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Effective degradation of COVID-19 related drugs by biochar-supported red mud catalyst activated persulfate process: Mechanism and pathway

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ABSTRACT
With the global spread of the COVID-19 pandemic, the water pollution caused by extensive production and application of COVID-19 related drugs has aroused growing attention. Herein, a novel biochar-supported red mud catalyst (RM-BC) containing abundant free hydroxyl groups was synthesized. The RM-BC activated persulfate process was firstly put forward to degrade COVID-19 related drugs, including arbidol (ARB), chloroquine phosphate, hydroxychloroquine sulfate, and acyclovir. Highly effective removal of these pharmaceuticals was achieved and even 100% of ARB was removed within 12 min at optimum conditions. Mechanism study indicated that SO4•− and HO• were the predominant radicals, and these radicals were responsible for the formation of DMPOX in electron spin resonance experiments. Fe species (Fe2+ and Fe3+) and oxygen-containing functional groups in RM-BC played crucial roles in the elimination of ARB. Effects of degradation conditions and several common water matrices were also investigated. Finally, the degradation products of ARB were identified by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and possible degradation pathways were proposed. This study demonstrated that RM-BC/PS system would have great potential for the removal of COVID-19 related drug residues in water by the catalyst synthesized from the solid waste.

1. Introduction

Recently, COVID-19 caused by a new coronavirus named SARS-CoV-2 has raised international concern due to its rapid spread. Although World Health Organization (WHO) has not recommended any effective pharmaceuticals for COVID-19 treatment, there are some antiviral drugs, such as arbidol (ARB, also named umifenovir), chloroquine phosphate (CQ), hydroxychloroquine sulfate (HCQ), and acyclovir (ACV), have been proposed as promising therapeutic agents against SARS-CoV-2 infection (Amani et al., 2021; Cui et al., 2020; Gasmi et al., 2021; Heidary et al., 2021). Besides, ARB and CQ are also recommended for the treatment of COVID-19 in the ‘Diagnosis and Treatment of New Coronavirus Pneumonia’ (trial version 8 revised edition) by The National Health Committee of the People’s Republic of China (NHC) (NHC, 2021). Generally, ARB is a widely used antiviral drug for influenza and other respiratory viral infections. CQ and HCQ are beneficial in treating malaria, amebiasis, lupus erythematosus, and rheumatoid arthritis. ACV can be used for herpes zoster (shingles), genital herpes, and chickenpox treatment. In fact, only a small part of pharmaceuticals can be metabolized within the human body, while most of them are excreted into sewage. For example, the oral bioavailability of ACV is only 15–30% (Saifi et al., 2020). Furthermore, most pharmaceuticals are poorly eliminated by conventional wastewater treatment processes owing to their low concentration, hydrophobicity, and low biodegradability (Rodriguez-Narvaez et al., 2017; Yang et al., 2017). Thus, large amounts of drug residues generated from pharmaceutical factories, hospitals and human bodies will be released into the aquatic environment, leading to at least ng/L level of these drug residues in water. The concentration of ACV in influent of wastewater treatment plant is up to 2.0 μg/L, whereas in effluent reaches 0.2 μg/L (Prasse et al., 2011). Another research shows that The average concentration of chloroquine is 4.238–5.24 μg/L in the surface and groundwater collected from a pharmaceutical...
industrial area of Sango Ota, Ogun State—Nigeria (Olaitan et al., 2014). The negative impacts of many pharmaceuticals on the environment also have been reported due to their properties such as pseudo-persistence, bioaccumulation, and toxicity (Ebele et al., 2017; Wang and Wang, 2016a; Yang et al., 2017). Therefore, water pollution and potential ecosystem risks caused by the extensive use of COVID-19-related drugs should be taken into serious consideration. Currently, few publications have been reported about the effective treatment of COVID-19-related drugs. In order to control the organic contamination risks caused by the extensive use of COVID-19-related drugs, it is of great significance to develop economical and effective approaches to remove COVID-19 drug residues for environmental protection.

In this study, ARB was selected as a model pollutant. ARB can interact preferentially with aromatic amino acids and then affect multiple stages of the virus life cycle, thereby interfering the SARS-CoV-2 binding and intracellular vesicle trafficking (Vankadari, 2020; Wang et al., 2020c). A major drawback of ARB is that a large dose must be administered to achieve therapeutic efficacy (Kadam and Wilson, 2017; Wright et al., 2017), and approximate 40% of ARB intake is excreted by the human body without metabolism (Surov et al., 2015). The oral LD₅₀ (50% lethal dose) for mice of ARB, CQ, and ACV is 340, 500, >10,000 mg/kg, respectively (Blaising et al., 2014; Saiﬁ and Alanazi, 2014; Tucker et al., 1983), indicating that the toxicity of ARB is relatively higher than CQ and ACV. Besides, the ecotoxicological risk level caused by ARB in river water is high, and the resistance of wild animals to antiviral drugs is low (Kuroda et al., 2021). The half-time of ARB metabolites such as N-demethylsulfanilamidol, sulfanilamidol, and sulfonarylacidol (26.3, 25.0, and 25.7 h, respectively) are longer than that of ARB (15.7 h) (Deng et al., 2013), which would result in secondary pollution. Furthermore, arbidol provides a prolonged antioxidant effect compared to the standard compound Trolox. In detail, the free radical scavenging rate constant was $k_1 = 2000 \text{nM}^{-1}\text{min}^{-1}$ for Trolox, while $k_2 = 300 \text{nM}^{-1}\text{min}^{-1}$, $k_3 = 4 \text{nM}^{-1}\text{min}^{-1}$ for arbidol (Proskurnina et al., 2020). This antioxidant capability can make a serious contribution to the therapeutic performance of antiviral drugs, whereas the potent antioxidant property of ARB (Glushkov et al., 1996; Proskurnina et al., 2020) would reduce its degradation efficiency in the aqueous phase. A recent research reported that the concentration of ARB in municipal wastewater reaches 1 μg/L, and only 40% of ARB can be removed by biological wastewater treatment (Ul’yanovskii et al., 2022). A few studies have reported the stress degradation of ARB to investigate its stability under hydrolytic, oxidative, and photolytic conditions (Mukthinpthalapiti et al., 2018; Secretan et al., 2021), but systematic study concerning the effective degradation processes of ARB hasn’t been reported yet.

Persulfate-based advanced oxidation processes (AOPs) are effective methods for the degradation of pharmaceuticals and other organic pollutants through the activation of persulfate (PS), such as peroxysulfate (PDS) or peroxymonsulfate (PMS) (Matzek and Carter, 2016; Wang and Wang, 2016a). The degradation mechanisms of persulfate-based AOPs include both free radical and non-radical pathways. The free radical pathways are dominated by reactive oxidation species (ROS) such as SO•⁺, HO•, and O₂⁻, which are generated from the breakage of O−O bond in PS. The non-radical pathways mainly include the generation of singlet oxygen (O₂) and direct electron transfer mediated by carbon materials (Liu et al., 2020). In comparison with non-radical pathways, free radical pathways are more capable of mineralizing a wide variety of organic pollutants into CO₂ and H₂O because of their higher oxidative potential and relatively non-selectiveness feature (Ouan et al., 2018; Zhao et al., 2021). Generally, persulfate could be activated through a lot of methods and materials, including transition metals (e.g., Fe, Co, Cu, Mn, Zn, Ag, and Ni), carbon materials, base, and external energies (e.g., thermal, ultraviolet, microwave, electricity, and ultrasounds) (Khan et al., 2021; Li et al., 2020b; Matzek and Carter, 2016; Ushani et al., 2020). Among these initiators, Fe-based catalysts are the most preferable owing to their high activation efficiency, abundant geological reserves, low energy consumption, and low biotoxicity (Diao et al., 2018; Zhang et al., 2020).

