

Secondary amine-activated ferrate(VI) for isoquinoline degradation: Relationship between molecular structure and reactive performance

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(Article begins on next page)

1           **Secondary Amine-Activated Ferrate(VI): Relationship Between**  
2                           **Molecular Structure and Reactive Performance**

3  
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19     **Abstract**

20           This study systematically elucidates the electronic structure-activity relationship  
21 between secondary amines and ferrate (Fe(VI)) activation. Comparative experiments  
22 demonstrated that pyrrolidine (Py) significantly outperformed diethylamine (Di) in  
23 enhancing Fe(VI)'s oxidation capability across various dosage conditions and pollutant  
24 systems, with Py-Fe(VI) achieving approximately 7-fold higher rate constant than  
25 Fe(VI) alone for isoquinoline (IQL) degradation, versus a 2-fold improvement observed  
26 with the Di-Fe(VI) system. Mechanistic studies combining quenching experiments and  
27 EPR characterization corroborated Fe(IV)/Fe(V) as dominant reactive species for IQL  
28 degradation, with kinetic modeling revealing that Fe(IV) contributes >80% to IQL  
29 degradation in all processes. Electrochemical analyses suggested that Fe(VI) activation  
30 by Di and Py might involve the formation of iron-secondary amine complexes. Density  
31 functional theory calculations highlighted Py's lower energy barrier for Fe(VI)  
32 complexation (27.7 vs. Di's 29.1 kcal/mol), accelerating activation. Secondary amines  
33 were shown to stabilize Fe(IV) via coordination, extending its reactive lifetime.  
34 Systematic evaluation of various secondary amines revealed a significant negative  
35 correlation between the highest occupied molecular orbital energy levels of amines and  
36 Fe(VI) activation performance, indicating that moderate electron-donating capacity  
37 promotes iron complexation and pollutant degradation. This work establishes a  
38 molecular design framework for Fe(VI) activators while providing new insights into  
39 high-valent iron-mediated oxidation mechanisms, advancing sustainable water  
40 treatment strategies.

41

42     **Keywords**

43 Ferrate; Secondary amines; High-valent iron species; Kinetic model; Theoretical

44 calculations

45

## 46 **Synopsis**

47 This study established a quantitative correlation mechanism between secondary amine  
48 configuration and Fe(VI) activation efficiency.

49

## 50 **1. Introduction**

51 In recent years, ferrate (Fe(VI)) has attracted extensive research attention as an  
52 environmentally friendly and multifunctional water treatment agent due to its unique  
53 redox properties <sup>1,2</sup>. This compound combines strong oxidizing capacity with  
54 multifunctional synergistic effects <sup>3</sup>, enabling efficient pathogen inactivation <sup>4</sup>, organic  
55 pollutant degradation <sup>5,6</sup>, inorganic pollutant transformation <sup>7,8</sup>, and heavy metal ion  
56 removal <sup>9</sup>. Notably, it produces no halogenated disinfection by-products during  
57 treatment <sup>10</sup> and demonstrates superior resistance to water matrix interference compared  
58 to chlorine-based disinfectants and ozone <sup>11</sup>. Although Fe(VI) demonstrates  
59 multifunctional advantages, its practical implementation remains constrained by kinetic  
60 limitations in pollutant degradation compared to ozone, Fenton reagents, and other  
61 advanced oxidation processes (AOPs) <sup>11</sup>. Furthermore, its intrinsic instability poses  
62 critical challenges, such as rapid decomposition under acidic conditions <sup>12,13</sup>. These pH-  
63 dependent limitations collectively restrict its operational versatility across diverse water  
64 matrices. To address these bottlenecks, there exists an urgent demand for developing  
65 efficient Fe(VI) activation strategies while broadening its operational pH spectrum,  
66 thereby enabling more robust and adaptable water treatment applications.

67 Studies have demonstrated that the oxidative capabilities of highly reactive high-  
68 valent iron species (Fe(IV)/Fe(V)) markedly surpass those of Fe(VI) <sup>1,14</sup>. Existing

69 research confirms that strategies including acid activation <sup>15</sup>, coupling with carbon-  
70 based materials <sup>2,16</sup>, synergistic oxidation <sup>17-19</sup>, reduction agents <sup>20-23</sup>, metal oxide  
71 catalysis <sup>24-26</sup>, and energy field enhancement <sup>2,27</sup> can significantly increase the  
72 proportion of Fe(IV)/Fe(V) generation in Fe(VI) systems. Of particular interest are  
73 amine compounds, which are ubiquitous in natural water systems as reductive media  
74 derived from dissolved organic matter and anthropogenic pollutants, such as  
75 pharmaceuticals, personal care products, and pesticides <sup>28</sup>. Emerging studies have  
76 revealed that nitrogen-containing substances like creatinine <sup>29</sup>, aliphatic amines <sup>28</sup>, and  
77 amino acids <sup>1</sup> can activate Fe(VI) through electron transfer processes, substantially  
78 improving pharmaceutical pollutant degradation efficiency. Notably, the amine  
79 functional groups in pharmaceuticals play a decisive role in governing their oxidative  
80 transformation pathways mediated by Fe(VI). This structural dependence is particularly  
81 evident in sulfonamide antibiotics, where the electronic and steric properties of amine  
82 moieties dictate the selectivity of oxidation intermediates and final products <sup>30</sup>. A  
83 critical distinction lies in the activation mechanisms among primary, secondary, and  
84 tertiary aliphatic amines: secondary amines exhibit optimal enhancement effects by  
85 preferentially generating Fe(IV)-dominated active species, while structurally unique  
86 amines, e.g., proline, achieve efficient pollutant removal via Fe(V)-mediated pathways.

87 To systematically elucidate the structure-activity relationship between amine  
88 configurations and Fe(VI) activation mechanisms, this study selects diethylamine (Di,  
89 [Figure 1a](#)) and pyrrolidine (Py, [Figure 1b](#)) as model compounds. Despite their similar  
90 molecular weights and chemical compositions, Di possesses a flexible aliphatic chain  
91 structure, whereas Py features a rigid cyclic configuration. This structural difference  
92 provides an ideal comparative system for investigating the impact of molecular rigidity  
93 on Fe(VI) activation efficiency. The research focuses on four key objectives: (1)

94 comparing the differential enhancement effects of Di and Py on Fe(VI)-mediated  
95 degradation of pollutants; (2) identifying critical active species (radical/non-radical)  
96 and quantifying their contributions; (3) elucidating molecular mechanisms underlying  
97 Fe(VI) activation by different amines; (4) establishing quantitative structure-activity  
98 relationships between secondary amine configurations and Fe(VI) activation efficiency  
99 to provide guidance for designing high-performance Fe(VI) activators. This work not  
100 only advances fundamental understanding of Fe(VI)-amine interactions but also offers  
101 scientific foundations for developing ligand-regulated advanced water treatment  
102 technologies.

