

Overlooking the effect of alcohol quenchers can mislead mechanistic understanding in ferrate-based advanced oxidation processes

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1 **Overlooking the Effect of Alcohol Quenchers Can**
2 **Mislead Mechanistic Understanding in Ferrate-based**
3 **Advanced Oxidation Processes**

4
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20 **Abstract**

21 Alcohols serve as effective quenchers and are widely employed to assess the role
22 of reactive species in advanced oxidation processes (AOPs). However, this study
23 reveals that frequently used alcohol quenchers, including tert-butanol (TBA), methanol
24 (MA), ethanol (EA), and furfuryl alcohol (FFA), can substantially affect the ferrate
25 (Fe(VI)) system. Firstly, the presence of alcohols was found to influence the
26 decomposition of Fe(VI). In the pH range of 7–11, various alcohols promoted Fe(VI)
27 decomposition, especially at pH 7–8, namely, the pH conditions often used in Fe(VI)-
28 based advanced oxidation studies. The magnitude of Fe(VI) decomposition influenced
29 by the alcohols was ranked as FFA > EA > MA > TBA. Secondly, alcohols may alter
30 the formation and conversion of high-valent iron active species. **Using the**
31 **phenylmethyl sulfoxide (PMSO) probe**, we observed that MA and TBA inhibited the
32 removal of PMSO by Fe(VI), while FFA and EA substantially enhanced it. These results
33 indicate that alcohols may not only influence the decomposition of Fe(VI) itself, but
34 also affect the degradation of pollutants mediated by high-valent iron active species.
35 These phenomena may lead to misconceptions about the mechanisms and efficacy of
36 Fe(VI)-based AOPs. Overall, this work underscores the importance of carefully
37 selecting quenchers in complex oxidation systems involving Fe(VI) to avoid misleading
38 interpretations of Fe(VI) decomposition and oxidation behavior.

39

40 **Keywords**

41 **Alcohol; Scavengers; Quenchers; High-valent iron species; Advanced oxidation**
42 **processes**

43 **1. Introduction**

44 Ferrate (Fe(VI)) is an emerging green oxidant with strong oxidative ability [1].
45 Since the 1970s, researchers have been exploring its potential applications in water and
46 wastewater treatment [2]. Its unique features, such as multiple treatment capabilities,
47 minimal formation of disinfection by-products, and reduced susceptibility to water
48 components, position it as a promising alternative to traditional oxidants like chlorine,
49 ozone, and persulfate [3].

50 Nevertheless, Fe(VI) is prone to auto-decay reactions under environmentally
51 relevant conditions, presenting a major obstacle for its application in water and
52 wastewater treatment [2,4]. Consequently, various methods have been developed in
53 recent years to enhance the oxidative capacity of Fe(VI). These approaches generally
54 involve transforming Fe(VI) into more reactive species, such as generating sulfate
55 radicals, hydroxyl radicals, and singlet oxygen through combination with other oxidants
56 [5,6], or by introducing reductants [7,8], metal oxides [9–11], metal ions [12,13], or
57 carbonaceous materials [14,15] to reduce Fe(VI) to highly active high-valent iron
58 species [16]. The use of quenchers is a standard experimental technique for identifying
59 active species generated in advance oxidation processes (AOPs). By adding various
60 excess quenchers and observing their effects on the system, specific active species can
61 be inferred [17]. However, this quenching method relies on an implicit assumption: that
62 the high concentration of quencher solely removes its targeted reactive species without
63 significantly affecting other reaction mechanisms in the system. If this assumption does
64 not hold, the observed variability in the decrease of pollutant concentration in the
65 absence of the quencher may not be solely attributed to the quenched reactive species
66 but could instead result from other confounding effects induced by the quencher [18].

