, temp:25 °C	UV–VIS spectrophotometer at the wavelength of 247 nm	Removal efficiency >99 %	Barisci et al. (2015)
24	Ibuprofen	FeO <sub>4</sub> <sup>-2</sup> oxidant		pH:8.0, temp: 25 °C		Removal efficiency up to 40 %	Sharma and Mishra (2006)
25	Octylphenols	Fe(VI) oxidation		pH:7.0, temp:25 °C	Octylphenols conc. 0.001–1.44 µg L <sup>-1</sup>	Effective results	Sharma et al. (2009)
26	Nonylphenol (N.P.), and bisphenol-A (BPA)	Fe(VI) oxidation		pH:7.0, temp:25 °C	0.006–32.8, and 0.0005–4.0 µg L <sup>-1</sup> for NP, and BPA respectively	Maximum degradation	Sharma et al. (2009)
27	Sulfamethoxazole	K <sub>2</sub> FeO <sub>4</sub>		pH:7.0–9.5, temp:25 °C	10 mg L <sup>-1</sup> K <sub>2</sub> FeO <sub>4</sub>	N/A	Noorhasan et al. (2010)
28	Glycylglycine	K <sub>2</sub> FeO <sub>4</sub>		pH:9.5, temp:25 °C	10 mg L <sup>-1</sup> K <sub>2</sub> FeO <sub>4</sub>		Noorhasan et al. (2010)
29	Glycine	K <sub>2</sub> FeO <sub>4</sub>		pH:9.5, temp:25 °C	10 mg L <sup>-1</sup> K <sub>2</sub> FeO <sub>4</sub>		Noorhasan et al. (2010)
30	PPCPs and EDCs noted in secondary effluents of WWTPs	Fe(VI) oxidation		pH:7.0, temp:23 ± 2 °C	Fe(VI) dose 0–10 mg L <sup>-1</sup>	31 PPCPs and EDCs noted in secondary effluents.	Yang et al. (2012)
31	Sulfonamides (SNs)	Fe(VI) with UV	5 min	pH: 7.0	15 mg L <sup>-1</sup> SNs, UV/Vis spectrometer (UV–1600PC VWR) at a wavelength of 510 nm for Fe (VI) detection	Removal efficiency: 100 %	Acosta-Rangel et al. (2020).
32	trimethoprim (TMP)	Fe(VI)/UV–visible		pH:9.0, temp:25 °C	510 nm using UV–visible spectrophotometer	Fe(VI) would increase for complete removal of TMP from the secondary effluent water	Anquandah et al. (2011)
33	Polychlorinated diphenyl sulfides (PCDPSs)	Fe(VI) oxidation		pH: 8.0	Fe(VI) stock solution to 30 mL of 20.0 mM PCDPSs solution	Degradation of PeCDPS by Fe(VI) achieved with the loss toxicity from the parent compound.	Chen et al. (2018)
34	Cetylpyridinium chloride	UV/Fe(VI) oxidation		pH: 9.2	UV-1601PC spectrophotometer at 510 nm wavelength.	Removal efficiency >95 %	Eng et al. (2006)
35	Flumequine (FLU), fluoroquinolone (FQ), norfloxacin (NOR), enrofloxacin (ENR), marbofloxacin (MAR), and ofloxacin (OFL)	Fe(VI)	2 min	pH: 7.0	[Fe(VI)]:[FQ] ≤ 20.0	Removal efficiency 85 %	Feng et al. (2016)
36	Metal Cyanides (K <sub>2</sub> [Zn(C.N.) <sub>4</sub> ], K <sub>2</sub> [Cd(C.N.) <sub>4</sub> ], K <sub>2</sub> [Ni(C.N.) <sub>4</sub> ], and K <sub>3</sub> [Cu(C.N.) <sub>4</sub> ])	Fe(VI)		pH: 9.0	Solid K <sub>2</sub> FeO <sub>4</sub> was added to solutions (10 mL) of 0.1 m cyanides	Fe(VI) has high degradation potential for Cd, Zn, and Cu ion while lower for Ni ions.	Filip et al. (2011)
37	Organic contaminants (DEET, phenol, TMP, and FLU)	Fe(VI)/sulfite and Fe(VI)/thiosulfate e (PMSO)		pH:9.0		PMSO degradation efficiency in sulfite presence ~90 %, while negligible with Fe(VI) alone.	Gao et al. (2020)
38	Acesulfame potassium (ACE)	Fe(VI)	240 min	pH:7.6–8.1	[Fe(VI)]:[ACE], molar ratio 6.0 M	Removal efficiency; 67 %	Ghosh et al. (2019)
39	Azo dye X–3B	Fe(VI)		pH:9.0, 60 °C		Removal/decolorizing efficiency >80 %	Han et al. (2013)
40	Produced water (PW)	Fe (VI)	5–90 min	pH:1–7.0	Fe <sup>6+</sup> dosage of 1–25 mg L <sup>-1</sup>	Promising method for the degradation of organic compounds in produced water	Haneef et al. (2020)

