



Molybdenum phosphide (MoP) with dual active sites for the degradation of diclofenac in Fenton-like system

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ARTICLE INFO

Article history:

Received 28 April 2021

Revised 23 July 2021

Accepted 26 July 2021

Available online 31 July 2021

Keywords:

MoP

Dual active sites

Fenton-like

Diclofenac degradation

ABSTRACT

The leaching and non-recoverability of metal ions have always limited the practical application of Fenton-like processes. For the first time, we synthesized molybdenum phosphide (MoP) with dual active sites for the degradation of diclofenac (DCF) in the Fenton-like process. The DCF degradation rate constant (k) of MoP + H₂O₂ process was calculated to be 0.13 min⁻¹ within 40 min, indicating a highly efficient catalytic ability of MoP. In addition, this catalyst exhibits a stable structure and good activity, which could apply in a broad pH range, different ions solution and real wastewater condition. Accordingly, this efficient catalytic capability may be attributed to the presence of the metal sites Mo^{δ+} and the electron-rich sites P^{δ-} in MoP, which could induce the generation of hydroxyl radical ([•]OH) and superoxide radical ([•]O₂⁻) through electron transfer, resulting in the effective removal of DCF. This study provides an idea for the optimization of Fenton-like technologies and environmental remediation.

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Diclofenac (DCF) is a kind of anti-inflammatory drugs that is widely used to treat inflammatory, painful diseases, and other pains [1]. It has been reported that the annual consumption of DCF reached more than 60 tons in many countries [2]. However, the excretions of DCF are poorly eliminated in the wastewater treatment plants, resulting in the residual of DCF in surface water and groundwater. For example, high concentration of DCF is detected in Llobregat River [3]. In addition, DCF with low concentration would cause cytological alterations in rainbow trout [4], suggesting that DCF may have a risk to the aquatic ecosystems. Thus, DCF exposed to the natural environment needs to be removed urgently.

Fenton-like processes with strong oxidation capacity can produce hydroxyl radicals ([•]OH), which are considered as promising technologies to treat refractory pollutants [5–10]. Although traditional Fenton process has lots of advantages such as high efficiency and simple operation, the production of iron sludge and the difficulty in the recycle of Fe²⁺ both limit its practical application [11].

Hence, it is necessary to find an efficient and recyclable catalyst to replace Fe²⁺.

Transformation metal compounds are a group of common catalysts used to replace metal ions in Fenton-like reaction, among which P-based compounds with low-cost and earth-abundant have been widely used to be hydrogen agent, photocatalyst or electrocatalyst [12–14]. In addition, the formation of metal-P bonds in P-based compounds can result in a “weak ligand” effect on P atom and adjust the surface charge state of metal atoms, which may perform the potential to be applied in Fenton-like reactions [15–17]. In recent years, P-based compounds have been gradually used to treat organic pollutants in Fenton-like processes. For example, Luo *et al.* prepared nanostructured CoP as an efficient peroxymonosulfate (PMS) activation catalyst for the degradation of orange II, which could achieve a ratio of 97.2% for orange II degradation in 4 min [18]. As an important member of P-based compounds, MoP presents high electronic conductivity and superior chemical stability, which gets more and more attention in recent years [15]. With the charged nature of molybdenum (Mo^{δ+}) and phosphorus (P^{δ-}), MoP may own unique dual active sites like Ni₂P [19–21], which may be also conducive to the optimization of the Fenton-like systems. Generally, Mo is considered as the active center among the

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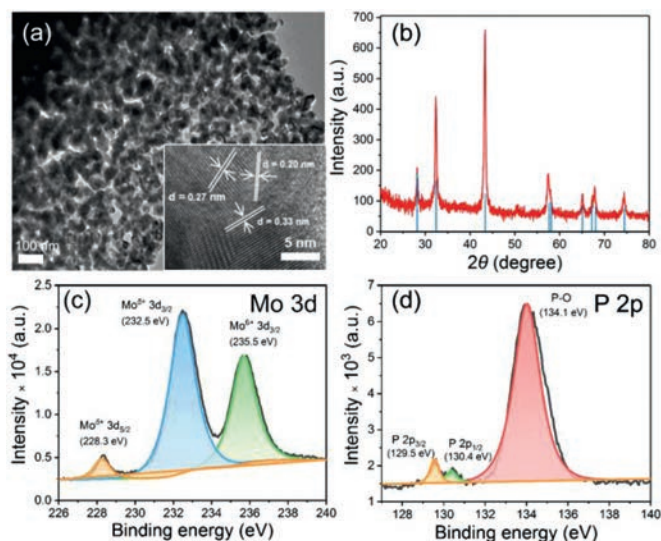


Fig. 1. (a) TEM image and (b) XRD pattern of MoP. (c) Mo 3d and (d) P 2p XPS spectra of MoP.