67 Notably, recent findings suggest that the basic assumptions of the quenching

68 method may not be applicable to persulfate-based AOPs. Alcohols have been shown to
69 generate alkoxy radicals, which can decompose peroxydisulfate (PDS) into sulfate
70 radicals ($\text{SO}_4^{\cdot-}$), thereby increasing PDS consumption and mitigating the inhibitory
71 effects of alcohols on pollutant degradation [18]. This interaction can lead to
72 misunderstandings regarding the contribution of active species. Additionally, reports
73 indicate that alcohols can react with Fe(VI) and high-valent iron active species to
74 produce aldehydes/ketone [19,20]. This phenomenon raises concerns that alcohols may
75 affect the Fe(VI)-based oxidation processes, thus potentially altering their effectiveness
76 in oxidizing pollutants and leading to incorrect assessments of the contributions of
77 active species in complex systems. Therefore, it is essential to clarify this issue to
78 enhance the mechanistic understanding of Fe(VI)-based AOPs.

79 The primary aim of this study is to assess the effectiveness of quenching methods
80 in Fe(VI)-based AOPs. Specifically, it examines the impact of commonly used alcohol
81 quenchers—methanol (MA), ethanol (EA), tert-butanol (TBA), and furfuryl alcohol
82 (FFA)—on the decomposition of Fe(VI) under different pH conditions. The study
83 explores the effect of dosages of these alcohol quenchers on Fe(VI) decomposition and
84 investigates their influence on the removal of methyl phenyl sulfoxide (PMSO) probes,
85 as well as the formation of methyl phenyl sulfone (PMSO₂) by Fe(VI). Additionally,
86 based on density functional theory calculations, a mechanistic hypothesis for the
87 reaction between ferrate and alcohols is proposed.

88

89 **2. Materials and Methods**

90 **2.1. Chemicals and Reagents**

91 All chemicals and reagents are detailed in the Supporting Information Text S1. The
92 preparation method for Fe(VI) is in Text S2.

93 2.2. Decomposition and Degradation Tests

94 All Fe(VI) decomposition and methyl phenyl sulfoxide (PMSO) degradation
95 experiments were conducted in 100 mL glass beakers with magnetic stirring at $25 \pm$
96 1°C . Reactions were initiated by introducing Fe(VI) (200 μM) and alcohols (0–20 mM)
97 to the system. The pH was maintained within a range of 7.0–11.0 using a 10 mM borate
98 or carbonate buffer (see Text S3 for information on buffer selection). For Fe(VI)
99 decomposition, samples were taken at intervals and measured with UV-visible
100 spectroscopy at 510 nm (Text S4). For PMSO (10 μM) degradation, 1 mL samples were
101 quenched with hydroxylamine hydrochloride, then filtered through a 0.22 μm filter into
102 a UPLC vial before analysis. Other experiments followed the same procedure. All
103 operations were repeated at least twice, with data reported as averages with standard
104 deviations.

105 2.3. Analytical Methods

106 The concentrations of PMSO and PMSO₂ were determined by UPLC (LC-16,
107 Shimadzu, Japan) with a UV detector and Shim-pack GIST C18 (5 μm , 4.6×250 mm),
108 under conditions in Table S1.

109 2.4 Quantum Chemical Calculations

110 The quantum chemical calculations were performed with the Gaussian 16 [21]
111 program using the M06-2X functional in combination with the 6-311G(d,p) basis set.
112 Nucleophilicity index (ω^-), and quantum chemical descriptors (E_{HOMO} , E_{LUMO} , E_{LUMO}
113 $- E_{\text{HOMO}}$, ionization potential (IP), electron affinity (EEA)), were chosen for this study
114 [22]. All the descriptors and their formulas are tabulated in Table S2. The calculation
115 of the Fukui index for each alcohol was performed using the Multiwfn software [23,24].
116 To visualize the molecular orbitals, molecular electrostatic potential, and Fukui indexes,
117 color-filled isosurface graphs were generated using the Visual Molecular Dynamics

118 (VMD) program [25]. Details are provided in [Text S5](#).