#### 4. Ferrate application for the degradation of micro pollutant (pharmaceuticals)

In recent years, a lot of focus has been paid to the incidence of micro pollutants in water. Unrestricted toxins, which include endocrine

disrupters, pharmaceutical, and personal care products (PPPs), have traditionally been referred to as environmental contaminants (Picó and Barceló, 2015). The growing use of pharmaceutical products globally and eventually in waste water is a problem (Jiang et al., 2013; Khetan and Collins, 2007). Through water treatment, many of these

pharmaceuticals are not completely removed, and industrial waste is normally distributed directly into surface sources. Therefore in the marine world, pharmaceuticals are also found (Banjac et al., 2015; Evgenidou et al., 2015). Case studies of water supply, freshwater, and water medicines include Germany's conjugating x-ray (ICM) newspapers, Canadian and U.S. medicines, narcotics in Australia, and many other pharmaceutical molecules in the European Union, China, and the United States reported presence of pharmaceuticals (Michael et al., 2013; Postigo and Richardson, 2014). The presence of pharmaceuticals in numerous rivers will place marine life and environmental lives in danger (Cizmas et al., 2015; Gan et al., 2015). Advanced oxidation techniques are effective but have some disadvantages in the removal of drugs (Huber et al., 2005a; Huber et al., 2005b). For example, water chlorination has also been known to generate toxic chlorinated whilst also-products of decontamination (Gan et al., 2015; Sharma et al., 2014a). The ability to shape carcinogenic chlorite/bromate complexes is chlorine dioxide with ozone. The use of chloramine will contribute to nitrosamine production (Krasner et al., 2013; Sharma et al., 2011).

In contrast, in the renewable diagnostic process, Fe(VI) has arisen as an environmentally friendly oxidant. Several scientists are actively researching micropollutant oxidative removals, including pharmaceutical, by using Fe(VI) (Jiang et al., 2007; Lee et al., 2009; Sharma et al., 2008). A collection of pharmaceutical drugs treated using Fe(VI) as an oxidizing agent (Li et al., 2008). The compounds analysed include endocrine disfunction (sulfonamides,  $\beta$ lactams, fluoroquinolones, trimethoprim, triclosants),  $\beta$ -blocking substances (Atenolol, metoprolol, propranolol, analgesic (diazepam), anti-carcinogenic substances (diclofenac and ibuprofen) and x-ray comparison medium (ditrizoic acid), anticonvulsants (Tramadol), and co-inflammatory substances (diclofenac and ibuprofen) (Sharma et al., 2014b). The thermodynamic properties of the reactions among Fe(VI) and certain molecules, as depicted by X, are accompanied by the kinetics of the second order, given in Eq.13.

$$-d [\text{Ferrate}]/dt = k_{\text{app}}[\text{Ferrate}][X] \quad \text{Eq 13}$$

where  $k_{\text{app}}$  is the obvious variable of the second-order scale, [Ferrate] and [X] are simultaneously, Fe(VI) and medicinal concentrations.  $K_{\text{app}}$  values were calculated for these reactions at various pHs. In general, pH declines from neutral to alkaline conditions are indicated. The pH-responsive rate reduction pattern was consistent with multiple reactions of ferrate reduction agents (Casbeer et al., 2013; Noorhasan et al., 2010). The pH-responsive rate reduction pattern was consistent with multiple reactions of Fe(VI) reduction agents (Hübner and Jekel, 2013; Karlesa et al., 2014; Wilde et al., 2013; Yang et al., 2012). Table 4 contains more information concerning each pharmaceutical type.

