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Ultrafast degradation of Cu(II)-EDTA by peroxymonosulfate activated with polyoxometalate clusters intercalated layered double hydroxides: Simultaneous decomplexation and resourcelization

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Abstract

Technologies used to handle metal pollution are often ineffective for complexed metals, which have refractory biodegradability, high solubility, and strong mobility, posing significant threats to the ecological environment. This work proposed a novel catalytic system for the proper disposal of Cu(II)-EDTA pollution. Polyoxometalate cluster intercalated CaFe layered double hydroxide (LDH-CoPW) prepared through a mild and convenience method was applied to activate peroxymonosulfate (PMS) for the degradation of Cu(II)-EDTA and the simultaneous immobilization of the released Cu(II). Compared to direct waste or complex regeneration of catalysts, the application of used LDH-CoPW in clean energy production was proposed to further reduce carbon emissions. Under the combination of 0.1 g/L of LDH CoPW and 0.1 mM of PMS, nearly 100% of Cu(II)-EDTA was removed within 3 min of reaction time, and 49.6% of Cu(II) was adsorbed within 60 min of reaction time. The second-order reaction kinetic constants of Co(IV)=O with various probes were confirmed by competition kinetics method. Based on this, Co(IV)=O was identified as the dominant RSs using a scientific probe-based kinetic model. Furthermore, CaFe-LDH did not directly activate PMS but ensured the reactivity of the catalytic system by promoting the redox cycle of cobalt species. Finally, due to the regulation of Cu on the electronic structure of the catalyst, the electrochemical performance of the used LDH-CoPW surpassed that of fresh LDH-CoPW and CaFe-LDH, showing great potential in clean energy production.

Keywords: Layered double hydroxides; Polyoxometalates; High valence metal;

Resourcelization.

1. Introduction

Increasing heavy metal pollution has attracted global public attention due to its environmental persistence and lethal toxicity [1, 2]. Due to the stable coordination of heavy metals with organic compounds, complexed metals with refractory biodegradability, high solubility and strong mobility can easily across water treatment process and pose potential threats to the ecological environment [3]. Therefore, efficient strategies are urgently needed to mitigate the harmfulness of complexed metals.

Although traditional methods such as precipitation, adsorption, and ion exchange are sufficient for removing free metals ions, they are powerless to handle complexed metals. Given the molecular structure of complexed metals, a two-step strategy is considered feasible. Heavy metal ions, released from complexed metals via oxidative decomplexation, can be subsequently removed by chemical precipitation [4]. Currently, several advanced oxidation processes (AOPs) have been employed to destruct the organic part of complexed metals [5, 6]. Of which, sulfate radical ($SO_4^{\bullet-}$) based AOPs are found to possess higher decomplexation efficiency than hydroxyl radical ($^{\bullet}OH$) based AOPs. Xu et al. compared the degradation of Cu(II)-EDTA by UV/persulfate and UV/peroxide systems, and proposed that the advantages of UV/persulfate system were mainly attributed to the better selectivity of $SO_4^{\bullet-}$ [7]. Despite the efficiency of precipitation and coagulation in removing free metal ions, the cost of chemical agents and sludge treatment is often unaffordable [8, 9]. Fortunately, some elaborately designed AOPs systems have achieved the goal of simultaneous decomplexation and metal recovery. For instance, satisfactory Cu(II)-EDTA degradation and Cu(II) recovery were realized in a combined electro-oxidation and electro-coagulation (EO-EC) reactor, with COD and Cu(II) removal of 85.01% and 99.85%, respectively [3]. Zhao et al. introduced a method for the photolysis of Cu(II)-EDTA and the simultaneous reduction of Cu(II) under UV irradiation, where EDTA was mineralized by radicals and Cu(II) was reduced to recoverable Cu^0 [10]. Notably, while decomplexation requires only oxidants, the recovery of heavy metal ions depends on energy input, complicating pollution remediation.

Developments in heterogeneous catalysts with activation and adsorption functions have alleviated this issue. The simultaneous decomposition of complex and the immobilization of free metal ions by a catalyst/oxidant system can effectively control the risk diffusion of complexed metals [11, 12]. For example, $Ti_3C_2T_x$ played the triple roles as activator for peroxymonosulfate (PMS) activation, reductant for triggering Cu(II)/Cu(I) cycle and absorbent for Cu ions recovery in the $Ti_3C_2T_x$/PMS system [13]. Layered double hydroxides (LDHs) with special spatial structure and abundant surface functional groups have been widely used in catalysis and adsorption, especially in the treatment of heavy metal pollution [14-16]. Efficient Cu(II) removal was achieved through $Cu(OH)_2$ precipitation on the LDH surface or by isomorphic substitution of divalent metals at the octahedral sites of LDH layers [17, 18]. Importantly, the interlayer confined space of LDHs serves as an ideal catalyst immobilization site, preventing catalyst loss and alleviating active site passivation [19]. Chen et al. constructed a LDHs confined single-atom cobalt catalyst for the PMS activation. The positively charged LDHs can stabilize PMS and enable it to be effectively activated by the intercalated single-atom cobalt [20].

Based on the above, we designed a $[Co_4(PW_9O_{34})_2]$ polyoxometalate cluster (CoPW) intercalated CaFe-LDH (LDH-CoPW) to activate PMS for simultaneous Cu(II)-EDTA decomplexation and Cu(II) resourcelization. The physicochemical properties and microstructure of LDH-CoPW were thoroughly characterized. The removal of Cu(II)-EDTA and the control of released Cu(II) by the LDH-CoPW/PMS system was assessed. Furthermore, we revealed the underlying catalytic mechanism of the LDH-CoPW/PMS system and evaluated its resourcelization prospect based on the electrochemical performance of the used LDH-CoPW. This study not only proposes a reasonable method for handling complexed metal pollution, but also provides a new idea for the reuse of waste catalysts.

2. Materials and methods

2.1. Chemicals

Potassium peroxymonosulfate was acquired from Sigma-Aldrich®, and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All reagents were analytical grade and used as received without further purification. Ultrapure water was used in all experiments.

