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Persistent free radicals (PFRs) were mainly reported as negative species. Here we report a positive role of PFRs in enhancing reactive oxygen species (ROS) generation for an extreme rate enhancement in environmental pollutants decomposition.

Persistent free radicals (PFRs) were widely observed in nature, such as combustion-generated matters, airborne PM2.5, soils and sediments. The importance of this class of reactive intermediate has been duly noted in environmental, chemical and biological systems due to their persistence and radical reactivity. Generally, the current researches mainly focus on regarding PFRs as deleterious species, which initiated adverse health impacts, such as DNA damage and pulmonary dysfuction. Despite several reports in the discovery of PFRs as oxidants activators to oxidize organic compounds, the positive roles of PFRs were still poorly considered so far.

PFRs are stable in air for a prolonged time and their half-lifetimes are on the order of hours or even days. Such long lifetimes of the radicals are unique, however, they do not preclude radical reactivity. It has been reported that the unpaired electrons in PFRs can be sustainably transferred to electron-acceptors such as higher valent metals. This distinctive property might feature the capability to accelerate some important catalytic redox processes such as iron-mediated cycle involved the intrinsic drawback of slow iron reduction rate to generate reactive oxygen species (ROS) for the degradation of environmental pollutants. Hence, PFRs may be beneficial species in promoting the catalytic efficiency for contaminants decomposition, while comparatively, the knowledge about this role of PFRs is rather limited.

Lately, carbonaceous materials were reported to contain PFRs and gradually received attention in the related researches. Meanwhile, carbonaceous materials were widely used as catalyst supports, which might endow PFRs potential applications in environmental catalysis. Among various carbonaceous materials, activated carbon fiber (ACF) has remarkable advantage: it may be formed into felts or fabrics of various shapes, and is therefore amenable to handling in different applications. Moreover, ACF also has the similar characteristics of other carbonaceous materials, such as large specific surface area, unusual chemical and structural stability. Herein, we selected ACF as the representative of PFRs, iron porphyrin (hemin) as the catalyst and H2O2 as the oxidant to construct a novel catalytic oxidation system of hemin-ACF/H2O2 for contaminants decomposition. However, during the reaction process, continuous electron transfer from PFRs (ACF) to hemin will inevitably cause the loss, or even complete consumption of PFRs, which would decrease the catalytic efficiency. Inspired by the discharging and charging process of battery, a “charging” process (electron donor) is highly desired to supply electron to ACF for the regeneration of PFRs.

Ascorbic acid (AA) is an unsaturated polyhydroxy compound, which enable AA to be an ideal candidate as the electron donor. Moreover, compared with other electron donors such as polyphenols, hydroxylamine hydrochloride and sodium sulfite, AA is nontoxic, relatively cheap, and has extensive sources. Herein, AA was introduced to hypothetically supply electrons for the electron sink, i.e., “charging”. These “discharging” (electron transfer from ACF to hemin) and “charging” (electron transfer from AA to ACF) processes could allow for a higher catalytic efficiency in the production of ROS, resulted in an extreme rate enhancement in contaminants decomposition. This research offers a new insight into the PFRs-enhanced catalytic performance and initiates an inspiring research domain of PFRs in the environmental field.

Fig. 1A showed the electron paramagnetic resonance (EPR) spectra of hemin-ACF at room temperature after different reaction time in the hemin-ACF/H2O2 system. The narrow singlet signal located at 3513G was attributed to the PFRs in the system located at 3513G. The narrow singlet signal located at 3513G was attributed to the PFRs in the system.
pH 7.3, at 50°C.

Fig. 1. (A) EPR spectra of hemin-ACF at room temperature after different reaction time in the hemin-ACF/H$_2$O$_2$ system. (B) EPR spectra of hemin-ACF at room temperature after different reaction time in the hemin-ACF/H$_2$O$_2$/AA system. (C) Intensity of PFRs in hemin-ACF in the hemin-ACF/H$_2$O$_2$ and hemin-ACF/AA/H$_2$O$_2$ system at different reaction time. Conditions: [hemin-ACF]=10 g/L, [H$_2$O$_2$]=50 mM, initial pH 7.3, at 50°C.

3402G and 3513G decreased $9.38 \times 10^6$ and $7.47 \times 10^6$, respectively (Fig. 1A and C), implying the decrease of the PFRs concentration in hemin-ACF, which might be attributed to the electron transfer from ACF to hemin. Meanwhile, the reduction of hemin(Fe$^{III}$) to hemin(Fe$^{II}$) in hemin-ACF was evidenced by XPS (Fig. S2), which was in agreement with the literature, indicating that ACF could transfer electrons to hemin. In this sense, ACF could serve as an electron sink providing electrons to hemin to accelerate the catalytic cycle of hemin(Fe$^{III}$)/hemin(Fe$^{II}$).

