Performance of high temperature phase-stable high entropy oxide \((\text{MgCuMnCoFe})\text{O}_x\) in catalytic wet air oxidation of chloroquine phosphate

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ABSTRACT

With the continuous spread of COVID-19, the water pollution problems caused by the abuse of chloroquine phosphate (CQP) as an antiviral drug have attracted wide attention. The cubic \(Fm\text{-}3m\) spinel high entropy oxide (HEO)—\((\text{MgCuMnCoFe})\text{O}_x\) was prepared by coprecipitation method as the catalytic wet air oxidation (CWAO) catalyst to treat CQP simulated wastewater. Through electron spin resonance (ESR) analysis, HEO will stimulate the production of superoxide radical \((-\text{O}_2^+\)) and hydroxyl radical \((-\text{OH})\) in the wet air oxidation (WAO) process, which accelerates the degradation and mineralization of CQP. Through response surface method (RSM) optimization, the optimal degradation conditions of CQP in CWAO were proposed: initial oxygen pressure of 15 bar, catalyst dosage of 1.4 g/L and temperature of 230 \(\text{°C}\). The advantages of HEO in CWAO were analyzed by principal component analysis (PCA). The degradation mechanism of CQP in CWAO by \((\text{MgCuMnCoFe})\text{O}_x\) were explored. This work provides a new idea for the rapid development of HEO in the field of environmental catalysis.

Introduction

Chloroquine phosphate (CQP), as one of the three antimalarial drugs (quinoline, artemisinin and pyrimidine), has been used in clinic for nearly 70 years [1]. At present, CQP is still the first choice to fight malaria [2]. Since February 2020, CQP is recommended as a clinically effective drug for the treatment of COVID-19 [3]. However, with the global spread of COVID-19, the over dosage of CQP may lead to a sharp increase in the resistance of water parasites, which poses a potential threat to the stability of water environment and the safety of human life [4]. In addition, as a kind of synthetic...
pharmaceutical and personal care products (PPCPs), CQP is difficult to be effectively and completely removed from the water environment [5]. In the face of this dilemma, it is imperative to explore an economic, efficient and environmentally friendly treatment technology to remove CQP.

As a member of advanced oxidation methods (AOPs) together with Fenton, like-Fenton, ozone oxidation, and photocatalysis, catalytic wet air oxidation (CWAO) is a significant part of refractory wastewater treatment process [6, 7]. The catalyst can affect the reaction temperature and pressure of wet air oxidation (WAO) system without reducing the treatment effect [8, 9]. For example, Serra-P’erez et al. [8] showed that in WAO, the maximum degradation rate of naproxen was 77% within 180 min at 160 °C, while CWAO system achieved this goal within 60 min at 110 °C. Now, CWAO catalysts mainly include homogeneous and heterogeneous catalysts [10]. Homogeneous catalyst has higher activity and faster reaction rate than heterogeneous catalyst, which is due to its more uniform contact with the reactant interface and easier exposure to the active sites of the reaction system [11, 12]. However, the homogeneous catalyst is difficult to recover, and the loss of heavy metals in the homogeneous catalyst with the reaction products is easy to cause secondary pollution, which means that the use of homogeneous catalyst in CWAO is tremendously limited [13]. Heterogeneous catalysts mainly include noble metals and non-noble metals [10]. Common noble metal elements include ruthenium (Ru), platinum (Pt), palladium (Pd), rhodium (Rh) and iridium (Ir). However, the high price of noble metals and large one-time investment limit their wide application in CWAO industry [14, 15]. Non-noble metal catalysts include Fe-based, Cu-based, Ce-based, Mo-based catalysts, polynuclear supported catalysts and poly-metallic oxate catalysts [16, 17]. In general, Fe-based and Cu-based catalysts are widely used in heterogeneous catalysis because they show great advantages over other metal-based catalysts, such as high activity, easy access and low toxicity[17]. Due to the limited catalytic performance of single-phase catalysts, heterogeneous catalysts are prone to serious dissolution of catalyst active components in the process of use due to the limitations of synthetic methods (commonly used coprecipitation and impregnation) [9]. This dissolution will cause the loss of catalyst, reduce its activity and slash its repeated service life. Therefore, the development of stable and efficient heterogeneous catalysts is the critical factor to solve the shortage of catalysts in CWAO.

High entropy oxide (HEO), first proposed by Rost et al. [18] in 2015, a kind of oxide with single crystal phase, in which five or more different metal cations with equal atomic ratio affect the phase stability of solid solution by accurately controlling the configuration entropy ($S_{\text{config}}$) of materials. Compared with the traditional doped transition metal oxides, the chemical composition and atoms distribution of HEOS are often disordered, which lead to excellent performance in thermodynamic, structural and kinetic properties [19]. Since their inception (at 2015), due to their unique structure and chemical properties, HEO has been widely studied in the fields of organic catalytic oxidation, electrode energy storage materials and electrocatalytic hydrogen production [20, 21]. For example, Liu et al. [22–24] and Fu et al. [25–27] confirmed the reversible lithium storage performance of HEO and the effect of entropy stability on the electrochemical performance of the battery, showing the high catalytic activity and good stability of HEO. HEO not only has the high catalytic performance of traditional heterogeneous catalysts, but also has a more stable phase structure than traditional heterogeneous catalysts due to the accurate regulation of $S_{\text{config}}$, which is not easy to lead to the rapid dissolution of active components of the catalyst and greatly prolong the service life of the catalyst. For instance, nano HEO synthesized by Sundara et al. [28] shows good material phase stability, which is reflected in 100% capacitance retention and coulomb efficiency after 15,000 charge discharge cycles.

HEO is widely used in the fields of electrode energy storage and electrocatalytic hydrogen production materials, but it has not been reported in CWAO, which is closely related to the time when HEO was proposed (first proposed in 2015). HEO not only has the advantages of high catalytic activity of CWAO traditional heterogeneous catalyst, but also its stable phase structure is not possessed by traditional heterogeneous catalyst [29], consequently, it has broad development prospects in the field of CWAO in future. In this study, the cubic $Fm-3m$ spinel HEO—(MgCuMnCoFe)O$_3$ was prepared by coprecipitation method as the CWAO catalyst, and the simulated CQP pollutant was taken as the target pollutant. Further, the rapid removal and mineralization performance indexes of CQP were investigate,
the catalytic performance and mechanism of (MgCuMnCoFe)Oₓ as CWAO catalyst were explored. It provided a certain experimental basis for the rapid development of HEO in CWAO.