2.2. Synthesis of LDH-CoPW

CaFe-LDH was first prepared as the host of CoPW. Briefly, 4.72 g of $Ca(NO_3)_2{\cdot}4H_2O$ and 4.04 g of $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in 100 mL of ultrapure water labeled as A. Then, 2.4 g of NaOH was dissolved in another 100 mL of ultrapure water labeled as B. Subsequently, A solution was dropwise added to B solution with vigorous stirring under nitrogen atmosphere. Subsequently, the obtained suspension was aged at 60 ℃ for 10 h to gain CaFe-LDH. CoPW was synthesized according to the previous literature [21]. LDH-CoPW was synthesized via a convenience ion exchange method at room temperature. CaFe-LDH and CoPW were ultrasonically dispersed in 200 mL of ultrapure water at the mass ratio of 1:1. Then, the reaction was kept at 60 ℃ for 3 h. After filtration, washing and drying, the collected powder was named LDH-CoPW.

Characterization, experimental and analytic methods are provided in Texts S1-S6 and Tab. S1 in Supporting Information.

3. Results and discussion

3.1. Catalysts characterization

XRD analysis was employed to ascertain the crystalline phase of LDH-CoPW and CaFe-LDH. Fig. S1 illustrates distinct peaks observed at 2θ = 6.8°, 18.7° and 28.8°, corresponding to the (003), (006) and (009) lattice planes of CaFe-LDH (JCPDS#44-0445), respectively [22, 23]. Upon substituting NO_3^- with CoPW in the interlayer of CaFe-LDH, a notable shift in lattice reflection toward lower 2θ values was observed compared to pristine CaFe-LDH, indicative of successful CoPW intercalation [24, 25]. Particularly, the primary diffraction peak corresponding to the *d* value provides crucial insights into the interlayer distance [26, 27]. Calculation reveals that the basal spacing of LDH-CoPW (17.9 Å) significantly surpassed that of CaFe-LDH (8.2 Å), consistent with previous observations [21, 28]. Furthermore, the interlayer spacing, determined as 13.1 Å by subtracting the height of the host layer (4.8 Å), aligned well with the diameter of the *b* axis of CoPW [21, 28].

The elemental valence information of LDH-CoPW and CaFe-LDH were analyzed using

XPS. Fig. S2a shows that no significant difference between the elemental valence of Fe in CaFe-LDH and LDH-CoPW, suggesting that the intercalated CoPW would not react with CaFe-LDH and lead to the structural collapse of CaFe-LDH. Furthermore, for the XPS spectra of O1s (Fig. S2b), the intercalation of CoPW resulted in the decrease of adsorbed oxygen (O_O) and the increase of hydroxyl oxygen (O_{OH}) in CaFe-LDH. This can be attributed to the increase in interlayer spacing of CaFe-LDH, which led to the escape of adsorbed oxygen and the exposure of surface hydroxyl groups, which was beneficial for the adsorption of metal ions.

HR-TEM was utilized to examine the microstructure of LDH-CoPW. As depicted in Fig. 1a, LDH-CoPW displayed the characteristic lamellar structure of brucite, with nanosheets standing up in bulk aggregates, exhibiting a mean size of 50 nm. This observation suggests the structural stability of CaFe-LDH during the ion exchange process, as CaFe-LDH also possessed typical layered structure (Fig. S3). The lattice plane distances were measured to be 0.47 and 0.31 nm corresponding to the (006) and (009) planes, respectively, which was indeed evidenced in the polycrystalline diffraction rings of LDH-CoPW. Furthermore, elemental content analysis and EDS mapping of LDH-CoPW (Fig. 1b and c) confirm the uniform distribution of Ca, Fe, O, Co, P and W elements in the prepared catalyst. Notably, the relative content of Co attributed to CoPW was significantly lower than that of Fe, representing CaFe-LDH, indicating that CoPW was more likely to be intercalated within the CaFe-LDH interlayer rather than simply loaded onto the surface.

3.2. Catalytic performance evaluation

As depicted in Fig. 2a, the combination of LDH-CoPW and PMS led to 98.3% of Cu(II)-EDTA removal within 3 min of reaction time. Conversely, LDH-CoPW could barely adsorb Cu(II)-EDTA, and negligible removal was achieved through direct PMS oxidation, underscoring the enhancement of PMS activation by LDH-CoPW. The catalytic activity of CaFe-LDH was also examined. Only ~20% of Cu(II)-EDTA was removed under the same conditions. Furthermore, the pseudo-first-order reaction rate constant (k_{obs}) for the LDH-CoPW/PMS and CaFe-LDH/PMS systems were 0.41 and 0.03 min^{-1}, respectively, indicating that the catalytic site responsible for PMS activation was CoPW rather than CaFe-LDH. Moreover, the turnover frequency values (TOF) of some reported catalysts were calculated by dividing the product of Cu(II)-EDTA concentration and k_{obs} values by the product of catalyst dosage and PMS dosage. As calculated, the TOFs of calcite, MSBC, and ZIF-67 were 0.0007 [29], 0.007 [30], and 0.08 [31], which were much lower than that of LDH-CoPW (0.41). This indicates that the proposed catalytic system possessed advantages in the rapid elimination of Cu(II)-EDTA from water.