The kinetics of the reactions between Fe(VI) and alkyl phenol is examined with octylphenol, nonylphenol, bisphenol (BPA), and tetrabromobisphenol A (TBBPA) (Anquandah and Sharma, 2009; Li et al., 2008; Yang et al., 2014). For the removal of alkyl phenols in seconds, Fe (VI) reacted quickly with these phenols. The reaction materials for BPA and TBBPA oxidation have been tested (Han et al., 2015; Li et al., 2008; Yang et al., 2014). The production of oxidised materials is thus calculated as per the molar proportion and also relies on selective sedimentation of BPA to inorganic material. The ratio of molar to  $\sim$ 30% DOC was 4:1 ([ferrate]:[BPA]) (Li et al., 2008). DOC declining after complete oxidative transformation of BPA. by Fe(VI) have been calculated for oxidised product of BPA (Li et al., 2008). The proposed reaction scheme displays nine known oxidised products (Li et al., 2008).

P-isopropenyl, phenol, and 4-isopropanol phenol (1-phenyl-1-butenyl) benzene were mildly toxic and present as reaction intermediate of BPA. This will lead to a disruption in the interaction between two phenyl groups. Styrene, 4-isopropyl-cyclohexa-2,5-dienone, p-hydroxyl-aceto-fenone, propane dioic acid, and oxalic acid can be oxidised by this precursor. Any compounds may have reacted with Fe(VI) to cause a partial Fe(VI) mineralization of BPA. Similar transformations of BPA/

**Table 4**  
Apparently second-order reaction rates for Fe(VI) reactions of pharmaceuticals.

Compound	Reactive agent	pKa	$k_{\text{app}}$ (kinetic rate constant of pseudo first-order reaction)	Reference
Cimetidine	Ferrate	6.9	1.6 ( $\pm 0.2$ ) $\times$ $10^3$	(Nie et al., 2020)
Famotidine	Ferrate	8.4	7.8 ( $\pm 0.3$ ) $\times$ $10^2$	(Nie et al., 2020)
Sulfamethazine	Electrophoresis	2.3 7.4	158.7 ( $\pm 5.8$ )	Lin et al. (1997)
Sulfamethoxazole	Ferrate	6.4 7.8 ( $\pm 0.2$ ) ( $\pm 0.3$ )	55.7 ( $\pm 8.1$ )	Kim et al. (2015)
Diclofenac	Ferrate	4.2	32	Lee et al. (2009)
Carbamazepine	Ferrate	13.9 $\pm 0.2$	16	Lee et al. (2009)
Trimethoprim	Ferrate	3.2 7.2	7.2 ( $\pm 5.0$ )	(Qiang and Adams, 2004; Roth and Strelitz, 1969)
Atenolol	Ferrate	9.6	$\sim 7$	Lee and Von Gunten (2010)
Nalidixic acid		5.95	2.6 ( $\pm 0.4$ )	Ross and Riley (1990)
Ronidazole	Activated carbon	1.32	1.7 ( $\pm 0.1$ )	Rivera-Utrilla et al. (2009)
Dimetridazole	Activated carbon	2.81	0.9 ( $\pm 0.3$ )	Rivera-Utrilla et al. (2009)
Tinidazole	Activated carbon	2.30	0.2 ( $\pm 0.1$ )	Rivera-Utrilla et al. (2009)