103

## 104 **2. Materials and Methods**

### 105 **2.1. Chemicals and Reagents**

106 All the chemicals and reagents used were at least analytical grade; detailed  
107 descriptions are provided in the Supporting Information (SI), [Text S1](#). The synthesis  
108 procedure for potassium ferrate (Fe(VI)) is presented in [Text S2](#) of the SI

### 109 **2.2. Experiment Procedures**

110 All batch degradation experiments were conducted at  $25 \pm 1$  °C in glass beakers  
111 on a magnetic stirrer (300 rpm). Each pollutant was individually added to the 100 mL  
112 system at a concentration of 10  $\mu$ M. The reaction was initiated by simultaneously  
113 adding the target amount of amine compounds and solid Fe(VI). The pH was  
114 maintained at  $9.0 \pm 0.05$  with 10 mM borate buffer. At predetermined time intervals, a  
115 1 mL sample was collected and immediately quenched with excess hydroxylamine  
116 hydrochloride (100  $\mu$ L of 0.1 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ ), and then filtered (0.22  $\mu$ m) into UPLC  
117 vials before analysis. Other experiments under different conditions also followed the  
118 above procedures. All experiments were performed in at least duplicates and the results

119 are presented as average data with one standard deviation.

### 120 **2.3. Analytical Methods**

121 The pH values were monitored with a pH meter (FE-28, Mettler Toledo, USA).  
122 The measurement of Fe(VI) concentration is detailed in [Text S3](#) Measurements of  
123 micropollutant concentrations are described in [Text S4](#) and [Table S1](#). Electron  
124 paramagnetic resonance (EPR) analysis is presented in [Text S5](#). Electrochemical tests  
125 were conducted in a three-electrode electrochemical cell ([Text S6](#)).

126

### 127 **2.4. Theoretical calculations**

128 Structure optimizations were carried out with Gaussian 16, Revision A.03 package  
129 <sup>31</sup> at the B3LYP <sup>32,33</sup> level of theory including Grimme's D3 dispersion corrections with  
130 Becke-Johnson damping (D3BJ) <sup>34,35</sup> with a def2SVP basis set <sup>36-39</sup>. To identify each  
131 stationary point as either an energy minimum or a transition state, analytical frequency  
132 calculations were carried out at the same level of theory. On the basis of the gas-phase  
133 optimized structures, single point energy values were calculated using the B3LYP  
134 functional with a def2-TZVP basis set <sup>36-39</sup>. All reported energies are based on gas-  
135 phase Gibbs free energies for which the electronic energies were corrected to B3LYP  
136 with def2-TZVP basis set and solvent effects. The calculation of the Fukui index for Di  
137 and Py molecule was performed using the Multiwfn software <sup>40</sup> (details shown in [Text](#)  
138 [S7](#)).

### 139 **2.5. Kinetic Modeling**

140 The program Kintecus V6.51 ([www.kintecus.com](http://www.kintecus.com)) was used for kinetic fitting and  
141 simulation for IQL oxidation in the Fe(VI) alone, Di-Fe(VI), and Py-Fe(VI) systems.  
142 The reaction equations employed in the kinetic model are displayed in [Tables S2-S4](#),  
143 and the models were validated by the model sensitivity analysis ([Texts S8-S10](#) and

144 [Figures S10–S19](#))<sup>41</sup>.

145

### 146 **3. Results and Discussion**

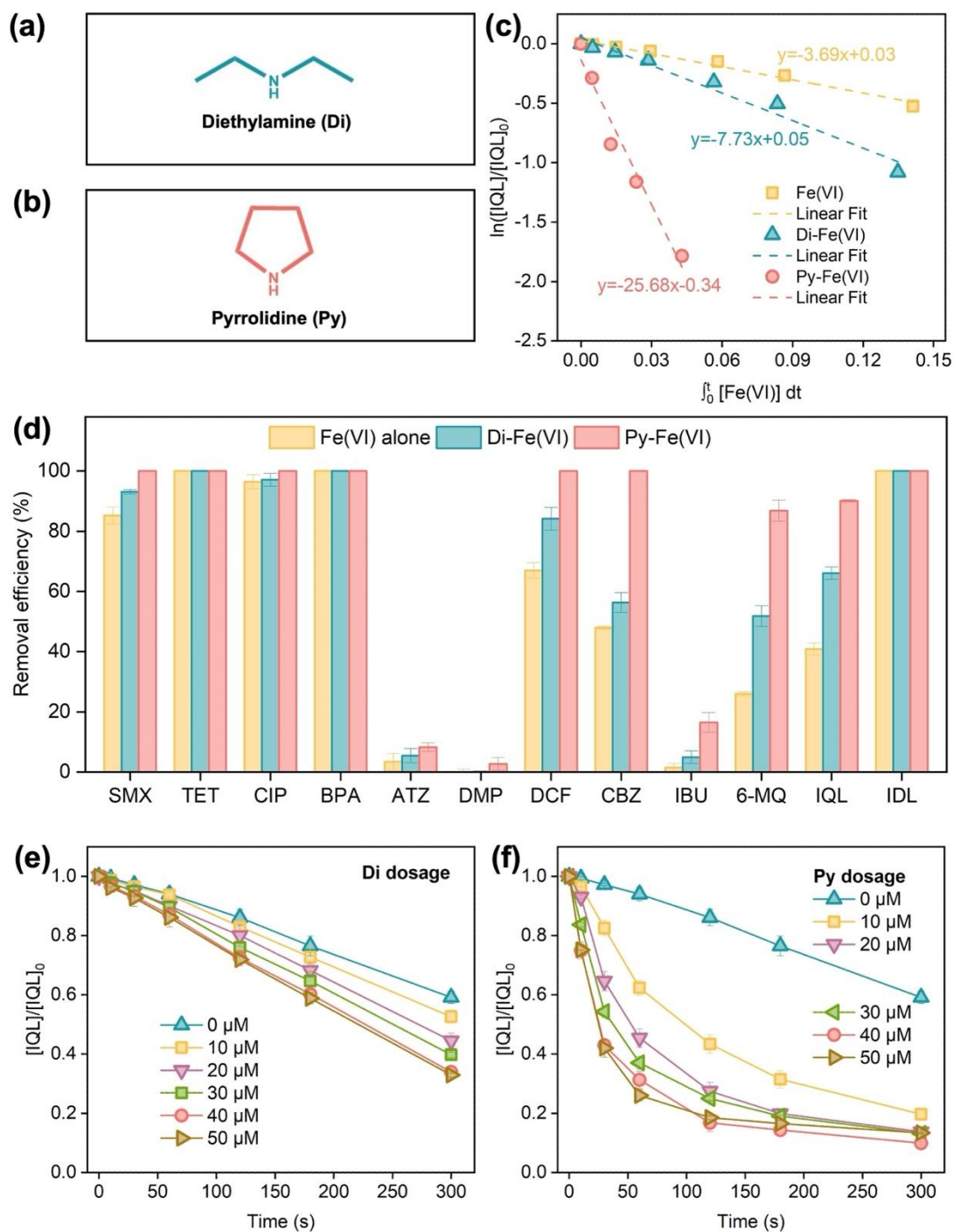
#### 147 **3.1. Oxidation Performance of secondary amine-Fe(VI)**

148 The degradation of isoquinoline (IQL) by individual systems (Di alone, Py alone,  
149 Fe(VI) alone) and combined systems (Di-Fe(VI), Py-Fe(VI)) was systematically  
150 investigated. As shown in [Figure S1](#), neither Di nor Py alone exhibited any IQL  
151 degradation capability within 300 seconds of reaction. In contrast, the Fe(VI) alone, Di-  
152 Fe(VI), and Py-Fe(VI) systems achieved IQL removal efficiencies of 40.9%, 66.1%,  
153 and 90.1%, respectively. As depicted in [Figure 1c](#), all the three processes followed  
154 second-order kinetics. The rate constants for Di-Fe(VI) and Py-Fe(VI) were determined  
155 to be  $7.73 \text{ M}^{-1}\text{s}^{-1}$  and  $25.7 \text{ M}^{-1}\text{s}^{-1}$ , respectively, representing approximately 2-fold and  
156 7-fold enhancements compared to the sole Fe(VI) process ( $3.69 \text{ M}^{-1}\text{s}^{-1}$ ). It is obvious  
157 that the introduction of Di or Py significantly enhanced the Fe(VI)-mediated  
158 degradation of IQL.