Fig. 2b shows the synchronous removal of released Cu(II) by LDH-CoPW. Compared to the rapid degradation of Cu(II)-EDTA, the immobilization of Cu(II) took longer. However, 49.6% of Cu(II) was still adsorbed within 60 min of reaction time, indicating that the LDH-CoPW/PMS system possessed potential of controlling pollution diffusion. The adsorption of Cu(II) on the LDH-CoPW surface was further verified using XRD and XPS analysis. As shown in Fig. S4a, compared to the XRD pattern of fresh LDH-CoPW, the typical diffraction peak representing (006) and (009) crystal planes shifted from low angle to high angle, suggesting the successful substitution of Ca(II) by Cu(II), which was consistent with previous literatures. As can be seen in Fig. S4b, the formation of Cu-OH and Cu-O in the used LDH-CoPW suggests the isomorphic substitution of Ca(II) with Cu(II) at the octahedral sites of LDHs layers. Moreover, the shift of O 1s towards higher binding energy indeed confirms this process (Fig. S4c) [32, 33]. It should be noted that the adsorption efficiency of Cu(II) was much lower than the decomplexation efficiency of Cu(II)-EDTA. This could be attributed to the strong oxidation environment induced by the catalytic system caused the high concentration of Cu(II) to be released rapidly, while the adsorption sites of LDHs was limited. Therefore, more attention should be paid to the concentration variation of Cu(II) in aqueous solution rather than the degradation efficiency of Cu(II)-EDTA in real-world application.

To evaluate the mineralization capacity of the LDH-CoPW/PMS system, TOC removal was monitored during the reaction. As depicted in Fig. 2c, with 98.3% of Cu(II)-EDTA was degraded, only 17.0% of TOC was eliminated within 3 min of reaction time, suggesting the recalcitrance of EDTA in the environment. Notably, extending the reaction time to 20 min led to an improved mineralization rate of 17.2%, underlining the sustained oxidation capacity of the LDH-CoPW/PMS system. However, with extending the reaction time from 20 min to 60 min, TOC removal only increased from 34.2% to 48.3%, which may be due to the lack of oxidants in the later stage of the reaction. The effect of reaction temperature on Cu(II)-EDTA degradation was investigated (Fig. 2d), revealing that higher temperatures facilitated PMS activation by LDH-CoPW. The k_{obs} values for Cu(II)-EDTA degradation at 15 °C, 25 °C, 35 °C and 45 °C were 0.16, 0.41, 1.39, and 2.61 min^{-1}, respectively. Additionally, a linear relationship between ln(k_{obs}) and the reciprocal of the reaction temperature (1/T) was observed, with the activation energy (Ea) for PMS by LDH-CoPW calculated to be 67.4 kJ/mol. Considering that the Ea for diffusion-controlled reactions is typically between 10-13 kJ/mol, therefore, the catalytic reaction was governed by surface chemical reactions rather than mass transfer [34].

3.3. Catalytic mechanisms analysis

3.3.1. Reactive species identification

Various reactive species (RSs) has been found that could be generated in the catalytic system during PMS activation [35, 36]. Hence, it is imperative to identify the RSs present in the LDH-CoPW/PMS system. ESR analysis was employed to recognize $SO_4^{\bullet-}$, $^{\bullet}OH$, superoxide radical ($O_2^{\bullet-}$) and singlet oxygen ($^1O_2$) using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-Tetramethylpiperidine (TEMP) as the trapping agents [37, 38]. Fig. 3a reveals a weak characteristic signal attributed to 5,5-dimethyl-1-pyrrolidone-2-oxy-l (DMPOX) adducts in the LDH-CoPW/PMS system, instead of the signals of DMPO-$SO_4^{\bullet-}$ and DMPO-$^{\bullet}OH$ adducts. Recent studies have proposed that Co(IV)=O can directly oxidize DMPO to form DMPOX, potentially leaving misleading information [39]. Moreover, compared with the feeble signals of DMPO-$O_2^{\bullet-}$, the three-line characteristic signals observed in Fig. 3b were attributed to TEMP-$^1O_2$ adducts, indicating the formation of $^1O_2$ in the LDH-CoPW/PMS system [40].

Then, methanol (MeOH) ($k_{[MeOH,OH]}=1.2–2.8\times10^7$ M^{-1}s^{-1}; $k_{[MeOH,SO4−]}=1.7–7.7\times10^7$

$M^{-1}s^{-1}$), tert-butanol (TBA) ($k_{[TBA,OH]}$=3.8–7.6×10^8 $M^{-1}s^{-1}$), furfuryl alcohol (FFA) ($k_{[FFA,OH]}$=1.5×10^{10} $M^{-1}s^{-1}$; $k_{[FFA,1O2]}$=1.2×10^8 $M^{-1}s^{-1}$) and dimethylsulfoxide (DMSO) ($k_{[DMSO,Co(IV)=O]}$=2.4×10^6 $M^{-1}s^{-1}$) were used as quenching agents to further confirm the RSs in the system [41]. As shown in Fig. S5, with 100 mM of TBA and MeOH was added into the solution, Cu(II)-EDTA removal decreased to 78.5% and 9.6%, respectively, highlighting the significant role of $SO_4^{\bullet-}$ in the system. In addition, the presence of 1 mM FFA almost terminated the reaction, with the k_{obs} value for Cu(II)-EDTA degradation decreasing to 0.02 min^{-1}. As for Co(IV)=O, Cu(II)-EDTA degradation was barely effected by the addition of 100 mM DMSO. However, the results did not correspond well with ESR analysis. Generally, it is impossible for MeOH and FFA to completely terminate Cu(II)-EDTA degradation simultaneously, as they are capture agents for $SO_4^{\bullet-}$ and $^1O_2$, respectively.