119

120 **3. Results and Discussion**

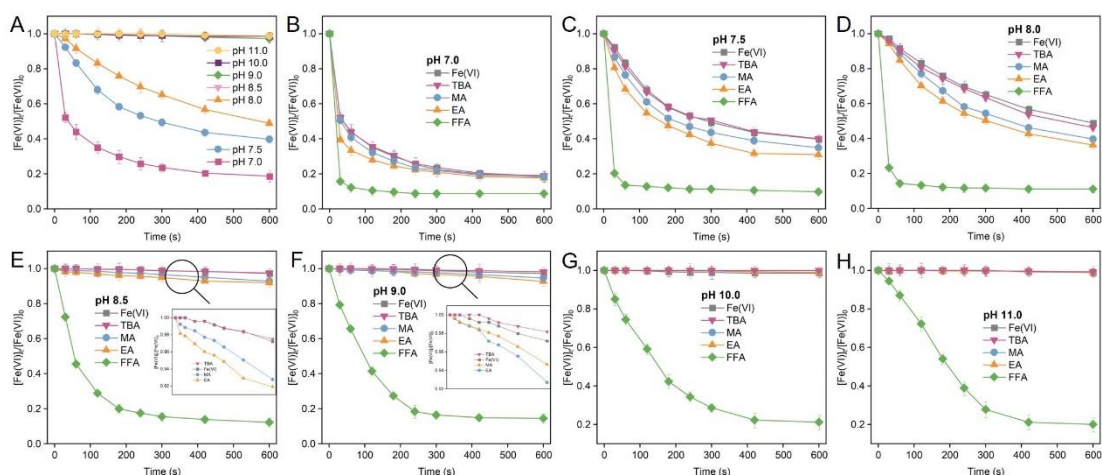
121 **3.1. Fe(VI) Self-decay and Impact of Alcohols**

122 Fe(VI) has a high rate of loss due to its spontaneous decomposition [11]. Fig. 1A
123 shows results regarding the self-decomposition of Fe(VI) in the pH range of 7.0–11.0.
124 **When the pH increased from 8.0 to 11.0, the decomposition rate of Fe(VI) substantially**
125 **decreased from 51% (at pH 8.0) to 1% (at pH 11.0).** This result indicates a slower
126 decomposition rate of Fe(VI) and a more stable system under basic pH conditions. The
127 differences in Fe(VI) decay under various pH conditions are mainly attributed to: 1)
128 differences in the form of Fe(VI); 2) differences in the decay mechanisms [26].
129 **Furthermore, we investigated the effect of initial Fe(VI) concentration on its self-**
130 **decomposition (Fig. S1). The results suggest that Fe(VI) self-decomposition**
131 **accelerated with increasing initial concentration, indicating that elevated concentrations**
132 **promoted self-decomposition, which may be related to the self-catalytic effect of Fe(VI)**
133 **[27].**

134 Fig. 1B–1H illustrate the impact of tert-butanol (TBA), methanol (MA), ethanol
135 (EA), and furfuryl alcohol (FFA) on the self-decomposition of Fe(VI) under various pH
136 conditions. **Within the pH range of 7.0–11.0, the decomposition rate decreased from 81%**
137 **to 1% in the presence of TBA, closely matching the auto-decomposition rate of Fe(VI),**
138 **indicating negligible effects of TBA. In contrast, the addition of MA, EA, or FFA**
139 **considerably accelerated Fe(VI) decomposition, increasing the rate by 1%–83% at pH**
140 **7.0–9.0. However, their effects diminished at pH >9.0.** The impact of alcohols was most
141 pronounced between pH 7.0 and 8.0, possibly due to the higher chemical activity of
142 Fe(VI) in this range. When the pH exceeded 9, except for FFA, alcohols showed

143 decreasing impact with pH on Fe(VI) decomposition, likely because Fe(VI) is
 144 increasingly stable under more basic pH conditions. Similarly, in the tap water and river
 145 water matrices (Fig. S2), the same effects were observed, implying the universal
 146 applicability of this effect.