Mo-based catalysts like MoS₂ and Mo₂C [22–26]. However, the activation capacity of MoP for H₂O₂ has not been reported and the mechanism of MoP + H₂O₂ process is unknown.

In this study, MoP was used as a catalyst for DCF degradation in Fenton-like process for the first time. The purpose of this study is to (i) determine the DCF degradation efficiency in MoP + H₂O₂ process; (ii) investigate the effects of experimental parameters such as MoP, H₂O₂ and DCF concentration; (iii) evaluate the practical application potential of MoP + H₂O₂ process; (iv) clarify the mechanism of MoP + H₂O₂ process; and (v) propose the degradation pathways and products of DCF.

The specific materials and methods are supported in the Text S1 (Supporting information). To determine the successful synthesis of MoP, characterizations such as transmission electron microscope (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were conducted and the results are shown in Fig. 1. The TEM image suggests that MoP is a group of irregular nanoparticles. Through observing the crystal lattice of the synthesized material, three lattice fringes with the interval of around 0.20, 0.27 and 0.33 nm were found, corresponding to the (101), (100) and (001) lattice plane of MoP crystalline [21,27]. In addition, the crystallinity of the sample was characterized by XRD. As shown in Fig. 1b, XRD pattern displays diffraction peaks at 2θ of 28.0°, 32.2°, 43.2°, 57.4°, 57.9°, 64.9°, 67.0°, 67.8° and 74.4°, which well correspond to the (001), (100), (101), (110), (002), (111), (200), (102) and (201) of the orthorhombic MoP standard card (JCPDS No. 24-0771), respectively. Furthermore, XPS was carried out to study the valence situation of the as-prepared MoP (Figs. 1c and d). Two peaks at 228.3 eV and 232.5 eV performed in Mo 3d XPS spectrum are the typical peaks of MoP assigning to Mo^{δ+} [27], while another peak at 235.5 eV corresponds to Mo⁶⁺ 3d_{3/2}, resulted by the slight oxidation on the surface of MoP [21]. Additionally, P 2p XPS spectrum clearly exhibits a predominant peak at 134.1 eV corresponding to P–O bond, which could be attributed to the oxidation of surface P [21]. Moreover, the peaks located at 129.5 eV and 130.4 eV corresponding to P 2p_{3/2} and P 2p_{1/2} are the P^{δ-} species in MoP, which are consistent with previous research [21,27,28].

Before testing the catalytic capacity of MoP in Fenton-like process for DCF degradation, the adsorption capability of MoP for DCF was studied. As shown in Fig. S1 (Supporting information), the adsorption ratio of DCF in 120 min reached about 30%, indicating a limited adsorption capability of MoP. In addition, the adsorption

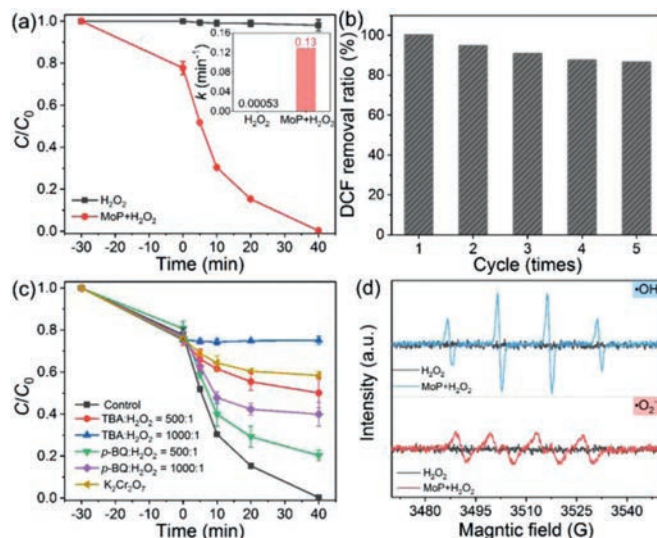


Fig. 2. (a) Degradation ratio and reaction rate constant of DCF in MoP + H₂O₂ system. (b) Cycle experiments in MoP + H₂O₂ system for the DCF degradation. (c) Degradation ratios of DCF using various scavengers and (d) ESR in the MoP + H₂O₂ system. Experimental conditions: [H₂O₂] = 2.0 mmol/L, [MoP] = 0.10 g/L, [DCF] = 20 mg/L, pH 6.0, T = 25 °C, scavenger:H₂O₂ = 500:1 and 1000:1 molar ratio.