3.3.2. Reactive species exposure

Due to the varying reactivity of different RSs towards Cu(II)-EDTA, we reassessed the contribution of $SO_4^{\bullet-}$, $^{\bullet}OH$, $^1O_2$, and Co(IV)=O to Cu(II)-EDTA degradation. To avoid potential misinterpretations from traditional probe experiments, a probe-based kinetic model proposed by Wang's group was employed to evaluate the exposure and contribution of RSs to Cu(II)-EDTA removal (details in Text S4) [42]. Notably, all four probes were rapidly degraded by the LDH-CoPW/PMS system, affirming the presence of these RSs in the solution. It is worth noting that the probes can hardly be removed within 0.5 min, which may be due to the mass transfer limitation of PMS (Fig. S6a). Subsequently, we determined RSs exposure by selectively fitting the probes degradation. As illustrated in Fig. S6b, the k_{obs} for

ATZ, PMD, MTZ, and PMSO degradation were calculated as 0.48, 0.57, 1.43 and 0.56 min^{-1}, respectively. Through calculations, $^{\bullet}OH$ exposure was nearly undetectable, while the exposures of $SO_4^{\bullet -}$, $^1O_2$, and Co(IV)=O continuously increased during the catalytic reaction, reaching 3.4×10^{-10}, 7.7×10^{-9} and 5.4×10^{-7} M s at 3 min, respectively (Fig. 3c). Furthermore, the transient concentration variations of RSs during the reaction were estimated (details in Text S5). As indicated in Fig. 3d, the concentrations of $SO_4^{\bullet -}$, $^1O_2$, and Co(IV)=O gradually increased to 8.8×10^{-14}, 2.0×10^{-12}, and 1.4×10^{-10} M within 3 min, respectively. Remarkably, the concentration of Co(IV)=O remained approximately 10^2-10^4 times higher than that of $SO_4^{\bullet -}$ and $^1O_2$ throughout the reaction, underscoring the dominant role of Co(IV)=O in the LDH-CoPW/PMS system. Based on these observations, we calculated the contributions of different RSs to Cu(II)-EDTA degradation as described in the inserted figure in Fig. 3c (details in Text S5). Although the concentration of $^1O_2$ in the LDH-CoPW/PMS system was two orders of magnitude higher than that of $SO_4^{\bullet -}$, its contribution to Cu(II)-EDTA attenuation was only 3.8%, while the contribution of $SO_4^{\bullet -}$ was 14.7%. Conversely, the contribution of Co(IV)=O, with its long-acting oxidation capacity, selectivity, and high concentration, to Cu(II)-EDTA degradation was as high as 80.9%. [43]. As demonstrated by the advantages of catalytic systems in TOC removal, the longer half-life of Co(IV)=O compared to free radicals endows it with sustained oxidative activity. In addition, as a nonradical pathway, its inertness to water substrates also endows Co(IV)=O with flexibility in environmental remediation, as Co(IV)=O is not as easily quenched as free radicals. This makes the LDH-CoPW/PMS system a favorable candidate for the remediation of

Cu(II)-EDTA pollution.

3.3.3. Mechanism of PMS activation

To explore the mechanism of PMS activation by LDH-CoPW, the element valence of fresh and used LDH-CoPW were determined using XPS. From Fig. 4, the 2p orbit can be divided into $2p_{1/2}$ and $2p_{3/2}$, representing the same elemental information. Herein, taking $2p_{3/2}$ as an example, Co(III) and Co(II) are represented by peaks at binding energies of 780.8 and 784.9 eV, respectively (Fig. 4a). Significantly, both single-electron transfer processes related to free radicals and double-electron transfer processes related to Co(IV)=O involve the oxidation of lower-valence cobalt species to higher-valence states [44, 45]. However, the relative content of Co(II) decreased after the reaction (Tab. S3). Given the catalytic inertness of CaFe-LDH, this result is unlikely due to competitive activation of PMS by iron species. Therefore, it can be reasonably concluded that although iron species cannot directly activate PMS, it can endow LDH-CoPW with high catalytic activity of by promoting the redox cycle of cobalt species. As shown in Fig. 4b, the peak intensities of Fe(III) and Fe(II) at binding energies of 712.2 and 710.0 eV changed from 31.6% and 68.4% to 37.5% and 62.5%, respectively (Tab. S3), confirming this process.

Therefore, the process of Cu(II)-EDTA degradation and Cu(II) immobilization by the LDH-CoPW/PMS system is described in Fig. 5, Upon addition of PMS, CoPW confined in the CaFe-LDH interlayer can capture PMS to form CoPW-$OOSO_3^-$ intermediate. Hence, the bonded PMS would be reduced to SO_4^{2-} through a double-electron transfer process. Meanwhile, Co(IV)=O with strong oxidation was concomitantly produced, which possesses high selectivity for Cu(II)-EDTA. Along with the oxidation of Cu(II)-EDTA, Co(IV)=O is continuously converted into non renewable Co(III). Fortunately, Fe(II) on the CaFe-LDH layer can accelerate the reduction of Co(III) to Co(II), thus ensuring the continuous production of Co(IV)=O. Meanwhile, due to the buffering of CaFe-LDH, the coordination of CoPW and PMS via inner/outer sphere interaction would not be interfered with by ClO_4^- and PO_4^{3-} (Fig. S7), ensuring the environmental resistance of the LDH-CoPW/PMS system. Under the attack of Co(IV)=O, Cu(II)-EDTA can be rapidly degraded. Of which, EDTA is deeply mineralized to inorganic carbon/nitrogen, and the released Cu(II) is immobilized on the CaFe-LDH layer via isomorphic substitution of Ca(II).

3.4. Effect of key parameters

The broad operational range of pH is crucial for the potential application of LDH-CoPW. In Fig. S8a, the LDH-CoPW/PMS system exhibited satisfactory performance across acidic and alkaline solutions, with the k_{obs} values for Cu(II)-EDTA degradation at pH 3.0, 5.0, 7.0, and 9.0 being recorded as 0.27, 0.25, 0.60 and 0.92 min^{-1}, respectively. The slight suppressed performance of the LDH-CoPW/PMS system at lower pH conditions can be attributed to the scavenging of $SO_4^{\bullet-}$ and $^1O_2$ by H^+ might inhibit their secondary contribution to Cu(II)-EDTA degradation [46, 47]. Then, the zeta potential of LDH-CoPW was tested to further understand the effect of electrostatic force on the catalytic process (data not provided). LDH-CoPW was negatively charged within the studied range of pH, and its potential decreased with the elevation of pH. However, this was not consistent with the better performance of catalytic system under alkaline conditions, as negatively charged catalyst exhibits significant electrostatic repulsion with PMS molecule. Therefore, the better catalytic efficiency of the catalytic system at higher pH conditions may be due to the fact that the higher reactivity of SO_5^{2-} than HSO_5^-, and the negative impact of electrostatic repulsion in the catalytic reaction process is not the decisive factor [48].

