



Short communication

# Hydrazine drastically promoted Fenton oxidation of bisphenol A catalysed by a Fe<sup>III</sup>–Co Prussian blue analogue

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## ABSTRACT

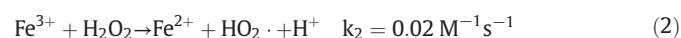
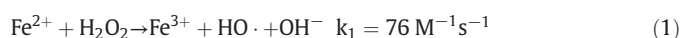
Herein, for the first time it has been demonstrated that hydrazine (Hz) could significantly promote the bisphenol A (BPA) degradation in the Fenton reaction catalysed by Fe[Co(CN)<sub>6</sub>]•2H<sub>2</sub>O Prussian blue analogue (Fe<sup>III</sup>–Co PBA). Results indicate that the dramatic enhancement of BPA degradation could be partly attributed to the induced homogeneous Fenton reaction by the enhanced dissolution of Fe<sup>III</sup>–Co PBA. Meanwhile, the Hz coordinated iron site (H<sub>2</sub>NH<sub>2</sub>N–Fe), which is evolved from the original water coordinated iron site (H<sub>2</sub>O–Fe), was identified as the main active site. A possible reaction pathway involving the proposed active iron species was proposed.

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## 1. Introduction

Among various advanced oxidation processes (AOPs), Fenton and Fenton-like processes have been widely investigated in view of their high efficiency, simplicity and environmental friendliness [1,2]. Reactive oxygen species (HO•, HO<sub>2</sub>• etc.), generated during the Fenton process at room temperature through Eqs. (1)–(2), are highly efficient in degrading nearly all organic compounds rapidly and none selectively [3]. However, because the reaction rate of ferric ions with H<sub>2</sub>O<sub>2</sub> (Eq. (2)) is much slower than that of ferrous ions with H<sub>2</sub>O<sub>2</sub> (Eq. (1)), ferric ions are quickly accumulated during the Fenton reactions. Therefore, a large amount of research focuses on accelerating the Fe<sup>II</sup>/Fe<sup>III</sup> redox cycle to increase the pseudo first-order rates of the Fenton system [4–15]. Reducing agents (RAs), such as hydroxylamine [7], ascorbic acid [9], quinone [11], humic acid [12], etc., were reported to be effective in accelerating the reduction of Fe<sup>III</sup> to Fe<sup>II</sup>, which further enhances the oxidation performance of the Fenton system. However, they may also compete for the active sites of the catalyst with organic compounds and the oxidant (H<sub>2</sub>O<sub>2</sub>), leading to the decrease of Fenton activity [15–17]. In addition, the limited understanding of the mechanism of heterogeneous Fenton reactions in the presence of RAs hinders any significant

advances in Fenton chemistry.



Previously, we developed two kinds of Fe–Co Prussian blue analogues (PBAs) as excellent photo-Fenton catalysts for in-depth investigation of the heterogeneous Fenton reaction mechanism [18]. The efficient redox cycling of iron species in the Fe–Co PBAs photo-Fenton process was identified and the water coordinated iron was proposed as the main active site. However, until now, the reaction intermediates and fate of the active iron species in the heterogeneous Fenton system are still unclear and need further investigation [10,19–21]. As is well known, the intermediates of a catalyst-activated reaction are often very difficult to detect. The reducing agents in the Fenton process may compete for the active sites of a catalyst and thus change the coordination environments of active iron species. Owing to the advantage of <sup>57</sup>Fe Mössbauer techniques, which is an ideal technique for determining the coordination environment and oxidation state of iron ions in a catalyst [4,18,22,23], the reaction intermediates and its subsequent reaction pathways of iron species can be investigated and may shed some light on the heterogeneous Fenton mechanism.

In this work, hydrazine (Hz), due to its strong reducing ability, low cost, and minimizing impurities in the products (N<sub>2</sub> and H<sub>2</sub>O) [24,25],

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was recently introduced to enhance the oxidation performance of the Fenton system despite its associated toxicity. The effects of Hz on the heterogeneous Fenton oxidation of bisphenol A (BPA) catalysed by  $\text{Fe}^{\text{III}}$ -Co PBA, as well as on the homogeneous Fenton reaction, were systematically investigated. The reaction intermediates and pathway of active iron species in the Hz/ $\text{Fe}^{\text{III}}$ -Co PBA Fenton system were explored by  $^{57}\text{Fe}$  Mössbauer spectroscopy and X-ray photoelectron spectroscopy (XPS).