Materials and methods

Reagents

Chloroquine phosphate (C₁₈H₂₆ClN₃·2H₂PO₄≥99%, CAS No: 50-63-5) was purchased from Sigma-Aldrich. Iron (II) sulfate heptahydrate (FeSO₄·7H₂O, CAS No: 7782-63-0), copper (II) sulfate pentahydrate (CuSO₄·5H₂O, CAS No: 7758-99-8), cobalt sulfate heptahydrate (CoSO₄·7H₂O, CAS No: 10026-24-1), magnesium sulfate heptahydrate (MgSO₄·7H₂O, CAS No: 7787-88-9), and manganese sulfate (MnSO₄·5H₂O, CAS No: 7775-87-7), Sodium carbonate decahydrate (Na₂CO₃·10H₂O) were purchased from Sinopharm Chemical Reagent Co., Ltd. Except for chloroquine phosphate, all of the chemicals used were of analytical grade.

Preparation of HEO

The coprecipitation method was used to prepare the precursor of type (MgCuMnCoFe)Oₓ high entropy oxide [30]. Firstly, each 0.01 mol metal (Mg, Cu, Mn, Co, Fe) salt and 0.07 mol Na₂CO₃·10H₂O were dissolved in 400 mL distilled water to obtain mixture A and B, respectively. Secondly, solution A was added to solution B at a rate of about 20 mL/min while magnetic stirring (900 r/min) was kept 30 min. Then, the gel like co precipitate was filtered, washed repeatedly with distilled water, and dried at 60°C for the night. The sample was labeled CP.

HEO was prepared by calcining the synthesized CP powder particles in a temperature programmed muffle furnace. Initially calcine at 450 °C for 1 h (heating rate = 10 °C/min) to completely gasify the water in the material. Then, it was sintered in a muffle furnace at 1050 °C at a heating rate of 10 °C/min in a static air atmosphere for 1.5 h. After cooling, take it out to obtain the formed HEO catalyst and store it at room temperature and vacuum.

Analytical method

The HEOs before and after reaction were characterized by X-ray diffractometry (XRD, Bruker AXS, D8 Advance) using copper-potassium alpha radiation (40 kV, 30 mA). The 2θ range was 10°-90°, and the scanning speed was 10° min⁻¹. The adsorption-desorption isotherm of nitrogen was determined using a micromeritics ASAP 2020 M + C analyzer at a liquid nitrogen temperature (77 K) over a relative pressure range of 0 to 1. The specific surface area and pore structure characteristics of the materials were analyzed using the Brunauer–Emmett–Teller ( BET) method and the Barrett-Joyner-Halenda (BJH) model. Scanning electron microscopy (SEM, HITACHI SU8010) equipped with an Oxford Instruments X-max spectrometer (EDS) for studying the chemical composition was used to observe the nanomaterial morphology and size. Magnetism was assessed using a magnetic measurement system (Squid-VSM, USA). An ultraviolet-visible spectrophotometer was used for rapid measurements of chloroquine phosphate concentration after 0.22 µm filter membrane was removed at different times [31]. A HACH DRB200 COD digester was used for the digestion of CQP water samples, and a HACH DR3900 visible spectrophotometer was used for the quantitative analysis of COD in water samples after digestion. The presence of reactive free radicals in CWAO process was directly detected by electron spin resonance (ESR) analysis. During CWAO, the samples were taken out of the reactor through the sampling valve after 5 and 30 min and quickly cooled to room temperature. Then, a mixture of 50 µL of sample and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was immediately tested on a Bruker ELEXSYS-II E 500 spectrometer (Germany), where the concentration of DMPO was 100 mM. For comparison, a control experiment was carried out in which there was no temperature rise to the system. Briefly, the chromatographic separation was performed on a Hypersil GOLD C18 column (2.1 × 100 mm, 1.9-µm particle size, Thermo Fisher Scientific). The gradient began with 5% methanol and 95% ultrapure water (v/v), increased to 95% methanol in 12 min, then returned to 5% methanol and held for 3 min. MS detection was acquired using a heated electrospray ionization source in positive ion mode, with a scan range of m/z 50–500, and the data were recorded in the data-dependent MS/MS (dd-MS2) mode.
CWAO experiments

A batch autoclave (YZMR-2250D, \(V_{max} = 250 \text{ mL}\)) was used as an evaluation device for the performance and stability of HEO catalyst in the catalytic degradation of chloroquine phosphate. The schematic diagram of evaluating catalyst was as shown in Fig. 1, and the numbers 1–5 in the figure represent: 1 oxygen cylinder, 2 mixing device, 3 CWAO reactor, 4 control device, 5 heating device. In addition to the above main components, CWAO reactor is also equipped with safety blasting valve, with blasting pressure of 200 bar and upper temperature control limit of 300 °C.

The steps of degradation of chloroquine phosphate by HEO in CWAO are as follows: firstly, add an appropriate amount of HEO catalyst and 150 mL 30 mg/L simulated CQP solution to the reactor lining. Secondly, seal the reactor, control the temperature at the set temperature with a temperature programmed instrument (the error is 0.1 °C), fill the reactor with a certain amount of oxygen, and start timing after the reactor temperature reaches the specified temperature. Take samples through the liquid phase sampling valve on the reactor. Finally, after the reactor is cooled to room temperature, release the gas in the reactor and open the reactor.

The response surface analysis experiment is designed and analyzed by the design software design expert 12. The reaction temperature, oxygen pressure and catalyst dosage in the CWAO of CQP were investigated to clarify the rapid removal and mineralization effect of CQP catalyzed by HEO. Box–Behnken (BBD) method was used to obtain the optimal reaction parameters under the condition of optimal catalytic performance, which provided experimental support for further revealing the catalytic mechanism of HEO catalyst for CQP in CWAO.