The effect of coexisting anions on the LDH-CoPW/PMS system was investigated. As depicted in Fig. S8b, the presence of Cl^- notably inhibited Cu(II)-EDTA degradation, particularly at higher Cl^- concentrations, resulting in a decline in k_{obs} for Cu(II)-EDTA degradation to 0.05 min^{-1} at a Cl^- concentration of 10 mM. This inhibition could be attributed to the direct consumption of PMS by excessive Cl^-, leading to the formation of chlorine oxidants, which cannot be effectively utilized by LDH-CoPW [49, 50]. Meanwhile, the addition of SO_4^{2-} slightly compromised the catalytic efficiency of the LDH-CoPW/PMS system, with the k_{obs} values for Cu(II)-EDTA degradation being recorded as 0.38, 0.35, and 0.37 min^{-1} in the presence of 1, 5, and 10 mM of SO_4^{2-}, respectively (Fig. S8c). From Fig. 5, it can be seen that PMS bonds to the active site and undergoes oxygen transfer to form Co(IV)=O, which involves the release of SO_4^{2-}. Therefore, the addition of SO_4^{2-} can lower the decomposition potential of HSO_5^-, thereby suppressing the formation of Co(IV)=O [51]. However, with the buffer of confined space, this negative impact was reduced to an acceptable level. Similarly, the slight inhibitory effect of NO_3^- on the reactivity of the LDH-CoPW/PMS system can also be attributed to the protection of the internal catalytic sites by CaFe-LDH. Overall, the influence of coexisting anions on the performance of the catalytic system was limited, indicating promising application prospects for the LDH-CoPW/PMS system.

As shown in Fig. S9a, the effect of initial pH on Cu(II) immobilization was consistent with the degradation of Cu(II)-EDTA. Along with the rapid degradation of Cu(II)-EDTA under alkaline conditions, the released Cu(II) did not accumulate significantly in the solution, which can be attributed to the alkaline environment promoting surface hydroxylation of CaFe-LDH, thereby facilitating the isomorphic substitution reaction between CaFe-LDH and free Cu(II). Furthermore, we investigate the influence of coexisting anions on the adsorption of Cu(II). As shown in Fig. S9b, the presence of Cl^- inhibited Cu(II)-EDTA degradation and also possessed adverse effect on the subsequent Cu(II) immobilization. The low efficiency of the decomplexation process prevented Cu(II) from being captured by the adsorption sites of CaFe-LDH. For SO_4^{2-} and NO_3^- (Fig. S9c and d), the slight suppression of Cu(II) immobilization might only be induced by the decrease in the efficiency of Cu(II)-EDTA decomplexation, and these coexisting anions barely effected the adsorption process of Cu(II) by CaFe-LDH.

The multi-cycle durability of the LDH-CoPW/PMS system was assessed as shown in Fig. S10, the catalytic system not only possessed remarkable potential in removing Cu(II)-EDTA, but also exhibited satisfactory stability. Cu(II)-EDTA removal in the first, second, third, and fourth cycles were 98.3%, 100%, 97.5%, and 94.5%, respectively. However, compared with the superior degradation efficiency, the recovery performance of Cu was almost completely lost in only the second cycle (data not provided). This suggests that Cu(II) immobilized by chemical adsorption cannot be removed by simple washing methods, which forced us to seek a more reasonable way of catalyst reuse.

3.5. Copper resourcelization

Promoting the use of clean energy is crucial to achieving carbon neutrality. Thus, exploring more efficient strategies for obtaining clean energy has attracted great attention. Water splitting is a promising approach to obtain hydrogen energy, a type of clean energy with zero pollution emissions. Unfortunately, due to the kinetic sluggishness of the four electron transfer process, oxygen evolution reaction (OER), as the half reaction of water splitting, is considered the bottleneck of electrochemical water splitting [52]. Therefore, low-cost and high activity OER electrocatalysts are urgently needed to alleviate the embarrassment. Among all the materials capable of catalyzing OER, LDHs stand out as one of the most effective electrocatalysts owing to their compositional and structural flexibility. Specifically, LDHs composed of transition metals (Co, Fe, Ni, et al.) have been proven to exhibit superior OER performance [53]. Recent studies indicate that the high electron conductivity and d-electron abundance of Cu can promote the OH^- adsorption and electron transport at active sites, thus improving the OER kinetics of the catalyst [54]. Thus, used LDH-CoPW is expected to be as a potential OER catalyst.

Firstly, the OER performance of CaFe-LDH, fresh LDH-CoPW and used LDH-CoPW in 1.0 M KOH was tested. From the linear sweep voltammetry (LSV) curves (Fig. 6a), it is evident that CaFe-LDH was electrochemically inert, and the slope of used LDH-CoPW was higher than that of fresh LDH-CoPW. These results manifest that used LDH-CoPW possessed better electrocatalytic OER activity than CaFe-LDH and fresh LDH-CoPW [55]. Moreover, electrochemical impedance spectroscopy (EIS) test was performed to compare the charge transfer properties. The EIS curves consist of two distinct semicircles. The high-frequency semicircle and the low-frequency semicircle are associated with charge transfer resistance and mass-diffusion process, respectively [56]. As shown in Fig. 6b, it can be found that used LDH-CoPW exhibited a smaller high-frequency semicircle diameter compared to CaFe-LDH and fresh LDH-CoPW, indicating lower charge transfer resistance for water oxidation in the used LDH-CoPW compared to CaFe-LDH and fresh LDH-CoPW [55].

