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

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Abstract

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

Keywords

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

1. Introduction

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

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

Notably, recent findings suggest that the basic assumptions of the quenching method may not be applicable to persulfate-based AOPs. Alcohols have been shown to generate alkoxy radicals, which can decompose peroxydisulfate (PDS) into sulfate radicals ($SO_4^{\bullet-}$), thereby increasing PDS consumption and mitigating the inhibitory effects of alcohols on pollutant degradation [18]. This interaction can lead to misunderstandings regarding the contribution of active species. Additionally, reports indicate that alcohols can react with Fe(VI) and high-valent iron active species to produce aldehydes/ketone [19,20]. This phenomenon raises concerns that alcohols may affect the Fe(VI)-based oxidation processes, thus potentially altering their effectiveness in oxidizing pollutants and leading to incorrect assessments of the contributions of active species in complex systems. Therefore, it is essential to clarify this issue to enhance the mechanistic understanding of Fe(VI)-based AOPs.

The primary aim of this study is to assess the effectiveness of quenching methods in Fe(VI)-based AOPs. Specifically, it examines the impact of commonly used alcohol quenchers—methanol (MA), ethanol (EA), tert-butanol (TBA), and furfuryl alcohol (FFA)—on the decomposition of Fe(VI) under different pH conditions. The study explores the effect of dosages of these alcohol quenchers on Fe(VI) decomposition and investigates their influence on the removal of methyl phenyl sulfoxide (PMSO) probes, as well as the formation of methyl phenyl sulfone ($PMSO_2$) by Fe(VI). Additionally, based on density functional theory calculations, a mechanistic hypothesis for the reaction between ferrate and alcohols is proposed.

2. Materials and Methods

2.1. Chemicals and Reagents

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

2.2. Decomposition and Degradation Tests

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

2.3. Analytical Methods

The concentrations of PMSO and $PMSO_2$ were determined by UPLC (LC-16, Shimadzu, Japan) with a UV detector and Shim-pack GIST C18 (5 μm, 4.6 × 250 mm), under conditions in Table S1.

2.4 Quantum Chemical Calculations

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

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

3. Results and Discussion

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

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

Fig. 1B–1H illustrate the impact of tert-butanol (TBA), methanol (MA), ethanol (EA), and furfuryl alcohol (FFA) on the self-decomposition of Fe(VI) under various pH conditions. Within the pH range of 7.0–11.0, the decomposition rate decreased from 81% to 1% in the presence of TBA, closely matching the auto-decomposition rate of Fe(VI), indicating negligible effects of TBA. In contrast, the addition of MA, EA, or FFA considerably accelerated Fe(VI) decomposition, increasing the rate by 1%–83% at pH 7.0–9.0. However, their effects diminished at pH >9.0. The impact of alcohols was most pronounced between pH 7.0 and 8.0, possibly due to the higher chemical activity of Fe(VI) in this range. When the pH exceeded 9, except for FFA, alcohols showed decreasing impact with pH on Fe(VI) decomposition, likely because Fe(VI) is increasingly stable under more basic pH conditions. Similarly, in the tap water and river water matrices (Fig. S2), the same effects were observed, implying the universal applicability of this effect.