ratio kept stable after 30 min, suggests that the adsorption equilibrium was determined to be 30 min. Furthermore, it can be clearly observed that H₂O₂ alone could not remove DCF, suggesting the insufficient oxidant capability of H₂O₂ (Fig. 2a). However, MoP catalyzed H₂O₂ process got a surprising degradation of DCF, in which almost 100% of DCF was degraded in 40 min (Fig. 2a). These results manifest that MoP could react with H₂O₂ to remove organic pollutant effectively. The reaction kinetics of MoP, H₂O₂ and MoP + H₂O₂ processes were calculated using pseudo-first-order kinetic model $-\ln(C/C_0) = kt$ for further comparing the degradation performance of DCF in different processes. The observed rate constant (*k*) value of MoP + H₂O₂ process was calculated to be 0.13 min⁻¹ (Fig. 2a). Moreover, as shown in Fig. S2 (Supporting information), the reaction rate constant of DCF in different Fenton-like systems are lower than that in MoP + H₂O₂ process, indicating an excellent performance of the MoP. In addition, the synergy factor (SF) of MoP + H₂O₂ process was further calculated by Eq. S1 (Supporting information) and the calculation result is 15 (> 1), indicating a significant synergistic effect between MoP and H₂O₂. Therefore, the prepared MoP displayed efficient activation efficiency on H₂O₂ for DCF degradation, which would widen the application areas of P-based compounds.

Additionally, the key operational factors would also have an important impact on the degradation of pollutants, thereby the impact of MoP dosage, H₂O₂ dosage, DCF concentration and pH were explored. As shown in Fig. S3 (Supporting information), with the increase of MoP or H₂O₂, the degradation ratio of DCF gradually increased, which may be attributed to the increase in surface reaction sites of MoP and reactive oxidative species (ROSs). Moreover, the higher concentration of DCF would cause the lower degradation efficiency of DCF, because the generated ROSs might be not insufficient to degrade excess DCF in the MoP + H₂O₂ process (Fig. S3c). In addition, the MoP + H₂O₂ system would work over a broad pH range (4.0–8.0), among which the removal ratio of DCF could be achieved almost 100% when pH = 6.0. According to the above optimization experiments, the MoP dosage, H₂O₂ dosage, DCF concentration and pH were subsequently set as 0.10 g/L, 2.0 mmol/L, 20 mg/L and 6.0, respectively.

To evaluate the practical application potential of MoP, several experiments were conducted. Firstly, the common ions in wastewater were added in the reaction solution to examine the effect of ions. It is obviously to find that 5 mmol/L of ions in the reaction solution could slightly decrease the degradation efficiency of DCF, which reached 80%, 85%, 88% and 90% with the addition of Cl^- , HCO_3^- , NO_3^- and SO_4^{2-} , respectively. This indicates that the addition of ions would slightly inhibit the ability of MoP activation of H_2O_2 (Fig. S4a in Supporting information). Furthermore, the degradation ratio of DCF in different actual wastewater was slightly lower than that in ultrapure water matrix. Thus, even though the addition of ions and actual wastewater would affect the treatment efficiency of DCF, they were all greater than 70% (Fig. S4b in Supporting information), revealing a high potential for DCF removal in real water in the MoP + H_2O_2 process. In addition, MoP exhibits a good activity after the reaction, which could maintain 86% of DCF degradation ratio in 5 cycles (Fig. 2b). These all suggest the high application potential for the pollutant degradation in real wastewater by MoP + H_2O_2 system.