4. Conclusion

Proper disposal of Cu(II)-EDTA pollution was achieved by the LDH-CoPW/PMS catalytic system in this work. The following conclusions can be drawn.

i) The combination of LDH-CoPW and PMS enabled both ultrafast Cu(II)-EDTA removal and acceptable Cu recovery.

ii) Instead of free radical and $^1O_2$, Co(IV)=O was determined as the dominate RSs using a scientific probe-based kinetic model.

iii) Although CaFe-LDH was incapable of activating PMS, it ensured the reactivity of the catalytic system by promoting the redox cycle of cobalt species.

iv) The regulation of Cu on the electronic structure of the catalyst improved the electrochemical performance of used LDH-CoPW compared to fresh LDH-CoPW and CaFe-LDH.

Conflicts of interest

The authors declare no conflict of interest.

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References

[1] Duan, G., Li, X., Ma, X., Zhong, W., Wang, S. High-efficiency adsorption removal for Cu(II) and Ni(II) using a novel acylamino dihydroxamic acid chelating resin. *Sci. Total Environ.* **2023**, 864, 160984.

[2] Wang, L., Guo, C., Qian, Q., Lang, D., Wu, R., Abliz, S., Wang, W., Wang, J. Adsorption behavior of UV aged microplastics on the heavy metals Pb(II) and Cu(II) in aqueous solutions. *Chemosphere* **2023**, 313, 137439.

[3] Song, P., Sun, C., Wang, J., Ai, S., Dong, S., Sun, J., Sun, S. Efficient removal of Cu-EDTA complexes from wastewater by combined electrooxidation and electrocoagulation process: Performance and mechanism study. *Chemosphere* **2022**, 287, 131971.

[4] Bai, W., Tang, R., Wu, G., Wang, W., Yuan, S., Xiao, L., Zhan, X., Hu, Z.-H. Co-precipitation of heavy metals with struvite from digested swine wastewater: Role of suspended solids. *J. Hazard. Mater.* **2023**, 455, 131633.

[5] Zong, Y., Ji, W., Xie, Y., Wu, D. Overlooked oxidative role of Ni(III) in the enhanced mineralization of Ni(II)–EDTA complex by ozonation. *Sep. Purif. Technol.* **2023**, 306, 122697.

[6] Zhang, Y., Li, D., She, L., Guo, F., Jia, F., Zhang, L., Ai, Z., Liu, X. Ball-milled zero-valent iron with formic acid for effectively removing Cu(II)-EDTA accomplished by EDTA ligands oxidative degradation and Cu(II) removal. *J. Hazard. Mater.* **2024**, 465, 133009.

[7] Xu, Z., Shan, C., Xie, B., Liu, Y., Pan, B. Decomplexation of Cu(II)-EDTA by UV/persulfate and UV/H_2O_2: Efficiency and mechanism. *Appl. Catal. B-Environ.* **2017**, 200, 439-447.

[8] Yang, X., Liu, L., Wang, Y., Lu, T., Wang, Z., Qiu, G. Sustainable and reagent-free cathodic precipitation for high-efficiency removal of heavy metals from soil leachate. *Environ. Pollut.* **2023**, 320, 121002.

[9] Liu, J.-W., Fu, T., Sun, G.-D., Shen, X.-R., Liu, S., He, Y., Xu, Y., Zhao, H.-Z. A versatile organic silicate aluminum hybrid coagulant for broad-spectrum removal of heavy metal ions. *Chem. Eng. J.* **2023**, 472, 145005.

[10] Zhao, J., Hu, X., Kong, L., Peng, X. UV irradiation induced simultaneous reduction of Cu(II) and degradation of EDTA in Cu(II)-EDTA in wastewater containing Cu(II)-EDTA. *J. Hazard. Mater.* **2024**, 465, 133131.

[11] Wu, L., Garg, S., Xie, J., Zhang, C., Wang, Y., Waite, T.D. Electrochemical removal

of metal–organic complexes in metal plating wastewater: A comparative study of Cu-EDTA and Ni-EDTA removal mechanisms. *Environ. Sci. Technol.* **2023**, 57, 12476-12488.

[12] Huang, J., Miao, X., Zhang, L., Yu, X., Liu, W., Huang, C. Synergistic effect and mechanism of zero-valent iron activated persulfate on Cu(II)–EDTA decomplexation enhanced with weak magnetic field. *J. Environ. Chem. Eng.* **2023**, 11, 111042.

[13] Zu, D., Song, H., Li, C., Wang, Y., Du, R., Zhou, R., Zhang, W., Pan, S., Cai, Y., Shen, Y., Yang, Z. Understanding the self-catalyzed decomplexation mechanism of Cu-EDTA in $Ti_3C_2T_x$ MXene/peroxymonosulfate process. *Appl. Catal. B-Environ.* **2022**, 306, 121131.

[14] Zeng, H., Yang, B., Zhang, J., Zhu, H., Deng, J., Shi, Z., Zhou, S., Zhang, H., Cai, A., Deng, L. MnFe layered double hydroxides confined MnO_x for peroxymonosulfate activation: A novel manner for the selective production of singlet oxygen. *Environ. Pollut.* **2024**, 348, 123865.

[15] Zeng, H., Zhu, H., Deng, J., Shi, Z., Zhang, H., Li, X., Deng, L. New insight into peroxymonosulfate activation by CoAl-LDH derived CoOOH: Oxygen vacancies rather than Co species redox pairs induced process. *Chem. Eng. J.* **2022**, 442, 136251.

[16] Farhan, A., Khalid, A., Maqsood, N., Iftekhar, S., Sharif, H.M.A., Qi, F., Sillanpää, M., Asif, M.B. Progress in layered double hydroxides (LDHs): Synthesis and application in adsorption, catalysis and photoreduction. *Sci. Total Environ.* **2024**, 912, 169160.

[17] Rojas, R. Effect of particle size on copper removal by layered double hydroxides. *Chem. Eng. J.* **2016**, 303, 331-337.

[18] González, M.A., Pavlovic, I., Barriga, C. Cu(II), Pb(II) and Cd(II) sorption on different layered double hydroxides. A kinetic and thermodynamic study and competing factors. *Chem. Eng. J.* **2015**, 269, 221-228.