159 Additionally, the degradation of 12 micropollutants were systematically evaluated  
160 with Di alone, Py alone, Fe(VI) alone, Di-Fe(VI), and Py-Fe(VI) processes. The target  
161 contaminants included: antibiotics, i.e., sulfamethoxazole (SMX), tetracycline (TET),  
162 ciprofloxacin (CIP); endocrine disruptors, i.e., bisphenol A (BPA, atrazine (ATZ),  
163 dimethyl phthalate (DMP); pharmaceuticals, i.e., diclofenac (DCF), carbamazepine  
164 (CBZ), ibuprofen (IBU); representative organics in shale gas wastewater, i.e., IQL, 6-  
165 Methylquinoline (6-MQ), indoline (IDL) (see [Figure S2](#) and [Figure 1d](#)). Within 300 s,  
166 Di and Py alone exhibited negligible degradation for all tested micropollutants. Fe(VI)  
167 achieved partial degradation of 9 out of 12 contaminants within 5 minutes, with the  
168 exceptions of DMP, IBU, and ATZ, likely because Fe(VI) typically exhibits high

169 reactivity toward electron-rich contaminants but inertness toward electron-deficient  
170 ones <sup>27</sup>. Notably, except for DMP, TET, BPA, and IDL, the latter three having already  
171 achieved 100% degradation by Fe(VI) alone, the addition of Di and Py enhanced the  
172 degradation of all tested micropollutants. Py consistently exhibited a stronger catalytic  
173 enhancement than Di, with this phenomenon observed across different pollutant  
174 categories, implying the broad applicability of the observed catalytic behavior.

175 The dosage-dependent effects of secondary amines on IQL degradation were  
176 evaluated in Di-Fe(VI) and Py-Fe(VI) processes. As shown in [Figures 1e–f](#), increasing  
177 the Di or Py concentrations from 10 to 40  $\mu\text{M}$  initially enhanced IQL degradation  
178 efficiency, followed by a slight decline at 50  $\mu\text{M}$ . This phenomenon likely arised from  
179 excessive Di or Py reducing high-valent iron species (Fe(VI)/Fe(V)/Fe(IV)) to less  
180 reactive lower-valence states (Fe(III)/Fe(II)), which commonly exhibit diminished  
181 oxidative capacity for IQL degradation. Notably, Py exhibited persistent catalytic  
182 superiority over Di across all tested dosages under identical experimental conditions,  
183 thereby emphasizing the reproducibility and mechanistic stability of this enhancement  
184 phenomenon. Investigations into additional influencing parameters (e.g., pH,  
185 coexisting ions) are provided in [Figures S3–S4](#) and [Text S11–S12](#).



186

187 **Figure 1.** Structural formula of Di (a) and Py (b); Degradation kinetics of IQL by Fe(VI),

188 Di-Fe(VI), and Py-Fe(VI) processes (c); Removal of various pollutants by Fe(VI) alone,

189 Di-Fe(VI), and Py-Fe(VI) processes (d); Effect of Di dosage (e) and Py dosage (f) on

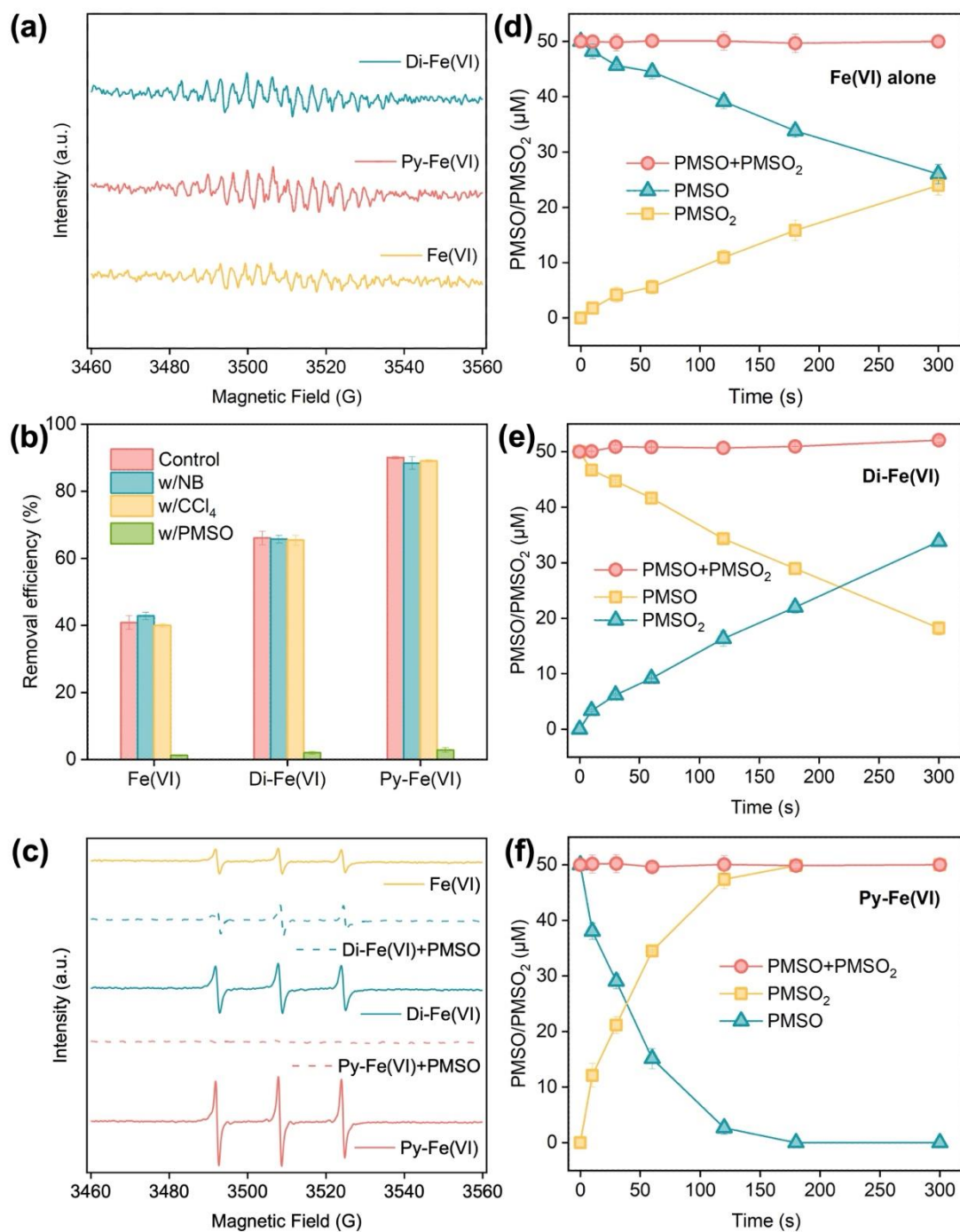
190 IQL removal. Experiment conditions: pH = 9.0,  $[IQL]_0 = 10 \mu$ M,  $[Di]_0 = [Py]_0 = 40 \mu$ M,

191  $[Fe(VI)]_0 = 500 \mu$ M.