In recent years, red mud (RM), a kind of iron-rich solid waste generated from aluminum production by the Bayer process, has attracted increasing attention on its utilization as a Fe-based catalyst for persulfate activation (Du et al., 2020b; Feng et al., 2016; Ioannidou et al., 2020; Matthaiou et al., 2018; Qian et al., 2016). However, the reactivity is greatly limited by the form of Fe species (Fe₂O₅) in red mud. To solve this problem, a novel biochar-supported red mud catalyst (RM-BC) is prepared by a hydrothermal pretreatment and co-precipitation process, which reduces the Fe₂O₅ to Fe³⁺ and Fe₂O₃ in red mud using coconut shells as electron donors. The formed biochar (BC) acts as the carrier to stabilize and disperse Fe nanoparticles while increasing the specific surface area of RM. Besides, biochar is also reported as an efficient adsorption material and catalyst for many organics in the water environment (Yang et al., 2020). This prepared RM-BC catalyst exhibits excellent degradation performance for several dyes and antibiotics through persulfate activation. Compared to many iron-based catalysts combined PS system, RM-BC exhibited outstanding advantages, such as high removal efficiency within a short time, less PS and catalyst consumption, and lower Fe leaching (Guo et al., 2021). Furthermore, RM-BC is synthesized from red mud and coconut shells to realize the resource utilization of solid waste for treating water pollution. Since the concentration of drugs in real water is in trace amounts, a high adsorption capacity of RM-BC would be conducive to the enrichment of the pollutants, thereby enhancing the catalytic degradation process by promoting the contact of pollutants and ROS. RM-BC has exhibited excellent catalytic performance, but its adsorption capacity is limited. Therefore, it is necessary to improve the adsorption capacity of RM-BC for the effective elimination of COVID-19 drug residues by the synergy degradation from both adsorption and catalytic functionality.

In this study, we developed a novel RM-BC catalyst containing abundant free hydroxyl groups by improving our published method. This RM-BC combined PS system was applied to remove ARB as well as other COVID-19 related drugs. The removal performance, mechanism, and degradation pathway were also studied.

2. Materials and methods

2.1. Chemical reagents

All chemical reagents were used directly without further purification and are listed in Text S1. Properties of pollutants include arbidol (ARB, AR), acyclovir (ACV, AR), chloroquine phosphate (CQ, AR), and hydroxychloroquine sulfate (HCQ, AR) used in this study were shown in Table 1. De-ionized water was employed throughout the experiments.

2.2. Fabrication and characterization of RM-BC

RM-BC was synthesized following our earlier reported method with some modifications by omitting the final rinsing step and optimizing the ratio of each component (Text S2) (Guo et al., 2021). The catalysts prepared by the same route of RM-BC but without RM or without CS were designated as BC(HP) and RM(HP), respectively. Microstructures and compositions of the RM-BC were characterized through a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared (FTIR), and Raman spectroscopy (Text S2). The characterization results of RM-BC were basically consistent with those in the earlier report except IR. A new sharp peak at 3640 cm⁻¹ appeared in the FTIR spectrum of RM-BC as the stretching vibration of free OH groups (Fig. 3b) (Xiong et al., 2015).

2.3. Experimental procedures

The batch experiment was performed in a brown Erlenmeyer flask
placed in a shaker bath with a rotation rate of 180 rpm at ambient temperature. In a typical procedure, 100 mL of ARB solution was added to the flask followed by the addition of RM-BC and PS without adjusting the pH of the solution. Unless otherwise specified, the reaction conditions were established as follows: \([\text{ARB}]_0 = 20 \text{ mg/L}, \ [\text{RM-BC}]_0 = 0.2 \text{ g/L}, \text{ and } [\text{PS}]_0 = 0.6 \text{ mM}.\) Sampling was performed once per 3 min for a total reaction time of 15 min, and 2 mL of the reaction solution was filtered by a 0.45 μm syringe filter, then immediately used to determine the ARB concentration. In addition to ARB, the degradation performance for other pharmaceuticals including CQ, HCQ, and ACV were also investigated with the initial concentration of 20 mg/L. Although the concentration of these drugs in real water is in trace amount, which is below the detection limit of the conventional HPLC analysis method. Therefore, a higher initial concentration in the range of mg/L was adopted in this study to investigate the reaction kinetics and degradation mechanism of these drugs.

The effects of reaction parameters including ARB concentration, RM-BC dosage, PS concentration, and initial pH were examined. Similarly, the same experiments were also conducted to estimate the influence of cations (Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\)), anions (Cl\(^-\), SO\(_4^{2-}\) and NO\(_3^-\)), and DOM (humic acid, ascorbic acid, and citric acid). In the recycle experiment, the used catalyst was rinsed with MeOH five times and dried at 80 °C in a vacuum oven, then reused in the next run. The concentration of Fe in solution after catalysis reaction was measured by ICP-MS (Agilent 8800, US).

2.4. Analytical methods

The concentration of ARB and ACV was determined by an Agilent 1200 HPLC system coupled to a DAD detector. The separation was performed on a C18 column (2.7 μm, 3.0 × 150 mm, Agilent) at a flow rate of 0.5 mL/min with an injection volume of 10 μL. The mobile phase for simultaneous detection of ARB consisted of 40% water (containing 0.2% formic acid) and 60% acetonitrile, while 90% water (containing 0.2% formic acid) and 10% methanol for ACV. The detection wavelength was set at 316 nm and 254 nm for ARB and ACV, respectively. The concentration of HCQ and CQ was measured by UV–vis spectrophotometer (HORIBA Aqualog®, US) at 352 nm. The current density in RM-BC/PS system was measured by a linear sweep voltammetry (LSV) method using CHI 660D electrochemical workstation (Text S3). The zeta potential of RM-BC at various pH values was determined by a Malvern Zetasizer Nano ZS90 instrument.

Ethanol (EtOH), tert-butyl alcohol (TBA), isopropyl alcohol (IPA), p-Benzoquinone (p-BQ), and L-Histidine (L-His) were employed to evaluate the effect of different scavengers on ARB removal. The reactive oxidation species (ROS) were examined by an Electron spin resonance (ESR) spectrometer (Bruker ELEXSYS-II E500 CW-EPR, Germany) adopting 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidinol (TEMP) as spin trapping reagents. The formation of HO• was also detected by the fluorescence spectrum technique with terephthalic acid (TA) as a probe (Text S4).

2.5. Extraction and FT-ICR-MS analysis of intermediate products

The intermediate products of ARB degradation were identified by Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) (Bruker Solari X) equipped with a 7.0 T superconducting magnet and an electrospray ionization (ESI) source. Prior to the FT-ICR-MS analysis, solid-phase extraction (SPE) cartridges including C18 (Supelclean ENVII-18, 1 g, 6 mL) and PPL cartridges (Agilent, 200 mg, 3 mL) coupled with pressure extraction equipment were employed to purify and enrich the samples. In detail, the SPE cartridges were pre-activated sequentially with ten times the cartridge volumes of HPLC grade methanol and ultrapure water. Then, 10 mL of reaction solution were
passed through the SPE cartridges at around 2 mL/min. After that, the cartridges were rinsed with ultrapure water with ten times of the cartridge volumes, and eluted with 5 mL of HPLC grade methanol. The eluent was further used for FT-ICR-MS analysis. All the samples were analyzed in both positive and negative ionization mode with the ESI voltage set at 4.5 kV. A total of 16 continuous 4 M data FT-ICR transients were accumulated with an ion accumulation time of 0.05 s.