intermediate products, including cleavage of C-C bonding phenol, hydroquinone, benzoquinone, styrene, and low molecular weight dicarboxylic acids also have been identified by a later study of the oxidized product for Fe(VI) reaction with bisphenol-A (Han et al., 2015). The reaction pathways suggested in both experiments were also identical (Han et al., 2015; Li et al., 2008). The analysis of tetrabromobisphenol-A oxidation by Fe(VI) found that the target pollutant was quickly transformed with Fe(VI) (Yang et al., 2014). The existence of the inorganic ingredient metal oxides in the drinking water did not cause Fe(VI) oxidation for tetrabromobisphenol-A. However, organic fertilizer might compete with tetrabromobisphenol-A for Fe(VI), a typical constituent of tainted water. This will limit Fe(VI)'s potential to destroy tetrabromobisphenol-A entirely. Tetrabromobisphenol-A has been entirely removed in the existence of humic acid where an excess of Fe (VI) has been added. The results of the processes showed that TBBPA was degraded by  $\beta$  fracturing, which resulted in de-brominated oxidised products with low molecular weight (Yang et al., 2014). Importantly, tetrabromobisphenol-A's oxidative Fe(VI) based transition has led tetrabromobisphenol-A to lose some hormone functions, including generally pro-estrogenic, valerate, and anti-androgenic (Yang et al., 2014).

The kinetic reactions between Fe(VI) and phenolic estrogens showed effective steroid elimination. The degradation of estrogen in fresh water, wastewater, and milk-based waste lagoons by Fe(VI) has shown this (Hu et al., 2008; Lee et al., 2005; Remsberg et al., 2008). While this occurrence of organic manures in polluted water has impaired the 17  $\alpha$ -ethinyl-estradiol (EE2) breakdown, the growing dose of Fe(VI) means that the waste water sample obtained the entire estrogen extracted (Hu et al., 2008; Lee et al., 2005). The estrogenic content of

$\alpha$ -ethinyl-estradiol after Fe(VI) therapies has been analysed and disclosed that the original manufacturing products also have in situ anti-oxidant activities (Lee et al., 2008).

Nevertheless, Fe(VI) has been used to convert the initially generated products to eliminate the estrogenic activity of  $\alpha$ -ethinyl-estradiol by oxidation (Lee et al., 2008). The pharmaceutical pollutants including cimetidine, nalidixic acid, famotidine, caffeine and tinidazole can effectively degrade at pH 8.0 with the second order reaction rate. The rate constant of these pollutant ranges from 5.0 to 9.5 and conclude that the  $k_{app}$  decrease with the increase in reaction pH. The fluorescence surrogate accuracy was determined by field sample for the elimination of pharmaceutical pollutants. During Fe(VI) treatment, authors conclude that the fluorescence of the pollutant change as the pollutant degrade. Fe (VI) with three different exposure dose (100–213 mgL<sup>-1</sup> min) was deployed, the result conclude that carbamazepine, trimethoprim and diclofenac can be degraded with low dose of Fe(VI) (26–38.8 mgL<sup>-1</sup> min) (Ni et al., 2020).

#### 4.1. Reductants and products obtained by Fe(VI)

In the study of Fe(VI) oxidation reactions, the interplay between Fe (VI) and the aqueous solution should be taken in account (Lee et al., 2014; Sharma, 2011). Initial Fe(VI) concentration, temperature, pH, water components, and the composition of the oxides/hydrous iron oxide provide a significant effect on ferrate oxidation level.

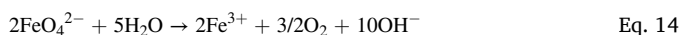
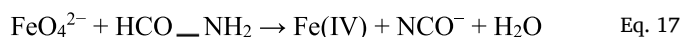
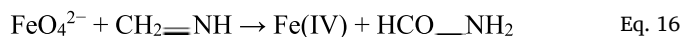
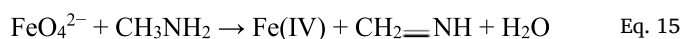


