NJC

PAPER



Cite this: New J. Chem., 2021, 45, 2167

Received 27th October 2020, Accepted 23rd December 2020

DOI: 10.1039/d0nj05271j

rsc.li/njc

1. Introduction

With the rapid development in industrialization, various wastewaters with concentrated organic pollutants and inorganic salts are produced daily. These wastewaters are usually hazardous and toxic, and thus have to be disposed before discharge and recycle utilization.^{1,2} However, the high salinity makes it impossible to degrade by conventional biological degradation (anaerobic and aerobic digestions) because of the bacteriostasis of inorganic salts.³⁻⁵ Besides, some of the organic pollutants in wastewater are usually recalcitrant to oxidation and decomposition.^{2,6,7} Taking phenol as an example, it is not only hazardous and toxic, but also frequently existing in industrial wastewaters such as the process wastewaters from benzene oxidation and maleic anhydride synthesis. Phenol is also an intermediate product during the oxidation of aromatic compounds.^{8,9} For these reasons, phenol-containing wastewater treatment has attracted much attention for the past few decades.^{7,10–12}

High-efficiency catalytic wet air oxidation of high salinity phenolic wastewater under atmospheric pressure in molten salt hydrate media[†]

Hongzi Tan, (10) ‡ Shuai Wang, ‡ Jinghua Wang, Feng Song, Xiuyu Sun, Rongrong Zhao, Yuan Zhang and Hongyou Cui (10) *

An improved catalytic wet air oxidation (CWAO) process for high salinity phenolic wastewater is reported for the first time by using molten salt hydrates (MSHs) as reaction media. One feature of such a process is that it allows the operation to be conducted at atmospheric pressure owing to the temperatureincreasing effect of MSHs. Another feature is that the inorganic salts in phenolic wastewater can be separated readily, taking advantage of the common-ion salting-out effect between inorganic salts and MSHs. Continuous catalytic oxidation degradation of the simulated high salinity phenolic wastewater demonstrated that more than 92% of phenol can be removed with chemical oxygen demand (COD) as high as 85% after reacting in CaCl₂·3H₂O medium at 150 °C with air as an oxidant. Meanwhile, the desalination efficiency of NaCl in continuous operation could reach up to 100%. It was found that CeCl₃ was an excellent catalyst for CWAO of phenol. XPS and UV-vis spectral characterization as well as radical scavenger experiments proved that [•OH/Ce⁴⁺] was responsible for the synergistic catalytic degradation mechanism of phenol. Current work not only paves the way for developing a highefficiency CWAO technology for concentrated organic wastewaters with high salinity, but also helps to better understand MSHs as reaction media.

> Advanced oxidation processes (AOPs) have been testified to be very effective to remove the organic pollutants in wastewater because the strongly oxidative hydroxyl radical (•OH) can be generated in these processes.^{13–15} Various AOP techniques have been developed, such as photochemical oxidation,¹⁶ phonooxidation,17 chemical electrochemical oxidation.18 ozonation,¹⁹⁻²¹ Fenton method,^{11,22} etc. In most of these developed AOP techniques, hydrogen peroxide and ozone are indispensably used as the oxidants. The high cost of these oxidants makes it economically unacceptable for the concentrated organic wastewater treatment. Although oxygen and air can sometimes be used as the oxidants in photochemical and electrochemical oxidation processes, the efficiency in light or electricity utilization is still a challenging issue.

> Catalytic wet air oxidation (CWAO) also belongs to the AOP family, which is particularly suitable for wastewater with high chemical oxygen demand (COD) (COD = 104–105 mg L⁻¹) because of the cheapness of air. In comparison with other AOP techniques, the operation cost of CWAO is usually much lower. In the CWAO process, large molecular weight organic pollutants are either oxidized partially into lower molecular weight organic compounds or completely into CO₂ and $H_2O.^{23,24}$ E. Castillejos-López *et al.* reported that phenol could be completely removed after reacting at 140 °C and 2.0 MPa



View Article Online

School of Chemistry & Chemical Engineering, Shandong University of Technology, Zibo, Shandong, 255049, P. R. China. E-mail: cuihy@sdut.edu.cn

 [‡] Electronic supplementary information (ESI) available: Theoretical and experimental desalination efficiency calculation, catalyst stability recycles and SEM-mapping images. See DOI: 10.1039/d0nj05271j
‡ These two authors contributed equally.