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

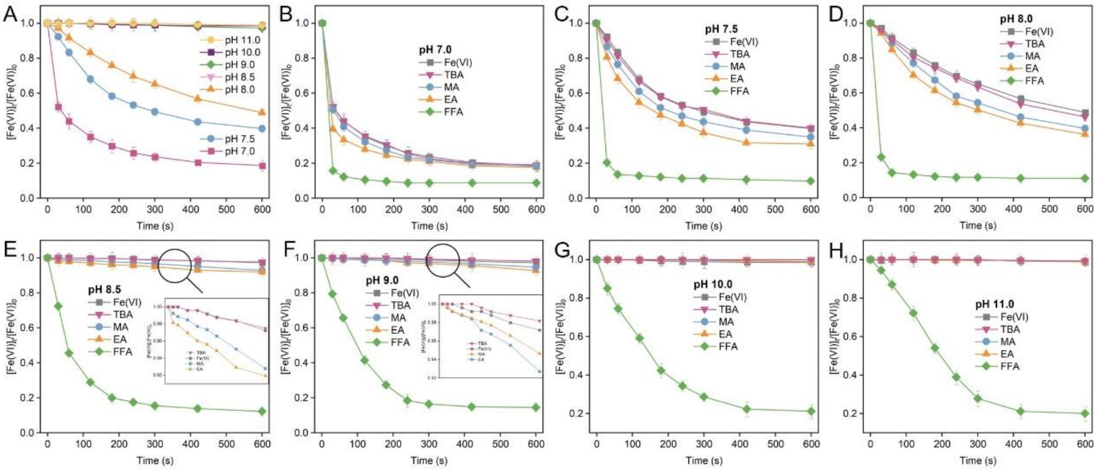

Fig. 1. Self-decomposition of Fe(VI) at pH 7.0–11.0 (A). Effect of TBA, MA, EA, and FFA on Fe(VI) decomposition at pH 7.0 (B), pH 7.5 (C), pH 8.0 (D), pH 8.5 (E), pH 9.0 (F), pH 10.0 (G), and pH 11.0 (H). Experimental conditions: $[\mathrm{Fe(VI)}]_0 = 200\ \mu\mathrm{M}$, $[\mathrm{TBA}]_0 = [\mathrm{MA}]_0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

As shown in Fig. 2, the ratio of alcohol quenchers to Fe(VI) substantially affected the decomposition rate of Fe(VI). As the amount of alcohol quencher increased (from a ratio of 0:1 to 10:1), the decomposition rate accelerated markedly. When the ratio reached 50:1 or 100:1, the decomposition rate remained relatively constant, indicating that the alcohol quenchers were in excess. Overall, the data imply that alcohol quenchers substantially influence the stability of Fe(VI) under different conditions.

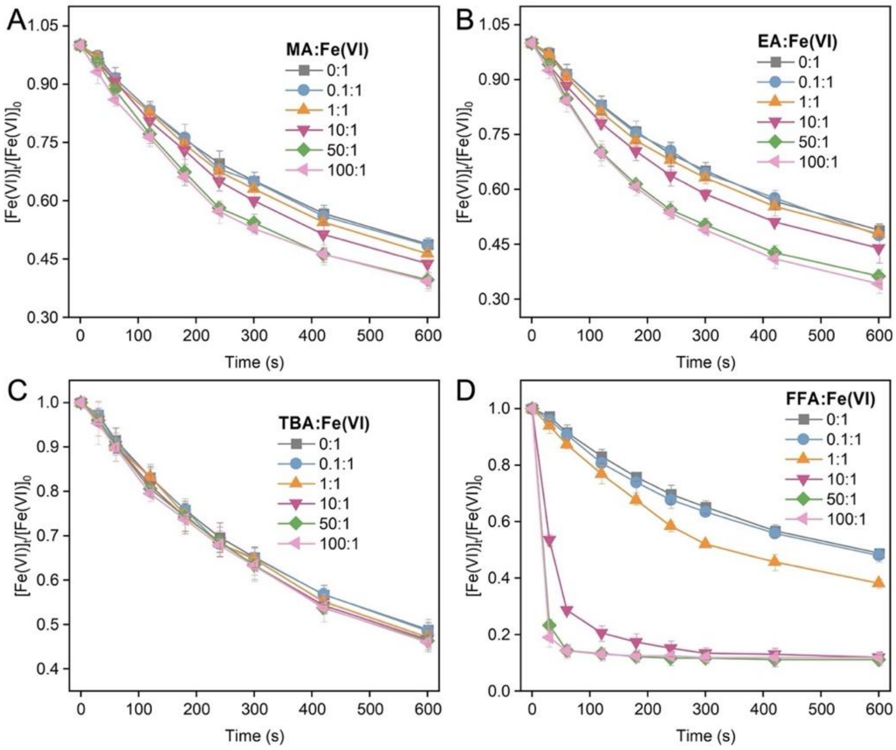

Fig. 2. Effect of MA (A), EA (B), TBA (C), and FFA (D) on the decomposition of Fe(VI) at varying ratios of alcohol quenchers to Fe(VI). Experimental conditions: pH = 8.0, $[Fe(VI)]_0 = 200$ μM, $[TBA]_0 = [MA]_0 = [EA]_0 = [FFA]_0 = 20$ μM–20 mM.