## 2. Experimental

See Supporting Information, SI (Text S1).

## 3. Results and discussion

### 3.1. Enhanced removal of BPA by addition of Hz

The effects of Hz on the heterogeneous Fenton oxidation of BPA catalysed by  $\text{Fe}^{\text{III}}$ -Co PBA were investigated and are shown in Fig. 1. A control test using only  $\text{Fe}^{\text{III}}$ -Co PBA as the heterogeneous Fenton catalyst shows that less than 5% of BPA was degraded in 6 min, revealing that its activation of  $\text{H}_2\text{O}_2$  for production of reactive radicals was very limited at current reaction conditions. The activation of  $\text{H}_2\text{O}_2$  by Hz was also negligible with BPA decrease of less than 2%. However, the addition of both  $\text{Fe}^{\text{III}}$ -Co PBA and Hz led to a significant enhancement of the BPA removal efficiency. As high as 99% BPA removal efficiency could be achieved within only 6 min, which is even higher than that of the  $\text{Fe}^{\text{II}}$ -Co PBA catalysed heterogeneous Fenton system. As shown in Fig. S1, Hz also shows a better performance as compared to HA in the same reaction system. According to our previous report [18], the whole Fenton processes could be fitted with a pseudo first-order kinetics model as shown in Table S1, the addition of Hz increased the BPA degradation rate with more than two orders of magnitude in this Fenton oxidation system at pH = 4.0. The effect of Hz concentration on  $\text{Fe}^{\text{III}}$ -Co PBA Fenton activity for BPA degradation was quantitatively examined (Figs. S2, S3). Although the increase of Hz concentration could largely enhance the BPA removal efficiency and the rate constant, further increasing the concentration of Hz decreased the rate constant, which is most probably because of the competitive reactions that adversely affect the generation of reactive species ( $\text{HO}\cdot + \text{NH}_2\text{NH}_2 \rightarrow \cdot\text{NHNH}_2 + \text{H}_2\text{O}$   $k = 1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) [26]. All these results suggest the important role of Hz on the significantly promoted BPA degradation in the  $\text{Fe}^{\text{III}}$ -Co PBA catalysed Fenton system.

The effect of pH on BPA degradation in Hz promoted  $\text{Fe}^{\text{III}}$ -Co PBA Fenton process was also investigated (Fig. S4). The rate constant as

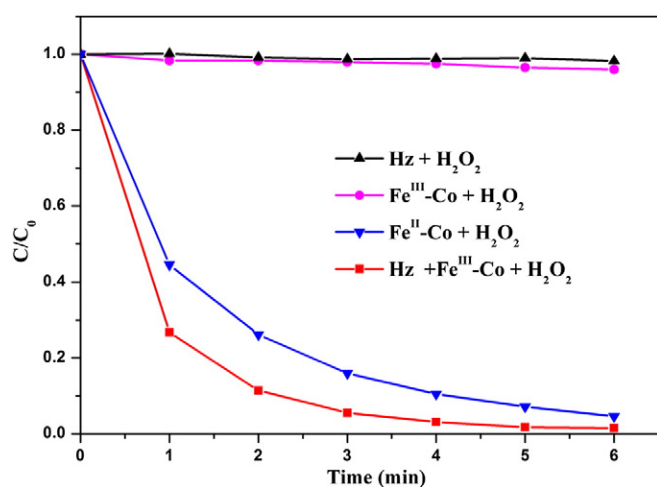


Fig. 1. Removal efficiency of BPA in different reaction systems within 6 min. Reaction conditions: [BPA] = 20 mg L<sup>-1</sup>, [H<sub>2</sub>O<sub>2</sub>] = 2 mM, [Hz] = 0.8 mM (if needed), catalyst = 0.2 g L<sup>-1</sup>, T = 298 K, pH = 4.0.

well as the BPA degradation efficiency decrease significantly while the solution pH is increasing, suggesting that acidic condition is more suitable for the reaction system.