Paper

pressure with supported Ru nanoparticles as catalyst.²⁵ P. Albin et al. also investigated the CWAO of aqueous solutions with formic acid, acetic acid and phenol in a continuous flow trickle-bed reactor over Ru/TiO2 catalyst. In terms of total organic carbon (TOC), formic acid can be removed completely at 110 °C, while removal of acetic acid and phenol needs relatively higher temperatures (230 °C and 210 °C) and 10 bar oxygen partial pressure, affording TOC abatements of 95% and 99%, respectively.²⁶ Moreover, A. Garg and A. Mishra investigated the degradation of phenol at 120 °C and 0.5 MPa pressure using CuSO₄ as the catalyst, obtaining removal rates of phenol and TOC of 90% and 67%, respectively.²⁷ Unfortunately, a traditional CWAO process must be manipulated at high temperature (150-320 °C) and high pressure (2-15 MPa). In spite of the highefficiency in removing organic pollutants, the harsh operation conditions (high temperature and high pressure) tremendously increase the facility investment. In a homogeneous catalysis process, catalyst recycling is very difficult, while in a heterogeneous catalysis process, the leaching of active components is unavoidable due to the harsh operation conditions, leading to quick catalyst deactivation and secondary contamination of the wastewater being treated.^{28,29} When some corrosive inorganic salts like NaCl, KCl and NH4Cl exist in the wastewater or can be formed such as in the oxidation degradation of wastewater with chlorinated pollutants, these salts significantly accelerate equipment corrosion, deposition and clogging of the pipelines or reactors, and thus augment maintenance cost. Therefore, it is urgent to explore an innovative CWAO process to degrade phenolic wastewater in particular those containing concentrated inorganic salts.

It has been well-known that some molten salt hydrates (MSHs) have a temperature-increasing effect and thus can act as reaction media, enabling the CWAO process to be operated under high temperature but low pressure conditions. In addition, the common-ion salting-out effect of MSHs makes it feasible to salt out the inorganic salts that have identical cations or anions to those in MSHs. For these reasons, MSHs are expected to act as excellent reaction media for deep catalytic oxidation degradation of organic pollutants using air as an oxidant without operating under high pressure. As such, materials such as glass, quartz, ceramics and silicon carbide, which possess excellent corrosion resistance but low pressure tolerance, can be used to manufacture the catalytic oxidation reactor and equipment, significantly reducing the investment and operation costs. To the best of our knowledge, little research has been reported using MSHs as reaction media for catalytic oxidation of organic wastewater.

Herein we investigate the feasibility of the CWAO process for treating high salinity phenolic wastewater by use of $CaCl_2 \cdot 3H_2O$ as the reaction medium. Saturated NaCl solution containing phenol (30 g L⁻¹) was used as simulated high salinity phenolic wastewater. The desalination efficiency of NaCl in the trihydrate of CaCl₂ at various temperatures was examined. Several metal chlorides (Mn²⁺, Fe³⁺, Co²⁺, Cu²⁺, and Ce³⁺) were evaluated as the homogeneous catalysts in batch operation. A continuous operation coupling desalination with catalytic oxidation of the

simulated high salinity phenolic wastewater was also carried out. Based on the characterization of XPS and UV-vis spectra as well as radical scavenger experiments, the synergistic catalytic degradation mechanism of phenol was reasonably speculated.

2. Experimental section

2.1 Catalytic evaluation

1

2.1.1 Desalination in batch operation. To salt out the dissolved NaCl, anhydrous CaCl2 was introduced into the saturated NaCl solution, as illustrated in Scheme 1. Firstly, saturated NaCl solution at different temperatures was prepared and simulated high salinity wastewater with m_1 g NaCl per 100 mL H₂O. Then, a slight excess of CaCl₂ was added to obtain a absolutely saturated CaCl₂ solution. With the introduction of CaCl₂, dissolved NaCl was salted out gradually because the ion product of NaCl is lower than that of CaCl₂ in aqueous solution. The precipitate mixture including the salted-out NaCl and the undissolved CaCl₂ were separated by filtration, dried, weighed $(m_2 \text{ g})$, and further completely dissolved in pure water, to which Na₂CO₃ was added so as to completely convert CaCl₂ to the CaCO₃ precipitate. Finally, the CaCO₃ precipitate was separated by filtration followed by drying and weighing $(m_3 g)$. In this way, the desalination efficiency of NaCl can be calculated according to the following equation:

Desalination efficiency (%) =
$$\frac{m_2 - \frac{W_{CaCl_2}}{W_{CaCO_3}}m_3}{m_1} \times 100\%$$

where W_{CaCl2} and W_{CaCO3} are the molecular weights of CaCl₂ and CaCO₃, respectively.

2.1.2 Catalytic oxidation in batch operation. The CWAO process of phenolic wastewater in trihydrate of $CaCl_2$ was performed in a three-necked flask with a reflux condenser. In a typical test, 1.5 mol of $CaCl_2$ and 80 mL of phenol solution (30 g L^{-1}) were mixed in a flask, corresponding to a $CaCl_2/H_2O$ molar ratio equal to 1:3. Upon reaching the desired reaction temperature, 0.01 mol of $CeCl_3$ catalyst was added and compressed air was introduced continuously in a bubbling mode. During the reaction, the liquid phase was sampled at intervals. To determine the reaction products, the samples were extracted



 $\label{eq:Scheme 1} \begin{array}{l} \mbox{Diagram of the desalination process of NaCl owing to the common-ion salting-out effect of anhydrous CaCl_2. \end{array}$

with ethyl acetate before analysis by gas chromatography (GC) and high performance liquid chromatography (HPLC).

To assess the reusability of the MSH medium and $CeCl_3$ catalyst, five cycle experiments were conducted. After one run of batch degradation, an equivalent of phenol was added directly into the reaction medium without any other treatment and the next run was performed.

2.1.3 Desalination and catalytic oxidation in continuous operation. The coupling of desalination with catalytic oxidation for high salinity phenolic wastewater in trihydrate of CaCl₂ was performed on a home-made continuous operation setup, as illustrated in Scheme 2. The setup is mainly composed of a quartz reactor (40 mm inner diameter and 600 mm length), an air compressor, a centrifuge and a condenser. To start the operation, 0.01 mol of CeCl₃ catalyst, 1.5 mol of anhydrous CaCl2 and 80 mL of saturated NaCl solution containing phenol (30 g L^{-1}) were charged into the reactor. After the mixture was heated to the reaction temperature, compressed air was introduced from the bottom of the reactor in a bubbling mode. During the reaction, the wastewater was continuously pumped into the reactor undergoing oxidation and then evaporated out from the reactor so as to keep the liquid phase constant. The vapor effluent from the reactor was cooled through a condenser and collected in a condensate trap. To obviate the accumulation of the NaCl precipitate in the reaction medium, the reaction solution was centrifuged and the supernatant was pumped back to the reactor continuously. After the system reached a steady operation, the condensate was sampled for analysis purpose.

2.2 Analytic method

astewaters

Quantitative determination of the organic compounds was performed on a GC (Agilent 6890) equipped with an Innowax 199091N-136 column (60 m \times 0.25 mm \times 0.25 µm) and a flame ionization detector. Carrier gas: 1 mL min⁻¹ N₂; column temperature was programmed: from 120 °C to 210 °C with a ramp rate of 5 °C min⁻¹. A gas chromatograph-mass spectrometer (Agilent, GC 6890-MS 5973N) was employed to identify the intermediate products.

Quantitative determination of the intermediate products with high boiling point or poor thermostability (such as maleic

www-

thermodetecto



acid and oxalic acid) was conducted on a HPLC (Waters e2695) equipped with a Rezex RHM-Monosaccharide column (300 mm \times 7.8 mm \times 5 μm) and a Waters 2489 ultraviolet detector. Column temperature: 30 °C; mobile phase: 5 mM H₂SO₄ solution with a flow velocity of 0.5 mL min⁻¹.

COD measurement of liquid samples was analyzed on a DR1010 benchtop spectrophotometer (HACH) according to the standard methods for the examination of water and wastewater in China (HJ/T 399-2007).