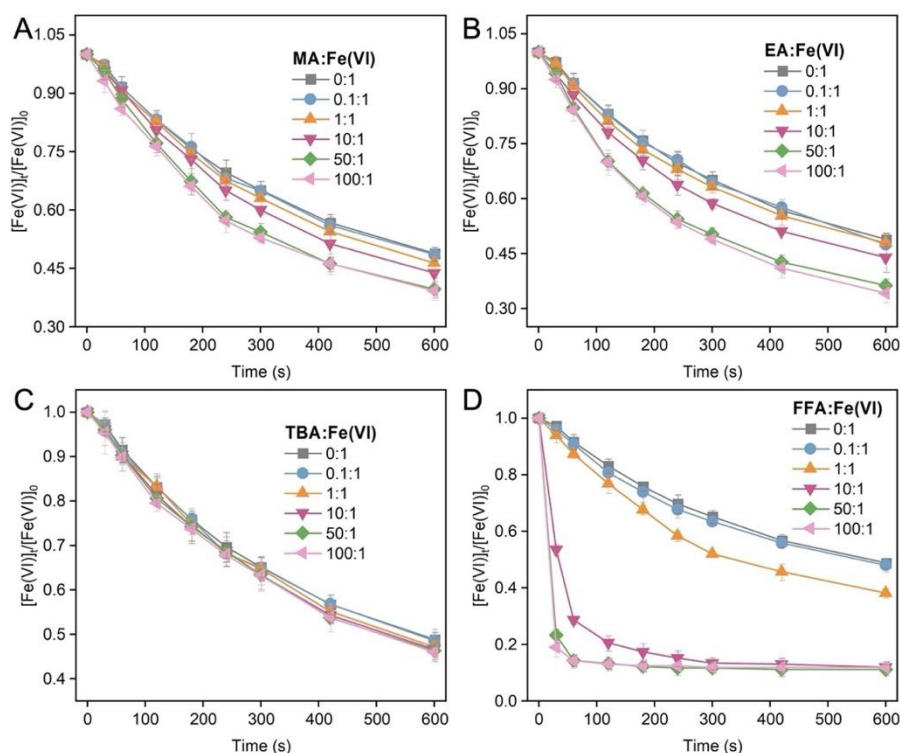
147 However, many studies on the advanced oxidation technique using Fe(VI) are
 148 conducted under pH 7.0–8.0 conditions [28–30], and quenching experiments often use
 149 the same alcohols [17,18] assessed in this study. Although research reports indicate that
 150 traditional alcohol quenchers do not quench high-valent iron active species, these
 151 studies may thus overlook the potential impact of alcohols on Fe(VI) itself.



152
 153 Fig. 1. Self-decomposition of Fe(VI) at pH 7.0–11.0 (A). Effect of TBA, MA, EA, and
 154 FFA on Fe(VI) decomposition at pH 7.0 (B), pH 7.5 (C), pH 8.0 (D), pH 8.5 (E), pH
 155 9.0 (F), pH 10.0 (G), and pH 11.0 (H). Experimental conditions: $[Fe(VI)]_0 = 200 \mu M$,
 156 $[TBA]_0 = [MA]_0 = [EA]_0 = [FFA]_0 = 10 \text{ mM}$.

157
 158 As shown in Fig. 2, the ratio of alcohol quenchers to Fe(VI) substantially affected
 159 the decomposition rate of Fe(VI). As the amount of alcohol quencher increased (from
 160 a ratio of 0:1 to 10:1), the decomposition rate accelerated markedly. When the ratio
 161 reached 50:1 or 100:1, the decomposition rate remained relatively constant, indicating

162 that the alcohol quenchers were in excess. Overall, the data imply that alcohol
163 quenchers substantially influence the stability of Fe(VI) under different conditions.



