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# Improving Fenton-like System with Catechin, an Environmental-friendly Polyphenol: Effects and Mechanism

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**Abstract:** Fenton-like system had long been modified to promote its adaptability and efficiency by adding extra components like metal chelators or reducers. Nonetheless, chelator such as ethylene diamine tetraacetic acid (EDTA) was harmful in high dosage. While strong reducers could efficiently promote the generation speed of hydroxyl radicals (HO<sup>•</sup>), they could also get oxidized easily during storage time, for which further application was costly. In this study, (+)-catechin (CAT), an environmental-friendly component, was proved to be an efficient promoter of Fenton-like system on Bisphenol A (BPA) degradation. The modified system achieved 92% of BPA removal in one hour. The mechanism was studied, and the reaction procedure between CAT and Fe(III) together with the degradation pathways of CAT were identified. Fe(III) got chelated first by CAT and quickly reduced to Fe(II) via a single inner-compound electron transfer. The intermediates of CAT could further reduce one and a half more portion of Fe(III) on average. Consequently, massive amount of Fe(II) turned Fenton-like procedure to Fenton reaction and thus promoted the generation of HO<sup>•</sup>.

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The main radicals contributed on BPA degradation was HO<sup>•</sup>. BPA could be efficiently degraded at pH 6.5 or acidic pH range, but the degradation was completely inhibited with the pH higher than 8.0. The optimal mole ratio between Fe(III) and CAT was 6:1 and the degradation pathway of BPA was deduced.

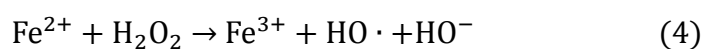
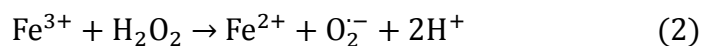
**Keywords:** Fenton system, plant polyphenol, catechin, hydroxyl radical, reduction mechanism

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## 1. Introduction

Since the Fenton reagent was firstly introduced by H.J.H Fenton in 1894 [1], it had been developed to several branches, such as Fenton-like process, photo-Fenton process, and ligand-modified Fenton process to extend its applicability and improve efficiency. Those processes had shown high efficiency of degrading some persistent organic pollutants (POPs) or endocrine disruptor chemicals (EDCs) by producing large amount of HO<sup>•</sup> based on the reaction illustrated as Eqs (1)-(4) (Fenton-like process: 1-4; Fenton process: 4). In latest cases, the Fenton and Fenton-like processes had already been applied in industrial wastewater treatment in real situation. Bautista et al. [2] utilized traditional Fenton system to treat wastewater of low BOD<sub>5</sub>/COD rate from cosmetic industry. Changotra et al. [3] treated real pharmaceutical wastewater with three different Fenton processes combined with aerobic biological treatment. Although those applications were proved to be successful to some extent, there were still some defects yet to improve. The major limitation of Fenton processes was pH value. To overcome the limitation on pH, chelators such as EDTA, oxalate, citrate and [S,S]-Ethylene diamine-*N,N'*-disuccinic acid (EDDS) were added to promote the system. Hu et al. [4] achieved 92.7% malachite green degradation in neutral pH with EDTA-modified Fenton-like system. Manenti et al. [5] tested oxalate, citrate and

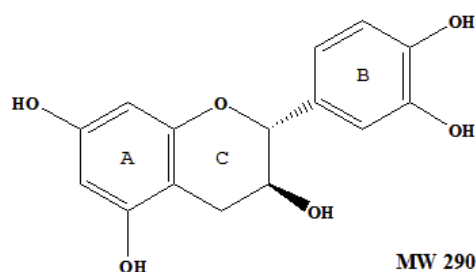
EDDS as organic ligands and accomplished 69.1% mineralization with modified photo-Fenton system. However, EDTA had low biodegradability [6-8]. Hence, it was crucial to find an efficient chemical compound which i) improved the Fenton process efficiency and ii) was easy to degrade.



Plant polyphenols were a group of organic compounds with multiple phenol structures generated in plant metabolism procedure. They were often detected in a vast amount in roots, leaves, fruits, mass-produced food and beverage made from plants. According to previous researches, fruits such as grapes and berries might contain 0.3% of polyphenol in fresh weight, especially in tea leaves [9]. The concentration of polyphenols could reach up to 30% in dry weight of green tea [10]. The naturally high productivity showed the potential for exploitation and manufacture of certain polyphenol. Polyphenols were also believed to bring health benefits on cardiovascular protection and anti-oxidation, and they were becoming popular as the additive or health care products [11-13]. The associated benefits of these compounds were often based on the reducibility of polyphenols [14]. From the perspective of chemical structure, the sensitivities toward oxidant of both *o*-phenolic hydroxyl group and *p*-phenolic hydroxyl group were accounted for the reducibility of polyphenol which raised the possibility to modify traditional Fenton-like system as a reducer.