Results and discussion

Characterization of HEO catalyst

In order to understand the crystal structure of HEOs material—\((\text{MgCuMnCoFe})_x\)O, the HEO samples before and after the reaction were characterized by XRD in Fig. 2a. As shown by XRD, when the calcination temperature reached 1100 °C, the five components (Cu, Mn, Fe, Mg, Co) were completely transformed into a single solid solution because high treatment temperature is essential for the formation of high entropy metal oxides [32]. As shown in Fig. S1 and Table S1, the metal elements on the surface of \((\text{MgCuMnCoFe})_x\)O are not in equal proportion, which shows that although the precipitation method is fast and convenient, the process for preparing HEO needs to be further optimized. Previous studies have shown that entropy stable solid solutions can be formed when the calcination temperature is higher than 900 °C [33], and their combination will lead to the formation of single-phase \(Fm-3m\) solid solution [34]. Therefore, 1100°C was selected as the calcination temperature in this study. Meanwhile, compared with the previously reported XRD patterns [35] and standard cards (ICSD No 77-0010), the peaks were attributed to the (111), (220), (311), (222), (400), (422), (511), (440), (620), (533), (622), (444) and (642) planes of cubic \(Fm-3m\) spinel HEOs—\((\text{MgCuMnCoFe})_x\)O were observed. In order to further confirm the uniformity of spinel samples, EDS mapping was carried out (Fig. 2b). No tendency toward segregation or formation of other phases was visible.

Degradation of CQP by HEO in CWAO system

The prepared cubic \(Fm-3m\) spinel HEOs—\((\text{MgCuMnCoFe})_x\)O was applied to CWAO system to evaluate the degradation efficiency of CQP. As shown in Fig. 2c, HEO has little adsorption on CQP in water environment at room temperature. Compared with traditional adsorbents such as activated carbon \((926.1–1137.5 \text{ m}^2/\text{g})\) [36], the specific surface area of HEO is smaller \((0.14 \text{ m}^2/\text{g})\). At the same time, HEO, which is mainly macropore, has a large pore size and

![Figure 1 Schematic diagram of CWAO catalyst evaluation device.](image-url)
lacks adsorption sites for CQP. The degradation efficiencies of no HEO/no O₂, no HEO/O₂, HEO/no O₂, HEO/O₂ in wet oxidation systems. Experimental conditions: initial CQP concentration of 30 mg/L, reaction temperature of 200 °C, initial oxygen pressure of 10 bar and catalysts dosage of 1.0 g/L.

Response surface methods in optimization and mineralization experiment

Temperature, initial oxygen pressure and catalyst dosage are considered to be extremely important factors affecting the CWAO system [8, 37]. Therefore, the effects of temperature, initial oxygen pressure and HEO dosage on the CQP degradation efficiency of CWAO were studied. In this experiment, the response surface method (RSM) is carried out through the design software design expert 12. The experimental design and analysis are carried out by Box–Behnken method (BBD) [38]. The experimental design is shown in Table 1.

The results show that the response \( \frac{C}{C_0} \) conforms to the quadratic polynomial model listed in Formula (1). From Formula (1), it can be seen that the influence of temperature, initial oxygen pressure and HEO dosage on the CQP degradation efficiency of CWAO is not a simple linear relationship, but an interactive relationship. Therefore, a simple single factor analysis will cause error to the results.

\[
\frac{C}{C_0} = 0.1557 - 0.2334 A - 0.1874 B - 0.1103 C \\
+ 0.0730 AB + 0.0370 AC - 0.0645 BC \\
+ 0.1704 A^2 + 0.1690 B^2 + 0.1241 C^2
\]  

In the RSM analysis experiment on the degradation efficiency of CQP in CWAO by BBD (Table 2), the model F value is 189.26, \( p \) value < 0.0001, and lack of fit \( p \) value = 0.1432 > 0.05, indicating that the
regression model was at the very significant level without any lack of fit factor [37]. At the same time, the correction determination coefficient of the model $R_{adj}^2 = 0.9918$, indicating that more than 99.18% of the response values in the response surface quadratic model can be explained by the model, and the regression equation model has good fitting. Among them, the $F$ values of reaction temperature, oxygen pressure and HEO dosage are 691.14, 445.62 and 154.31, respectively, and the $p$ values are less than 0.0001, indicating that the effects of reaction temperature, oxygen pressure and HEO dosage on the response value are significant. In addition, from the value of $F$, the influence degree of various factors on the degradation efficiency of CQP in CWAO is: $A$—temperature $> B$—oxygen pressure $> C$—dosage of HEO. Among the interaction terms, the interaction terms of $AC$ and $BC$ have a significant effect on the response value ($p < 0.05$), indicating that the catalyst can prominently affect the degradation efficiency of CQ by temperature and oxygen pressure.

The response surface diagram can reflect the influence of the interaction of various factors on the response value and predict the optimal reaction conditions for CWAO to degrade CQP. Firstly, as can be seen from Fig. 3a, the comparison between the predicted and measured equilibrium adsorption capacity. Since the slope of the straight line is close to

| Run | Factor 1 | Factor 2 | Factor 3 | Response 1 |
|-----|---------|---------|---------|-----------|
|     | A: Temperature °C | B: Oxygen pressure bar | C: Dosage of HEO g/L | C/C0 |
| 1   | 250     | 10      | 2       | 0.126837 |
| 2   | 200     | 20      | 2       | 0.112697 |
| 3   | 200     | 0       | 0       | 0.65592  |
| 4   | 200     | 10      | 1       | 0.152955 |
| 5   | 150     | 0       | 1       | 0.95252  |
| 6   | 200     | 0       | 2       | 0.589932 |
| 7   | 250     | 0       | 1       | 0.43907  |
| 8   | 250     | 20      | 1       | 0.092354 |
| 9   | 200     | 20      | 0       | 0.436745 |
| 10  | 200     | 10      | 1       | 0.144822 |
| 11  | 150     | 10      | 2       | 0.527479 |
| 12  | 200     | 10      | 1       | 0.169222 |
| 13  | 150     | 10      | 0       | 0.847621 |
| 14  | 250     | 10      | 0       | 0.298838 |
| 15  | 150     | 20      | 1       | 0.496488 |