The phenol removal rate (R_{phenol}) and COD removal rate (R_{COD}) were calculated as follows:

$$R_{\text{phenol}} (\%) = \frac{C_{\text{ph}}^{\text{i}} - C_{\text{ph}}^{\text{f}}}{C_{\text{ph}}^{\text{i}}} \times 100\%$$
$$R_{\text{COD}} (\%) = \frac{C_{\text{COD}}^{\text{i}} - C_{\text{COD}}^{\text{f}}}{C_{\text{COD}}^{\text{i}}} \times 100\%$$

where $C_{\rm ph}^{i}$ and $C_{\rm COD}^{i}$ are the initial values of phenol concentration and COD, respectively; and $C_{\rm ph}^{f}$ and $C_{\rm COD}^{f}$ are the final values of phenol concentration and COD, respectively.

3. Results and discussion

1

MSH is referred to as a concentrated liquid solution of inorganic salt, the concentration of which is determined by the number of crystal waters coordinated to the salt cation.³⁰ In a perfect MSH, all water molecules serving as crystal waters are tightly bound to the inner coordination sphere of the salt cation, leaving the salt anion naked in the medium.^{30–33} Because of the strong interaction between crystal waters and inorganic salt cations, the boiling point of MSHs is much higher than that of pure water at identical pressure. This phenomenon is known as the temperature-increasing effect.

The temperature-increasing effect of MSHs strongly depends on the properties of inorganic salts and the number of coordinated crystal waters. To sieve a suitable MSH, four common metal chlorides with different numbers of crystal waters were examined. As can be seen from Fig. 1, with decreasing number of coordinated crystal waters from 6 to 1, the boiling points of LiCl, CaCl₂, ZnCl₂ and CuCl₂ increased remarkably. For example, the boiling point of ZnCl₂·6H₂O is about 120 °C, while it can be enhanced to about 180 °C for ZnCl₂·H₂O in a normal atmosphere. Evidently, CaCl₂ and CuCl₂ demonstrated much higher boiling points as compared to LiCl and ZnCl₂. In view of the economy, ease in availability, safety and low toxicity, trihydrate of CaCl₂ was chosen as the optimal MSH medium.

Owing to the common-ion effect in trihydrate of CaCl₂, NaCl is expectedly salted out as it has the same anion (Cl⁻). To estimate the desalination efficiency (Table S1, ESI[†]), the maximum solubility of NaCl in the mixed solution in the temperature range of 0–100 °C was firstly calculated based on their solubility product constants (K_{sp}). Taking 100 °C as an example, the solubilities of NaCl and CaCl₂ in pure water are 39.8 g and 159 g per 100 mL H₂O, which correspond to 6.80 mol L⁻¹ and 4.32 mol L⁻¹ in molar volume concentration. The calculated K_{sp}

NJC

heating furnace



Fig. 1 The boiling point of various metal chloride salts with different crystal waters at atmospheric pressure.

values are 46.29 for NaCl and 11756.62 for CaCl₂, respectively. The solubility maxima of CaCl₂ and NaCl in the mixed solution, which mean that both the ion product of $[Ca^{2+}]$ and $[Cl^{-}]$ and the ion product of $[Na^+]$ and $[Cl^-]$ do not exceed their $K_{\rm sp}$, can be calculated as 13.80 mol L⁻¹ and 1.59 mol L⁻¹. In this sense, when a sufficient amount of CaCl₂ is introduced into a saturated NaCl aqueous solution (6.80 mol L⁻¹), the maximum desalination efficiency of NaCl is about 76.62%.

The theoretical and measured desalination efficiencies of NaCl at various temperatures are illustrated in Fig. 2a. The detailed experimental results for desalination efficiency of NaCl are summarized in the ESI† (Table S2). With increasing temperature, the desalination efficiency of NaCl increased rapidly below 40 °C, and then increased tardily. Within the tested temperature range, the maximum desalination efficiency of NaCl reached up to 74.36% at 100 °C. The solubility at temperatures above 100 °C was not measured as it required to be performed in an autoclave with sight glass. However, assuming that the variation tendencies in the solubilities of CaCl₂ and NaCl with temperature remain as those at 100 °C (Fig. 2b), the desalination efficiency of NaCl is expectedly further enhanced at higher temperatures that the CWAO process requires. These results reveal preliminarily that salting-out of NaCl from the CaCl₂·3H₂O medium is feasible.