3. Results and discussion

3.1. Removal of COVID-19 related drugs

The removal efficiencies of COVID-19 related drugs by RM-BC/PS system were shown in Fig. 1. The removal of ARB was negligible in the PS alone system due to the weak oxidative ability of PS with the redox potential of 2.01 V (Fig. 1a) (Wang and Wang, 2018). Approximately 68% of ARB was removed within 15 min in the RM-BC alone system, which was caused by the adsorption of ARB on the RM-BC. Notably, a combination application of the RM-BC and PS drastically increased the ARB removal rate that reached 100% within 12 min. This great enhancement is likely caused by the reactive oxidation species such as $\text{SO}_4^{•-}$ and $\text{HO}^{•}$ generated from the activation of PS by RM-BC. Therefore, both adsorption and degradation processes were involved in the removal of ARB by RM-BC/PS system. Both BC\textsubscript{HP}/PS system and RM\textsubscript{HP}/PS system showed poor removal performance for ARB, indicating that both the red mud and coconut shells were essential in RM-BC. The presence of red mud facilitated the formation of free-OH groups in RM-BC and protected other OFGs from breaking at a high temperature (800 °C) (Fig. 4b and d). These OFGs were vital adsorption sites as well as catalytic sites for ARB removal. Besides, the addition of coconut shells promotes the phase transformation from Fe\textsubscript{2}O\textsubscript{3} to Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{0}, which have been proved as the main catalytic sites in RM-BC (Guo et al., 2021).

The reusability of RM-BC was shown in Fig. 1c. Approximately 100% and 96.3% of the ARB were degraded during the first and second cycles, respectively. The degradation efficiency gradually decreased with the number of repetitions and finally achieved 65.5% at the 4th run. Similar to other iron-based catalysts, oxidation of Fe\textsubscript{0} and Fe\textsubscript{2}+ was the main reason for the deactivation of the catalyst. Additionally, the incomplete desorption of adsorbed ARB and its degradation products on RM-BC would also decrease the removal rate of ARB in the recycle experiment. The concentration of dissolved iron after the reaction was measured by ICP-MS (Fig. 1c). The maximum Fe concentration in the solution was only 0.48 mg/L after the reaction, which is much lower than that of other iron-based catalysts (Li et al., 2014; Wang et al. 2017, 2020a). To investigate the effect of the homogeneous catalytic process caused by dissolved Fe from RM-BC, 0.2 g/L RM-BC was added into 100 mL water and shook at 180 rpm for 15 min, then the leachate was collected by vacuum filtration and combined with PS to degrade ARB. As shown in Fig. 1a, only 11.7% of ARB was removed in this process, indicating that heterogeneous catalysis was mainly responsible for the ARB degradation.

In addition to ARB, the removal performance for chloroquine phosphate (CQ), hydroxychloroquine sulfate (HCQ), and acyclovir (ACV) were also studied. Although these drugs were more resistant to removal,
RM-BC/PS system also exhibited excellent removal capacity by increasing the dosage of RM-BC and PS. The removal efficiencies of CQ, HCQ and ACV within 40 min were 84.8%, 87.7%, and 90.8%, respectively (Fig. 1b). According to Fig. 1b, the removal of CQ, HCQ, and ACV was quick in the first 10 min, after which the reaction rate slowed down gradually. This might be caused by the rapid adsorption of CQ, HCQ, and ACV on RM-BC. In addition, the type and amounts of intermediate products accumulated as the reaction progresses, which would compete
with the pristine drugs for radicals. Table S1 showed the comparison of degradation performance for these drugs with previous studies. It was found that RM-BC/PS system could achieve high removal rates for these drugs within a relatively shorter reaction time. In addition, ACV is more resistant to degrade than HCQ and CQ (Bensalah et al., 2020; Hu et al., 2014; Peng et al., 2022), which is consistent with this study. Comparison of RM-BC with other RM-biochar or RM-related catalysts on drug degradation was shown in Table S2. It was suggested that RM-BC catalyst had some outstanding advantages, such as 100% removal rate, short reaction time, low PS, and catalyst consumption.

The current density in different systems was measured by linear sweep voltammetry (LSV) with RM-BC coated glassy carbon electrode (GCE). As shown in Fig. 1d, when RM-BC coated GCE was employed as the working electrode, the current density was significantly higher than that of pure GCE, indicating that RM-BC has better electron transfer capacity. Moreover, the current density was remarkably higher in the system containing both PS and ARB compared with that without PS or RM-BC. These results further indicated that massive electron transfer occurred in the oxidation process of ARB.

3.2. Identification of reactive oxidation species

3.2.1. Effect of scavengers

To investigate the mechanism, different radical scavengers (i.e., EtOH, TBA, IPA, p-BQ, and L-His) were applied to identify the dominant ROS (i.e., SO$_4^{•-}$, HO$^•$, O$_2^{•-}$, and 1O$_2$). EtOH was a commonly used scavenger for both HO$^•$ (k = 1.6–7.8 × 10$^7$ M$^{-1}$ s$^{-1}$) and SO$_4^{•-}$ (k = 1.2–2.8 × 10$^9$ M$^{-1}$ s$^{-1}$) (Zhou et al., 2020), while TBA and IPA were both effective quenchers for HO$^•$ (Du et al., 2020a). O$_2^{•-}$ and 1O$_2$ were often quenched by p-BQ (k = 0.9–1.6 × 10$^9$ M$^{-1}$ s$^{-1}$) (Lyu et al., 2019) and L-His (k = 3.2 × 10$^9$ M$^{-1}$ s$^{-1}$) (Luo et al., 2020), respectively. As shown in Figs. S1a–c, the enhanced inhibitory effects were observed with the increasing concentration of the scavengers (EtOH, TBA, and L-his). But some interesting phenomena were observed in the quenching experiments. For example, the removal rate of ARB was only 57% and 37% with 5 mM EtOH and TBA (Fig. 2a), respectively, which was lower than that of ARB caused by RM-BC adsorption (68%) (Fig. 2b). The addition of p-BQ (1.5 mM) also showed similar results, reducing the rate to 44% (Fig. 2a). Furthermore, the addition of L-his at a low concentration (6 mM) even promoted ARB removal a little, while inhibited it with a high concentration (50 mM) (Fig. S1c). To verify if there was competition adsorption between scavengers and ARB, the same quenching experiments were conducted in the RM-BC alone system. As shown in Fig. 2b, the adsorption removal rate was considerably decreased to 4%, 10%, and 22% with the addition of 5 M TBA, IPA, and EtOH, respectively. A similar hindering effect of TBA for the biochar adsorption process was also reported (Magioglou et al., 2019). FITR spectrum (Fig. 3b) indicated that abundant hydrophilic functional groups (hydroxyl and carboxyl) existed on the RM-BC, which could be easily occupied by both ARB and the hydrophilic quenchers. The adhesion of quenchers on catalyst would compete for adsorption site with target substances or prevent the electron and mass transfer processes.