| Source     | Sum of Squares | df | Mean Square | $F$ value | $p$ value |
|------------|----------------|----|-------------|-----------|-----------|
| Model      | 1.07           | 9  | 0.1193      | 189.26    | < 0.0001  | Significant |
| A-Temperature | 0.4357    | 1  | 0.4357      | 691.14    | < 0.0001  |
| B-Oxygen pressure | 0.2809  | 1  | 0.2809      | 445.62    | < 0.0001  |
| C-Dosage of HEO | 0.0973   | 1  | 0.0973      | 154.31    | < 0.0001  |
| AB         | 0.0030        | 1  | 0.0030      | 4.74      | 0.0814    |
| AC         | 0.0055        | 1  | 0.0055      | 8.70      | 0.0319    |
| BC         | 0.0166        | 1  | 0.0166      | 26.41     | 0.0036    |
| $A^2$      | 0.1072        | 1  | 0.1072      | 170.07    | < 0.0001  |
| $B^2$      | 0.1055        | 1  | 0.1055      | 167.35    | < 0.0001  |
| $C^2$      | 0.0569        | 1  | 0.0569      | 90.23     | 0.0002    |
| Residual   | 0.0032        | 5  | 0.0006      |           |           |
| Lack of fit| 0.0028        | 3  | 0.0009      | 6.14      | 0.1432    | Not significant |
| Pure error | 0.0003        | 2  | 0.0002      |           |           |
| Cor total  | 1.08          | 14 |             |           |           |
1, the prediction result of the model is fine, which can be used to predict the best reaction conditions for the degradation efficiency of CQP in CWAO. Secondly, Fig. 3b–d showed the interaction of various factors on CQP degradation efficiency in CWAO. The degradation efficiency of CQP by WAO can be effectively improved by increasing the reaction temperature, initial oxygen pressure and HEO catalyst dose. However, too high temperature will not only increase energy consumption, but also aggravate the chemical corrosion of the reactor in the presence of oxygen. In order to effectively degrade CQP under mild conditions, adding HEO catalyst has become an effective solution. Therefore, through RSM optimization, the optimal degradation conditions of CQP in CWAO are as follows: initial oxygen pressure of 15 bar, catalyst dosage of 1.4 g/L and temperature of 230 °C.

At the same time, we also investigated the changes of CQP mineralization effect (COD/COD₀) during CWAO by RSM as shown in Tables S2–S3. According to Figure S1a–d, temperature, initial oxygen pressure and HEO dosage are still important factors affecting the mineralization effect of CQP in CWAO. In addition, under the condition of initial oxygen pressure of 15 bar, catalyst dosage of 1.4 g/L and temperature of 230 °C, the mineralization effect of CQP reaches the best, up to 0.25, indicating that CWAO can effectively mineralize CQP.

**Reactive radicals in the CWAO with HEO**

The existence of superoxide radical ($\text{O}_2^-$) and hydroxyl radical (OH) in CWAO was confirmed by quenching experiment and electron spin resonance (ESR). It is well known that $p$-benzoquinone ($p$-BQ)

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**Figure 3**

- a) Comparison of measured and predicted values for degradation efficiency of CQP by HEO/O₂ in wet oxidation systems.
- b–d) Response surface graphs of A temperature, B oxygen pressure and C dosage of HEO on CQP degradation by HEO/O₂ in wet oxidation systems.

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reacts specifically with superoxide radicals [39]. At the same time, the reaction rate of tert butyl alcohol (TBA) with hydroxyl radical is very fast ($k = 3.8-7.6 \times 10^7$ M$^{-1}$ S$^{-1}$) [40]. Therefore, p-BQ and TBA are often used as scavengers for quenching ·$\text{O}_2^-$ and ·$\text{OH}$. Firstly, 10 mM and 100 mM p-BQ and TBA were added to CWAO, respectively, to explore the existence of ·$\text{O}_2^-$ and ·$\text{OH}$ by investigating the degradation effect of CQP, as shown in Fig. 4a. 10 mM p-BQ and TBA significantly inhibited the degradation of CQP in CWAO. Meanwhile, when the concentration of BQ and TBA increased to 100 mM, the degradation of CQP in CWAO basically stagnated, indicating that the possible ·$\text{O}_2^-$ and ·$\text{OH}$ in CWAO are the fundamental active components for the degradation of CQP. Secondly, the existence of ·$\text{O}_2^-$ and ·$\text{OH}$ in CWAO was further confirmed by EPR, as shown in Fig. 4b, c. At room temperature (0 min), there is no peak in the reaction system, which means that temperature is the decisive condition for the production of free radicals. However, when the CWAO reaction lasted for 5 and 30 min, obvious 1:1:1 triplet signal peak and 1:2:2:1 quadruplet signal peak corresponding to ·$\text{O}_2^-$ and ·$\text{OH}$ were observed, which means that ·$\text{O}_2^-$ and ·$\text{OH}$ will be produced in CWAO, and the intensity will gradually strengthen until the end of the reaction [41].

**Figure 4** a Effects of scavengers on CQP degradation in CWAO system. Experimental conditions: initial CQP concentration of 30 mg/L, reaction temperature of 230 °C, initial oxygen pressure of 15 bar, catalysts dosage of 1.4 g/L. b ESR spectra of ·$\text{OH}$ generated in in CWAO system. c ESR spectra of ·$\text{O}_2^-$ generated in in CWAO system. d PCA for reaction parameters in catalytic wet and hydrogen peroxide oxidation (CWAO and CWPO).
PCA for reaction parameters in CWAO and CWPO