[19] Wu, J., Xie, Y., Li, Y., Jin, M., Liu, L., Pan, G., Wang, C., Li, F. Layered double hydroxides-based metal nanocatalysts: Confinement engineering, microenvironment effect and applications in catalytic conversion of biomass. *Coord. Chem. Rev.* **2023**, 497, 215437.

[20] Chen, C., Yan, M., Li, Y., Hu, Y., Chen, J., Wang, S., Wu, X.-L., Duan, X. Single-atom co sites confined in layered double hydroxide for selective generation of surface-bound radicals via peroxymonosulfate activation. *Appl. Catal. B-Environ.* **2024**, 340, 123218.

[21] Yin, Q., Tan, J.M., Besson, C., Geletii, Y.V., Musaev, D.G., Kuznetsov, A.E., Luo, Z., Hardcastle, K.I., Hill, C.L. A fast soluble carbon-free molecular water oxidation catalyst based on abundant metals. *Science* **2010**, 328, 342-345.

[22] Xiong, W., Yang, M., Wang, J., Wang, H., Zhao, P., Li, Z., Liu, B., Kong, X., Duan, H., Zhao, Y. Removal, recycle and reutilization of multiple heavy metal ions from electroplating wastewater using super-stable mineralizer Ca-based layered double hydroxides. *Chem. Eng. Sci.* **2023**, 279, 118928.

[23] Jiménez, A., Trujillano, R., Rives, V., Soria, M.A., Madeira, L.M., Vicente, M.Á. CaAlFe–mixed metal oxides prepared from an aluminum salt–cake and their evaluation as CO_2 sorbents at moderate temperature. *Chem. Eng. J.* **2023**, 473, 145165.

[24] Yang, Q., Li, Z., Xu, B. Layered double hydroxide with interlayer quantum dots and laminate defects for high-performance supercapacitor. *Adv. Funct. Mater.* **2023**, 33, 2300149.

[25] Hu, W., Chen, L., Geng, B., Song, Y., Wu, Z., Zheng, Q., Shan, G., Du, M. Effect of intercalated anion in nickel-cobalt-layered double hydroxide on its supercapacitive properties. *Chem. Eng. J.* **2023**, 468, 143694.

[26] Li, C., Yan, B., Xue, T., Tao, R., Song, Z., Qi, F., Zhang, F., Lei, X., Wang, Y. Electron transfer degradation of ciprofloxacin by peroxydisulfate intercalated MgAlFe-layered double hydroxides: Roles of laminate structure and interlayer peroxydisulfate. *Sep. Purif. Technol.* **2023**, 312, 123385.

[27] Chen, Z., Wang, X., Han, Z., Zhang, S., Pollastri, S., Fan, Q., Qu, Z., Sarker, D., Scheu, C., Huang, M., Cölfen, H. Revealing the formation mechanism and optimizing the synthesis conditions of layered double hydroxides for the oxygen evolution reaction. *Angew. Chem. Int. Ed.* **2023**, 62, e202215728.

[28] Terzi, C.M., dos Santos, E.H., Carvalho, C., Prevot, V., Wypych, F., Forano, C., Nakagaki, S. MgAl and ZnAl layered double hydroxides modified with molybdate and tungstate anions as catalysts for oxidation of cyclohexane. *Catal. Today* **2023**, 422, 114221.

[29] Chu, Z., Han, Z., Liu, H., Chen, T., Zou, X., Wang, H., Sun, F., Wang, H., Chen, D. Autocatalytic degradation of Cu-EDTA in the Calcite/PMS system: Singlet oxygen and Cu(III). *J. Hazard. Mater.* **2024**, 477, 135286.

[30] Xie, J., Liang, Z., Zhang, J., Zhao, Z., Cui, F. Synchronous decomplexation and mineralization of copper complexes by activating peroxymonosulfate with magnetic bimetallic biochar derived from municipal sludge. *Chemosphere* **2023**, 338, 139358.

[31] Wang, S., Guo, S., Du, X., Liu, Z., Yang, Y., Song, Y., Zhang, Q. One-step rapid removal of Cu(II) complexes via dual-active-site MOF catalysis with Peroxymonosulfate: Cooperative oxidation and adsorption. *Chem. Eng. J.* **2024**, 495, 153604.

[32] Li, Z., Zheng, S., Yan, J., Qian, P., Ye, S. Design and preparation of CaFe layered double hydroxides for efficient treatment of fluorinated water deduced by tailored sustained-release of Ca^{2+}. *Chem. Eng. J.* **2024**, 480, 147950.

[33] Vasseghian, Y., Sezgin, D., Nguyen, D.C., Hoang, H.Y., Sari Yilmaz, M. A hybrid nanocomposite based on CuFe layered double hydroxide coated graphene oxide for photocatalytic degradation of trimethoprim. *Chemosphere* **2023**, 322, 138243.

[34] Saputra, E., Muhammad, S., Sun, H., Ang, H.-M., Tadé, M.O., Wang, S. Manganese oxides at different oxidation states for heterogeneous activation of peroxymonosulfate for phenol degradation in aqueous solutions. *Appl. Catal. B-Environ.* **2013**, 142, 729-735.

[35] Yin, K., Wu, R., Shang, Y., Chen, D., Wu, Z., Wang, X., Gao, B., Xu, X. Microenvironment modulation of cobalt single-atom catalysts for boosting both radical oxidation and electron-transfer process in Fenton-like system. *Appl. Catal. B-Environ.* **2023**, 329, 122558.

[36] Yin, K., Shang, Y., Chen, D., Gao, B., Yue, Q., Xu, X. Redox potentials of pollutants determining the dominate oxidation pathways in manganese single-atom catalyst (Mn-SAC)/peroxymonosulfate system: Selective catalytic mechanisms for versatile pollutants. *Appl. Catal. B-Environ.* **2023**, 338, 123029.

[37] Asif, M.B., Kang, H., Zhang, Z. Gravity-driven layered double hydroxide nanosheet membrane activated peroxymonosulfate system for micropollutant degradation. *J. Hazard.*

Mater. **2022**, 425, 127988.