Catechin was polyphenol classified under flavonoid category. They were typical flavan-3-ols, characterized by a resorcinol group on its A ring, and a catechol group

on its B ring. Due to the two chiral carbons, there were four isomers, including (+)-catechin, (-)-catechin, (-)-epicatechin and (+)-epicatechin. However, (+)-catechin (Scheme 1) was the major catechins present in green tea [15, 16] and was chosen as the research target in this study. As stated in previous studies [17], the catechol group on its B ring provides possible chemical reactivity both in chelation and reduction, whereas the process was not clear. Wang et al. [18] studied the photodegradation of inderal in a UV/Fe(III)/CAT system at near neutral pH. The high degradation efficiencies were obtained and they were strongly dependent on pH, following the order  $\text{pH } 3.0 < 5.0 < 7.0 < 6.0$ . The reaction between Fe(III) and CAT was considered as chelation. Wu et al. [19] reported the degradation of atenolol in Fe(III)/CAT/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system at acid condition (pH=3.3). The mechanism was concluded as the reduction of Fe(III) by CAT to produce Fe(II) and PS was activated by Fe(II) to produce large amount SO<sub>4</sub><sup>•-</sup>. In general, there were three major explanations of the reaction between Fe(III) and CAT respectively, regarding CAT as a ligand [18], a reducer [19, 20] or both a ligand and reducer at the same time [17], yet none of these theories had been fully confirmed. Based on the chemical reactivity and its environmental-friendly feature as a plant polyphenol, CAT was potentially suitable to modify the conventional Fenton system.



**Scheme 1.** Structure of (+)-catechin

BPA was a kind of EDCs which had estrogenic activity by interacting with estrogen receptors in human body. As reported in previous study, the maximum

concentration in wastewater could reach 0.15 mg/L in some Canadian and US municipal wastewater treatment plants [21], and because it was hard to biodegrade [22-23], leftover BPA in effluent could still be detected. In this study, BPA was used as a model pollutant. The effect of CAT on the modified Fenton-like system on BPA degradation was investigated. Mechanism of the reaction between CAT and Fe(III), radical identification, effect of pH value and key influencing factors were carefully studied. The degradation pathway of BPA was also reported.

## **2. Methods and materials**

### **2.1 Chemicals**

H<sub>2</sub>O<sub>2</sub> (≥30%), NaCl (≥99.5%), NaNO<sub>3</sub> (≥99.0%), H<sub>2</sub>SO<sub>4</sub> (~98.0%), NaH<sub>2</sub>PO<sub>4</sub> (≥99.0%), ascorbic acid (≥99.7%) and *p*-hydroxyphenylacetic acid (POPHA, 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Bisphenol A (BPA, 99%) and (+)-catechin (CAT, 99%) were obtained from J&K Scientific. Methanol, isopropanol, chloroform, acetonitrile, and formic acid all in HPLC grade were also supplied by J&K Scientific. Fe(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (Fe 10.7% w/w) and catalase (2,000~5,000 units/mg) were purchased from Sigma-Aldrich. Peroxidase (≥150 units/mg) were obtained from Macklin Inc.. Ferrozine (97%) was supplied by Aladdin Inc..

### **2.2 Degradation Experiments.**

The degradation experiments basically involved four solutions: BPA, CAT, H<sub>2</sub>O<sub>2</sub> and Fe(III) as the target contaminant, modifier, and elementary components of Fenton-like system, respectively. Previous researches and pre-experiments both confirmed that little decomposition of BPA or CAT would occur when H<sub>2</sub>O<sub>2</sub> was added at the concentration level of this study [24]. Fe(III) were the last one to be mixed into the solution of BPA, CAT and H<sub>2</sub>O<sub>2</sub>, working as a trigger of the degradation procedure and making this step the time zero point. Immediately after each sampling, methanol was added to the samples in order to scavenge radicals and stop the degradation. To prevent photolysis, the experiments were conducted in dark

brown glass vials and HPLC vials were sheltered from light using an auto-sampler with a hood. All degradation experiments were conducted at least twice.

### **2.3 Analysis method**

The concentration of BPA was determined by high-performance liquid chromatography (U3000, Dionex, USA) with Diode Array Detector (HPLC-DAD). The detecting wavelengths were set at 226 nm and 280 nm to preclude the interference from the signal of intermediates. Samples of 10  $\mu\text{L}$  each, pretreated with methanol were injected into a C-18 reversed phase column (150 mm  $\times$  4.6 mm  $\times$  5  $\mu\text{m}$ , Kromasil, Sweden). The temperature of the column oven was set at 40°C. The mobile phase containing 70% of methanol (phase A) and 30% of water (phase B) was pumped into the system at the flow rate of 1 ml min<sup>-1</sup> [25]. Fe(II) concentration were spectrophotometrically measured based on the reaction between Fe(II) and ferrozine which formed a complex that was detected by UV-vis spectrophotometer at 562 nm [26]. H<sub>2</sub>O<sub>2</sub> concentration was determined by a dosage method based on the reaction between H<sub>2</sub>O<sub>2</sub> and POPHA under the catalysis of peroxidase [27]. Electron spin resonance (ESR) experiments were carried out on a Bruker spectrometer (JEOL, FA200). 5,5-Dimethyl-1-Pyrroline-N-Oxide (DMPO) was used as a spin trap to detect HO $\cdot$  and O<sub>2</sub> $\cdot^-$  in water and ethanol, respectively. The reaction intermediates were analyzed by quadruple time-of-flight (Q-TOF) mass spectrometry (MS) coupled with an ultra high performance liquid chromatography (UHPLC) in full scan mode.