In order to highlight the advantages of HEO in CWAO, principal component analysis (PCA) is used to compare the seven conditions (hydrogen peroxide, pH, reaction time, temperature, oxygen pressure, dosage of catalyst and catalyst stability) of HEO and other catalysts in CWAO or catalytic hydrogen peroxide oxidation (CWPO) (Tables S5, S6 and Fig. S3). As shown in Fig. S3, the first two principal components (PC1 and PC2) can explain the property changes of 71.28% of the seven conditions. Firstly, the composition of CWAO (red spot in Fig. 4d) and CWPO (black spot in Fig. 4d) have obvious regional division. The distance (Bray–Curtis distance) of the red spot group to eigenvectors (reaction time, temperature, oxygen pressure and dosage of catalyst) is closer than that of black spot group along the coordinate axis (PC1, 51.27%), while the distance between black spot group and the eigenvectors (hydrogen peroxide, catalyst stability) is closer than that of red spot group, indicating that the addition of hydrogen peroxide makes CWAO and CWPO significantly different in reaction conditions. In addition, the purple dotted line circles the cross region of red and black spot group, which is highly dependent on the catalyst stability. For example, under the optimal conditions, under the first Zn-CNTs-Cu catalysis, the degradation effect of CWAO on 4-chlorphenol (4-CP) can reach 100%, but its fifth catalytic efficiency is reduced to 38.2% [42]. Similarly, Cu-UiO-66 catalyst showed excellent catalytic activity for the degradation of 4-CP in CWPO for the first time, and the conversion of 4-CP reached 98% in 20 min. However, the degradation efficiency of the used catalyst dropped sharply to about 20% in 20 min [43]. Secondly, as shown in Fig. 4d, except for HEO, other CWAO catalysts are distributed in the second or fourth quadrant. The distribution in the second quadrant shows that the catalyst is mainly dominated by the stability of the catalyst, indicating that the stability of the catalysts (Zn-CNTs-Cu [42] and 1x-Mo/Al2O3 membrane@300 [44]) in this quadrant are poor and cannot meet the long-term and efficient catalytic performance. At the same time, the catalysts (CeO2/CNT-M [45], 0.5%Ru@TiO2 [46] and Fe-CNF/ACB [47]) are distributed in the fourth quadrant are dominated by dosage of catalyst and reaction time, which means that although the catalyst has strong stability, the catalyst activity is low. It is necessary to increase the catalyst dosage or reaction time to improve the catalytic effect. Only HEO is in the first quadrant, indicating that the catalyst is mainly dominated by temperature and oxygen pressure, which means that the activity and stability of HEO catalyst are excellent, because it is not dominated by the two eigenvectors of catalyst stability and dosage of catalyst.

Degradation mechanism of CQP

It is well known that CWO catalysts require O2 to degrade organic compounds. Therefore, if CWAO is the main process leading to CQP degradation, the oxidation rate of CQP should be positively correlated with O2 concentration. As shown in Fig. 2c, the degradation efficiency of CQP in no HEO/no O2 system is about 6.3%, which is much lower than that in aerobic system such as no HEO/O2 (44.9%) and HEO/O2 (86.1%). The CWAO reaction mechanism proposed by Ma et al. [48, 49] can be used to explain degradation mechanism of CQP in CWAO system. According to the proposed model, Cu (II) in HEO catalyst is reduced to form Cu (I) (Formula 2) and further reacts with oxygen dissolved in aqueous solution (formula 3). As shown in Fig. S4a, the copper element in HEO contains not only Cu (II) but also Cu (I) before the reaction. After six CWAO reactions, Cu (I) gradually changes to Cu (II). At the same time, HEO gradually changes from the metal oxygen bond M–O on the surface before the reaction to OH after the reaction (Fig. S4b), which also indicates the reaction and formation of ·OH on the surface of HEO during CWAO reaction. Subsequently, H2O2 is generated by the reaction of ·O2– as an intermediate and H2O (Formula 4). Then ·OH may be produced during the decomposition of H2O2 by HEO (Formula 5). Finally, CQP molecule is decomposed by hydroxyl radical attack (formula 6). The results of quenching experiment and ESR strongly support that the decomposition of CQP occurs through free radical pathway.

\[
\text{RH} + \text{Cu(II)} \rightarrow \text{R} \cdot + \text{Cu(I)} + \text{H}^+ \\
\text{Cu(I)} + \text{O}_2 \rightarrow \text{Cu(II)} + \cdot \text{O}_2 \\
2 \cdot \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{OH}^- + \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{H}_2\text{O}_2 + \text{Cu(II)} \rightarrow 2 \cdot \text{OH} + \text{Cu(II)}
\]
\cdot\text{OH} + \text{CQP} \rightarrow \text{degradation products} \quad (6)

The degradation pathway of HEO to CQP in CWAO system was investigated under the optimum conditions (initial CQP concentration of 30 mg/L, reaction temperature of 230 °C, initial oxygen pressure of 15 bar, catalysts dosage of 1.4 g/L). After the reactor reaches the reaction temperature, the samples for 5, 10, 30 and 60 min are analyzed by liquid chromatography-mass spectrometry. Figure 5 shows the proposed degradation pathway of CQP in CWAO system based on LC–MS analysis (Fig. S3). The degradation of parent CQP \((m/z = 320.19)\) mainly proceeded from the substituents of the side chain, in which there are two primary pathways for CQP degradation \([50, 51]\). Specifically, under the action of active species (\(\cdot\text{O}_2^-\) and \(\cdot\text{OH}\)), CQP could first disconnect the carbon nitrogen bond on the side chain to form B \((m/z: 179.04)\), C \((m/z: 181.03)\) and D \((m/z: 124.04)\), respectively. B could form E \((m/z: 160.60)\), F \((m/z: 146.08)\) and G \((m/z: 93.03)\) through the process of dechlorination, decarbonization and denitrification, and further could generate H \((m/z: 99.51)\), I \((m/z: 90.51)\) and G \((m/z: 102.13)\). At the same time, the presence of free and non-free radical species were more likely to attack the side chain of CQP and generate K \((m/z: 146.08)\) and L \((m/z: 158.15)\) through dechlorination, hydroxylation and hydrogenation. L could be further decarburized, hydrogenated and carboxylated to form M \((m/z: 124.04)\), N \((m/z: 112.11)\) and O \((m/z: 116.93)\). M–O could be converted to H–G by oxidation, decarburization and hydroxylation. K and the resulting low molecular weight compounds

![Figure 5](image-url)

**Figure 5** a Proposed degradation mechanism and b proposed degradation pathways of CQP in CWAO system.
such as H–G were finally mineralized into H$_2$O, CO$_2$ and NO$_3^-$, and NH$_4^+$.