192

### 193 3.2. Evidence for the Fe(V)/Fe(IV) Contribution

194 To examine the possible reactive oxygen species (ROS, e.g., HO<sup>•</sup>, O<sub>2</sub><sup>•-</sup>, and <sup>1</sup>O<sub>2</sub>)  
195 and reactive iron species (Fe(IV)/Fe(V)) for IQL depletion during the Fe(VI)-based  
196 processes, a combination of EPR spectroscopy, quenching tests, and probe compounds  
197 was utilized (Text S13). As depicted in Figure 2a, HO<sup>•</sup> was likely not involved in any  
198 of the processes, since no signal of the DMPO-HO<sup>•</sup> adduct was observed. The role of  
199 HO<sup>•</sup> was also ruled out using the probe compound nitrobenzene (NB)<sup>42,43</sup>, as NB had  
200 no effect on the removal of IQL (Figure 2b), and no removal of NB was observed in  
201 these systems (Figure S5). Then, to identify the role of O<sub>2</sub><sup>•-</sup>, CCl<sub>4</sub> was chosen as a  
202 scavenger for O<sub>2</sub><sup>•-</sup>, since CCl<sub>4</sub> is relatively reactive with O<sub>2</sub><sup>•-</sup> ( $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>44,45</sup>.  
203 The presence of 50 mM CCl<sub>4</sub> showed a negligible inhibition on the abatement of IQL,  
204 indicating that O<sub>2</sub><sup>•-</sup> did not have substantial involvement in any of the systems, with or  
205 without secondary amines (Figure 2b and Figure S6). The employment of nitro blue  
206 tetrazolium (NBT) as a characteristic probe also ruled out the role of O<sub>2</sub><sup>•-</sup>, because the  
207 absorbance of NBT could not be reduced (Figure S7) and there was no characteristic  
208 absorption peak of NBT-O<sub>2</sub><sup>•-</sup> at 560 nm<sup>46</sup> (Figure S8). Furthermore, visible light-rose  
209 bengal (Vis-RB) process, a classical system that only produces <sup>1</sup>O<sub>2</sub><sup>47</sup>, was conducted  
210 to verify the role of <sup>1</sup>O<sub>2</sub>. As summarized in Figure S9, the Vis-RB process did not lead  
211 to the degradation of IQL, reflecting that the <sup>1</sup>O<sub>2</sub> was not responsible for IQL  
212 elimination. Although a TEMP-<sup>1</sup>O<sub>2</sub> signal was observed (Figure 2c), it may not be  
213 attributed to <sup>1</sup>O<sub>2</sub>, a mechanism that will be discussed below. The results collectively  
214 excluded the significant roles of ROS in IQL removal. In other words, active iron  
215 species oxidation should be the largely main mechanism responsible for removing IQL  
216 within the Fe(VI), Di-Fe(VI), and Py-Fe(VI) systems.



217

218 **Figure 2.** EPR spectra of DMPO-HO' in various processes (a); Influence of different  
 219 scavengers and probes on the removal of IQL by Fe(VI) alone, Di-Fe(VI), and Py-Fe(VI)  
 220 processes (b); EPR spectra of TEMP-<sup>1</sup>O<sub>2</sub> in various processes (c); Degradation of  
 221 PMSO and generation of PMSO<sub>2</sub> in Fe(VI) alone (d), Di-Fe(VI) (e), and Py-Fe(VI) (f)  
 222 processes. Experiment conditions: pH = 9.0, [IQL]<sub>0</sub> = 10 μM, [Di]<sub>0</sub> = [Py]<sub>0</sub> = 40 μM,  
 223 [Fe(VI)]<sub>0</sub> = 500 μM, [PMSO]<sub>0</sub> = 1 mM, [NB]<sub>0</sub> = 10 μM, [CCl<sub>4</sub>]<sub>0</sub> = 50 mM.

224 It is well known that methyl phenyl sulfoxide (PMSO) can be oxidized by high-  
225 valent iron (Fe(IV)/Fe(V)) into PMSO<sub>2</sub> through oxygen-atom transfer pathway, which  
226 observably differs from the radical-based oxidation pathway, during which PMSO  
227 mainly transforms into other products, such as hydrolyzed PMSO<sup>16,48</sup>. Typically,  
228 Fe(IV)/Fe(V) exhibits higher oxidation capability than Fe(VI) with PMSO. Thus,  
229 PMSO has been frequently used to check the formation of Fe(IV)/Fe(V) in Fe(VI)-  
230 based oxidation processes. When 1 mM of PMSO was added into Fe(VI), Di-Fe(VI),  
231 and Py-Fe(VI) systems, the removal performance of IQL was remarkably restrained  
232 (Figures 2b). For instance, when 1 mM PMSO was added to the reaction solution, only  
233 1.24%, 2.03%, and 2.84% of IQL abatement was obtained after 300s treatment for  
234 Fe(VI) alone, Di-Fe(VI), and Py-Fe(VI), respectively, while 40.9%, 66.1%, and 90.1%  
235 IQL removal was achieved by the corresponding three processes in the absence of  
236 PMSO. The obvious suppression phenomenon of IQL degradation may be attributed to  
237 PMSO and IQL competing for Fe(IV)/Fe(V). This also suggested that Fe(IV)/Fe(V)  
238 played a dominant role in IQL removal.

239 Furthermore, the degradation of PMSO by sole Fe(VI), Di-Fe(VI), and Py-Fe(VI)  
240 processes was explored. As reflected in Figures 2d–2f, the proportion of generated  
241 PMSO<sub>2</sub> to degraded PMSO consistently remained around 100% throughout the entire  
242 reaction sequence, demonstrating that nearly all PMSO degradation was converted into  
243 PMSO<sub>2</sub> through the oxygen transfer mechanism in all processes. The findings  
244 additionally confirm that the involvement of radicals may be considered negligible,  
245 with Fe(V) and Fe(IV) being identified as the key reactive species responsible for the  
246 removal of IQL. Importantly, compared with sole Fe(VI) process, Di-Fe(VI) and Py-  
247 Fe(VI) processes achieved faster degradation of PMSO and formation of PMSO<sub>2</sub>,  
248 which is attributed to the addition of Di and Py speeding up the generation of