In a CWAO process, the catalyst plays a vital role. To obtain a suitable catalyst, the catalytic performance of five homogeneous

catalysts (MnCl₂, FeCl₃, CoCl₂, CuCl₂ and CeCl₃) was examined in the CaCl₂·3H₂O medium. It can be seen from Fig. 3a that without any additional catalyst, both the phenol and COD removal rates were very poor, with a phenol removal rate of only about 5.4%. In contrast, all five tested metal chlorides are effective catalysts. Among them, CeCl₃ demonstrated very excellent catalytic activity, affording 92.2% phenol removal rate and 74.8% COD removal rate after reacting at 150 °C for 3 h. Fig. 3b shows the time course of phenol degradation and COD removal under the catalysis of CeCl₃ in CaCl₂·3H₂O at 150 °C. During the early 2 hours, the catalytic oxidation of phenol occurred rapidly, and then proceeded tardily, which might be related to the decreased substrate concentration. After 3 hour reaction, the COD removal rate seems to reach an equilibrium, indicating that some intermediate products are recalcitrant to oxidation under the used reaction conditions.

To assess the reusability of $CaCl_2 \cdot 3H_2O$ medium and $CeCl_3$ catalyst after reaction, five successive run experiments were carried out. 0.01 mol of $CeCl_3$ catalyst, 1.5 mol of $CaCl_2$ and 80 mL of phenol solution (30 g L⁻¹) were subjected to reaction at 150 °C for 3 h. After reaction, another 2.4 g phenol was recharged to go on to the next run reaction without any other modification. In this way, five successive runs are conducted. As shown in Fig. S1 (ESI†), the removal rates of phenol and COD showed unnoticeable loss in the degradation efficiency. After five runs, the removal percentages of phenol only declined from 94.7% to 91.8% with COD removal rates from 78.1% to 73.3%. These results prove that $CaCl_2 \cdot 3H_2O$ is an effective reaction medium for the catalytic oxidation of phenol in the presence of $CeCl_3$ as the catalyst.

In order to validate the feasibility of the proposed catalytic oxidation process coupled with desalination in MSH medium for high salinity phenolic wastewater, saturated NaCl solution containing phenol (30 g L^{-1}) was subjected to the CWAO process in continuous operation (Scheme 2). At the steady state, as shown in Fig. 4a, the removal rates of phenol and COD could remain steady within a stream on time of 24 h, with average removal rates of 92% for phenol and 85% for COD, respectively. The purity of the isolated NaCl was characterized by thermogravimetric analysis and compared with that of a NaCl sample, which was obtained by direct evaporation of the



Fig. 2 (a) The theoretical and measured maximum desalination efficiency of NaCl from saturated NaCl solution by adding anhydrous CaCl₂ at different temperatures and (b) the solubility tendency of NaCl and CaCl₂ in pure water with increasing temperature.



Fig. 3 (a) The removal rates of phenol and COD under various catalysts after reacting at 150 °C for 3 h in CaCl₂·3H₂O medium, and (b) the removal rates of phenol (green) and COD (yellow) as a function of reaction time reacting at 150 °C in CaCl₂·3H₂O medium under the catalysis of CeCl₃ catalyst. Reaction conditions: 0.01 mol of CeCl₃ catalyst, 1.5 mol of CaCl₂ and 80 mL of phenol solution (30 g L⁻¹).