**Catalyst stability and recyclability**

In order to evaluate the stability of HEO in the CWAO system of CQP, six consecutive experiments were carried out under the same conditions. At the end of each experiment, the used HEO catalyst was separated by magnet, washed three times with distilled water, and then dried in an oven at 60 °C for 2 h before use. After six cycle tests, the specific surface area of HEO increased by 1.55 times compared with that before the reaction, as shown in Table S4. Meanwhile, some HEO were broken during the stirring process in CWAO system, and more abundant active sites in HEO were exposed (Fig. 6a), so that the HEO catalyst can have more contact area with CQP. Since the entropy contribution of Gibbs free energy change is related to temperature ($\Delta G = \Delta H - T\Delta S$), higher temperature will lead to more disorder of multicomponent metal cations, thus increasing the stability of HEO without structural collapse or metal ion aggregation at high temperature [52, 53]. As a result (Fig. 6b), the degradation efficiency of CQP by HEO increased instead of decreased (from 86.5 to 90.7%), which shows that HEO has good thermal stability in CWAO system. Similarly, the room temperature hysteresis curve of HEO before and after reaction was measured by VSM to evaluate the recoverability of HEO in the CWAO system of CQP (Fig. 6c), which showed that they had room temperature ferromagnetism. Furthermore, the saturation magnetization of HEOs before and after six reactions are 20.20 and 17.93 emu/g, respectively. Some studies have shown that these magnetic materials can be separated from the solution under the action of external magnetic field when the saturation change is related to temperature ($\Delta G = \Delta H - T\Delta S$), higher temperature will lead to more disorder of multicomponent metal cations, thus increasing the stability of HEO without structural collapse or metal ion aggregation at high temperature [52, 53]. As a result (Fig. 6b), the degradation efficiency of CQP by HEO increased instead of decreased (from 86.5 to 90.7%), which shows that HEO has good thermal stability in CWAO system. Similarly, the room temperature hysteresis curve of HEO before and after reaction was measured by VSM to evaluate the recoverability of HEO in the CWAO system of CQP (Fig. 6c), which showed that they had room temperature ferromagnetism. Furthermore, the saturation magnetization of HEOs before and after six reactions are 20.20 and 17.93 emu/g, respectively. Some studies have shown that these magnetic materials can be separated from the solution under the action of external magnetic field when the saturation change is related to temperature ($\Delta G = \Delta H - T\Delta S$), higher temperature will lead to more disorder of multicomponent metal cations, thus increasing the stability of HEO without structural collapse or metal ion aggregation at high temperature [52, 53]. As a result (Fig. 6b), the degradation efficiency of CQP by HEO increased instead of decreased (from 86.5 to 90.7%), which shows that HEO has good thermal stability in CWAO system.

**Figure 6**

a Catalyst stability and reusability of HEO in CWAO system. Experimental conditions: initial CQP concentration of 30 mg/L, reaction temperature of 200 °C, initial oxygen pressure of 10 bar, catalysts dosage of 1.0 g/L. b SEM image of the fracture surface of HEO after six reactions in the CWAO system. c Room-temperature magnetization curve of HEO and HEO after six reactions in the CWAO system. d Simple magnetic experiment photos of HEO after six reactions in the CWAO system.
magnetization of magnetic materials is greater than 16.3 emu/g. In addition, the almost zero coercivity and remanence prove the superparamagnetism of the composite, which makes the magnetic properties of HEO conducive to the separation from the solution by using the external magnetic field and avoid aggregation after removing the external magnetic field. This shows that the recoverability of HEO is excellent, and it can be recovered by simple magnetic absorption (Fig. 6d).

Conclusion

The cubic $Fm-3m$ spinel high entropy oxide (HEO)—(MgCuMnCoFe)O$_x$ is used as a valuable attempt for catalytic wet air oxidation (CWAO) to degrade CQP simulated wastewater. Under anaerobic and aerobic conditions, the degradation efficiency of CQP in HEO system was 34.6% and 41.2% higher than that without HEO system. The quenching experiment and electron spin resonance (ESR) confirmed that the superoxide radical ($\cdot$O$_2^-$) and hydroxyl radical (⋅OH) in CWAO were the active substances for the degradation of CQP. Through PAC analysis, HEO is mainly controlled by temperature and oxygen pressure in CWAO system, which means that the activity and stability of HEO catalyst are excellent, because it is not controlled by the two eigenvectors of catalyst stability and catalyst dosage. Dechlorination, decarbonization, denitrification and hydroxylation were the main paths in the degradation and mineralization of CQP in CWAO system. After six consecutive reactions, the catalytic efficiency of HEO for CQP increased instead of decreased and the saturation magnetization with no obvious change, which showed that HEO had good thermal stability and excellent recovery performance in CWAO system.

Declarations

Conflict of 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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References