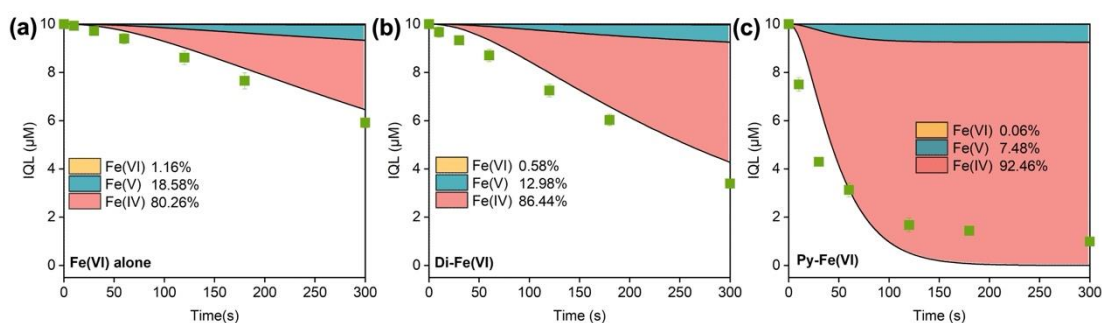
249 Fe(IV)/Fe(V). [Figure 2c](#) presents the EPR spectrum of TEMP-<sup>1</sup>O<sub>2</sub> in various processes:  
250 a signal for the TEMP-<sup>1</sup>O<sub>2</sub> adduct was observed in the Fe(VI) alone process, while the  
251 signals for adduct in the Di-Fe(VI) and Py-Fe(VI) systems were significantly stronger  
252 than that of the Fe(VI) alone. Previous research has reported that high-valent iron  
253 (Fe(IV), Fe (V), Fe(VI)) could lead to false positives in <sup>1</sup>O<sub>2</sub> EPR detection<sup>49</sup>. Therefore,  
254 the signals here were likely attributed to high-valent iron, since with the presence of  
255 PMSO the signals were significantly reduced. The enhanced signal in Di-Fe(VI) and  
256 Py-Fe(VI) process also indicated that the production of Fe(IV)/Fe(V) was increased. In  
257 summary, Fe(V)/Fe(IV) was likely the dominant reactive species for IQL removal in  
258 the Di-Fe(VI) and Py-Fe(VI) reaction processes.

259

### 260 **3.3. Identification of Fe(IV)/Fe(V)/Fe(VI) Contribution to IQL degradation**

261 The results discussed above corroborate that only Fe(IV), Fe(V), and Fe(VI) were  
262 involved in IQL oxidation. However, the specific contributions of ferrates in this  
263 process are still unknown. Thus, a model was built based on major reactions (details in  
264 [Tables S2–S4](#)) and employed to fit the kinetics of IQL degradation by Kintecus software.  
265 Based on the modeled results, Fe(V) and Fe(IV) contributed 18.6% and 80.3% to IQL  
266 oxidation in the Fe(VI) alone process, respectively. Fe(IV) was the dominant reactive  
267 species for IQL degradation in the Di-Fe(VI) process (86.4% contribution), while the  
268 contribution of Fe(V) was 12.9%. Similarly, Fe(IV) accounted for 92.5% of the IQL  
269 oxidation in the Py-Fe(VI) process, whereas Fe(V) contributed only 7.48% to IQL  
270 oxidation. Of note is that the contribution of Fe(IV) obviously increased in the Di-Fe(VI)  
271 and Py- Fe(VI) processes, in comparison with that of the sole Fe(VI) system ([Figures](#)  
272 [3](#)), suggesting the role of Fe(IV). The above models were tested with a sensitivity  
273 analysis and model validation ([Figures S10–S18](#)) and the results confirmed that the

274 fitting results were valid. Furthermore, the concentration profiles of ferrates in Fe(VI)  
 275 alone, Di-Fe(VI), and Py-Fe(VI) were also determined based on the simulation. [Figure](#)  
 276 [S19](#) shows that the concentration of Fe(IV) was about three orders of magnitude higher  
 277 than that of Fe(V) during IQL degradation by three different processes. Note that the  
 278 concentration of Fe(IV) in the Di-Fe(VI) and Py-Fe(VI) processes were increased  
 279 compared with the case of Fe(VI) alone, suggesting the increased amounts of reactive  
 280 species under the activation of Di and Py. In general, the results strongly suggest that  
 281 Fe(IV) played a dominant role in all the three processes.



282

283 **Figure 3.** Contributions of Fe(IV), Fe(V), and Fe(VI) to IQL degradation by Fe(VI)  
 284 alone (a), Di-Fe(VI) (b), and Py-Fe(VI) (c) processes.. Experiment conditions: pH =  
 285 9.0,  $[IQL]_0 = 10 \mu\text{M}$ ,  $[Di]_0 = [Py]_0 = 40 \mu\text{M}$ ,  $[Fe(VI)]_0 = 500 \mu\text{M}$ .

286

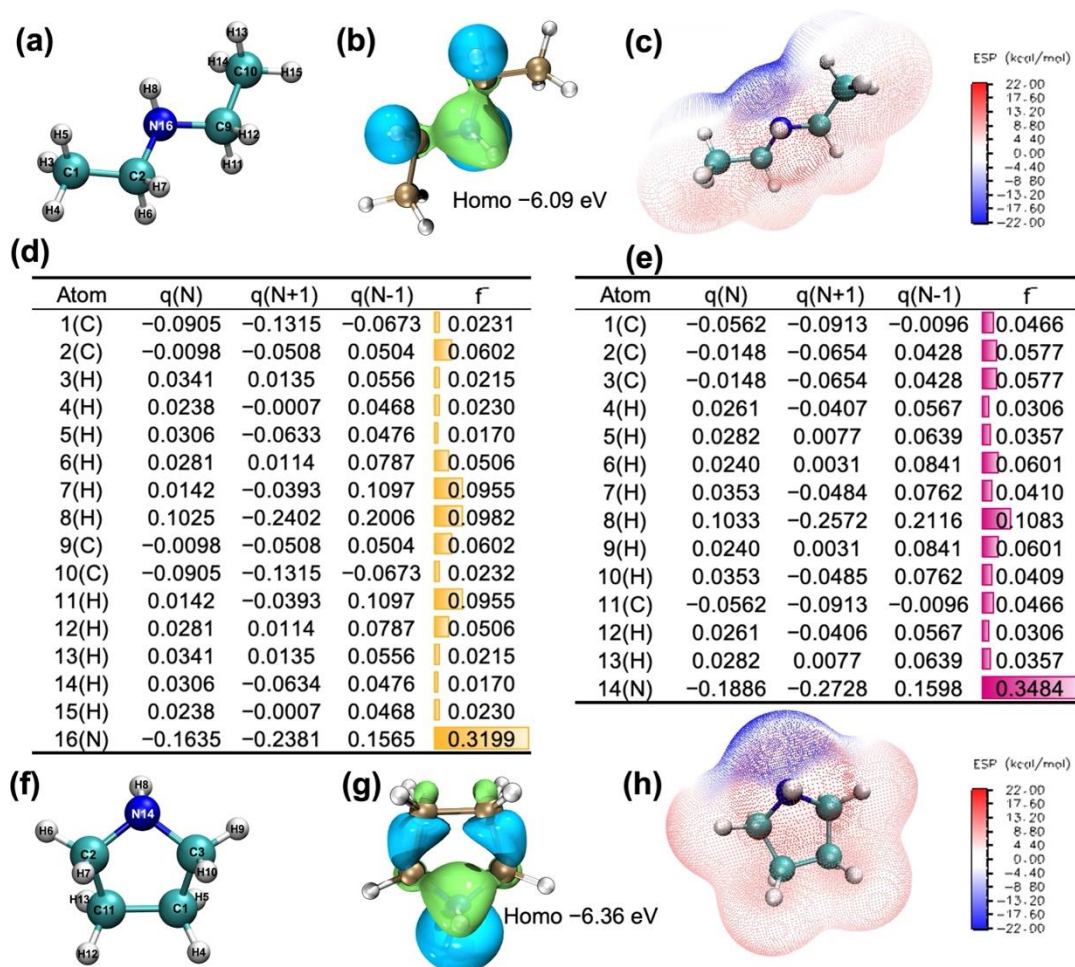
### 287 3.4. Activation Mechanism of Fe(VI) by Secondary Amines and Corresponding 288 Theoretical Calculations