164
165 **Fig. 2. Effect of MA (A), EA (B), TBA (C), and FFA (D) on the decomposition of Fe(VI)**
166 **at varying ratios of alcohol quenchers to Fe(VI). Experimental conditions: pH = 8.0,**
167 **[Fe(VI)]₀ = 200 μM, [TBA]₀ = [MA]₀ = [EA]₀ = [FFA]₀ = 20 μM–20 mM.**

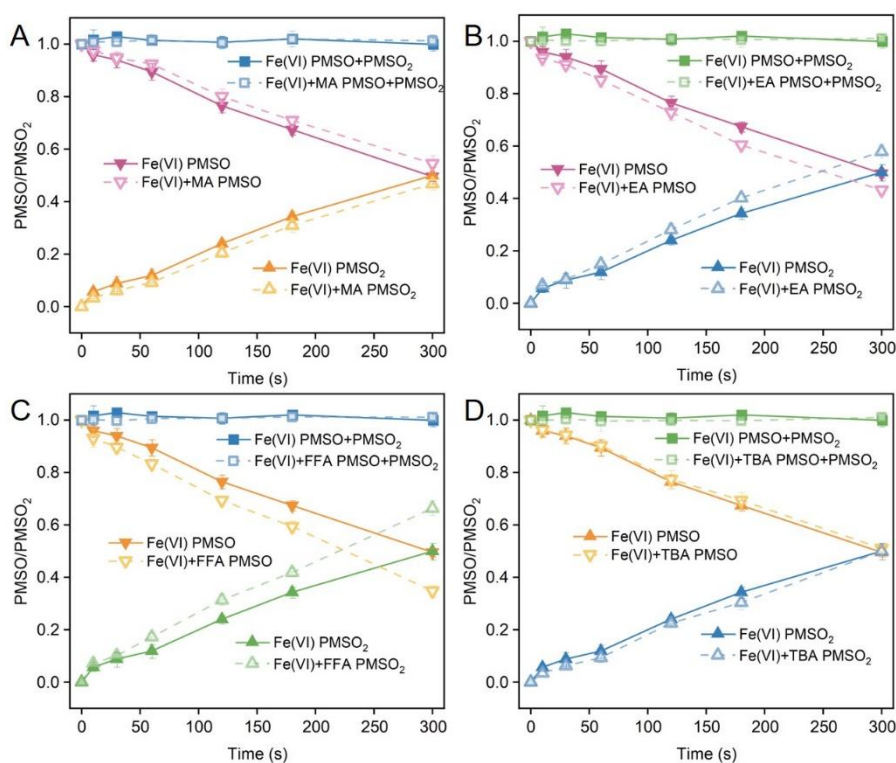
168

169 3.2. Effect of alcohols on the removal of PMSO by Fe(VI)

170 PMSO is a probe compound deployed to verify the nature of the high-valent iron
171 active species (Fe(IV)/Fe(V)), because it is specifically oxidized by Fe(IV)/Fe(V) into
172 PMSO₂, unlike other reactive species, such as hydroxyl radicals, which instead convert
173 PMSO into hydroxylated products [31]. Fig. 3 reports results obtained to assess the
174 effects of MA, EA, FFA, and TBA on the removal of PMSO by Fe(VI) and the
175 corresponding generation of PMSO₂. Each alcohol interacted differently with Fe(VI),
176 influencing the formation of Fe(IV)/Fe(V) and the degradation of PMSO. **Beside**
177 **promoting the decomposition of Fe(VI), MA inhibited PMSO removal by 5% compared**

178 to Fe(VI) alone, leading to a reduced amount of PMSO₂ formation. This result suggests
 179 that MA may facilitate the reduction of Fe(VI) to inactive lower-valent iron species
 180 (Fe(II)/Fe(III)). Unlike MA, both EA and FFA enhanced the removal of PMSO (7%–
 181 15%), implying that they reacted with Fe(VI) to produce the active Fe(IV)/Fe(V)
 182 species. TBA slightly inhibited PMSO removal (1%) and had minimal impact on Fe(VI)
 183 decomposition.

184 These observations emphasize the role of high-valent iron species in selective
 185 oxidation processes. Different types of alcohols can affect the reduction pathways of
 186 Fe(VI), thereby altering the oxidant selectivity. Therefore, when alcohol quenchers are
 187 used in complex Fe(VI)-based AOPs, they may either enhance or inhibit the system
 188 effectiveness. Such phenomena can obscure or mislead understanding of the roles
 189 played by reactive oxygen species, such as sulfate radicals, hydroxyl radicals, and
 190 singlet oxygen, in the removal of pollutants. Therefore, we do not recommend relying
 191 solely on quenchers to study the roles of active species in Fe(VI)-based AOPs. Instead,
 192 it is advisable to combine them with probe compounds or other detection methods.



