How to Accurately Assess the Intrinsic Activity of Catalysts in Peroxy Activation?

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Heterogeneous advanced oxidation processes (AOPs) with catalysts can remove recalcitrant organic pollutants in water by generating reactive oxygen species (ROS) through the activation of peroxy precursors (e.g., hydrogen peroxide, ozone, and peroxymonosulfate (PMS)). These AOPs involve not only adsorption and degradation of pollutants, but also oxidant activation over the catalyst surface. Oxidant concentration is widely recognized to affect the removal efficiency of organic pollutants, but its effect on the specific activity of catalysts has rarely been considered. Here, we use PMS-based AOPs as an example to illustrate how to more accurately evaluate the intrinsic activity of catalysts and optimize PMS activation and process performance.

Specific Degradation Rate Constants Do Not Accurately Reflect the Activity of Catalysts. To evaluate the catalytic activity of materials for PMS activation, apparent first-order rate constants \(k_{\text{app}}, \text{(min}^{-1})\) are commonly obtained from pollutant degradation tests under a certain PMS concentration, and further normalized by the surface area of catalysts \((S, \text{m}^2/\text{g})\) to obtain specific rate constants \(k_{\text{SA}}, \text{g} \cdot \text{m}^{-2} \cdot \text{min}^{-1}\). Generally, \(k_{\text{SA}}\) depends greatly on the initial oxidant concentration:\(k_{\text{SA}}\) usually increases with PMS dosages, but when PMS concentration exceeds a value that saturates the catalyst surface, \(k_{\text{SA}}\) no longer increases and excessive PMS can quench the generated radicals and decrease degradation rates.

As illustrated in Figure 1a, the effect of initial PMS concentration on \(k_{\text{SA}}\) varies for different catalysts. In this example, \(k_{\text{SA}}\) of catalysts A and B are linearly correlated to PMS concentrations with different slopes at the commonly used PMS concentration ranges. As a result, catalyst A outperforms catalyst B \((k_A > k_B)\) at the PMS concentration \(C_2\), while catalyst B has a higher activity \((k_A' > k_B')\) at \(C_2\). Thus, this would result in a contradictory conclusion regarding relative catalytic activity at different oxidant concentrations. As the cross points tend to be at low peroxy concentrations, this contradiction would more frequently happen in PMS activation tests, because efficient organic degradation can be achieved at relatively low PMS dosages. Inspired by the need to resolve this confounding effect, we re-evaluated the catalytic activity assessed by “\(k_{\text{SA}}\) comparison” based on previously reported data.\(^{1−3}\) The \(k_{\text{SA}}\) values are indeed linearly correlated to PMS concentrations with different slopes for 4-chlorophenol (Figure 1b) and bisphenol A (Figure 1c) degradation. Thus, it is not accurate to assess the catalytic activity of catalysts based on \(k_{\text{SA}}\) at just one oxidant concentration.

Implication of \(k_{\text{SA}}\) versus Initial PMS Concentration Slopes on Oxidant and Pollutant Adsorption Capacity and Reactivity. During pollutants degradation via heterogeneous PMS activation, both reactants (PMS and pollutant) interact with the active sites on the catalyst surface, and then undergo a bimolecular reaction, which follows the binary Langmuir–Hinshelwood mechanism. According to the surface coverage fractions of pollutant (\(\theta_1\)) and PMS (\(\theta_2\)) described in eqs 1 and 2, the initial reaction rate of pollutant degradation \((r, M \text{ min}^{-1})\) can be described in eq 3, where \(k_1 \text{ (M g m}^{-2} \text{ min}^{-1})\) is the surface normalized rate constant of the rate-limiting step, \(\theta^*\) represents the fractions of unoccupied surface sites, \(C_1\) (M) and \(C_2\) (M) represent the initial concentrations of pollutant and PMS, and \(K_{C_1} (M^{-1})\) and \(K_{C_2} (M^{-1})\) are equilibrium constants for pollutant and PMS adsorption.\(^{7}\) Considering the chemisorption nature of pollutants over catalysts, \(K_{C_1}\) would be much larger than 1.\(^{4}\) On the other hand, because the coverage of oxidant (\(\theta_2\)) is much lower than that of pollutants (\(\theta_1\)) due to the rapid conversion of oxidants over active sites, \(K_{C_2}\) is far less than \(K_{C_1}\). Thus, eq 3 can be simplified as eq 4. As the initial reaction rate can be described by a first-order kinetic eq (eq 5) with the specific apparent rate constants \(k_{\text{SA}}\), the combination of eqs 4 and 5 yields eq 6, which represents the relationship between specific reaction rate constant \(k_{\text{SA}}\) and oxidant concentration \((C_2)\).