3.2.2. ESR experiments and fluorescence detection

To further identify the radical species generated in RM-BC/PS system, ESR experiments adopting DMPO as spin trapping reagent were

Fig. 4. XRD patterns (a), FTIR spectra (b), and Raman spectra (c) of fresh and used RM-BC, FTIR spectra of BC (HP) and RM (HP) (d).
conducted in de-ionized water to detect HO• and SO4•-. As shown in Fig. 2c, no radical signals were detected in systems without PS or RM-BC. Interestingly, when DMPO was directly added to the RM-BC/PS system, a strong signal of seven main peaks was observed, which was assigned to 5,5-dimethylpyrroolidine-2(2)-oxyl-(1) (DMPO, α9 = 7.1 G, α9 = 4.0 G), an oxidized product of DMPO by some strong oxidation species, such as SO4•- and HO• (Yin et al., 2018). When the same ESR experiments were conducted in methanol, neither DMPO signal nor any radical signals related to SO4•-, HO• and O2•- were observed (Fig. 2d). Because methanol is a commonly used scavenger for SO4•- and HO•, the absence of DMPO signal implied that the formation of DMPOX was destroyed by the elimination of SO4•- and HO•. In order to directly observe the addition products of DMPO with SO4•- and HO•, the concentration of the radicals in the solution had to be controlled, otherwise, the DMPO would be quickly oxidized to DMPOX by a high concentration of radicals. Thus, DMPO was added into the filtered aqueous solution of the RM-BC/PS system, and a significant signal of DMPO-OH adduct (α9 = 15.0 G, α9 = 15.3 G) was detected (Fig. 2c). The formation of HO• was further confirmed by the fluorescence spectra technique taking TA as a probe (Fig. S2). The undetected DMPO-SO4• adduct could be caused by its low sensitivity and insignificant signal at a high background (Li et al., 2021), whereas HO• is more easily captured by DMPO to form an identifiable characteristic peak. In addition, it has been proved that the alkaline conditions (i.e., pH > 8.5) can induce the conversion of SO4•- to HO•, and the SO4•- also can react with water at all pHs to produce HO• (Furman et al., 2010, Liang and Su, 2009). Considering that the oxidant in the reaction system is PS instead of H2O2, the main source of HO• should be the conversion of SO4•-. Thus, the presence of HO• could indirectly prove the generation of SO4•-. Based on the above results, it was suggested that massive radicals (SO4•- and HO•) were quickly generated in the RM-BC/PS system, which may cause the direct oxidation of DMPO to DMPOX, or the indirect transformation of DMPO-SO4• and DMPO-OH to DMPOX (Li et al., 2020a; Wang et al., 2020b). The possible formation pathway of DMPOX was illustrated in Fig. S3. The ESR experiments were also conducted using TEMP as spin trapping reagents, but no apparent signals of •O2 were found in RM-BC/PS system (Fig. S4).

In summary, the results of ESR experiments and fluorescence spectra confirmed that SO4•- and HO• were the predominant radical species responsible for ARB degradation.

3.3. Mechanism of ARB removal

3.3.1. Characterization of fresh and used RM-BC

According to SEM images (Fig. 3a-c), honeycomb-like morphology containing many pores was observed on RM-BC, which was beneficial to the adsorption of ARB molecules. The RM-BC exhibits a surface area (S BET) of 246.47 m2/g and a total pore volume of 0.3056 cm3/g. The nitrogen adsorption-desorption isotherm at 77 K and the corresponding pore size distribution curve of RM-BC are presented in Fig. S5. According to the definition from the International Union of Pure and Applied Chemistry (IUPAC) (Sing, 1982), the isotherm of RM-BC was type IV, which is characteristic of mesoporous materials. The hysteresis loop is ascribed to type H3 loops, indicating that RM-BC contains slit-shaped pores (Wang et al., 2016). The volume adsorbed increases quickly at low relative pressure, which is attributed to the presence of micropores. The pore size distribution of RM-BC calculated by HK-plot shows that RM-BC contains micropores in the range of 0.5–2 nm with a peak at 0.54 nm. Besides, the BJH model also confirmed the existence of mesopores in the range of 2–100 nm. EDX image and XPS survey spectrum (Fig. 3f, Fig. S6a) indicated that the main elements on the surface of RM-BC were C, O, Fe, Ca, Al, and Si. The strong peak of Au presented in the EDX image was because that the RM-BC sample was sputtered with gold to increase conductivity before the SEM-EDX test. The element mapping images (Fig. 3d and e) showed that Fe was uniformly distributed on the surface of RM-BC. High-resolution XPS of Fe 2p (Fig. S6b) displayed two peaks corresponding to Fe 2p3/2 (710.9 eV) and Fe 2p1/2 (724.0 eV) of FeO4, respectively (Sun et al., 2020). XRD patterns (Fig. 4a) confirmed that the major forms of Fe species in RM-BC were Fe0 (JCPDS No. 06-0969) and FeO4 (JCPDS No. 19-0629). The mean particle size of Fe0 and FeO4 was calculated through Scherrer’s equation, which was 62.9 and 35.7 nm, respectively. These formed Fe0 and FeO4 nanoparticles have been proved to be the crucial active sites for PS activation (Guo et al., 2021). It is well known that XPS is a typical surface analytic technique. The Fe0 on the surface of RM-BC was easily oxidized by oxygen and water in the air. Normally, there was no peak of Fe0 detected in XPS unless the sample was quickly protected by the N2 after preparation (we were unable to do this). However, XRD can analyze the whole structure of the material, so the signal of Fe0 inside the RM-BC was detected. A similar phenomenon was also reported in other literature (Yi et al., 2020). A small peak located at 26.6° was observed both in the fresh RM-BC and used RM-BC, which belonged to either the graphite-like structure of RM-BC or the (101) planes of SiO2 (JCPDS No. 46-1045). The XRD pattern of RM-BC before and after the reaction (Fig. 4a) showed insignificant changes, as well as the relative proportions of Fe2+ and Fe3+ deconvoluted from the Fe 2p spectra (Fig. S6b and Table S3), indicating the excellent stability of RM-BC.

FTIR spectra of RM-BC were shown in Fig. 4b. Notably, compared with our earlier reported RM-BC catalyst (Guo et al., 2021), a new sharp peak at 3640 cm−1 corresponding to the stretching vibration of free OH appeared (Xiong et al., 2015). Around the free OH, there were no atoms or groups that could form hydrogen bonding with this OH. Of course, hydrogen bonding OH with a broad peak centered at 3350 cm−1 also existed in RM-BC. The peaks at 3640 and 1493 cm−1 (OH deformation) vanished after the reaction. The band at 1616 cm−1 was ascribed to C=O or C=O, and that at 1030 cm−1 represented O=O and Si–O stretching (Chen et al., 2008; Yu et al., 2019). Their intensities were weakened in the used RM-BC. XPS spectra of C 1s also showed similar changes (Fig. S6c, Table S3). The relative percentage of O=C–O (at 289.6 eV) decreased from 12.99% to 9.17% after the reaction. These results strongly indicated that oxygen-containing functional groups (OFGs) played vital roles in the ARB removal by the RM-BC/PS system. Firstly, the presence of oxygen-containing functional groups could enhance the adsorption of ARB on RM-BC through hydrogen bonding as well as π-π electron donor and acceptor (EDA) interactions (Dai et al., 2019b). The free OH groups in RM-BC can act as strong H-bond donors, which facilitated the adsorption of ARB on RM-BC by the formation of hydrogen bonding. Moreover, OFGs on the surface of biochar were also reported to be effective for PS activation (Zhu et al., 2019). Notably, these OFGs on iron-biochar materials could accelerate the Fe2+/Fe3+ redox recycles, thereby promoting the catalytic performance (Yan et al., 2015).

The Raman spectra of fresh and used RM-BC were shown in Fig. 4c, strong intensities of the D and G bands were observed at 1355 and 1593 cm−1, respectively. Generally, the D band corresponds to the defects and deformations of carbon atomic crystals, and the G band is associated with the in-plane vibrations of the sp2-bonded graphitic carbon structures (Guizani et al., 2017). The broad peak around 2850 cm−1 was identified as the 2D band that is related to the vibration of two phonon lattices, which was a typical symbol of graphitic carbon (Du et al., 2020a). These results suggested that RM-BC carbonized at a high temperature (800 C) contained large defect sites and presented a graphite-like structure. The defective sites of biochar were reported to be effective to PS activation (Ouyang et al., 2019). Furthermore, the existence of the graphite-like structure could act as π-electron donors as well as electron mediators, thereby contributing to PS activation (He et al., 2019).