### **2.4 Stopped-flow Method for Intermediates Analysis.**

Intermediates produced by the reaction between CAT and Fe(III) over the time span of several seconds were identified by UV-vis spectrum equipped with Stopped-flow mixing system (Applied Photophysics, SX20). The system was set to take 1000 scans in each time gap from 350 nm to 750 nm.

### **2.5 Computational method.**

The main computational methods were density functional theory (DFT) and time-dependent density functional theory (TDDFT). Gaussian09 program (Frisch et al., 2009) was used to perform both DFT and TDDFT calculations, and the

three-parameters hybrid density-functional (B3LYP) was used in all DFT calculations setting to 6–31 + g (d,p) basis. All excited-state geometry optimizations as open shell species were described with an unrestricted approach, while ground-state geometry optimizations as closed-shell species were explained with a restricted method.

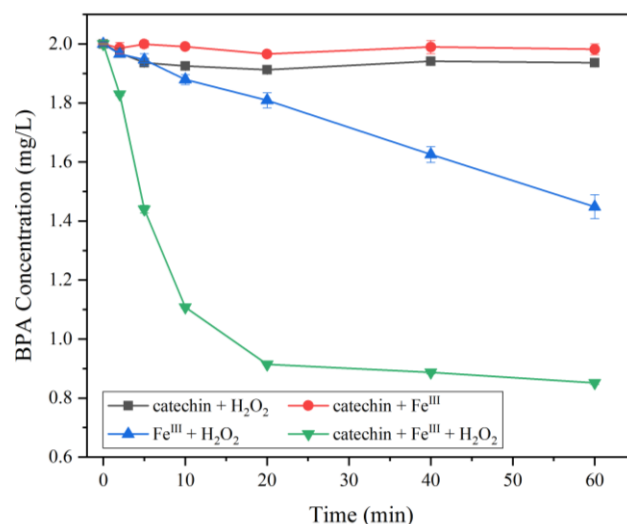
### **3. Results and discussion**

#### **3.1 Effect of Fenton-like system modified by CAT on BPA degradation**

The effect of CAT-modified Fenton-like system on degradation of BPA was compared with that of conventional Fenton-like system and photo-Fenton system. To rule out the effect attributed to potential reaction, in presence of CAT, between BPA and H<sub>2</sub>O<sub>2</sub> or reaction between BPA and Fe(III), experiments excluding one of that four basic components were also carried out (Fig. 1). The control experiment showed that the concentration of BPA decreased 27.6% in Fe(III)/H<sub>2</sub>O<sub>2</sub> system and it had an unstopped decomposition trend till 60 minutes. Further experiments revealed that the degradation would gradually slow down and stopped eventually after 150 minutes of experiments by which nearly 90% of BPA had been removed. In another experiment, BPA was slightly degraded in absence of Fe(III) which was possibly due to the weak oxidation ability of CAT/H<sub>2</sub>O<sub>2</sub> system (as shown in Fig. SM1, weak signal of HO<sup>•</sup> was found). There was almost no degradation of BPA in CAT/Fe(III) system.

When CAT was added, BPA got rapidly degraded to 45.7% in only 20 minutes and the concentration then gradually fell to 41.0% in 60 minutes. The efficiency of CAT/Fe(III)/H<sub>2</sub>O<sub>2</sub> system on BPA removal was almost doubled in an hour and the total amount of BPA that was removed remained nearly the same comparing to long-term (300 min) in Fe(III)/H<sub>2</sub>O<sub>2</sub> system experiment (near 90% of BPA degradation). The results proved that CAT can enhance the efficiency of the conventional Fe(III)/H<sub>2</sub>O<sub>2</sub> system on BPA removal.

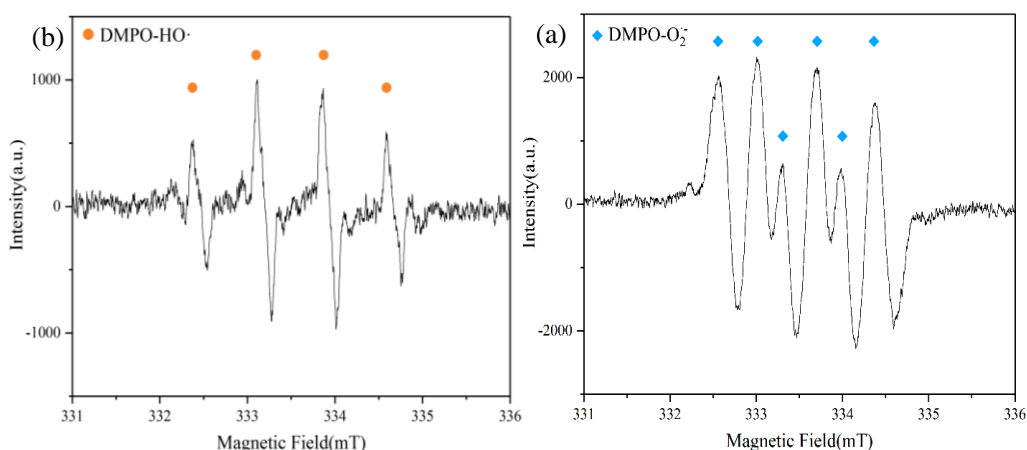




**Fig. 1.** Degradation of BPA in different system. ( $[BPA]_0 = 2 \text{ mg L}^{-1}/8.76 \text{ } \mu\text{M}$ ,  $[H_2O_2]_0 = [CAT]_0 = [Fe(III)]_0 = 50 \text{ } \mu\text{M}$ ,  $\text{pH}=6.5$ )