Table 5 gives the main products of Fe(VI) reactions with various organic substrates (Carr, 2008; Delaude and Laszlo, 1996; Huang et al., 2001a; Huang et al., 2001b; Johnson et al., 2008; Kim et al., 1984; Lee and Gai, 1993; Norcross et al., 1997; Ohta et al., 2001; Rush et al., 1995). Hydrocarbons are manufactured from natural hydroxylated compounds and alcohols via aldehydes/ketones (Kim et al., 1984; Lee and Gai, 1993). Fe(VI) amine degradation varies, with respect to temperature and because of different nature of amine (Table 5). Formalamide and cyanate have been the primary components of methylamine degradation, and formic acid has been the ultimate result of dimethylamine and trimethylamine oxidation (Johnson et al., 2008). This indicates that methylamine decay by Fe(VI) reactions vary from dimethylamine and trimethylamine degradation by Fe(VI). Due to aniline accumulation by Fe(VI), two forms of oxidised products were produced. When Fe(VI) content was more significant than aniline, nitrobenzene was perhaps the most abundant element. Azobenzene was produced when the aniline intensity was greater than the Fe(VI) levels (Huang et al., 2001a; Johnson et al., 2008). In another study, the author

**Table 5**  
Reaction intermediate products generated by ferrate degradation.

Reductant	Products	Reference
Hydrocarbons	Hydroxylated compounds	(Delaude and Laszlo, 1996; Kim et al., 1984)
Alcohols	Aldehyde and ketone	(Lee and Gai, 1993; Ohta et al., 2001)
Amines	Formamide, cyanate	Carr (2008)
• Methylamine (1 °C)	Formic acid	
• Dimethylamine (2 °C)	Formic acid	
• Trimethylamine (3 °C)		
Aniline	Nitrobenzene, azobenzene	(Huang et al., 2001a; Johnson et al., 2008)
Phenol	p-benzoquinone and biphenol	(Huang et al., 2001a; Rush et al., 1995)
Aliphatic sulfur compounds	Sulfenic, sulfenic, sulfonic, sulphate	Sharma (2011)
Thiols	Sulfonate, disulfide	(Delaude and Laszlo, 1996; Sharma, 2011)

revealed that the value of  $k_{app}$  of organic amine is much higher than aliphatic amine. The formation products of aliphatic amine are revealed as in the reaction equation (Eqs. 15–17) (Carr, 2008; Sharma, 2013).



In a recent study, the degradation of pharmaceuticals, antibiotics and personal care products were oxidized by Fe(VI) and biochar. The result revealed the increase in degradation rate from 3 to 14 time and TOC removal was enhanced by 2.4–8 times. The oxidant not only formed the intermediate but also cause detrimental effects to biochar structure (Tian et al., 2020). Two drugs, p-benzoquinone and biphenol, were obtained from phenol oxidation. Biphenol formation shows that during Fe(VI) phenol oxidation, a radical reaction has developed. The Fe(VI) can oxidize the aliphatic and aromatic sulfur compounds through an oxygen transfer mechanism (Huang et al., 2001a).

#### 4.2. Applications in wastewater treatment

The Fe(VI) has a superior range of applicability which can be theoretically associated with wastewater cleaning, but if manufactured in large amounts, the cost can be significantly decrease. Author studied the onsite waste water treatment by Fe(VI), the onsite utilization and production of Fe(VI) constructed with 220 mL electro-chemical reactor, dosing pump liked with storage tank. The electrochemical reactor is explained in Fig. 6, where 2mm thick anode and cathode with 3.6 mAc<sup>m-2</sup> were used. In the result, Fe(VI) significantly degraded the total phosphorus (56 %) and total soluble solids (79 %) (Alsheyab et al., 2010; Jiang et al., 2016). Further improvements have been observed to increase the efficiency like cleaning of anode with phosphoric acid solution. In a study Fe(VI) with combination of cationic polymer was used to remediate dyeing waste water. The treated pilot scale plant raised the conductivity, calcium and hardness while significantly reduced the iron and magnesium (Ciabatti et al., 2010). In another study, Fe(VI) and ozone were applied simultaneously to conclude the pilot scale comparison of waste water. The result conclude that Fe(VI) and ozone can remove 80 % and 60 % of the aniline respectively. Total organic carbon was significantly lower than the targeted pollutant which reflect that the complete mineralization has not been achieved (Liu et al., 2011).