193

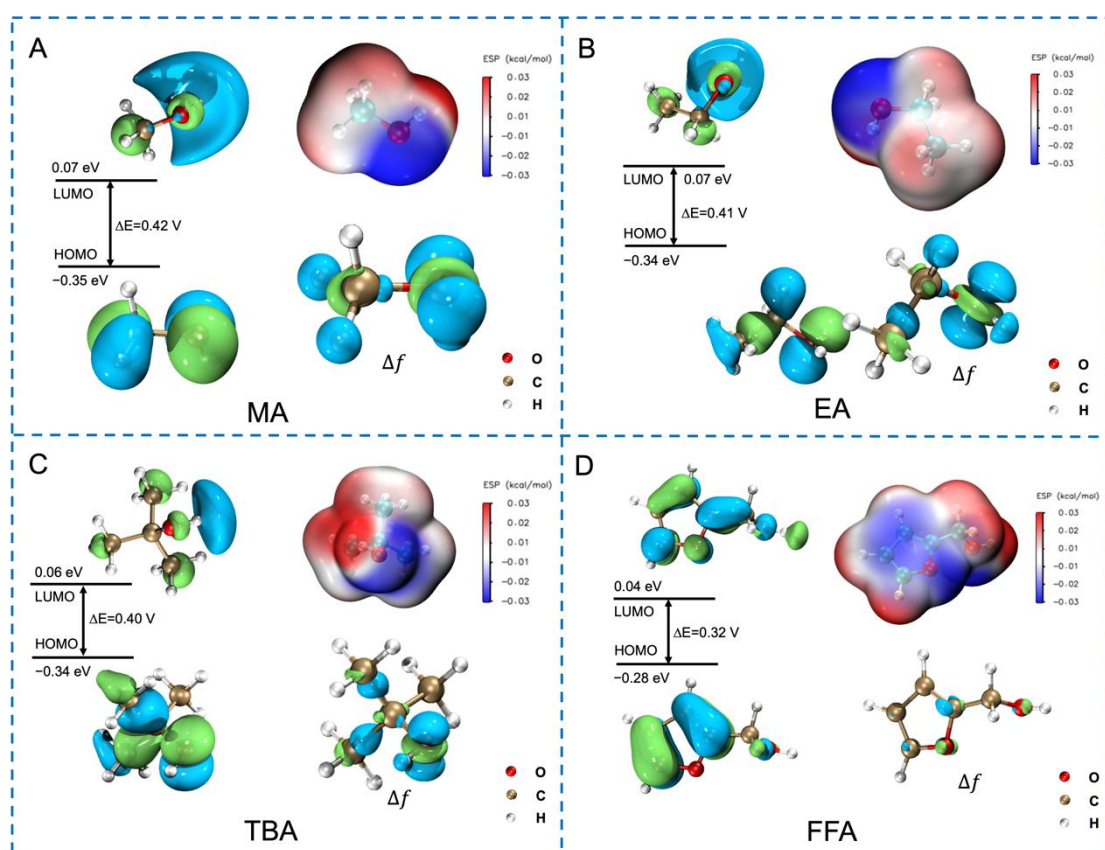
194 Fig. 3. Effect of MA (A), EA (B), FFA (C), and TBA (D) on the removal of PMSO and
195 the corresponding production of PMSO₂ in the Fe(VI) process. Experimental conditions:
196 pH = 8.0, [PMSO]₀ = 10 μM, [Fe(VI)]₀ = 200 μM, [TBA]₀ = [MA]₀ = [EA]₀ = [FFA]₀
197 = 10 mM.