Fig. 4 (a) Removal rates of phenol and COD in continuous operation under the catalysis of CeCl₃ catalyst reacting at 150 °C in CaCl₂·3H₂O medium as a function of reaction time. Reaction conditions: 0.01 mol of CeCl₃ catalyst, 1.5 mol of CaCl₂ and 80 mL of phenol solution (30 g L⁻¹). (b) Thermogravimetric analysis of the NaCl sample obtained from direct evaporation of the wastewater to dryness and the NaCl sample salted-out from the wastewater owing to the common-ion effect in continuous operation.

simulated high salinity phenolic wastewater to dryness. As shown in Fig. 4b, the mass loss of the salted-out NaCl was very low (<0.02%), while the NaCl obtained from evaporation showed about 0.6% mass loss, indicating the contamination by organic pollutants. Besides, the element contents in two NaCl samples were further analysed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). As shown in Fig. 5, the residual organic carbon in the NaCl sample obtained from evaporation was as high as 8.03%. In contrast, no residual organic carbon was detected from the salted-out NaCl sample, revealing the effectiveness of our proposed process. Only trace amounts of Ca and Ce were detected from the salted-out NaCl sample, with contents of 100 μ g Ca per g and 1900 μ g Ce per g, respectively. In spite of these, ICP analysis shows that the average contents of Ca and



Fig. 5 (a) and (d) EDS spectroscopy, (b) and (e) SEM scanned area and (c) and (f) element contents of the NaCl sample obtained from direct evaporation of the wastewater to dryness and the NaCl sample salted-out from the wastewater owing to the common-ion effect in continuous operation.

Ce in the recovered NaCl were very low, revealing that most of these impurities are present on the surface of the crystalline particles of NaCl. Such kinds of cationic impurities can be easily removed by conventional techniques such as rinsing with a small amount of water and ion-exchange. Therefore, it is feasible for the recovered NaCl to be used as a raw material in the chlor-alkali industry after simple further pre-treatment. It is well known that the content of organic pollutants in NaCl is strictly restricted due to their destructiveness to the ionic membrane that is used in the electrolysis ion-exchange film process. The SEM-mapping images of two NaCl samples are shown in Fig. S2 (ESI[†]). These results reveal that the salted-out NaCl is of high purity almost not contaminated by organic pollutants. Moreover, the desalination efficiency of NaCl in continuous operation could remain nearly 100%, because the residual NaCl has always saturated the solution of trihydrate of CaCl₂.

It should be noted that there is another difference between our proposed catalytic oxidation process and the conventional CWAO process. In our process, the treated water leaves the reactor in the vapor form while in the latter process it leaves in the liquid form, which might mean more energy consumption. For the wastewater with high salinity, however, evaporation is inevitable. Otherwise, the inorganic salts are very hard to recover. Given that the oxidation is a strong exothermic reaction, the energy consumption in the proposed process is still very competitive after optimizing the heat-exchange network as compared to that of other AOP.

To clarify the catalytic oxidative degradation mechanism of phenol in our MSH medium, UV-vis spectroscopy was employed to characterize the product change as a function of reaction time (Fig. 6). It can be seen that a maximum absorption peak appeared at 271 nm, which is attributed to the $n \rightarrow \pi^*$ electron transition of phenol.^{34,35} Under the catalysis of CeCl₃, the intensity of this characteristic peak declined rapidly within the initial 60 min time, and then changed unnoticeably, indicating that phenol has been removed almost completely. Meanwhile, a new absorption peak appeared around 253 nm, which can be assigned to the UV absorption of parabenzoquinone,³⁶ revealing the formation of *para*-benzoquinone as an intermediate product because the peak intensity presented a maximum and then declined with the reaction proceeding. For comparison, a blank experiment without catalyst was also conducted, in which the UV absorption intensity at 271 nm was



Fig. 6 UV-vis spectroscopy of the reaction product as a function of reaction time: (a) using $CeCl_3$ as catalyst and (b) without any additional catalyst.

almost unchanged, indicating that phenol oxidation proceeded very slowly in the absence of Ce^{3+} catalyst.

In order to figure out the subsequent degradation route, HPLC was used to monitor the intermediate products (Fig. 7a). There were four signal peaks in HPLC spectra, appearing at a retention time of 8.8 min, 9.5 min, 10.7 min and 19.1 min, which were identified as oxalic acid, maleic acid, *para*benzoquinone and acetic acid by comparison with the standard compounds. In addition, hydroquinone, *para*-benzoquinone and acetic acid as intermediate products were also detected by GC-MS (Fig. 7b). The absence of maleic acid and oxalic acid in GC-MS could be attributed to their high boiling point of 275 °C and thermal instability, respectively. Combined with the results of UV-vis spectroscopy, it can be deduced that hydroquinone, *para*-benzoquinone, maleic acid, oxalic acid and acetic acid were the sequential intermediate products in the catalytic oxidation degradation of phenol.