3.3.2. Mechanism of ARB removal by RM-BC/PS system

Based on the results mentioned above and previous studies, the possible mechanism of ARB removal by RM-BC/PS system was proposed (Fig. 5). It was suggested that once the AOPs were triggered by adding...
both RM-BC and PS into ARB solution, RM-BC could rapidly adsorb ARB while quickly activating PS to generate massive radicals (SO$_4^{\cdot-}$ and HO$^\cdot$), resulting in the effective oxidation and degradation of ARB. The porous RM-BC with large specific surface area, graphite-like structure, and abundant oxygen-containing functional groups could adsorb ARB through either hydrogen bonding or π-π EDA interactions. Due to the low concentration, the high adsorption capacity of RM-BC was conducive to the enrichment of the pollutants, thereby promoting the catalytic degradation performance and enhancing the removal efficiency.

Regarding the generation of radicals, transition metals in the RM-BC were of importance for the activation of PS. According to the analysis results of EDS, XRD, XPS, and our previous research, the main transition species either existed in Fe$_3$O$_4$ or formed by the continuous oxidation of Fe$^{\text{II}}$ were effective active sites for the PS activation (Eqs. (1)–(3)). Besides, Fe$^{\text{III}}$ also exhibited direct activation ability to PS by heterogeneous transportation of electrons from Fe$^{\text{III}}$ to PS (Eq. (4)) (Ye et al., 2020). The red mud also contains other transition metals with a much lower content (0.59 mg/g of Mn, 0.04 mg/g of Zn, and 0.018 mg/g of Co) (Guo et al., 2021), which might also be the PS activation sites (Matzek and Carter, 2016; Ushani et al., 2020).

$$\begin{align*}
\text{Fe}^{\text{III}} + 2\text{H}_2\text{O} &\rightarrow \text{Fe}^{\text{II}} + 2\text{OH}^- + \text{H}_2 \\
2 \text{Fe}^{\text{II}} + \text{O}_2 + 2\text{H}_2\text{O} &\rightarrow 2 \text{Fe}^{\text{III}} + 4\text{OH}^- \\
\text{Fe}^{\text{II}} + \text{SO}_4^{\cdot-} &\rightarrow \text{Fe}^{\text{III}} + \text{SO}_4^{2-} + \text{SO}_3^{\cdot-} \\
\text{Fe}^{\text{III}} + 2\text{SO}_4^{\cdot-} &\rightarrow \text{Fe}^{\text{II}} + 2\text{SO}_3^{\cdot-} + 2\text{SO}_4^{2-} 
\end{align*}$$

In addition, OFGs such as carboxyl and hydroxyl groups also played important roles in the activation of PS, which was widely reported by previous studies (Eqs. (5) and (6)) (Yan et al., 2015).

$$\begin{align*}
\text{BC}_{\text{surface}} - \text{O} &\rightarrow \text{BC}_{\text{surface}} - \text{O} + \text{HSO}_4^- + \text{SO}_4^{2-} \\
\text{BC}_{\text{surface}} - \text{O} &\rightarrow \text{BC}_{\text{surface}} - \text{O} + \text{HSO}_4^- + \text{SO}_4^{2-} 
\end{align*}$$

Finally, the defective structure and graphite-like structure of RM-BC (Zhao et al., 2021), as well as the persistent free radicals (PFRs) (Deng et al., 2020; Fang et al., 2015) that exist on biochar surface, might also contribute to PS activation to a certain extent.

3.4. Effect of reaction conditions and water matrices

3.4.1. Effect of reaction parameters on ARB removal

The effects of different reaction parameters including ARB concentration (10–40 mg/L), RM-BC dosage (0–0.4 g/L), PS concentration (0–2 mM), and initial solution pH (3–11) were investigated. The degradation of ARB was well fitted with the pseudo-first-order kinetic model (Eq. (7)) and the reaction rate constant ($k_{\text{obs}}$) was shown in Table S4.

$$\ln (C/C_0) = - k_{\text{obs}} t \quad (7)$$

As expected, the removal rate of ARB gradually decreased with the increase of initial ARB concentration (Fig. 6a). When the ARB concentration increased from 10 to 20 mg/L, the time required to achieve 100% ARB removal increased from 6 to 12 min. Further increasing the ARB concentration to 30 and 40 mg/L, the removal rate dropped to 95% and 72% within 15 min, respectively. These results were attributed to the insufficient number of active sites and ROS at high ARB concentration conditions.

In fact, the ARB removal efficiency was significantly affected by the dosage of RM-BC (Fig. 6b). ARB was hardly removed without RM-BC, while the ARB removal rate dramatically increased to 76% after adding only 0.1 g/L RM-BC, and the rate reached 100% within 15 min when the dosage of RM-BC increased to 0.2 g/L. Further increasing the dosage to 0.3 and 0.4 g/L, 100% ARB removal was achieved within only 6 and 3 min, respectively. The improved ARB removal efficiency was on account of the more reactive sites provided by the higher RM-BC dosage.

Similarly, the removal efficiency also improved with the increase of PS concentration (Fig. 6c). The efficiency improved from 68% to 100% as the PS concentration increased from 0 to 0.6. The addition of PS favored the generation of ROS such as SO$_4^{\cdot-}$ and HO$^\cdot$, thereby enhancing the efficiency. Further increasing the PS concentration from 0.6 to 2, the apparent rate constants moderately increased from 0.305 to 0.387 min$^{-1}$. In this case, the removal rate of ARB was limited by the number of active sites on RM-BC, and the optimum PS concentration in this study was 0.6 mM.

In addition, experiments were also conducted at different initial pH values (pH = 3, 5, 7, 9, and 11). As shown in Fig. 6d, the effect of initial pH was not significant. Although it was reported that acidic conditions are more favorable for the generation of SO$_4^{\cdot-}$ (Liu et al., 2018), the electrostatic repulsion between the positively charged RM-BC (the
isoelectric pH was 5.8) (Fig. S7) and protonated ARB (pK\textsubscript{a1} = 6.01, pK\textsubscript{a2} = 9.87) (Berendsen et al., 2012; Fong, 2020) hindered the adsorption of ARB on the BC surface. Therefore, the ARB removal rate at pH 3 (0.338 min\textsuperscript{-1}) was slightly decreased compared to that at pH 5 (0.446 min\textsuperscript{-1}). Although SO\textsubscript{4}\textsuperscript{2-} radicals are prone to transform to the HO\textsuperscript{·} radicals with redox potential (1.8–2.7 V) in the alkaline conditions (Eq. (7)), many organics could still be efficiently degraded by HO\textsuperscript{·} radicals due to its non-selective feature and high oxidative capacity. In addition, the phenol group of ARB under basic conditions is in a phenolate form, which can induce the formation of superoxide anion (O\textsuperscript{2-}·) by transferring an electron to molecular oxygen, then the formed O\textsuperscript{2-}· would further result in the degradation of ARB (Secretan et al., 2021). Therefore, considerable removal rates of ARB were also observed at pH 9 and 11 (Fig. 6d) under the synergistic effect of HO\textsuperscript{·} and O\textsuperscript{2-}· radicals.

\[
\text{SO}_{4}^{2-} + \text{OH}^- \rightarrow \text{SO}_{4}^{2-} + \text{OH}^* \tag{8}
\]

### 3.4.2. Effect of cations, anions, and DOM on ARB removal

Considering the practical application of the RM-BC/PS system, several common cations (Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, and Mg\textsuperscript{2+}), anions (Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, and NO\textsubscript{3}\textsuperscript{-}), and DOM (humic acid, ascorbic acid, and citric acid) existed in the water environment were employed to investigate their impacts on ARB removal.