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

PMSO is a probe compound deployed to verify the nature of the high-valent iron active species (Fe(IV)/Fe(V)), because it is specifically oxidized by Fe(IV)/Fe(V) into $PMSO_2$, unlike other reactive species, such as hydroxyl radicals, which instead convert PMSO into hydroxylated products [31]. Fig. 3 reports results obtained to assess the effects of MA, EA, FFA, and TBA on the removal of PMSO by Fe(VI) and the corresponding generation of $PMSO_2$. Each alcohol interacted differently with Fe(VI), influencing the formation of Fe(IV)/Fe(V) and the degradation of PMSO. Beside promoting the decomposition of Fe(VI), MA inhibited PMSO removal by 5% compared to Fe(VI) alone, leading to a reduced amount of $PMSO_2$ formation. This result suggests that MA may facilitate the reduction of Fe(VI) to inactive lower-valent iron species (Fe(II)/Fe(III)). Unlike MA, both EA and FFA enhanced the removal of PMSO (7%–15%), implying that they reacted with Fe(VI) to produce the active Fe(IV)/Fe(V) species. TBA slightly inhibited PMSO removal (1%) and had minimal impact on Fe(VI) decomposition.

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

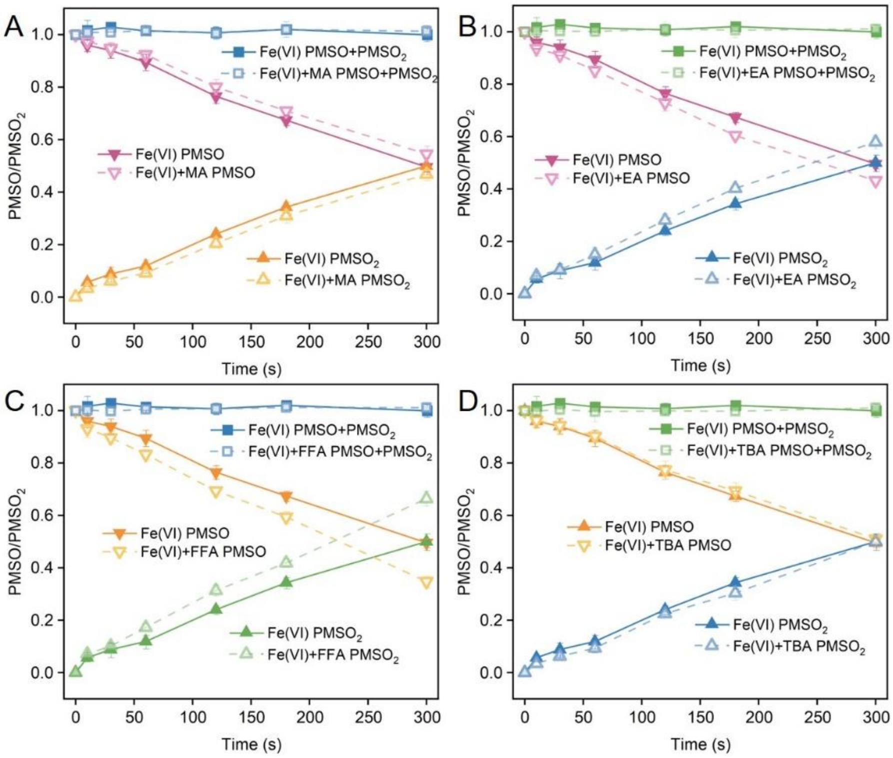

Fig. 3. Effect of MA (A), EA (B), FFA (C), and TBA (D) on the removal of PMSO and the corresponding production of $PMSO_2$ in the Fe(VI) process. Experimental conditions: pH = 8.0, $[PMSO]_0$ = 10 μM, $[Fe(VI)]_0$ = 200 μM, $[TBA]_0 = [MA]_0 = [EA]_0 = [FFA]_0$ = 10 mM.