[38] Sharmin, A., Asif, M.B., Zhang, G., Bhuiyan, M.A., Pramanik, B.K. Reactive layered hydroxide membrane for advanced water treatment: Micropollutant degradation and antifouling potential. *Chemosphere* **2024**, 359, 142318.

[39] Zeng, H., Zhu, H., Deng, J., Liu, B., Zhou, S., Shi, Z., Deng, L. Tunable peroxymonosulfate activation by (−111) crystal plane exposed δ-MnO_2: Oxidant concentration induced intrinsic mechanisms transformation. *Chem. Eng. J.* **2023**, 473, 145222.

[40] Yin, K., Peng, L., Chen, D., Liu, S., Zhang, Y., Gao, B., Fu, K., Shang, Y., Xu, X. High-loading of well dispersed single-atom catalysts derived from Fe-rich marine algae for boosting Fenton-like reaction: Role identification of iron center and catalytic mechanisms. *Appl. Catal. B-Environ.* **2023**, 336, 122951.

[41] Zeng, H., Deng, L., Zhang, H., Zhou, C., Shi, Z. Development of oxygen vacancies enriched CoAl hydroxide@hydroxysulfide hollow flowers for peroxymonosulfate activation: A highly efficient singlet oxygen-dominated oxidation process for sulfamethoxazole degradation. *J. Hazard. Mater.* **2020**, 400, 123297.

[42] Wang, H., Gao, L., Xie, Y., Yu, G., Wang, Y. Clarification of the role of singlet oxygen for pollutant abatement during persulfate-based advanced oxidation processes: Co_3O_4@CNTs activated peroxymonosulfate as an example. *Water Res.* **2023**, 244, 120480.

[43] Zhang, L., Qi, J., Chen, W., Yang, X., Fang, Z., Li, J., Li, X., Lu, S., Wang, L. Constructing hollow multishelled microreactors with a nanoconfined microenvironment for ofloxacin degradation through peroxymonosulfate activation: Evolution of high-valence cobalt-oxo species. *Environ. Sci. Technol.* **2023**, 57, 16141-16151.

[44] Anipsitakis, G.P., Dionysiou, D.D., Gonzalez, M.A. Cobalt-mediated activation of peroxymonosulfate and sulfate radical attack on phenolic compounds. Implications of chloride ions. *Environ. Sci. Technol.* **2006**, 40, 1000-1007.

[45] Wu, Q.-Y., Yang, Z.-W., Wang, Z.-W., Wang, W.-L. Oxygen doping of cobalt-single-atom coordination enhances peroxymonosulfate activation and high-valent cobalt–oxo species formation. *Proc. Natl. Acad. Sci.* **2023**, 120, e2219923120.

[46] Chen, X., Hu, X. Removal of NO_x and SO_2 from the coal-fired flue gas using a rotating packed bed pilot reactor with peroxymonosulfate activated by Fe(II) and heating. *Energy Fuels* **2019**, 33, 6707-6716.

[47] Zhao, Y., Sun, M., Zhao, Y., Wang, L., Lu, D., Ma, J. Electrified ceramic membrane actuates non-radical mediated peroxymonosulfate activation for highly efficient water decontamination. *Water Res.* **2022**, 225, 119140.

[48] Jijoe, P.S., Yashas, S.R., Shivaraju, H.P. Fundamentals, synthesis, characterization and environmental applications of layered double hydroxides: a review. *Environ. Chem. Lett.* **2021**, 19, 2643-2661.

[49] Zhu, K.-A., Chen, X.-J., Yuan, C.-W., Bai, C.-W., Sun, Y.-J., Zhang, B.-B., Chen, F. Orientated construction of visible-light-assisted peroxymonosulfate activation system for antibiotic removal: Significant enhancing effect of Cl. *J. Hazard. Mater.* **2023**, 445, 130476.

[50] Guan, Y.-H., Ma, J., Liu, D.-K., Ou, Z.-f., Zhang, W., Gong, X.-L., Fu, Q., Crittenden, J.C. Insight into chloride effect on the UV/peroxymonosulfate process. *Chem. Eng.*

J. **2018**, 352, 477-489.

[51] Lin, K., Liu, W., Gan, J. Oxidative removal of bisphenol a by manganese dioxide: Efficacy, products, and pathways. *Environ. Sci. Technol.* **2009**, 43, 3860-3864.

[52] Cai, Z., Bu, X., Wang, P., Ho, J.C., Yang, J., Wang, X. Recent advances in layered double hydroxide electrocatalysts for the oxygen evolution reaction. *J. Mater. Chem. A* **2019**, 7, 5069-5089.

[53] Lv, L., Yang, Z., Chen, K., Wang, C., Xiong, Y. 2D Layered double hydroxides for oxygen evolution reaction: From fundamental design to application. *Adv. Energy Mater.* **2019**, 9, 1803358.

[54] Chanda, D., Kwon, H., Meshesha, M.M., Gwon, J.S., Ju, M., Kim, K., Yang, B.L. Modulating interfacial electronic coupling of copper-mediated NiFe layered double hydroxide nanoprisms via structural engineering for efficient OER in wireless photovoltaic-coupled and anion exchange membrane water electrolysis. *Appl. Catal. B-Environ.* **2024**, 340, 123187.

[55] Zhai, Y., Ren, X., Sun, Y., Li, D., Wang, B., Liu, S. Synergistic effect of multiple vacancies to induce lattice oxygen redox in NiFe-layered double hydroxide OER catalysts. *Appl. Catal. B-Environ.* **2023**, 323, 122091.

[56] Chen, R., Hung, S.-F., Zhou, D., Gao, J., Yang, C., Tao, H., Yang, H.B., Zhang, L., Zhang, L., Xiong, Q., Chen, H.M., Liu, B. Layered structure causes bulk NiFe layered double hydroxide unstable in alkaline oxygen evolution reaction. *Adv. Mater.* **2019**, 31, 1903909.