289 As mentioned above, both Di and Py enhanced the oxidative performance likely  
 290 by activating Fe(VI) to generate Fe(IV)/Fe(V) intermediates. In this process, Fe(VI)  
 291 acts as an electron acceptor, while Di and Py serve as electron donors. This section will  
 292 delve into the specific activation sites of Fe(VI) by Di and Py, along with the relevant  
 293 functional groups, through DFT calculations. [Figure 4a](#), [4c](#), [4f](#), and [4h](#) illustrates the

294 distribution of negative and positive electrostatic potentials around Di and Py using a  
295 gradient from blue to red. The deep blue regions represent areas of concentrated  
296 negative charge, surrounding N atoms, which correlate with stronger affinity for high-  
297 valent Fe active species and greater potential for chemical activation. By analyzing the  
298 electron density isosurface maps of  $f^-$ ,  $f^+$ , and  $f^0$  on the surfaces of Di and Py, it is  
299 evident that the -NH groups in Di and Py are expected to exhibit higher reactivity  
300 (Figure S20). While the isosurface mapping of electron density provides intuitive  
301 insights, it does not facilitate detailed quantitative analysis of Fukui function values. To  
302 enable a more streamlined and intuitive interpretation, a simplified version of the Fukui  
303 function was employed to predict the sites in Di and Py molecules that are susceptible  
304 to attack by reactive species. The condensed Fukui function theory indicates that larger  
305  $f^-$ ,  $f^+$ , and  $f^0$  values correspond to atoms more prone to electrophilic, nucleophilic, and  
306 radical attacks, respectively. The 3N site in Di and the 1N site in Py display the highest  
307  $f^-$  values (Figure 4d–4e), suggesting these locations are likely the first to be targeted by  
308 Fe(VI).

309 The highest occupied molecular orbital (HOMO) is a critical indicator reflecting  
310 the electron-donating capacity of a molecule. Figure 4b and 4g reveals that the HOMOs  
311 of both Di and Py were apt to be localized on the -NH groups. Thus, the electrons in the  
312 -NH groups of Di and Py are readily delocalized. The HOMO value of Py (-6.36 eV)  
313 is more negative than that of Di (-6.09 eV), indicating that Di has superior electron-  
314 donating capability to Fe(VI) compared to Py. This observation, which exhibits an  
315 inverse correlation with the degradation trend of IQL, will be analyzed in subsequent

316 sections.



317

318 **Figure 4.** Chemical structure of Di (a) and Py (f); Highest occupied molecular orbital  
 319 (HOMO) of Di (b) and Py (g); Electrostatic potential (ESP) distribution of Di (c) and  
 320 Py (h); Natural population analysis (NPA) charge distributions and condensed Fukui  
 321 index ( $f^-$ ) of Di (d) and Py (e).

322

### 323 3.5. Coordination between Fe(VI) and Secondary Amines

324 In-situ electrochemical analysis was further used to investigate the promoting  
 325 mechanism of Di-Fe(VI) and Py-Fe(VI) processes. [Figure 5a](#) shows the variation curve  
 326 of the open circuit potential with time, using a mercury oxide electrode (HgO) as the

327 reference electrode and Pt sheet electrodes as the working and counter electrodes. After  
328 Fe(VI) was added to the solution, the potential rose immediately from initial 0.68 V to  
329 final 0.83 V after stabilization. Because Fe(VI) is a strong oxidizing agent, the addition  
330 of Fe(VI) enhanced the oxidizing power, resulting in a higher potential. After the  
331 subsequent addition of Di or Py, the potential began to decrease, indicating that Di and  
332 Py acted as reductants in the reaction, donating electrons and reducing Fe(VI) to low-  
333 valent forms, such as Fe(IV) and Fe(V). Next, the residual Fe(VI) concentrations for  
334 Fe(VI) alone, Di-Fe(VI), and Py-Fe(VI) processes were investigated (Figure 5b). After  
335 300 s reaction time, the value of  $[\text{Fe(VI)}]/[\text{Fe(VI)}]_0$  ratio was 0.94, 0.90, and 0.58 in the  
336 sole Fe(VI), Di-Fe(VI), and Py-Fe(VI) systems, respectively, indicating that the  
337 consumption of Fe(VI) could be remarkably improved with the presence of Di and Py.  
338 The consumption of Fe(VI) was effectively improved by Di and Py, while the Di-Fe(VI)  
339 and Py-Fe(VI) processes still showed higher performance for IQL abatement than sole  
340 Fe(VI). As a whole, these results indicate that more reactive species, such as active  
341 high-valent iron intermediate species, (Fe(IV), Fe(V)), may be formed by the  
342 combination of Di and Py with Fe (VI) <sup>14,28</sup>.

343 Cyclic voltammetry (CV) measurements were conducted for the three systems  
344 (Figure 5c). Redox peaks were observed in all three systems; given the limited  
345 electrochemical data for Fe(VI) in the existing literature, it is hypothesized that the  
346 observed reduction may correspond to the reductive conversion of high-valent Fe  
347 species to low-valent forms, such as Fe(IV) and Fe(V). The Py-Fe(VI) process exhibited  
348 the highest peak current, indicating the presence of more active iron species in the  
349 process. It is noteworthy that, compared to the Fe(VI) alone, both the Di-Fe(VI) and  
350 Py-Fe(VI) processes exhibited a positive shift in oxidation peaks and a negative shift in  
351 reduction peaks in their CV curves. This phenomenon could be attributed to the