3.3. Mechanistic analysis

Descriptors of the target compound, such as IP, electron affinity EEA, the difference of the energy levels of the lowest unoccupied and highest occupied molecular orbital ($E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$), and ω^-, usually correlate with its reactivity with Fe(VI) [22]. Based on DFT theoretical calculations, the ranking of IP and $E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$ values is: MA > EA > TBA > FFA (Table S3). A higher potential value implies that the alcohol is less reactive with Fe(VI). The EEA values for all the alcohols are negative, indicating that these substances are characterized by minimal electrophilicity. Conversely, the ranking of the ω^- value is: MA < EA < TBA < FFA, implying that MA has the least nucleophilic character and the weakest reactivity with Fe(VI), while FFA has the most nucleophilic character and the strongest reactivity with Fe(VI). Note that experimental results suggested that TBA had the smallest effect on Fe(VI) decomposition and reactive Fe species, which differs from the theoretical calculation results. The reason for this discrepancy is not entirely clear. In regions where the electrostatic potential is negative, electrons are more concentrated. Based on the analysis of electrostatic potentials, we observe that, aside from the negative electrostatic potential region on the five-membered ring of FFA, the negative regions for other alcohols are concentrated around the hydroxyl groups. Therefore, Fe(VI) is more likely to attack the hydroxyl parts of MA, EA, TBA molecules, and the five-membered ring of FFA. Fig. 4 illustrates the isosurface maps of electronic density on the surfaces of EA, FFA, EA, and MA molecules based on the Fukui function. In these maps, green and blue colors represent positive and negative values, respectively, with color intensity correlating with magnitude. Regions with higher positive values are more likely to be active sites for species attack. Clearly, the hydroxyl groups and alpha-hydrogen (α-H) in MA and EA, the hydroxyl group in TBA, and the O in FFA are more reactive. This result aligns with the findings by Kamachi et al. [20,32], who reported that Fe(VI) can mediate the extraction of hydrogen atoms from the O-H and C-H bonds of MA, forming organometallic intermediates with Fe-C bonds and hydroxymethyl radical intermediates, which are eventually oxidized to formaldehyde. Furthermore, Fe(IV) has been shown to oxidize cyclobutanol to cyclobutanone [19]. In other words, alcohols not only react with Fe(VI) itself, but also with the resulting high-valent iron species.

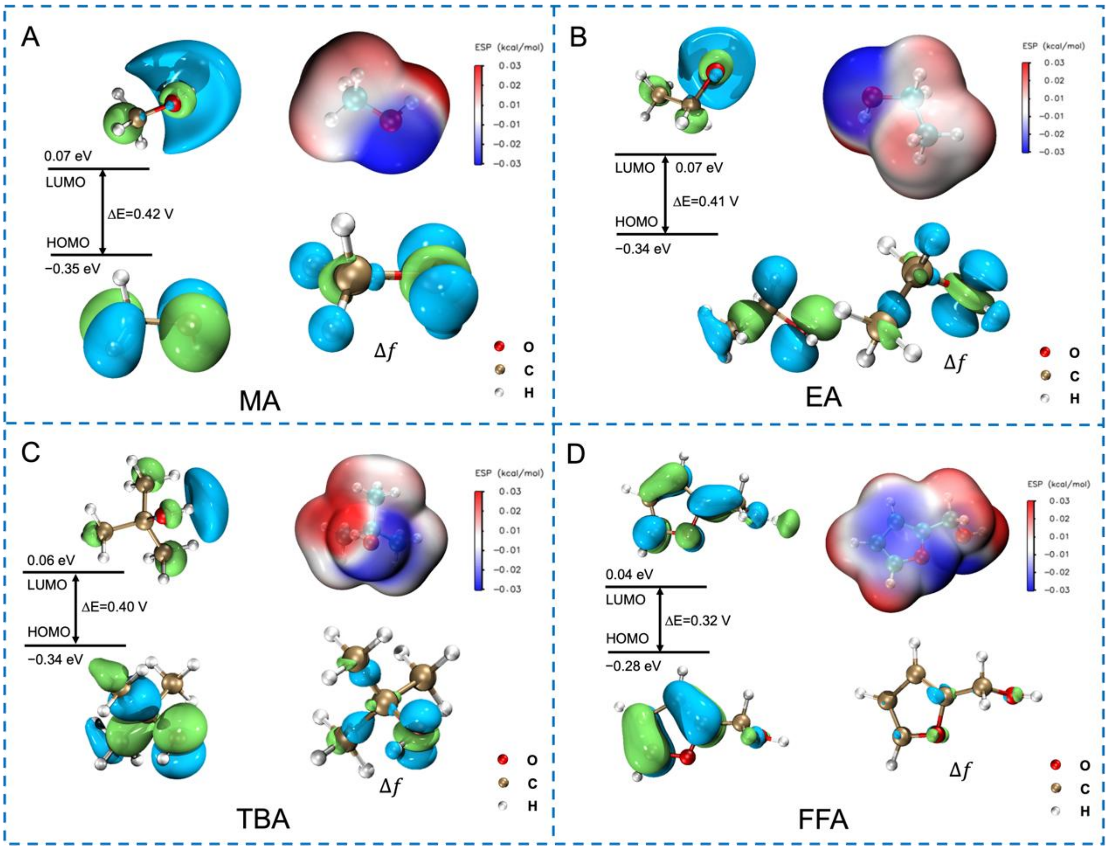

Fig. 4. Gap of E_{LUMO} and E_{HOMO}, orbital isosurface maps for Fukui function (Δf), and electrostatic potential (ESP) of MA (A), EA (B), TBA (C), and FFA (D).

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

4. Conclusion

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

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