[1] Hart CW, Naunton RF (1964) The ototoxicity of chloroquine phosphate. Arch Otalaryngol 80:407–412
[2] Valecha N, Savargaonkar D, Srivastava B, Rao BHK, Tripathi SK, Gogtay N, Kochar SK, Kumar NBV, Rajadhyaksha GC, Lakhani JD, Solanki BB, Jalali RK, Arora S, Roy A, Saha N, Iyer SS, Sharma P, Anvikar AR (2016) Comparison of the safety and efficacy of fixed-dose combination of arterolane maleate and piperaquine phosphate with chloroquine in acute, uncomplicated Plasmodium vivax malaria: a phase III, multicentric, open-label study. Malar J 15:42
[3] Cui C, Zhang M, Yao X, Tu S, Hou Z, Jie En VS, Xiang X, Lin J, Cai T, Shen N, Song C, Qiao J, Zhang S, Li H, Liu D (2020) Dose selection of chloroquine phosphate for treatment of COVID-19 based on a physiologically based pharmacokinetic model. Acta Pharm Sin B 10:1216–1227
[4] Horn S, Vogt B, Pieters R, Bouwman H, Bezuindenhout C (2020) Impact of potential COVID-19 treatment on South African water sources already threatened by pharmaceutical pollution. Environ Toxicol Chem 39:1305–1306
[5] Coelho AS, Chagas CEP, de Pádua RM, Pianetti GA, Fernandes C (2017) A comprehensive stability-indicating HPLC method for determination of chloroquine in active pharmaceutical ingredient and tablets: identification of oxidation impurities. J Pharm Biomed Anal 145:248–254
[6] Makatsa TJ, Baloyi J, Ntho T, Masuku CM (2021) Catalytic wet air oxidation of phenol: review of the reaction mechanism, kinetics, and CFD modeling. Crit Rev Environ Sci Technol 51:1891–1923
[7] Kim K-H, Ihm S-K (2011) Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: a review. J Hazard Mater 186:16–34
[8] Serra-Pérez E, Álvarez-Torrellas S, IsmaelÁgueda V, Larriba M, Ovejero G, García J (2021) Effective removal of naproxen from aqueous solutions by CWAO process using noble metals supported on carbon nanospheres catalysts. Separ Purif Technol 259:118084
[9] Luan M, Jing G, Xu X, Hou B, Wang Y, Meng D, Review A (2013) Wet oxidation and catalytic wet oxidation of industrial wastewater. Rec Patents Chem Eng 6:79–86
[10] Li D-B, Wang D, Jiang Z-S (2020) Catalytic wet air oxidation of sewage sludge: a review. Curr Organocatal 7:199–211
[11] Du K, He M, Lian M, Li Y (2016) Catalytic wet air oxidation treatment of oily wastewaters. Chem Technol Fuels Oils 52:85–89
[12] Collado S, Laca A, Díaz M (2010) Catalytic wet oxidation of thiocyanate with homogeneous copper(II) sulphate catalyst. J Hazard Mater 177:183–189
[13] Sushma M, Kumari AK, Saroha (2018) Performance of various catalysts on treatment of refractory pollutants in industrial wastewater by catalytic wet air oxidation: a review. J Environ Manag 228:169–188

[14] Bhargava SK, Tardio J, Prasad J, Föger K, Akolekar DB, Grocott SC (2006) Wet oxidation and catalytic wet oxidation. Ind Eng Chem Res 45:1221–1258

[15] Sushma M, Saroha (2019) Effectiveness of fresh and used supported noble and non-noble metal based catalysts for industrial organic raffinate oxidation by catalytic wet air oxidation at low operating parameters. J Environ Chem Eng 7:103382

[16] Yadav BR, Garg A (2014) Catalytic wet oxidation of ferulic acid (a lignin model compound) in the presence of non-noble metal based catalysts at mild conditions. Chem Eng J 252:185–193

[17] He S (2019) Catalytic wet oxidation: process and catalyst development and the application perspective. In: Catalysis, pp 37–71

[18] Rost CM, Sachet E, Borman T, Moballegh A, Dickey EC, Hou D, Jones JL, Curtarolo S, Maria J-P (2015) Entropy-stabilized oxides. Nat Commun 6:8485

[19] Musicò BL, Gilbert D, Ward TZ, Page K, George E, Yan J, Mandrus D, Keppens V (2020) The emergent field of high entropy oxides: design, prospects, challenges, and opportunities for tailoring material properties. APL Mater 8:040912

[20] Sun Y, Dai S (2021) High-entropy materials for catalysis: a new frontier. Sci Adv 7:eabg1600

[21] Albedwawi SH, AlJaberi A, Haidemenopoulos GN, Poly- 
schronopoulou K (2021) High entropy oxides-exploring a paradigm of promising catalysts: a review. Mater Des 202:109534

[22] Duan C, Li X, Wang D, Wang Z, Sun H, Zheng R, Liu Y (2022) Nanosized high entropy spinel oxide (FeCo-NiCrMn)3O4 as a highly active and ultra-stable electrocatalyst for the oxygen evolution reaction. Sustain Energy Fuels 6:1479–1488

[23] Tian K-H, Duan C-Q, Ma Q, Li X-L, Wang Z-Y, Sun H-Y, Luo S-H, Wang D, Liu Y-G (2022) High-entropy chemistry stabilizing spinel oxide (CoNiZnMnLi)3O4 (X = Fe, Cr) for high-performance anode of Li-ion batteries. Rare Met 41:1265–1275

[24] Jiang S, Tian K, Li X, Duan C, Wang D, Wang Z, Sun H, Zheng R, Liu Y (2022) Amorphous High-entropy Non-precious metal oxides with surface reconstruction toward highly efficient and durable catalyst for oxygen evolution reaction. J Colloid Interface Sci 606:635–644

[25] Wang X, Li X, Fan H, Miao M, Zhang Y, Guo W, Fu Y (2022) Advances of entropy-stabilized homologous compounds for electrochemical energy storage. J Energy Chem 67:276–289

[26] Wang X, Guo W, Fu Y (2021) High-entropy alloys: emerging materials for advanced functional applications. J Mater Chem A 9:663–701

[27] Wang X, Peng Q, Zhang X, Lv X, Wang X, Fu Y (2022) Carbonaceous-assisted confinement synthesis of refractory high-entropy alloy nanocomposites and their application for seawater electrolysis. J Colloid Interface Sci 607:1580–1588

[28] Lal MS, Sundara R (2019) High Entropy oxides—a cost-effective catalyst for the growth of high yield carbon nanotubes and their energy applications. ACS Appl Mater Interfaces 11:30846–30857

[29] Ma Y, Ma Y, Wang Q, Schweidler S, Botros M, Fu T, Hahn H, Brezesinski T, Breitung B (2021) High-entropy energy materials: challenges and new opportunities. Energy Environ Sci 14:2883–2905

[30] Biesuz M, Spiridigliozzi L, Dell’Agli G, Bortolotti M, Sglavo VM (2018) Synthesis and sintering of (Mg Co, Ni, Cu, Zn)O entropy-stabilized oxides obtained by wet chemical methods. J Mater Sci 53:8074–8085