### 3.2. Role of ROS in the degradation process

Reactive oxygen species (ROS) were often considered as the core of traditional Fenton-like system on contaminant removal. To fully understand the significant change brought by CAT and explore the role of different ROS in the degradation process, ESR analysis was performed with DMPO as spin trapping reagent. The results were shown in Fig. 2. In ultrapure water, ESR displayed signal around 333.5 mT in magnetic field with four peaks in 1:2:2:1 ratio, which were the characteristic pattern for  $HO^\bullet$  [28]. Ethanol was used as solvent in another test to quench  $HO^\bullet$ , so that patterns from other radicals were not affected by signal overlapping. As illustrated in Fig. 2b, the dominant signal was in 1:1:1:1 ratio, accompanied with two minor signals after the second and third peak which was often interpreted as the existence of superoxide anion radicals ( $O_2^{\bullet-}$ ) [29, 30]. It was concluded from the ESR analysis that both  $HO^\bullet$  and  $O_2^{\bullet-}$  were produced.



**Fig. 2.** ESR analysis performed in different solvent: (a) ultrapure water (b) ethanol.

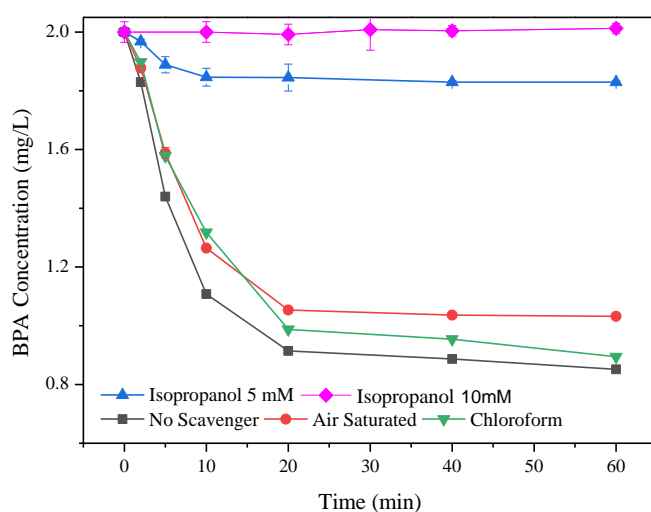
$$([\text{H}_2\text{O}_2]_0 = [\text{CAT}]_0 = [\text{Fe(III)}]_0 = 50 \mu\text{M}, \text{pH}=6.5)$$

To evaluate the role of radicals in the degradation process, two kinds of scavengers were added to the system simultaneously with Fe(III) and the results of quenching experiments were shown in Fig. 3. By adding isopropanol into the solution,  $\text{HO}^\bullet$  were quenched before they could attack target contaminants, and as consequence, the concentration of BPA stopped decreasing in just 10 minutes. While the concentration of isopropanol was increased from 5 mM to 10 mM, the BPA degradation was completely inhibited. Chloroform was added to quench  $\text{O}_2^{\bullet-}$  ( $k_{\text{CHCl}_3, \text{O}_2^{\bullet-}} = 3.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  [31]), but it did not show much impact on the BPA degradation. Comparing to experiments without any scavengers, just 3.7% of BPA degradation was inhibited at the end of the reaction. The 3.7% constraint on BPA removal was probably the result from the competition between chloroform and BPA in reacting with  $\text{HO}^\bullet$  instead of eliminating the effect of  $\text{O}_2^{\bullet-}$ , for the reaction rate constant between chloroform and  $\text{HO}^\bullet$  was  $k_{\text{CHCl}_3, \text{HO}^\bullet} = 5.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [31].

Although  $\text{O}_2^{\bullet-}$  were not involved in direct attack on BPA, they might still contribute to the reaction via reduction with Fe(III) or generating extra  $\text{H}_2\text{O}_2$  by the recombination of two  $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$  radicals. For dissolved oxygen (DO) was considered to enlarge the production of  $\text{O}_2^{\bullet-}$ , experiments with air-saturated solution were also conducted so that potential impact from DO or indirect contribution of  $\text{O}_2^{\bullet-}$  would not be omitted. Air flow was pumped into all the solutions with 20 minutes before the experiment. However, rather than promoting the BPA degradation, the result showed

the opposite trend. DO slowed down the speed of removal and increase the remaining concentration of BPA by nearly 10%. It was not surprised for this result. Actually, DO had two opposite effects on BPA degradation in this research. On the one hand, DO could enhance the production of  $O_2^{\bullet-}$  and should have a positive effect on the BPA removal. But the oxidation capacity of  $O_2^{\bullet-}$  was very low compared with  $HO^{\bullet}$ . So the positive effect on the BPA removal was limited. On the other hand, DO was able to oxidize Fe(II) to Fe(III) which would strongly inhibit the reaction between Fe(II) and  $H_2O_2$ . The degradation of BPA would be significantly reduced by the decreased formation of  $HO^{\bullet}$ . It became the dominant effect when the solution was bubbled by air.