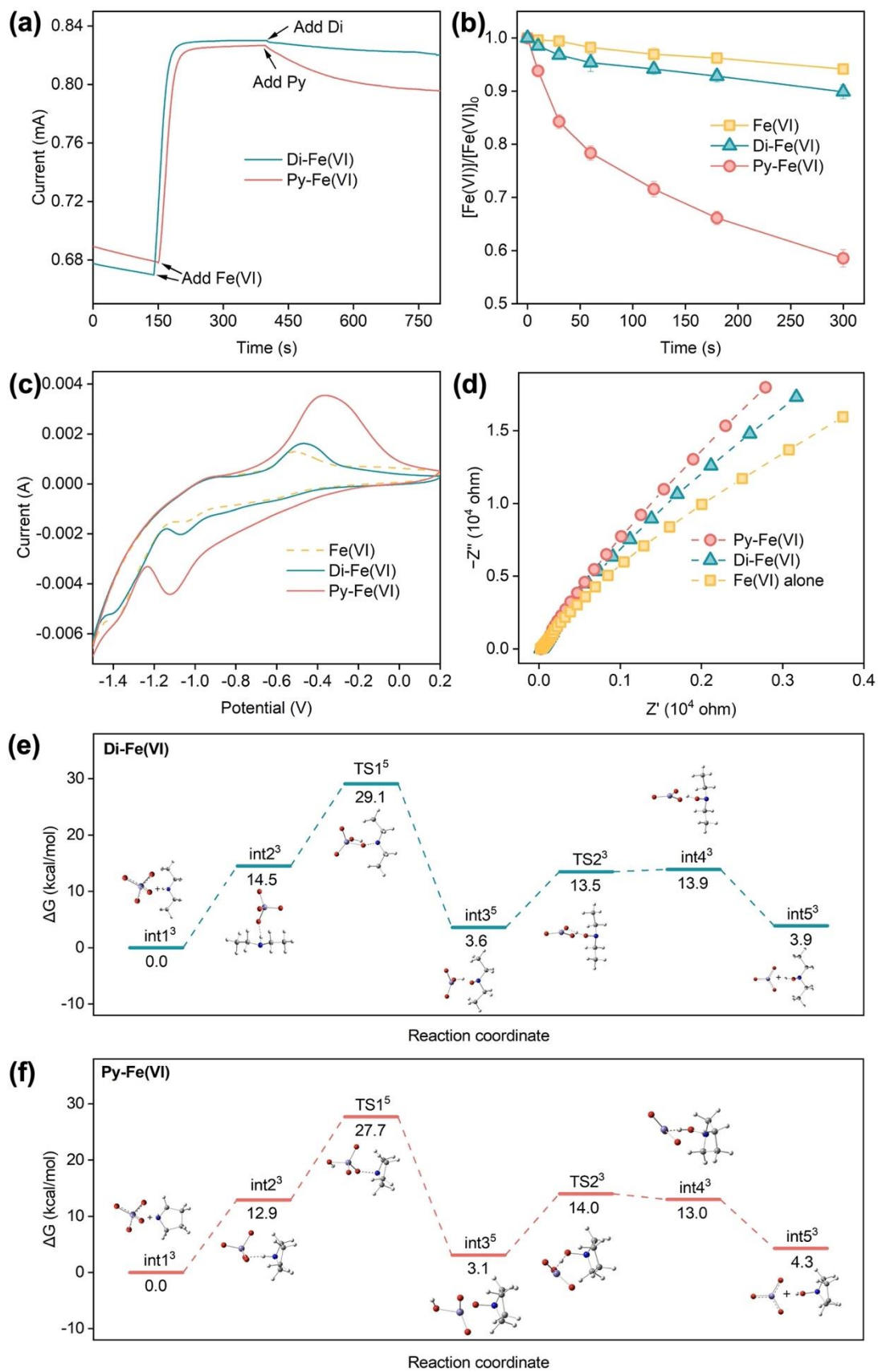
352 coordination of Di and Py with Fe(VI) to form complexes, where the complexation  
353 altered the redox potential of Fe(VI). The negative shift in reduction peaks indicates  
354 that the Fe(VI) complexes are more easily reduced than free Fe(VI), suggesting a  
355 lowering of their reduction energy barrier. Furthermore, electrochemical impedance  
356 spectroscopy (EIS) was employed to evaluate the charge transfer resistance of the  
357 catalysts during redox reactions <sup>50</sup> (Figure 5d). A lower Tafel slope indicates higher  
358 intrinsic activity and reduced transport limitations <sup>51</sup>. The order of the semicircle radii  
359 in the Nyquist plots was: Fe(VI) < Di-Fe(VI) < Py-Fe(VI), with Py-Fe(VI) process  
360 showing the largest radius. This phenomenon is due to the coverage of the electrode  
361 surface by the complexes after their formation, leading to an increase in resistance.  
362 These results validate the hypothesis discussed above: taken together, the efficacy of Di  
363 and Py in activating Fe(VI) for IQL removal appears to be influenced by their  
364 coordination properties.

365 To elucidate the superior activation performance of Py over Di in enhancing  
366 Fe(VI)-mediated IQL degradation and unravel the mechanistic origins of differential  
367 Fe(V)/Fe(IV) contribution ratios, we conducted density functional theory (DFT)  
368 calculations to compare the reaction energy barriers of the various systems.  
369 Thermodynamic parameters for reactants, transition states (TS), intermediates, and  
370 products in Di- and Py-Fe(VI) reaction systems are summarized in Tables S7–S9, with  
371 Gibbs free energies illustrated in Figures 5e and 5f. The results indicate that the  
372 activation energy barrier for Py to form transition state TS1 with Fe(VI) (27.7 kcal/mol)  
373 is lower than that of Di (29.1 kcal/mol), implying faster reaction kinetics for Py. This  
374 observation aligns with the enhancement trend discussed in Section 3.1, which  
375 suggested that Py-Fe(VI) exhibited superior IQL degradation compared to Di-Fe(VI).  
376 This phenomenon may arise from the conformational rigidity of Py's cyclic structure,

377 which facilitates optimal geometric alignment for hydrogen abstraction and oxygen  
378 transfer processes. Concurrently, intracyclic orbital conjugation and favorable lone-pair  
379 electron orientation within the pyrrolidine ring may synergistically promote Fe-O bond  
380 cleavage while stabilizing O-N bond formation. Although Di is characterized by a  
381 marginally lower TS2 barrier (13.5 vs. 14.0 kcal/mol for Py), the decisive TS1 disparity  
382 may govern the overall reaction kinetics, establishing Py's superiority.

383 Furthermore, we note that the energy barrier for the formation of complex int2  
384 between Py and Fe(VI) (12.9 kcal/mol) was found to be lower than the corresponding  
385 value for Di (14.5 kcal/mol), indicating that Py should coordinate more efficiently with  
386 Fe(VI). During the reaction between Py and Fe(VI), the energy barrier for the formation  
387 of complex int4 between Fe(IV) and Py(O) (13.0 kcal/mol) was also found to be lower  
388 than the corresponding value for Di (13.9 kcal/mol), suggesting that the Fe(IV)-Py(O)  
389 complex should be more stable and may effectively inhibit its conversion into less  
390 reactive Fe(II)/Fe(III). Based on [Tables S2–S4](#), Fe(V) in all three systems is primarily  
391 generated from the reaction between Fe(VI) and Fe(II). Consequently, the Fe(IV)  
392 contribution in the Py-Fe(VI) system is higher than that in the Di-Fe(VI) system, while  
393 the Fe(V) contribution is lower. Overall, Py may provide superior advantages in  
394 intermediate formation and stabilization, further supporting its kinetic dominance.

395 In summary, the findings discussed here suggest that the enhanced pollutant  
396 degradation performance of secondary amines (e.g., Di, Py) with Fe(VI) is closely  
397 related to their ability to form stable complexes with high-valent iron species  
398 (Fe(VI)/Fe(IV)/Fe(V)). Notably, differences in coordination capacity are hypothesized  
399 to directly determine the superiority or inferiority of the resulting catalytic performance.



400

401 **Figure 5.** Change of open-circuit potential in Di-Fe(VI) and Py-Fe(VI) processes (a);

402 Decomposition of Fe(VI) in reaction solution with or without Di and Py (b); Cycle  
403 voltammetry measurements of Fe(VI), Di-Fe(VI), and Py-Fe(VI) processes (c); EIS  
404 measurements of Fe(VI), Di-Fe(VI), and Py-Fe(VI) processes (d); Gibbs free energy  
405 pathway between Di and Fe(VI) (e), Py and Fe(VI) (f). Experiment conditions: pH =  
406 9.0, [IQL]<sub>0</sub> = 10 μM, [Di]<sub>0</sub> = [Py]<sub>0</sub> = 40 μM, [Fe(VI)]<sub>0</sub> = 500 μM.