In the case of cations (Fig. S8a–d), Na\textsuperscript{+} and K\textsuperscript{+} ions exhibited a negligible effect on ARB removal. However, ARB removal was significantly enhanced with the presence of Ca\textsuperscript{2+}, and slightly inhibited with the addition of Mg\textsuperscript{2+}. Actually, neither Ca\textsuperscript{2+} nor Mg\textsuperscript{2+} can activate persulfate. The inhibitory effect of Mg\textsuperscript{2+} on ARB removal may be attributed to the fact that Mg\textsuperscript{2+} adsorbed on the negatively charged RM-BC surface, which reduced the number of active sites. Dai et al. also reported that the presence of Mg\textsuperscript{2+} hindered the adsorption process of tetracycline by biochar (Dai et al., 2019a).

For the anions, the addition of Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}\textsuperscript{-} inhibited the ARB removal, and the inhibition effect followed the order of Cl\textsuperscript{-} > SO\textsubscript{4}\textsuperscript{2-} > NO\textsubscript{3}\textsuperscript{-} (Fig. S9a–d). It was reported that NO\textsubscript{3}\textsuperscript{-} could easily react with SO\textsubscript{4}\textsuperscript{2-} to produce nitrate radicals (NO\textsubscript{3}·) (Eq. (9)) having a lower redox potential of 2.3–2.7 V (Hou et al., 2019), and resulting in a lower ARB removal. The inhibition mechanism of Cl\textsuperscript{-} on ARB removal was similar to that of NO\textsubscript{3}·. The less reactive radicals such as Cl\textsuperscript{·} and Cl\textsubscript{2}· with the redox potential of 2.4 and 2.1V were generated by the reaction between SO\textsubscript{4}· and Cl\textsuperscript{-}, respectively (Eqs. (10) and (11)) (Armstrong et al., 2015). Furthermore, Cl\textsuperscript{-} could also quench hydroxyl radicals (Eq. (12)) (Fu et al., 2020). Actually, the reaction between SO\textsubscript{4}· and SO\textsubscript{4}· was very weak (Jiang et al., 2021), the inhibition of SO\textsubscript{4}· on ARB removal was attributed to the decreasing of the SO\textsubscript{4}·/SO\textsubscript{4}· redox potential. Assuming the oxidation process induced by SO\textsubscript{4}· could be expressed as Eq. 13, and a corresponding Nernst equation was described as Eq. (14) (Roy et al., 2020). According to Eq. (14), it could be inferred that the increase in the concentration of SO\textsubscript{4}· ions would cause the decrease in the redox potential of SO\textsubscript{4}·/SO\textsubscript{4}·, thus leading to the inhibition of ARB removal. Similar SO\textsubscript{4}· effects were also reported in other studies (Jiang et al., 2021).

\[
\text{SO}_{4}^{2-} + \text{NO}_{3}^{-} \rightarrow \text{NO}_{3}^{-} + \text{SO}_{4}^{2-} \tag{9}
\]
SO$_4^{2-} + $Cl$^-$ $\rightarrow$ ClO$^-$ + SO$_2^-$(10)

Cl$^-$ $\rightarrow$ Cl$^+_2$ (11)

HO$^+$ + Cl$^-$$\rightarrow$ ClOH$^+$ (12)

SO$_4^{2-} + e^{-}$$\rightarrow$SO$_2^{2-}$ (13)

$$E_{(SO_4^{2-}/SO_2^{2-})} = E_{(SO_4^{2-}/SO_2^{2-})}^{0} + \frac{RT}{nF} \ln \left[ \frac{[SO_4^{2-}]}{[SO_2^{2-}]} \right]$$ (14)

Similarly, the existence of DOM such as humic acid (HA), ascorbic acid (AA), and citric acid (CA) also reduced the ARB removal, and the inhibition extent of AA and CA was greater than that of HA (Fig. S10a–d). One possible reason was that these DOM adsorbed on active sites of RM-BC, then reduced the degradation of ARB by inhibiting the process of PS activation to produce ROS, or directly hindered the adsorption of ARB on RM-BC. Furthermore, DOM might quench radicals in this system. For example, humic acid could readily quench hydroxyl radicals with a reaction rate of $1 \times 10^8 - 2 \times 10^8$ M$^{-1}$ s$^{-1}$ (Lu et al., 2019). Huang et al. also reported that citric acid inhibited the degradation of 1-naphthol by reaction with HO$^*$ (Huang et al., 2019). On the other hand, the quinones, carboxyl, ketones, and hydroxyl groups in humic acid could accelerate the electron transfer and circulation of iron, thereby promoting the elimination of pollutants (Fu et al., 2020).

Therefore, the inhibition and promotion effects may simultaneously act on ARB removal, but the former was more important than the latter in this study.

3.5. Possible pathway of ARB degradation

The intermediate products of ARB during the degradation process were investigated using FT-ICR-MS. In addition to ARB (C$_{22}$H$_{23}$BrN$_2$O$_5$S), the intermediate products were successfully identified (Table S5 and Fig. S11). The molecules became smaller as the reaction time increased, suggesting that ARB was effectively decomposed. Based on these detected products and previous research (Deng et al., 2013; Secretan et al., 2021), subsequently, P2 (C$_{22}$H$_{23}$BrN$_2$O$_5$S) was formed by the oxidation of the methyl or methylene connected with the nitrogen on the benzene ring of P1. Then, P2 was converted to P3 (C$_{20}$H$_{20}$BrNO$_6$S) underwent the loss of dimethylamine and oxidation processes. After that, P3 was transformed to P4 (C$_{19}$H$_{18}$BrNO$_6$S) via a series of oxidation processes and ring fission. The pathway (2) was triggered by the removal of the 4-(dimethylamino)methyle group, resulting in the formation of P5 (C$_{21}$H$_{23}$BrN$_2$O$_5$S). Afterward, P5 was further transformed into P6 (C$_{20}$H$_{22}$BrN$_2$O$_5$S) through the demethylation process. Then, P6 was presumed to undergo a deamination and oxidation process to form P7 (C$_{19}$H$_{16}$BrNO$_6$S). Finally, these intermediate products mentioned above might be further oxidized to lower molecules and mineralized to carbon dioxide and water through a series of complicated degradation reactions.

4. Conclusions

In this study, a novel biochar-supported red mud catalyst (RM-BC) containing abundant free OH groups was prepared by improving our published method. This RM-BC catalyst activated persulfate process (RM-BC/PS) was firstly applied to eliminate COVID-19 related drugs containing abundant free OH groups. Highly effective removal of these pharmaceuticals was achieved; even 100% of ARB could be removed within 12 min. The results of ESR experiments and fluorescence detection indicated that SO$_4^{2-}$ and HO$^*$ were the predominant radicals in the degradation of ARB. Besides, it was proved that the formation of DMPOX in ESR experiments was closely related to SO$_4^{2-}$ and HO$^*$. In addition to Fe species (Fe$^{2+}$ and Fe$_2$O$_4$), OFGs such as carboxyl and hydroxyl groups played important roles in the activation of PS. The coexisting cations (Mg$^{2+}$), anions (Cl$^-$, SO$_4^{2-}$ and NO$_3^-$), and DOM (AA, HA, and CA) exhibited inhibition on the ARB removal, whereas Na$^+$ and K$^+$ had a negligible effect. Interestingly, the removal of ARB was significantly enhanced with the presence of Ca$^{2+}$. Finally, the intermediate products of ARB were identified by FT-ICR-MS and possible degradation pathways were proposed.