Based on experiments above,  $HO^{\bullet}$  were massively produced by the system and played as the mainly ROS in the BPA degradation process. Though ESR analysis revealed  $O_2^{\bullet-}$  was also in existence, the scavenger experiments proved that it had little influence on BPA degradation. Some previous studies regarded  $O_2^{\bullet-}$  as a considerable reducer for Fe(III) in Fenton-like process and generating extra Fe(II) [32-33], so the reaction should have been boosted by the radical. The phenomenon, nevertheless, was not shown in this study. The interesting contradiction on  $O_2^{\bullet-}$  lead us to seek further comprehension on the role of CAT.

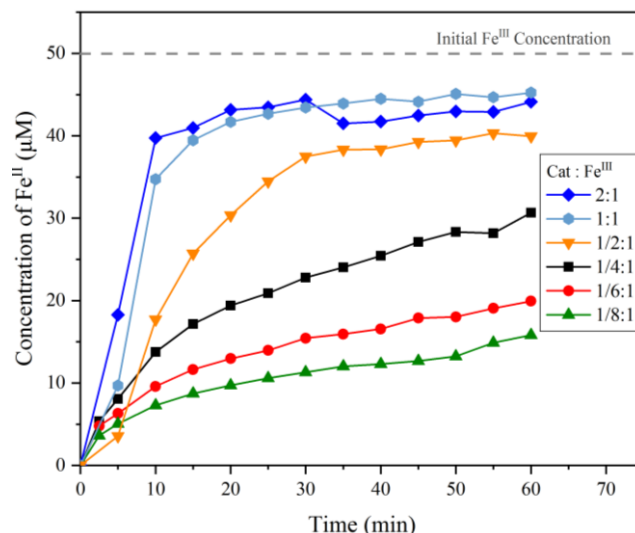


**Fig. 3.** Degradation of BPA with scavengers involved. ( $[BPA]_0 = 2 \text{ mg L}^{-1} / 8.76 \text{ } \mu\text{M}$ ,

$$[\text{H}_2\text{O}_2]_0 = [\text{CAT}]_0 = [\text{Fe(III)}]_0 = 50 \mu\text{M}, [\text{chloroform}] = 5 \text{ mM}, \text{pH}=6.5)$$

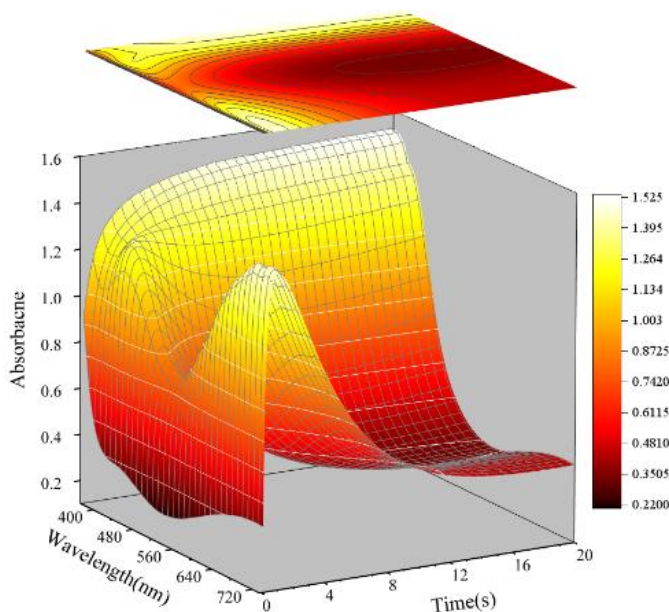
### 3.3. Role of CAT

As the result above showed, CAT barely changed the way how traditional Fenton-like system worked which still relied on the oxidation by  $\text{HO}^\bullet$ , but it improved the efficiency of BPA removal. Although the mechanism was unclear, it was inferred that Fe(III) might react with CAT. To test the assumption, Fe(II) was determined in the mixture solution of Fe(III) (50  $\mu\text{M}$ ) and CAT (6.25-100  $\mu\text{M}$ ) (Fig. 4). As the result, more than 80% of Fe(III) were reduced to Fe(II) in an hour, when CAT : Fe(III) was more than 1:2. While the concentration of CAT was less than a quarter of Fe(III), the formed Fe(II) concentrations were varied depending on initial concentration of CAT, but with a constant proportional relationship of roughly 2.5 times of CAT. The degradations of CAT were also followed and the results were shown in Fig. SM2. When the CAT concentrations were lower than 25  $\mu\text{M}$ , they were quickly 100% consumed at the beginning 3 min of the reaction. Data of the experiment revealed a reduction process between CAT and Fe(III), which was in accordance to some studies on catechol and other polyphenol substances [34]. Nonetheless, previous studies also hinted that catechol or compounds with similar functional group tended to react as a complex agent when Fe(III) was involved [35, 36]. The reduction procedure was, therefore, deduced to be a set of complicated reaction instead of a single elementary reaction.