The released Fe and Co ions during Hz/ $\text{Fe}^{\text{III}}$ -Co PBA Fenton reaction were determined to be about 2.0 and 2.3 mg L<sup>-1</sup>, respectively (Fig. S5). These are much higher than those of the Fenton system without Hz in our previous research [18], suggesting that the addition of Hz largely enhanced the dissolution of  $\text{Fe}^{\text{III}}$ -Co PBA during the Fenton reaction. As shown in Fig. 2, the BPA removal efficiency was less than 6% when catalysed by similar concentration of  $\text{Co}^{2+}$  and Hz, suggesting that the  $\text{Co}^{2+}$  is not the main active species in the Fenton reaction. The BPA removal efficiency catalysed by similar concentration of  $\text{Fe}^{3+}$  was also negligible. However, the addition of Hz to  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  system largely enhanced the BPA removal efficiency to about 35% in 6 min, suggesting the excellent promoter ability of Hz also on the homogeneous Fenton reaction. A similar concentration of  $\text{Fe}^{2+}$  resulted in the BPA removal efficiency as high as 83%, which was only slightly lower than that of 85% with the assistance of Hz. Combining with the pseudo first-order rate constants shown in Fig. S6, these results suggest that even though the heterogeneous Fenton reaction is the main contributor to the high BPA removal efficiency, the homogeneous Fenton reaction contributes about 40% to the rate constant by enhanced dissolution of  $\text{Fe}^{\text{III}}$ -Co PBA.

### 3.2. Plausible mechanisms of the Hz promoted $\text{Fe}^{\text{III}}$ -Co PBA Fenton process

The Mössbauer spectra of  $\text{Fe}^{\text{III}}$ -Co PBA before and after different reactions ( $\text{Fe}^{\text{III}}$ -Co + Hz and  $\text{Fe}^{\text{III}}$ -Co + Hz +  $\text{H}_2\text{O}_2$ ) were measured to explore the changes of the coordination environments of active iron species during the Fenton process (Fig. 3). The model employed to fit the spectra was similar to that reported in our previous works [18,27] and the corresponding Mössbauer parameters are shown in Table S2. As can be seen, the content of  $\text{Fe}^{\text{II}}$  in  $\text{Fe}^{\text{III}}$ -Co PBA increased from 4.5% to 7.7% after the reaction with Hz, suggesting that Hz is capable of reducing a part of  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$ . A more interesting phenomenon is that the content of  $\text{Fe}^{\text{III}}$  in  $\text{FeN}_6$  increased from 75.0% to 86.5% with the decrease of  $\text{Fe}^{\text{III}}$  in  $(\text{H}_2\text{O})\text{FeN}_5$  from 20.5% to 5.8%. This result indicates that the water coordinated iron site ( $\text{H}_2\text{O}-\text{Fe}$ ) was partly replaced by Hz coordinated iron site ( $\text{H}_2\text{NH}_2\text{N}-\text{Fe}$ ) during the Hz promoted Fenton process. However, when Hz and  $\text{H}_2\text{O}_2$  were coexisting in the reaction system, it was of great importance to find that the content of  $\text{Fe}^{\text{III}}$  in  $(\text{H}_2\text{O})\text{FeN}_5$  was higher than the one without  $\text{H}_2\text{O}_2$ . All these results suggest that the reaction of  $\text{H}_2\text{O}_2$  with  $[\text{Fe}(\text{CN})_5(\text{Hz})]^{2-}$  is most likely to occur during the Fenton process.

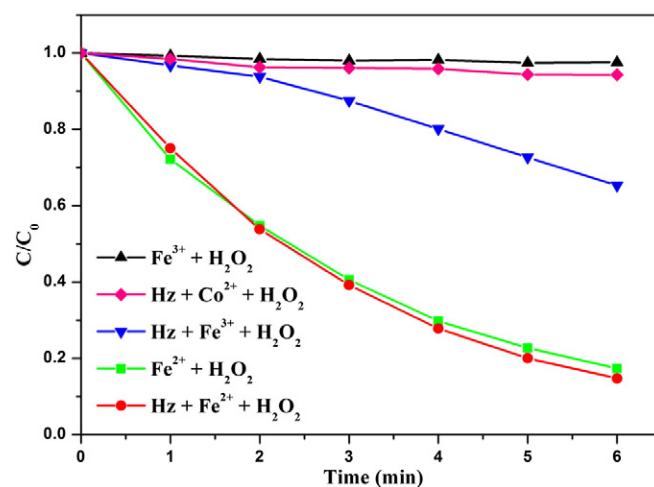


Fig. 2. Removal efficiency of BPA in Hz promoted homogeneous Fenton systems. Reaction conditions: [BPA] = 20 mg L<sup>-1</sup>, [H<sub>2</sub>O<sub>2</sub>] = 2 mM, [Hz] = 0.8 mM,  $[\text{Fe}^{2+/3+}/\text{Co}^{2+}] = 40 \mu\text{M}$ , T = 298 K, pH = 4.0.

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