In order to apply MoP + H_2O_2 process in actual wastewater treatment, it is necessary to understand its mechanism. Thus ROSs capture and electron spin resonance (ESR) experiments were carried out to determine the radical species during the MoP + H_2O_2 process. *Tert*-butanol (TBA) and *p*-benzoquinone (*p*-BQ) were used as $\cdot\text{OH}$ and superoxide radical ($\cdot\text{O}_2^-$) scavengers with the reaction rate constants of $(3.8\text{--}7.6) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ [29] and $2.9 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ [30], respectively. As displayed in Fig. 2c, the degradation ratio of DCF was strongly inhibited with the addition of TBA, which decreased to 50% in 40 min, indicating the significant role of $\cdot\text{OH}$ in the reaction. Furthermore, *p*-BQ also showed a suppression of DCF degradation, with the degradation ratio of 79%. With the ratio of TBA/*p*-BQ and H_2O_2 increasing to 1000, the degradation ratio of DCF further decreased to 24%/60%. Thus the ROSs quenching test signifies the coexistence of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, while $\cdot\text{OH}$ is the main ROSs that plays an important role. ESR experiment further certifies the result of ROSs test. Four peaks with the intensity ratio of 1:2:2:1 and 1:1:1:1 represent the signal of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, respectively [29]. As shown in Fig. 2d, there are no signal of $\cdot\text{OH}$ or $\cdot\text{O}_2^-$ in the only H_2O_2 system, indicating the lack of these two ROSs, while the signal of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ can be both detected in the MoP + H_2O_2 system, reconfirming the co-contribution of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ to DCF degradation in the MoP + H_2O_2 system.

Previous study has proved that the mechanism of P-based compounds-mediated PMS activation includes the dual role of $\text{P}^{\delta-}$ and metal ions ($\text{M}^{\delta+}$). Thus the XPS spectra of Mo 3d and P 2p of MoP after reaction were examined to investigate the valence changes of MoP during the reaction (Fig. S5 in Supporting information). It has been observed that there is no significant change of the XPS spectra of Mo 3d and P 2p of MoP after reaction compared to that before reaction, indicating a stable structure of MoP. However, the content of $\text{Mo}^{\delta+} 3d_{3/2}$ decreased from 58.37% to 56.23%, while the content of $\text{Mo}^{6+} 3d_{3/2}$ enhanced from 36.91% to 37.66%. This redox behavior of different Mo species manifests that $\text{Mo}^{\delta+}$ could react with the oxidant H_2O_2 to generate high valence Mo^{6+} , resulting in the increase of the Mo^{6+} content. Inductively coupled plasma (ICP) spectrometer was used to detect the dissolution of Mo ions and the result shows that about 5.17 mg/L Mo ions can be detected in the effluent, which indicated that Mo ions on the surface of MoP was dissolved in the reaction during redox reaction, reconfirming the generation of high valence Mo^{6+} during the reaction. In addition, $\text{P}^{\delta-}$ with rich electron is also an active site, which could react with O_2 or H_2O_2 to generate $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, followed by the release of oxidation-derived phosphate [19,31]. The concentration of phosphate ions were detected before and after the reaction and the results show that phosphate ions were increased

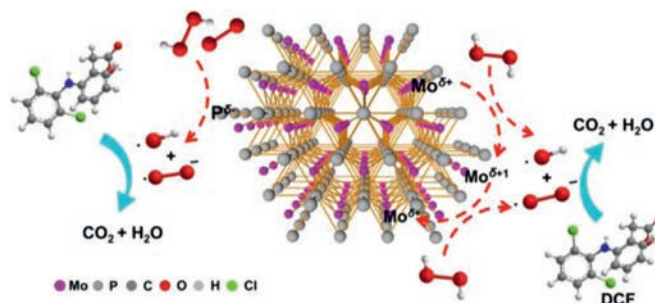
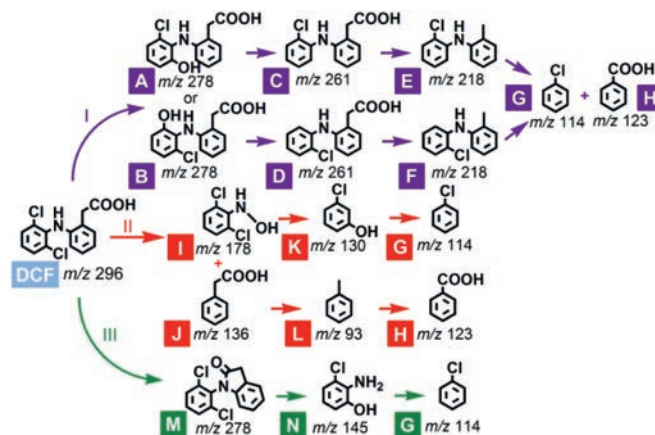


Fig. 3. Proposed mechanism of DCF degradation in the MoP + H_2O_2 system.