CRediT authorship contribution statement

Ziwei Guo: Conceptualization, Investigation, Formal analysis, Writing – original draft. Yue Zhang: Investigation. Shuchai Gan: Methodology, Supervision. Huan He: Writing – review & editing, Supervision. Nan Cai: Writing – review & editing, Review. Jingwei Xu:
Supervision, Writing – review & editing. Review & Writing. Pengran Guo: Conceptualization, Writing – review & editing. Supervision, Review & Supervision. Bo Chen: Conceptualization, Writing – review & editing, Supervision, Review & Supervision. Xuejun Pan: Supervision, Project administration.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2022.130753.

References

Amani, B., Amani, B., Zareei, S., Zareei, M., 2021. Efficacy and safety of arbidol (umifenovir) in patients with COVID-19: a systematic review and meta-analysis. Immuns. Inflamm. Dis. 1–12.

Armstrong, D.A., Huier, R.E., Koppenol, W.H., Lymar, S.V., Merce Foundation of China (No. 21777150), and the GDAS Science and Technology Development (No. 2020GDASYL-20200103044 and No. 2020GDASYL-20200103043).

Fang, G., Liu, C., Gao, J., Dionysiou, D.D., Zhou, D., 2015. Manipulation of Persistent Free Radicals in Biochar To Activate Persulfate for Contaminant Degradation. Environ. Sci. Technol. 49, 2572–2580.

Feng, Y., Wu, D., Liao, C., Deng, Y., Zhang, T., Shih, K., 2016. Red mud powders as low-cost and efficient catalysts for persulfate activation: pathways and reusability of mineralizing sulfadiazine. Separ. Purif. Technol. 167, 136–145.

Feng, C.W., 2020. Screening of novel biocatalysts from the Coronavirusidae Family Including SARS-CoV-2, SARS-CoV, MERS. Energiemysen Italy Australia.

Fu, C., Yi, X., Liu, Y., Zhou, H., 2020. CuO activated persulfate for sulfamethazine degradation. Chemosphere 257, 127924.

Farooq, O.S., Teel, A.L., Watts, R.J., 2010. Mechanism of base activation of persulfate. Environ. Sci. Technol. 44, 6423–6426.

Garmi, A., Prana, M., Noor, S., Lyrintz, P., Menzel, A., Garmi Benahmed, A., Bjerkland, G., 2021. Chloroquine and hydroxychloroquine in the treatment of COVID-19: the never-ending story. Appl. Microbiol. Biotechnol. 105, 1333–1343.

Glushkov, R., Gus’kova, T., Golikov, P., Davydov, B., Klychkovnikova, I., 1996. Study of the important properties of tetracyclines. Pharm. Chem. J. 30, 1–3.

Guizi, C., Haddad, K., Limousy, L., Jeguirim, M., 2017. New insights on the structural evolution of biomass char upon pyrolysis as revealed by the Raman spectroscopy and elemental analysis. Carbon 119, 519–521.

Guo, Z., Bai, G., Huang, B., Cai, N., Guo, P., Chen, L., 2021. Preparation and application of a novel biochar-supported red mud catalyst: Active sites and catalytic mechanism. J. Hazard Mater. 408, 128402.

He, J., Xiao, Y., Tang, J., Chen, H., Sun, H., 2019. Persulfate activation with sawdust biocatalyst in aqueous solution by enhanced electron donor-transfer effect. Sci. Total Environ. 690, 768–777.

Heidary, F., Madani, S., Ghareshaghi, R., Asadi-Amoli, F., 2021. Acyclovir as a potential adjuvant therapy in COVID-19 treatment regimens. Pharmaceut. Sci. 19.

Hou, X., Cui, Y., Yang, Q., Chen, F., Wang, J., Wu, Z., Zhou, X., Wang, D., 2019. Heterogeneous activation of peroxymonosulfate using Mn-Fe layered double hydroxide: performance and mechanism for organic pollutant degradation. Sci. Total Environ. 663, 453–464.

Hu, X., Z. Wang, C., Yu, N., Wang, J., 2014. Pharmaceuticals removal by novel nanoscale photocatalyst BiO3VO4Cl: influencing factors, kinetics, and mechanism. Ind. Eng. Chem. Res. 53, 14623–14632.

Huang, D., Wang, T., Zou, K., Zhao, S., Shi, Y., Ye, M., Wang, C., Jia, H., 2019. Low-molecular-weight organic acids impede the degradation of napthol in iron oxides/ persulfate systems: implications for research experiments in pure conditions. Chemosphere 225, 1–8.

Ismaili, A., Oulego, P., Collado, S., Petala, A., Arnellia, V., Frontistis, Z., Angelopoulou, G.N., Diaz, M., Manziavazzin, D., 2020. Persulfate activation by modified red mud for the oxidation of antibiotic sulfamethoxazole in water. J. Environ. Manag. 270, 110820.

Jiang, F., Li, Y., Zhou, W., Yang, S., Yang, Z., Ning, Y., Liu, D., Zhang, Y., Yang, B., Tang, Z., 2021. Cysteine enhanced degradation of monochlorobenzene in groundwater by ferrous ion/persulfate process: impacts of matrix species and toxicity evaluation in ISO. Chemosphere 271, 129520.

Kadam, R.U., Wilson, I.A., 2017. Structural basis of influenza virus fusion inhibition by the antiviral drug Arbidol. Proc. Natl. Acad. Sci. U.S.A. 114, 206–214.

Khan, S., Sohail, M., Han, C., Khan, J.A., Khan, H.M., Dionysiou, D.D., 2021. Degradation of highly chlorinated pesticide, lindane, in water using UV/persulfate: kinetics and mechanism, toxicity evaluation, and synergism by H2O2. J. Hazard Mater. 402, 125558.

Kuroda, K., Li, C., Dhangar, K., Kumar, M., 2021. Predicted occurrence, ecotoxicological risk and environmentally acquired resistance of antiviral drugs associated with COVID-19 in environmental waters. Sci. Total Environ. 769, 145760.

Li, H., Wang, J., Ma, Y., Wang, Y., Huang, M., 2014. Influence of particle size of zero-valent iron and dissolved silica on the reactivity of activated persulfate for degradation of acid orange 7. Chem. Eng. J. 237, 487–496.

Li, H., Yao, Z., Jiang, I., Du, X., Wang, C., Zhang, D., Tang, J., Zhao, H., Zhou, J., 2020a. Degradation of phenanthrene by peroxymonosulfate activated with bimetallic metal-organic frameworks: kinetics, mechanisms, and degradation products. Chem. Eng. J. 397, 125401.

Li, W., Li, S., Tang, Y., Yang, X., Zhang, W., Xian, H., Huang, Y., 2020b. Highly efficient activation of peroxymonosulfate by cobalt sulfide hollow nanospheres for fast ciprofloxacin degradation. J. Hazard Mater. 389, 121856.

Li, G., Guo, Y., Jin, Y., Tan, W., Liu, F., Yin, H., 2021. Intrinsinc mechanisms of calcium ion activation by siderite for atrazine degradation. Chem. Eng. J. 426, 131917.

Li, Y., Su, H.W., 2009. Identification of sulfate and hydroxyl radicals in thermally activated persulfate. Ind. Eng. Chem. Res. 48, 5558–5562.

Liu, C.-M., Diao, Z.-H., Hsueh, W.-Y., Kong, L.-L., Du, J.-J., 2018b. Simultaneous removal of Cu2+ and bisphenol A by a novel biochar-supported zero valent iron from aqueous solution: synthesis, reactivity and mechanism. Environ. Pollut. 239, 698–705.