**Fig. 4.** Formation of Fe(II) determined by Ferrozine method. ( $[\text{Fe(III)}]_0 = 50 \mu\text{M}$ ,  $\text{pH} = 5.5$  adjusted by acetate buffer)

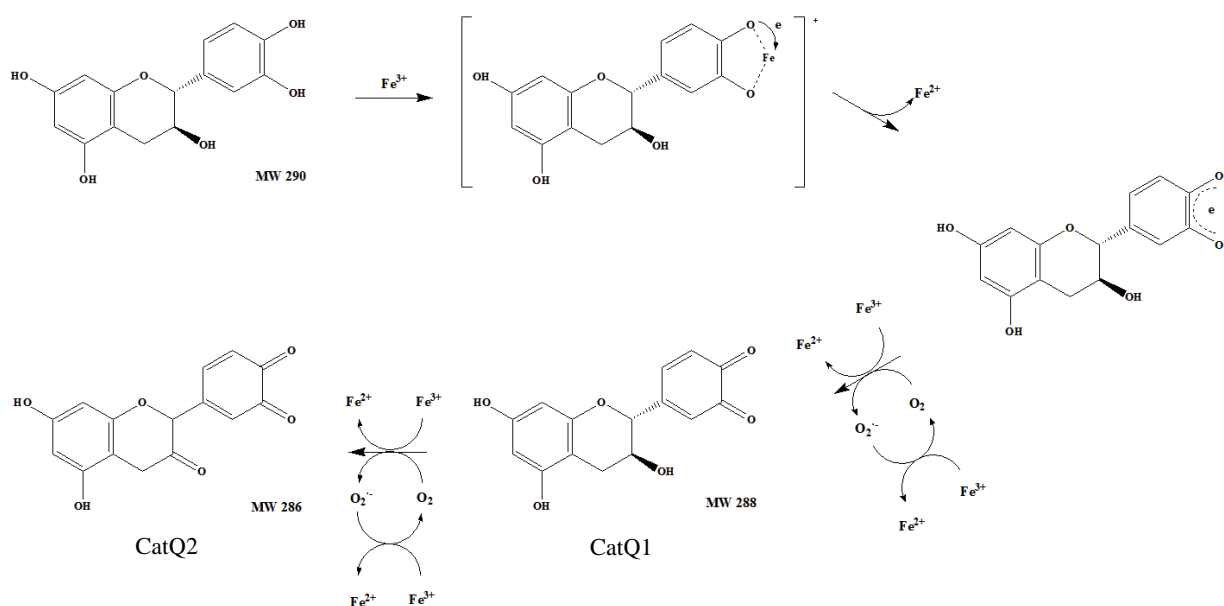
To gain a deeper insight into the reduction process, Stopped-flow UV-vis spectrum was obtained (as shown in Fig. 5). In the first second, absorbance rose steeply at 390 nm, 450 nm and 685 nm, implying formation of multiple compounds. Four seconds after mixing, absorbance at two wavelengths (450 nm and 685 nm) peaked and diminished gently to a low level while the other one (390 nm) still kept on growing. Since the peaked times at those wavelength were different from each other, it could be confirmed that one terminal product and two intermediates were produced during the reaction.



**Fig. 5.** Stopped-flow UV-vis spectrum of CAT and Fe(III) solution. ( $[\text{CAT}]_0 =$

$$[\text{Fe(III)}]_0 = 50 \mu\text{M}, \text{pH}=6.5$$

The intermediate with absorbance at 685 nm was consistent with catechol-group complexed Fe(III). The terminal product (named as CatQ<sub>2</sub>) and the other intermediate (named as CatQ<sub>1</sub>) both had strong absorbance near 390 nm, which were estimated to possess quinone, semi-quinone or comparable structure [17]. Grounded on the structure of CAT, the hydroxyl group on B ring was the only complexing group but the easiest part to be oxidized to quinone as well. It meant that the complex of Fe(III)-CAT would not exist if CAT was oxidized to quinone intermediate first. The deduction revealed the possible formation sequence of those three compounds: the complex of Fe(III)-CAT was formed first, followed by its decomposition generating quinone intermediate (CatQ<sub>1</sub>) and that intermediate was further reacted to the terminal product (CatQ<sub>2</sub>). To verify the procedure, products of the mixture was analyzed by UHPLC-QTOF-MS. The MS detected two related compounds in the samples with the mass weight of 288 and 286, which were in accordance with compounds possessing a flavanone structure with still a resorcinol group on its A ring, but an *o*-benzoquinone structure on its B ring, and a carbonyl group on its C ring as a result of oxidation of hydroxyl group. The possible reaction process was speculated as shown in Scheme 2.