Scheme 1. Pathways proposed for DCF degradation by the MoP + H_2O_2 system.

from 0.85 mg/L to 21.20 mg/L. Compared to the XPS spectrum of P 2p of MoP before reaction, the content of the peak of P–O bond after reaction decreased from 93.20% to 87.86%, which is consistent with the previous study resulting from the reaction of electrons and H_2O_2 [19,31]. Thus, $\text{K}_2\text{Cr}_2\text{O}_7$ has been used as an electrons scavenger to further verify the role of electrons. As shown in Fig. 2c, with the addition of $\text{K}_2\text{Cr}_2\text{O}_7$, the degradation ratio of DCF was severely suppressed, which was only 42%, indicating an important role of electrons.

According to the above investigation, it could be assumed that MoP with dual active sites $\text{Mo}^{\delta+}$ and $\text{P}^{\delta-}$ could effectively activate H_2O_2 . The specific reaction mechanism of MoP + H_2O_2 system is shown as Fig. 3. The positive site $\text{Mo}^{\delta+}$ could act as a metal activation sites to react with H_2O_2 , followed by the generation of ROSs ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$) and high valence Mo. Meanwhile, high valence Mo can also react with H_2O_2 to turn back to $\text{Mo}^{\delta+}$, achieving the redox cycle of $\text{Mo}^{\delta+}/\text{Mo}^{\delta+1}$. In addition, the negative site $\text{P}^{\delta-}$ is another highly reactive site, of which the surrounding electrons would react with H_2O_2 or O_2 , thereby producing the ROSs ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$) and phosphate. The generated ROSs will attack the pollutant and result in the degradation of DCF in the MoP + H_2O_2 process.

In order to discuss the degradation pathways of DCF, the degradation products of DCF in MoP + H_2O_2 system were detected by time-of-flight tandem mass spectrometer (TOF-MS). According to the detection results and previous investigation [32–36], three degradation pathways including fourteen degradation products are proposed as Scheme 1. In pathway I, hydroxylation might occur on DCF firstly by $\cdot\text{OH}$ attack, followed by undergoing the loss of $-\text{Cl}$, resulting in the generation of products A and B. Products C and D were produced by the dehydroxylation of products A and B, respectively, and further converted to products E and F through decarboxylation. Finally, products G and H were gained with the

cleavage of the N–C bond. The initial step of pathway II is the cleavage of the C–N bond of DCF, which would induce the generation of products **I** and **J**. Products **K** and **L** were yielded from products **I** and **J** via the loss of –NHOH and –CH₂COOH, respectively. Furthermore, the –OH release of product **K** and the –COOH addition of product **L** could at last bring out the products **G** and **H**, respectively. Additionally, in the pathway III, the DCF lost a –OH group to form product **M**, which is consistent with former research [32]. Then product **N** was engendered from product **M** via attack of the C–N bond, which could further undergo the loss of –NH₂ and –OH to product **G**. The formation small molecule intermediate products **G** and **H** would be further mineralized into H₂O and CO₂.

In summary, it is the first time to synthesize MoP as H₂O₂ activator for the degradation of DCF pollutant. DCF degradation ratio of almost 100% was achieved within 40 min in the MoP + H₂O₂ process, indicating an excellent activation efficiency of MoP. In addition, MoP + H₂O₂ process could be effectively applied in a wide pH range, different ions solution and different water substrates that could effectively remove organic pollutant, which suggested a practical application potential of MoP. Quenching experiment and ESR test confirmed that ·OH and ·O₂[–] are present in the MoP + H₂O₂ system, while ·OH played a more important role. Through comparing the XPS spectra before and after the reaction, Mo^{δ+} and P^{δ–} were the dual active sites of MoP. The positive site Mo^{δ+} could induce the generation of ROSs and the cycle of Mo^{δ+}/Mo^{δ+1}, while the electron-rich site P^{δ–} could also promote the formation of ROSs through electron transfer. Finally, the degradation products and pathways of DCF were proposed to further clarify the mechanism of the MoP + H₂O₂ system. In a word, this study provides a promising material MoP with dual active sites, which can provide robust support for the application of wastewater treatment based on its effectively catalytic activity.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by National Natural Science Foundation of China (No. 52070047), Guangzhou City Science and Technology Project (Nos. 201904010217, 202002010007), Guangdong Natural Science Foundation (No. 2021A1515011898), Featured

Innovation Project of Guangdong Education Department (No. 2019KTSCX135), State Key Laboratory of Pollution Control and Resource Reuse Foundation (No. PCRRF19010) and the Scientific Project of Guangzhou University (No. YG2020020).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2021.07.058.

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