Liu, L., Li, Y., Li, W., Zhong, R., Lan, Y., Guo, J., 2020. The efficient degradation of sulfadiazine by singlet oxygen (¹O2) derived from activated peroxymonosulfate (PMS) and Co3O4. Sci. Total Environ. 687, 105665.

Lu, H., Sui, M., Yuan, B., Wang, J., Li, Y., 2019. Efficient degradation of nitrobenzene by Cu-Co-Fe-LDH catalyzed peroxymonosulfate to produce hydroxyl radicals. Chem. Eng. J. 357, 140–149.

Luo, H., Qiu, Z., Zou, H., Xue, Z., Xiao, X., Li, J., 2020. Determining the key factors of nonradical pathway in activation of persulfate by metal-biochar nanocomposites for bisphenol A degradation. Chem. Eng. J. 391, 123555.

Luo, Y., Li, G., Zhang, Y., Zhang, Q., Wen, F., Wang, X., 2019. Cobalt hydroxide as an efficient heterogeneous catalyst of peroxymonosulfate activation for oil- contaminated soil remediation. Sci. Total Environ. 680, 61–69.
Prasse, C., Wagner, M., Schulz, R., Ternes, T.A., 2011. Biotransformation of the antiviral
Proskurnina, E.V., Izmailov, D.Y., Sozarukova, M.M., Zhuravleva, T.A., Leneva, I.A.,
Mukthinuthalapati, M.A., Valli, D.S., Chaitanya, S.M., 2018. New stability indicating
Matthaiou, V., Frontistis, Z., Petala, A., Solakidou, M., Deligiannakis, Y.,
Olaitan, O.J., Anyakora, C., Bamiro, T., Tella, A.T., 2014. Determination of
Qian, Y., Wang, Q., Yue, F., 2016. Remediation of TCE-contaminated water by enhanced
Roy, K., Agarkoti, C., Malani, R.S., Thokchom, B., Moholkar, V.S., 2020. Mechanistic
Sing, K.S.W., 1985. Reporting physisorption data for gas/solid systems with special
Ushani, U., Lu, X., Wang, J., Zhang, Z., Dai, J., Tan, Y., Wang, S., Li, W., Niu, C., Cai, T.,
Wang, N., Zhen, G., 2020. Sulfate radicals-based advanced oxidation technology in
various environmental remediation: a state-of-the-art review. Chem. Eng. J. 402,
Vankadari, N., 2020. Arbidol: a potential antiviral drug for the treatment of SARS-CoV-2
by blocking trimerization of the spike glycoprotein. Int. J. Antimicrob. Agents 56,
105998.
Wang, J., Wang, S., 2016a. Removal of pharmaceuticals and personal care products
(PPCPs) from wastewater: a review. J. Environ. Manag. 182, 620-649.
Wang, J., Wang, S., 2018. Activation of peroxide (PS) and persulfate oxide (PMS)
and application for the degradation of emerging contaminants. Chem. Eng. J. 334,
1502-1517.
Wang, P., Jiang, Z., Chen, L., Yin, L., Li, Z., Zhang, C., Tang, X., Wang, G., 2016. Pore
structure characterization for the Longmaxi and Niutitang shades in the Upper
Yangtze Platform, South China: evidence from focused ion beam–He ion microscopy,
nano-computerized tomography and gas adsorption analysis. Mar. Petrol. Geol. 77,
1323-1337.
Wang, J., Liao, Z., Iltihakar, J., Shi, L., Chen, Z., Chen, Z., 2017. One-step preparation
and application of magnetic sludge-derived biochar on acid orange 7 removal via both
adsorption and persulfate based oxidation. RSC Adv. 7, 18696-18706.
Wang, J., Shen, M., Gong, Q., Wang, X., Cai, J., Wang, S., Chen, Z., 2020a. One-step
preparation of ZVI-sludge derived biochar without external source of iron and its
application on peroxidase activation. Sci. Total Environ. 714, 136728.
Wang, W., Wang, H., Li, G., Wong, P.K., An, T., 2020b. Visible light activation of
peroxidase by magnetic hydrochar for bacterial inactivation: efficiency, recyclability
and mechanisms. Water Res. 176, 115746.
Wang, X., Cao, Z., Zhang, H., Liu, J., Xu, M., Hu, H., Li, Y., Zhao, L., Li, W., Sun, X.,
Yang, X., Shi, Z., Deng, F., Hu, Z., Zhong, W., Wang, M., 2020x. The anti-influenza
virus drug, arbidol is an efficient inhibitor of SARS-CoV-2 in vitro. Cell Discco 6, 28.
Yang, X., Ding, D., Chen, D., Waller, G., Bu, Y., Wang, Z., Liu, M., 2015. Three-
dimensional ultrathin Ni(OH)2 nanosheets grown on nickel foam for high-
performance supercapacitors. Nano Energy 11, 154-161.
Yan, J., Han, L., Gao, W., Xue, S., Chen, M., 2015. Biochar supported nanoscale
zervonial iron composite used as persulfate activator for removing
trichloroethylen. Bioresour. Technol. 175, 269-274.
Yang, Y., Ok, Y.S., Kim, K.-H., Kwon, I.E., Yang, Y.F., 2017. Occurrences and removal of
pharmaceuticals and personal care products (PPCPs) in drinking water and water/
sewage treatment plants: a review. Sci. Total Environ. 596-597, 303-320.
Yang, H., Ye, S., Zeng, Z., Zeng, G., Tan, X., Xiao, B., Wang, J., Song, B., Du, L., Qin, M.,
Yang, Y., Xu, F., 2020. Utilization of biochar for resource recovery from water: a
review. Chem. Eng. J. 397, 125502.
Ye, S., Cheng, M., Zeng, G., Tan, X., Wu, H., Liang, J., Shen, M., Song, B., Liu, J.,
Yang, H., Zhang, Y., 2020. Insights into catalytic removal and separation of attached
metals from natural-aged microplastics by magnetic biochar activating oxidation
process. Water Res. 179, 115876.
Yi, Y., Wang, X., Ma, J., Ning, P., 2020. An efficient Egeria najas-derived biochar
supported ZVI composite for Cu(II) removal: characterization and mechanism
investigation based on visual MINTEQ model. Environ. Res. 189, 109912.
Yin, R., Guo, W., Wang, H., Du, J., Zhou, X., Wu, Q., Zheng, H., Chang, J., Ren, N., 2018.
Enhanced persulfate oxide activation for sulfamethazine degradation by ultrasound irradiation: performances and mechanisms. Chem. Eng. J. 335, 145-153.
Yue, J., Wang, T., Yang, Z., Zeng, G., Wang, J., Deng, Y., Liu, Y., Feng, H., Chen, S., Ren, X.,
2019. Magnetic nitrogen-doped sludge-derived biochar catalysts for persulfate
activation: internal electron transfer mechanism. Chem. Eng. J. 364, 146-159.
Zhang, N., Yi, Y., Lian, J., Fang, Z., 2020. Effects of Co doping on the Fenton-like
reactivity of Cu-based catalyst to the flavonol. Bioresour. Technol. 290, 126499.
Zhou, Y., Yuan, X., Li, X., Jiang, L., Wang, H., 2021. Bursting prospects of biochar and its
composite in persulfate-advanced oxidation process. J. Hazard Mater. 409, 126499.
Zhu, K., Wang, X., Chen, D., Ren, W., Lin, H., Zhang, H., 2019. Wood-based biochar as an
excellent activator of persulfate for Acid Orange 7 decolorization.
Chemosphere 231, 32–40.