The conclusive aspects of Fe(VI) with wate water treatment are:

- Electrochemical produced Fe(VI) has more wide application as compare to wet oxidised method in waste water treatment
- The cleaning of anode surface and composition of analyte can improve the efficacy.
- The composition of liquid Fe(VI) with highly alkaline and soluble/residual content are another problematic concern.
- It produces a Fe(OH)<sub>3</sub> gel that drops and contains other particles.
- The reaction condition (pH, anions, cations, chemical structure and concentration of the contaminant greatly influence the degradation trend).

#### 5. Limitations and perspective

There are number of future prospective which can be induced in oxidative degradation includes:

- Stability concern:** The stability concern is the main and major goal in Fe(VI) oxidation. The self-decay of Fe(VI) may lead to poor oxidation. Fe(VI) is very unstable at acidic pH and show maximum reactivity at basic pH. The most of the reaction shows second-order reaction kinetics. But their decay mechanism is

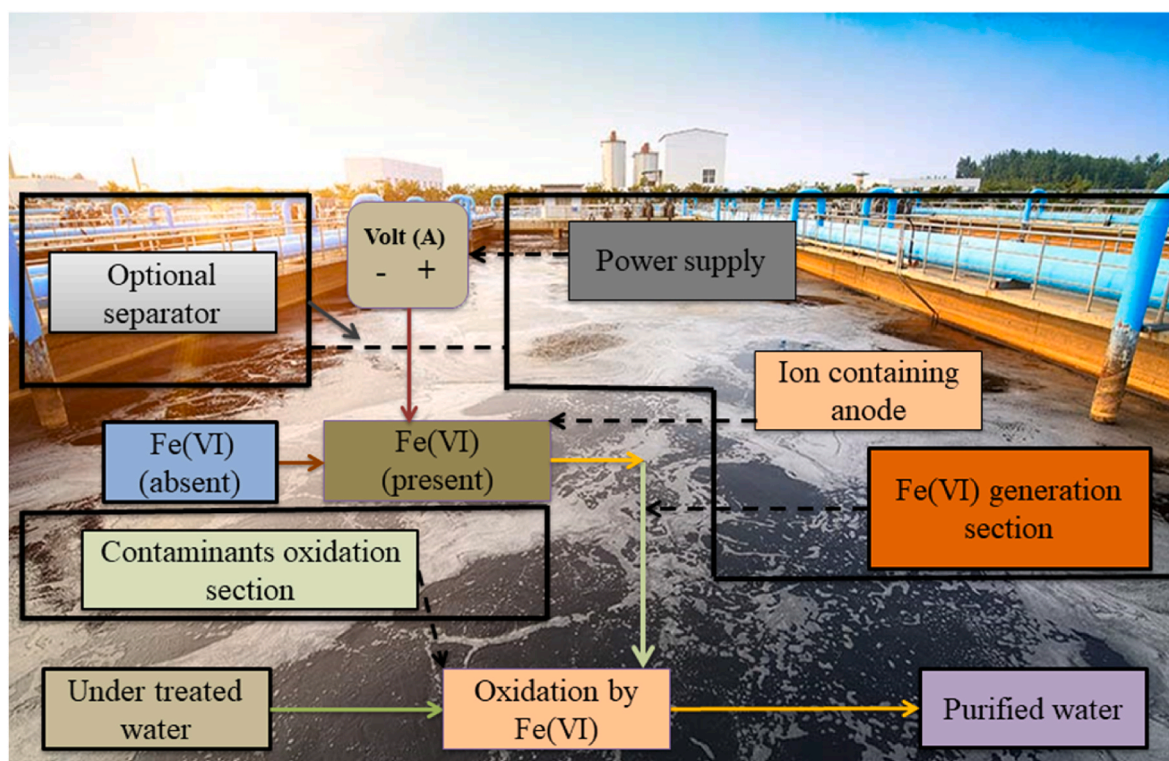


Fig. 6. Complete pathway of wastewater treatment by ferrate.

confused and controversial under different reaction conditions. A new method can be introduced to approach maximum degradation, like frozen Fe(VI) can be an innovative method, as basically we need a slow release of Fe(VI) in the reaction system. Because in most of the reaction, up to 70 % degradation takes place in early few minutes. So frozen Fe(VI) can be an effective method for the slow release of Fe(VI).