\[
\theta_1 = K_{C_1} \theta^* \tag{1}
\]

\[
\theta_2 = K_{C_2} \theta^* \tag{2}
\]

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As described in eq 6, $k_{SA}$ shows a linear relationship with $C_2$ (below excessive PMS concentrations that promote radical quenching), which is consistent with the experimental results (Figure 1). Accordingly, plotting $k_{SA}$ versus the initial oxidant concentration ($C_2$) yields a linear trend with the following slope:

$$\text{slope} = k_2K_2/C_1^2$$  \hspace{1cm} (7)

Equation 7 reflects the intrinsic properties of catalysts and provides valuable information for the design of high-performance catalysts. For example, (1) a high concentration ($C_1$) and strong adsorption ($K_1$) of pollutants would inhibit oxidant activation due to occlusion of available active sites. Thus, separation of the active sites for pollutant adsorption and oxidant activation is necessary and effective to enhance pollutant degradation. (2) $k_r$, which is the reaction rate constant between the adsorbed pollutants and the reactive species, may vary over several orders of magnitude. As shown in Figure 1c, the slope for Fe$_3$O$_4$/PMS that is dominated by hydroxyl and sulfate radicals is 1 order of magnitude higher than the other one based on singlet oxygen mechanism. Thus, reactive species with stronger oxidative capacity result in higher slope values. (3) $K_2$, which is the equilibrium constant for the adsorption of oxidants on the catalysts, depends on the Gibbs free energy for the oxidant adsorption. Generally, nonradical pathways for PMS activation have less negative PMS adsorption energies than radical pathways, resulting in significantly lower $K_2$ values.\(^5\) Diverse pathways for persulfate activation result in different slopes, which make the assessment of catalytic performance more intricate.

Catalysts for AOPs have long been screened by comparing pollutant degradation efficiency at a certain oxidant concentration, which is inaccurate and possibly misleading. Here, we propose that the intrinsic activity of a catalyst to activate peroxy can be evaluated by the slope of $k_{SA}$ versus the initial oxidant (e.g., PMS) concentration. Factors that contribute to a larger slope and higher activity include separating the active sites for pollutant adsorption and oxidant activation, producing reactive species with higher oxidation potential, and increasing affinity between catalysts and oxidants. This slope-based approach can thus help compare the intrinsic activity of different catalysts, determine optimal initial oxidant concentrations for different applications, and provide insight into the pertinent activation pathways.

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Notes

The authors declare no competing financial interest.
Biography

Mingce Long, Ph.D., is a professor in the School of Environmental Science and Engineering at Shanghai Jiao Tong University. His research focuses on heterogeneous advanced oxidation processes for environmental cleanup. He has authored over 130 peer-reviewed papers and one edited book. He serves as a member of the Editorial Board of Nano-Micro Letters, and Toxics and as early career Editorial Board member of Chinese Journal of Catalysis. He has been awarded as the “Tang Lixin Excellent Scholar of Shanghai Jiao Tong University” in 2018 and “Thermo Fisher Young Researcher Academic New Artist” in 2010. He received his Ph.D. degree in Environmental Engineering from Shanghai Jiao Tong University in 2007, after completing his bachelor and master studies at Harbin Institute of Technology.

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