**Scheme 2.** The process of the reaction between CAT and Fe(III)

The structures were also double checked via computational method. To further confirm the structure of three products, the UV-vis spectrum of them were compared with the computational result of DFT model. The DFT model simulated the possible spectrum based on the input structure, and the results were in accordance with the spectrum obtained by the Stopped-follow UV-vis spectrum instrument (Table 1). According to the results of ESR, HO<sup>•</sup> and O<sub>2</sub><sup>•-</sup> were both formed in Fe(III)/CAT/H<sub>2</sub>O<sub>2</sub> system. Moreover, the formation of Fe(III)-CAT complex, CatQ<sub>1</sub> and CatQ<sub>2</sub> were confirmed by stopped-flow UV-vis spectra, UHPLC-QTOF-MS and DFT model calculation. So the Scheme 2 was further confirmed.

**Table 1.** Comparison between observed peak wavelengths of CAT related compounds and DFT results

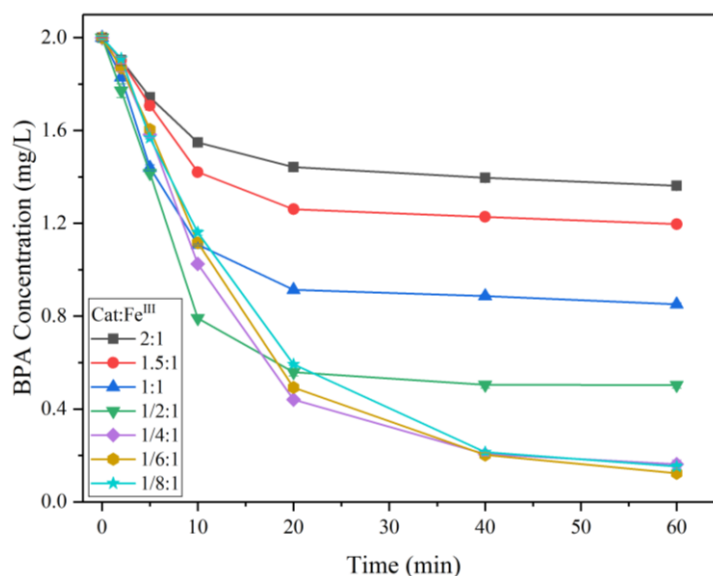
| Compounds         | Observed $\lambda_{\max}$ (nm) | DFT Results (nm) |
|-------------------|--------------------------------|------------------|
| catechin          | 280                            | 280.14           |
| complex           | 685                            | 673.02           |
| CatQ <sub>1</sub> | 450                            | 455.73           |
| CatQ <sub>2</sub> | 390                            | 387.95           |

In summary, most of the Fe(III) were complexed with CAT and then reduced by an inner-complex electron transfer to form Fe(II). Since Fe(II) could barely complex with catechol group [34, 36], the complex decomposed quickly and released a huge quantity of Fe(II) to the system, which promoted the generation of HO<sup>•</sup> in presence of H<sub>2</sub>O<sub>2</sub>. On the other side, CAT became extremely reducible as a radical after losing an electron on its catechol group. The radical form of CAT might react with any kind of oxidant including Fe(III), H<sub>2</sub>O<sub>2</sub>, DO and convert to quinone intermediate. Since the intermediate was still reactive to oxidant, the flavonol structure was soon transformed to the terminal product, flavanone structure. DO might compete for electrons with Fe(III) in last two steps, O<sub>2</sub><sup>•-</sup> was produced as the consequence, which was also reactive to reduce Fe(III). Despite that O<sub>2</sub><sup>•-</sup> could be increased by pumping air, it would not promote the reduce procedure. Because the total amount of electrons available to transfer, regardless of its carrier (O<sub>2</sub> or CAT), was only tied to the CAT

concentration. It well explained the contradictory on the effect of  $O_2^{\cdot-}$ .

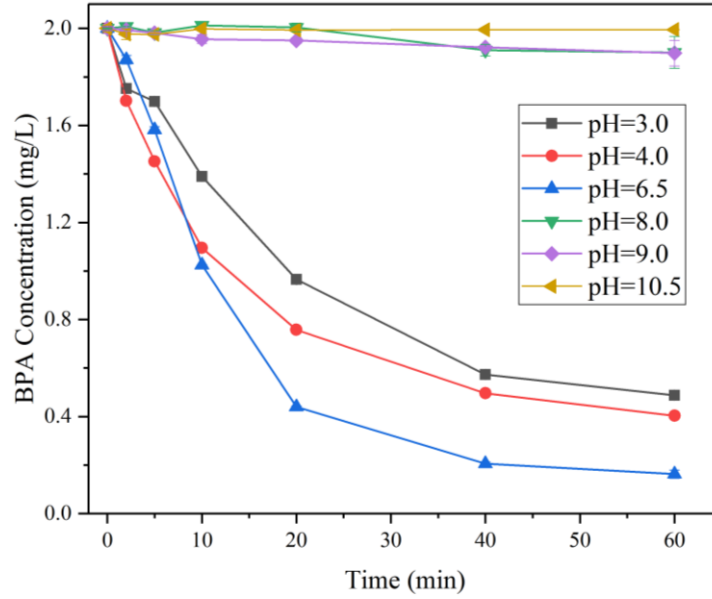
### 3.4. Effect of CAT/Fe(III) ratio, pH and common anions