407

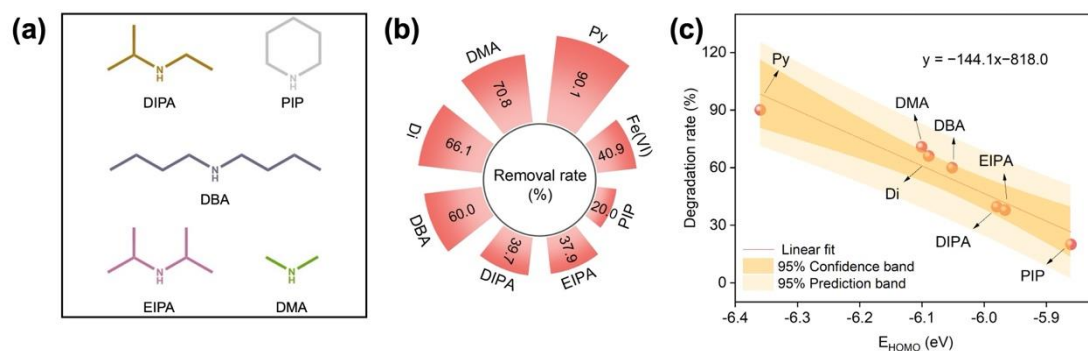
### 408 **3.6. Structure Effects of Secondary Amine**

409 The regulatory effects of seven structurally distinct secondary amines was  
410 investigated in the Fe(VI)-mediated degradation of isoquinoline (IQL). The tested  
411 amines included five linear secondary amines: dimethylamine (DMA), Di,  
412 dibutylamine (DBA), diisopropylamine (DIPA), and N-ethylisopropylamine (EIPA),  
413 along with two cyclic secondary amines, namely, Py and piperidine (PIP). Among the  
414 linear amines, DMA, Di, and DBA possess straight-chain alkyl groups, whereas DIPA  
415 and EIPA feature branched structures (Figure 6a). Results indicated that DMA, Di, DBA,  
416 and Py enhanced Fe(VI)- mediated IQL degradation, with efficacy following the order:  
417 Py > DMA > Di > DBA (Figure 6b). Notably, the cyclic amine Py exhibited superior  
418 activation performance compared to linear amines, likely attributed to its rigid  
419 molecular structure facilitating stable complexation with Fe(VI). Such coordination  
420 may effectively stabilize reactive iron intermediates. In linear amine systems,  
421 shortening the alkyl chain length improved activation efficiency, highlighting the  
422 critical role of steric hindrance, with longer chains hindering optimal coordination.  
423 However, DIPA, EIPA, and PIP inhibited degradation. This anomaly may arise from  
424 unique steric effects imposed by their branched structures or electronic interference  
425 with Fe(VI) redox processes.

426 Although preliminary comparisons between Di and Py showed a positive

427 correlation trend between their coordination ability with Fe(VI) and IQL removal  
428 efficiency, directly quantifying the coordination capabilities of various secondary  
429 amines with Fe(VI) faces significant challenges. Coordination strength is influenced by  
430 multiple factors, including solvent effects, steric hindrance, and dynamic reaction  
431 conditions, which complicate precise measurement or quantitative estimation.<sup>52</sup> In  
432 contrast, the HOMO energy levels ( $E_{\text{HOMO}}$ ) calculated via quantum chemical methods  
433 should offer a stable theoretical measure of the intrinsic electron-donating properties of  
434 amines. Moreover, as discussed in Sections 3.4 and 3.5, there appears to be a theoretical  
435 relationship between  $E_{\text{HOMO}}$  and coordination ability: higher  $E_{\text{HOMO}}$  values were  
436 associated with weaker coordination. Based on this premise, we investigated the  
437 correlation between IQL removal and  $E_{\text{HOMO}}$  values for seven secondary amines.  
438 Quantum chemical calculations revealed a significant negative correlation between IQL  
439 degradation and the  $E_{\text{HOMO}}$  levels (Figure 6c, Figure S21). This finding suggests that  
440 the electron-donating capacity of secondary amines inversely correlates with their  
441 coordination ability. Effective Fe(VI) activation requires moderate electron-donating  
442 capacity: excessive electron donation (high HOMO levels) may trigger over-reduction  
443 of Fe(VI) to Fe(II)/Fe(III), prematurely depleting its oxidative potential.

444 In summary, this study suggests that the electron-donating capacity of secondary  
445 amines exhibits a negative correlation with Fe(VI) activation, thus providing theoretical  
446 guidance for designing high-performance Fe(VI) activators, while also unveiling the  
447 intricate relationships between ligand electronic properties and oxidant activation  
448 mechanisms.



449

450 **Figure 6.** Chemical structure of DIPA, PIP, DBA, EIPA, and DMA (a); Degradation  
 451 efficiencies of IQL by Fe(VI) with and without secondary amines (b); Correlation  
 452 between the HOMO energy levels ( $E_{\text{HOMO}}$ ) and IQL degradation rate (c); HOMO and  
 453 LUMO of Py, Di, DIPA, PIP, DBA, EIPA, and DMA (d). Experiment conditions: pH =  
 454 9.0,  $[\text{IQL}]_0 = 10 \mu\text{M}$ ,  $[\text{secondary amines}]_0 = 40 \mu\text{M}$ ,  $[\text{Fe(VI)}]_0 = 500 \mu\text{M}$ .

455

#### 456 4. Environmental Implications

457 This study discusses the critical role of secondary amines in enhancing Fe(VI)-  
 458 based oxidation systems. By identifying Di and Py as high-performance activators  
 459 (degradation kinetics accelerated by ~2-fold and 7-fold compared to Fe(VI) alone,  
 460 respectively), the findings should enable reductions in Fe(VI) dosage and treatment  
 461 time, thereby minimizing secondary sludge generation and chemical costs. The  
 462 dominance of Fe(IV) over free radicals in pollutant degradation further reduces risks of  
 463 toxic byproduct formation (e.g., halogenated organic compounds), aligning with safer  
 464 water purification strategies. Importantly, the revealed negative correlation between the  
 465 HOMO energy levels of secondary amines and their activation efficiency provides a  
 466 molecular blueprint for designing eco-friendly amine ligands, guiding synthetic  
 467 chemistry toward non-toxic, electronically tunable alternatives. The iron-amine  
 468 complexation mechanism may also inspire low-carbon solutions that could convert  
 469 nitrogen-containing waste compounds into Fe(VI) activators. Furthermore, the amine-

470 coordination-mediated extension of Fe(IV) lifetime enhances pollutant mineralization  
471 efficiency, which is crucial for eliminating persistent micropollutants in aquatic  
472 environments.

473 It should be emphasized that due to the structural complexity of secondary amines,  
474 the impacts and underlying mechanisms of Fe(VI)-mediated pollutant degradation by  
475 secondary amines containing additional functional groups (e.g., -COOH, -OH) remain  
476 unclear. Further investigations into the fundamental mechanisms of introducing other  
477 functional groups into Fe(VI)-based pollutant oxidation systems are essential. Such  
478 studies will deepen the understanding of secondary amine-Fe(VI) interactions and  
479 strengthen the theoretical foundation for designing highly efficient secondary amine-  
480 based compounds to activate Fe(VI).

481

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