198

199 3.3. Mechanistic analysis

200 Descriptors of the target compound, such as IP, electron affinity EEA, the
201 difference of the energy levels of the lowest unoccupied and highest occupied molecular
202 orbital ($E_{LUMO} - E_{HOMO}$), and ω^- , usually correlate with its reactivity with Fe(VI) [22].
203 Based on DFT theoretical calculations, the ranking of IP and $E_{LUMO} - E_{HOMO}$ values is:
204 MA > EA > TBA > FFA (Table S3). A higher potential value implies that the alcohol is
205 less reactive with Fe(VI). The EEA values for all the alcohols are negative, indicating
206 that these substances are characterized by minimal electrophilicity. Conversely, the
207 ranking of the ω^- value is: MA < EA < TBA < FFA, implying that MA has the least
208 nucleophilic character and the weakest reactivity with Fe(VI), while FFA has the most
209 nucleophilic character and the strongest reactivity with Fe(VI). Note that experimental
210 results suggested that TBA had the smallest effect on Fe(VI) decomposition and
211 reactive Fe species, which differs from the theoretical calculation results. The reason
212 for this discrepancy is not entirely clear. In regions where the electrostatic potential is
213 negative, electrons are more concentrated. Based on the analysis of electrostatic
214 potentials, we observe that, aside from the negative electrostatic potential region on the
215 five-membered ring of FFA, the negative regions for other alcohols are concentrated
216 around the hydroxyl groups. Therefore, Fe(VI) is more likely to attack the hydroxyl
217 parts of MA, EA, TBA molecules, and the five-membered ring of FFA. Fig. 4 illustrates
218 the isosurface maps of electronic density on the surfaces of EA, FFA, EA, and MA

219 molecules based on the Fukui function. In these maps, green and blue colors represent
 220 positive and negative values, respectively, with color intensity correlating with
 221 magnitude. Regions with higher positive values are more likely to be active sites for
 222 species attack. Clearly, the hydroxyl groups and alpha-hydrogen (α -H) in MA and EA,
 223 the hydroxyl group in TBA, and the O in FFA are more reactive. This result aligns with
 224 the findings by Kamachi et al. [20,32], who reported that Fe(VI) can mediate the
 225 extraction of hydrogen atoms from the O-H and C-H bonds of MA, forming
 226 organometallic intermediates with Fe-C bonds and hydroxymethyl radical
 227 intermediates, which are eventually oxidized to formaldehyde. Furthermore, Fe(IV) has
 228 been shown to oxidize cyclobutanol to cyclobutanone [19]. In other words, alcohols not
 229 only react with Fe(VI) itself, but also with the resulting high-valent iron species.



230

231 Fig. 4. Gap of E_{LUMO} and E_{HOMO} , orbital isosurface maps for Fukui function (Δf), and
 232 electrostatic potential (ESP) of MA (A), EA (B), TBA (C), and FFA (D).

233

234 This study challenges the traditional use of alcohols as quenchers in ferrate-based
235 processes. The results reveal that alcohols impact the decomposition of Fe(VI) and the
236 formation of Fe(IV)/Fe(V), raising concerns about the accuracy of active species
237 detection methods. These findings underscore the necessity for cautious use of alcohol
238 quenchers to ensure reliable assessment of active species in ferrate-based processes.

239

240 **4. Conclusion**

241 In this study, we assessed the effects of MA, EA, TBA, and FFA alcohols on the
242 decomposition of Fe(VI) and the behavior of high-valent iron active species.
243 Experimental observations suggest the need for caution when selecting alcohol
244 quenchers in complex systems, to avoid misleading interpretations regarding the
245 oxidative behavior of Fe(VI) and the contributions of reactive species. Some
246 contradictory conclusions from previous studies using quenching methods may also
247 need to be revisited, based on the results discussed in this work. However, we
248 acknowledge that, when the target pollutants react quickly with Fe(VI) or when Fe(VI)
249 concentrations are low, the influence of MA, EA, TBA, and FFA on the oxidative
250 behavior of Fe(VI) may be minimal or negligible. A key aim of this study is to
251 emphasize the careful use of alcohol quenchers in complex systems involving Fe(VI)
252 and high-valent iron active species to avoid misinterpretation of reactive species
253 contributions. Further research is warranted on accurately identifying and detecting
254 active species involved in the advanced oxidation process based on Fe(VI).

255

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