- (2) Fe(III) and Fe(IV) generation: As with comprehensive support of this article, the redox potential of Fe(III) is more valuable than Fe(VI). Even the generation of Fe(IV) and their reaction mechanism still need to be studied. So, there should be more studies focusing on the generation of Fe(III) and Fe(IV).
- (3) Nanopores entrapment and nanopore capsules: A number of studies have incorporated in homogenous reaction, while there is significant potential in the heterogeneous reaction system. Nanopores, with the help of zeolite and silicon dioxide, can be generated and apply with Fe(VI), as they have more absorbance capacity. In addition, nano pore which has a smaller pore than Fe(VI), can be used to form capsule shell, once capsule formed it will not allow escaping/self-decay. When the capsule needs to dissociate, some external signal (It may UV, temperature) may require, Fe(VI) will be able to degrade the pollutant. Besides, we may also intrude some other methods like UV method to reach out the mechanistic approach.
- (4) Activation and synergetic effects: Fe(VI) activation by different agents, including photocatalyst, can be an effective approach to overcome the time-consuming process (like encapsulated Fe(VI)). The generation of an electron during photocatalytic activity may enhance the degradation efficiency, and meanwhile, synergetic effects can be generated.

## 6. Conclusion

Fe(VI) is a substance that oxidizes the hydrocarbon, alcoholic and phenolic derivatives, nitrogen compounds. This study offers previous

comprehensive studies and a comparative comparison of Fe(VI) alternative treatment strategies for environmental pollutants. At the beginning, we elucidated the characteristics of different advanced oxidation processes. Although research on these deterioration methods has shown a steady global rise over the last 20 years, these studies comprise a number of limitations, which are briefly addressed in this review. The Fe(VI) reaction mechanism addresses the generation of one and two electrons which mediate the degradation intermediate. The generation of Fe(III) and their redox potential are more concerning in degradation than Fe(V) and Fe(VI).

The recent advancement in Fe(VI) provides the Fe(VI) activation by different activation agent, and these studies offer the more comprehensive details as compared to Fe(VI) alone. These are summarized as (1) Fe(VI) was able to activate C-H hydrocarbon bond by the related heterogeneous catalysts and to turn benzyl alcohol into benzaldehyde by stoichiometry without over-oxidation into benzoic acid. (2) The photocatalytic intermediates often establish environmental toxicity to different species. The scientific establishment should pay particular attention to these limits. (3) Petrochemical waste is toxic and, even at very low concentrations, has numerous harmful effects on human health and the environment. It takes hour to establish a practical methodology for the degradation of this organic pollutant, economically and sustainably. It is important to ensure technical advances in implementing the various biological and photocatalytic systems in petrochemical waste management. (4) Advances have been made on the kinetics of Fe(VI) oxidation of pharmaceuticals, but there is a lack of knowledge on stoichiometry and reaction products including reaction intermediates, self and cross coupling products. The synergetic effects can be achieved by implementing photoactivation reagent with Fe(VI). This approach can provide real-life information about treatment processes. Finally, research on organic molecule synthesis and transformation will begin to find viable new applications in greener processing and therapy for earth-abundant iron-based products.

## Author's statement

Afzal Ahmed Dar and Chuanyi Wang conceptualized the initial draft, Eric Lichtfouse, and Usman reviewed and highlighted the gaps, Bao, Zhu and Qin helped in data collection, and moderation. All authors reviewed, edited, and agreed on the final version of the manuscript. In addition, authors declare no financial and competing interest.

## Authors' contributions

Afzal Ahmed Dar and Chuanyi Wang conceptualized the initial draft, Eric Lichtfouse, and Usman reviewed and highlighted the gaps, Bao, Zhu and Qin helped in data collection, and moderation. All authors reviewed, edited, and agreed on the final version of the manuscript.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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