Moreover, when AA was added into the hemin-ACF/H$_2$O$_2$ system (Fig. 1B and C), we interestingly found that the signal intensity of PFRs located at 3513G observed for the hemin-ACF firstly increased $3.66 \times 10^6$ in 30 min, suggesting that AA acted as an electron donor to supply electrons to the hemin-ACF, thus increasing the signal intensity of PFRs. Then the intensity decreased $9.36 \times 10^6$ from 30 min to 60 min, which was obviously higher than that of $4.21 \times 10^6$ in the hemin-ACF/H$_2$O$_2$ system (Fig. 1C). These findings suggested that AA coupled with ACF significantly accelerated the electron transfer from ACF to hemin. Furthermore, the effect of AA on the PFRs concentration after cyclic utilizations was investigated. As shown in Fig. S3, the PFRs of hemin-ACF decreased obviously after cyclic utilizations in the hemin-ACF/H$_2$O$_2$ system. However, after the introduction of AA, the PFRs of hemin-ACF (at 3513G) conversely increased after cyclic utilizations in the hemin-ACF/AA/H$_2$O$_2$ system, demonstrating that hemin-ACF could work like a rechargeable electron sink, which could be repeatedly “charged” by the electron donor AA after “discharging” (i.e. transferring electrons to hemin).

To further testify the role of PFRs in enhancing the generation of ROS, spin-trap experiments were carried out. First, the types of ROS in the systems were identified as shown in Fig. 2A, the hemin/H$_2$O$_2$ system exhibited 1:2:2:1 quartet of lines in the electron paramagnetic resonance (EPR) spectrum with the hyperfine coupling parameters ($\alpha_N=14.9$ G), which is attributed to DMPO•OH and DMPO•R adducts. Meanwhile, the reduction of hemin(Fe$^{III}$) to hemin(Fe$^{II}$) in hemin-ACF was evidenced by XPS (Fig. S2). Other detailed conditions and methods were demonstrated in the Supplementary Information.

Second, the amounts of •OH, •R and hemin(Fe$^{IV}$=O) in the systems were further investigated. The relative amounts of •OH and •R were calculated according to EPR signal intensity of DMPO•OH and DMPO•R adducts in various catalytic systems. It was found that the introduction of ACF and AA resulted in the promoted formation of •OH with the order of
participation of AA caused the generation of •R with the order of hemin/AA<hemin/ACF/AA, while the generation of •OH than that of the hemin/HO2 system was considerably enhanced (Fig. 2D), indicating that both ACF and AA enhanced the hemin(FeIII=O) formation. It is of note that the hemin/AA/HO2 system generated higher intensity of •OH and hemin(FeIII=O) than that of the sole hemin/HO2 (Fig. 2), indicating that AA could transfer electron to hemin, enhancing hemin-catalyzed generation of ROS. However, the ROS generation in the hemin/AA/HO2 system was obviously much less than that of the hemin-ACF/AA/HO2 system (Fig. 2), implying that the direct electron transfer from AA to hemin was not mainly responsible for the dramatically enhanced generation of ROS, while the electron transfer from AA to ACF might be the dominant reason for the ROS enhancement in the hemin-ACF/AA/HO2 system.

Based on these findings mentioned above, we envisioned that PFRs could be applied in catalytic decomposition of organic pollutants due to the generation of ROS,50-53 Reactive Red M-3BE (RR M-3BE) was employed as the target contaminant to test the performance of our system, as shown in Fig. 3A. Hemin/HO2 could not efficiently remove RR M-3BE (curve a), while the introduction of sole AA or ACF accelerated the dye decomposition with over 80% removal rate in 60 min (curves b and c). Amazingly, when AA and ACF were co-introduced, we found that 100% of RR M-3BE was rapidly eliminated in 1 min (curve d). All of the RR M-3BE decomposition curves obeyed pseudo-first-order kinetics (Fig. 3B). The RR M-3BE decomposition rate constant was calculated to be 3.9039 min⁻¹ in the hemin-ACF/AA/HO2 system, which was about 2169 times that (0.0018 min⁻¹) in the hemin/HO2 system, 114 times that (0.0342 min⁻¹) in the hemin/HO2/AA system and even 48 times that (0.0815 min⁻¹) in the hemin-ACF/HO2 system.

These findings mentioned above suggested that PFRs (ACF) played a key role of electron sink, continuously transferring electrons to hemin (i.e. “discharging”). When the PFRs were gradually consumed during the process of electron transfer, AA could serve as an electron donor to supply electrons to the electron sink (i.e. “charging”), thus maintaining the amounts of PFRs in ACF. Therefore, PFRs coupled with AA sustainably provided electrons for the rate-determining conversion of hemin(FeII) to hemin(FeIII), thus accelerating the catalytic cycle of hemin, resulting in strongly enhanced production of •OH and hemin(FeIII=O) (Route 2), further promoting the oxidative decomposition of RR M-3BE by 2169-folds compared with that of the sole hemin/HO2 system (Route 1) (Scheme 1). In addition, from the perspective of structure change of hemin-ACF and electrochemistry, the mechanism for extremely enhanced decomposition was also investigated (Fig. S21, Schemes S1 and S2).

The current work provides a new insight into the role of PFRs in extremely enhancing the generation of ROS for the contaminants decomposition. In the hemin-ACF/HO2/AA system, •OH and hemin(FeIII=O) were the main ROS for the extremely enhanced decomposition of organic pollutants, while the novel radicals •R derived from the decomposition of AA with a strong signal intensity were proved not able to effectively destroy the pollutants, but might find promising applications in other fields. The findings of this study provide a new insight into the PFRs-enhanced catalytic performance for environmental pollutants decomposition, which might bring an inspiring research domain of PFRs in the environmental field.

**Scheme 1.** The proposed catalytic cycle of hemin with or without the introduction of AA and ACF.
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Notes and references