To seek the best condition of the modified system on BPA degradation, several influencing factors were tested or introduced to the system. Ratio impact of CAT and Fe(III) was tested from 1/8:1 to 2:1. Based on the data, two different trends which were divided by inflection point between 1/2:1 and 1/4:1 were noticed (Fig. 6a). When ratio went down from 2:1 to 1/2:1, BPA got removed much faster and more thoroughly over the experiment. As the ratio went deeper down to 1/4:1 or even lower, BPA removal gradually slowed down, but the similar removal effect was achieved. The outcome was partially in conformity with the pattern of Fe(II) generation: as the CAT outnumbered Fe (III) in 1/3 or more, some CAT was spared and might compete on  $HO^{\cdot}$  that hindered BPA removal [37]. As for the similarity in removal effect in low CAT/Fe(III) ratio, it showed the efficiency of CAT modification was quite high. Nonetheless, numerous products were created during the degradation process, which blocked further degradation. In order to get the best degradation result, following experiments applied the ratio of CAT and Fe(III) as 1/6:1.

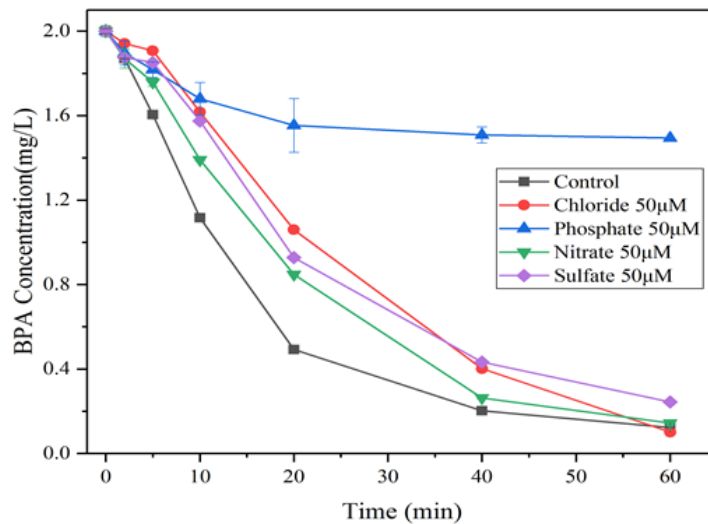


(a)





(b)



(c)

**Fig. 6.** The impact of the ratio between CAT and Fe(III) (a), initial pH (b) and common anions (c) on BPA degradation ( $[BPA]_0 = 2 \text{ mg L}^{-1}/8.76 \text{ } \mu\text{M}$ ,  $[H_2O_2]_0 = [Fe(III)]_0 = 50 \text{ } \mu\text{M}$ ,  $[CAT]_0 = 8.3 \text{ } \mu\text{M}$ ,  $\text{pH}=6.5$ )

Concerning that Fe(III) formed different hydroxide species under different pH, the initial pH value was tested as another influencing factor. The data illustrated in Fig. 6b showed that the system worked well in both acidified and neutral environment. There were more than 70% of BPA removal but the degradation of BPA was completely stopped if the pH value was above 8.0. It was known that Fe(III) and Fe(II)

would completely precipitate in pH 8.0 or above, and as a result, the system stopped yielding HO<sup>•</sup>. On the other hand, less BPA was degraded as the pH went down in high acidity solution (pH=3). This phenomenon happened since H<sup>+</sup> competed with Fe(III) on CAT complexation and changed the distribution of Fe(III) species. Either of the factors might have negative impacts on BPA degradation.

In this study, all chemicals were solved in deionized water or HPLC class organic solvent, while in real water treatment, inlet water possibly contained varieties of anions that may bring unknown influence. To ensure the modified system was also suitable for water treatment accompanied with anions, several common anions were selected to add in the reaction solution (Fig. 6c). In the experiments, all the tested anions including chloride (Cl<sup>-</sup>), phosphate (PO<sub>4</sub><sup>3-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>) and sulfate (SO<sub>4</sub><sup>2-</sup>), reduced the speed of BPA degradation. The effects of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were similar and negligible. However, the reason for the obvious inhibition effect of PO<sub>4</sub><sup>3-</sup> was the precipitation of Fe(II) or Fe(III) with PO<sub>4</sub><sup>3-</sup> ( $K_{sp} = 4 \times 10^{-27}$  and  $K_{sp} = 1 \times 10^{-36}$ , respectively).

#### 4. Conclusion

The addition of CAT promoted the reduction reaction from Fe(III) to Fe(II) through a five-step process: complexation, reduction, release, second reduction and final reduction, leading to a higher productivity of HO<sup>•</sup> in the Fenton-like system. Thus, CAT was proved to be an efficient agent to modify Fenton-like system in neutral pH on BPA degradation and very possibly on removal of many other compounds which was also sensitive towards HO<sup>•</sup>. Moreover, the result demonstrated that the modified system kept its efficiency not only in neutral pH in deionized water, but also in acidic environment or with common anions. The degradation pathway of BPA had also been studied (shown in Fig. SM3). Considering the high potential for massive production of CAT and other plant polyphenols, together with their negligible risk of ecosystem and human health, results of this study present a promising future of applying plant polyphenols in Fenton-like system to promote its efficiency in real

water treatment.

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