[31] Midassi S, Bedoui A, Bensalah N (2020) Efficient degradation of chloroquine drug by electro-Fenton oxidation: effects of operating conditions and degradation mechanism. Chemosphere 260:127558

[32] Akrami S, Edalati P, Fuji M, Edalati K (2021) High-entropy ceramics: review of principles, production and applications. Mater Sci Eng R Rep 146:100644

[33] Chen H, Sun Y, Yang S, Wang H, Dmowski W, Egami T, Dai S (2020) Self-regenerative noble metal catalysts supported on high-entropy oxides. Chem Commun 56:15056–15059

[34] Gu K, Wang D, Xie C, Wang T, Huang G, Liu Y, Zou Y, Tao L, Wang S (2021) Defect-rich high-entropy oxide nanosheets for efficient 5-hydroxymethylfurfural electrooxidation. Angew Chem Int Ed 60:20253–20258

[35] Deng C, Wu P, Zhu L, He J, Tao D, Lu L, He M, Hua M, Li H, Zhu W (2020) High-entropy oxide stabilized molybdenum oxide via high temperature for deep oxidative desulphurization. Appl Mater Today 20:100680

[36] Liu Y, Wang C, Sui Z, Zou D (2018) Degradation of chlortetracycline using nano micro-electrolysis materials with loading copper. Sep Purif Technol 203:29–35

[37] Isgoren M, Gengec E, Veli S, Hassandoost R, Khataee A (2021) The used automobile catalytic converter as an efficient catalyst for removal of malathion through wet air oxidation process. Int J Hydrogen Energy. https://doi.org/10.1016/j.ijhydene.2021.08.020

[38] Ordoñez-Ordoñez A, Revelo-Romo DM, García-Mora AM, Hidalgo-Troya A, Galeano L-A (2019) MS2 coliphage inactivation by Al/Fe PILC-activated catalytic wet peroxide
oxidation: multiresponse statistical optimization. Heliyon 5:e01892
[39] Peng X, Wu J, Zhao Z, Wang X, Dai H, Wei Y, Xu G, Hu F (2022) Activation of peroxymonosulfate by single atom Co-N-C catalysts for high-efficient removal of chloroquine phosphate via non-radical pathways: electron-transfer mechanism. Chem Eng J 429:132245
[40] Liao X, Shen L, Jiang Z, Gao M, Qiu Y, Qi H, Chen C (2021) NDMA formation during ozonation of metformin: roles of ozone and hydroxyl radicals. Sci Total Environ 796:149010
[41] Yu H, Liu Y, Xu M, Cong S, Liu M, Zou D (2021) Hydroxylamine facilitated heterogeneous fenton-like reaction by nano micro-electrolysis material for rhodamine B degradation. J Clean Prod 316:128136
[42] Fu T, Gong X, Guo J, Yang Z, Liu Y (2021) Zn-CNTs-Cu catalytic in-situ generation of H2O2 for efficient catalytic wet peroxide oxidation of high-concentration 4-chlorophenol. J Hazard Mater 401:123392
[43] Pan Y, Jiang S, Xiong W, Liu D, Li M, He B, Fan X, Luo D (2020) Supported CuO catalysts on metal-organic framework (Cu-Uio-66) for efficient catalytic wet peroxide oxidation of 4-chlorophenol in wastewater. Microporous Mesoporous Mater 291:109703
[44] Bao Y, Lee WJ, Wang P, Xing J, Liang YN, Lim T-T, Hu X (2021) A novel molybdenum-based nanocrystal decorated ceramic membrane for organics degradation via catalytic wet air oxidation (CWAO) at ambient conditions. Catal Today 364:276–284
[45] Ali S, Xiong W, Liao Z, Aslam MJ, Zhou C, Seong KK, Zhang P, Zhang N, Zheng J, Fu J, Chen B (2021) Noble metal free catalyst with High activity and stability for catalytic wet air oxidation of N, N-dimethylformamide. Appl Catal A 620:118172
[46] Gai H, Liu X, Feng B, Gai C, Huang T, Xiao M, Song H (2021) An alternative scheme of biological removal of ammonia nitrogen from wastewater–highly dispersed Ru cluster @mesoporous TiO2 for the catalytic wet air oxidation of low-concentration ammonia. Chem Eng J 407:127082
[47] Gupta P, Verma N (2021) Evaluation of degradation and mineralization of glyphosate pollutant in wastewater using catalytic wet air oxidation over Fe-dispersed carbon nanofibrous beads. Chem Eng J 417:128029
[48] Srikhao A, Smith SM (2013) Preparation of Cu2(OH)3NO3/ZnO, a novel catalyst for methyl orange oxidation under ambient conditions. Appl Catal B 130–131:84–92
[49] Ma H, Zhuo Q, Wang B (2007) Characteristics of CuO—MoO3—P2O5 catalyst and its catalytic wet oxidation (CWO) of dye wastewater under extremely mild conditions. Environ Sci Technol 41:7491–7496
[50] Yi X-H, Ji H, Wang C-C, Li Y, Li Y-H, Zhao C, Wang A, Fu H, Wang P, Zhao X, Liu W (2021) Photocatalysis-activated SR-AOP over PdINH/MIL-88A(Fe) composites for boosted chloroquine phosphate degradation: performance, mechanism, pathway and DFT calculations. Appl Catal B 293:120229
[51] Dan J, Rao P, Wang Q, Zhang M, He Z, Zhang W, Gao N, Deng J, Chen J (2022) Catalytic performance of wrapped CoO by MgO in oxidative degradation of chloroquine phosphate with peroxymonosulfate. Appl Surf Sci 573:151430
[52] Chen H, Jie K, Jafeta CJ, Yang Z, Yao S, Liu M, Zhang Z, Liu J, Chi M, Fu J, Dai S (2020) An ultrastable heterostructured oxide catalyst based on high-entropy materials: a new strategy toward catalyst stabilization via synergistic interfacial interaction. Appl Catal B 276:119155
[53] Gao Y, Liu Y, Yu H, Zou D (2022) High-entropy oxides for catalysis: status and perspectives. Appl Catal A 631:118478

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