In addition, *para*-benzoquinone and maleic acid, which have been confirmed by HPLC as intermediate products, were subjected to catalytic oxidation under identical conditions to phenol. As shown in Fig. 8, complete removal of *para*-benzoquinone and maleic acid could be achieved in 120 min and 12 min,



Fig. 7 (a) HPLC and (b) GC-MS analysis of the intermediate products reacting in trihydrate of $CaCl_2$ with $CeCl_3$ catalyst. Ethyl acetate was used as the dilution solvent for GC-MS analysis.



Fig. 8 Catalytic oxidation of *para*-benzoquinone and maleic acid under catalysis of CeCl₃ catalyst reacting at 150 °C in CaCl₂·3H₂O medium as a function of reaction time. Reaction conditions: 0.01 mol of CeCl₃ catalyst, 1.5 mol of CaCl₂ and 80 mL of *para*-benzoquinone solution (35 g L⁻¹) or maleic acid solution (37 g L⁻¹).

respectively. The quick decomposition rate of maleic acid might explain why a very low concentration of maleic acid was detected in the phenol oxidation product. Besides, the much slower decomposition rate of *para*-benzoquinone demonstrated that the ring-opening process of *para*-benzoquinone is the rate-controlling step in the whole process, which is in accord with the results of UV-vis spectroscopy.

Ce 3d XPS was used to characterize the trihydrate of CaCl₂ with $CeCl_3$ after reaction as well as a physical mixture ($CaCl_2$ + $CeCl_3$) for comparison (Fig. 9). The characteristic V and U bands are related to the spin-orbit splitting of Ce 3d_{5/2} and Ce $3d_{3/2}$, which can be deconvoluted into eight peaks: U''' $(\sim 916.5 \text{ eV}), U'' (\sim 906.5 \text{ eV}), U' (\sim 904.6 \text{ eV}), U (\sim 901.1 \text{ eV}),$ V''' (~897.7 eV), V" (~887.6 eV), V' (~886.3 eV), and V (~882.7 eV). The four U bands are characteristic of Ce $3d_{3/2}$, and the four V bands are characteristic of Ce3d_{5/2}.^{37,38} For the physical mixture (CaCl₂ + CeCl₃), only the peaks of U', U and V', V were observed, which represent Ce³⁺ 3d_{3/2} and Ce³⁺ 3d_{5/2}, respectively. For the mixture of trihydrate of CaCl₂ and CeCl₃ used after reaction, however, new peaks of U''', U" and V''', V" appeared, revealing that part of the initial Ce^{3+} species was oxidized to Ce^{4+} species with the Ce(m)-Ce(m)-Ce(m) recycle during reaction.

In the Fenton process, it has been reported that reactive oxygen species such as 'OH radicals could be generated when using H_2O_2 as a strong oxidant to degrade the organic pollutants in wastewaters.^{39,40} Several authors also have demonstrated that because of their electrophilic nature •OH radicals would attack aromatic compounds such as phenol.41-43 Therefore, it is assumed that the oxidation degradation of phenolic wastewater proceeds mainly through the attack of electrophilic •OH radicals. The presence of Ce³⁺ catalyst would accelerate the production of •OH radicals. Besides, para-benzoquinone is well known as an effective trapping agent for 'OH radicals,^{44,45} which might account for the high degradation efficiency to some extent. To further verify the degradation mechanism, a radical quenching experiment was performed. As a well-known scavenger of •OH radicals, different amounts of H₂PO₄²⁻ were added competing with para-benzoquinone to eliminate the •OH radicals. The effect of the radical scavenger on R_{phenol} is shown in Fig. 10, which decreased obviously with the increase of $H_2PO_4^{2-}$ concentration. In the presence of $H_2PO_4^{2-}$ with a concentration of 80 mg L^{-1} , the removal rate of phenol decreased from 49.4% to 24.3% at 60 min, which indicated



Fig. 9 XPS of (a) physical mixture (CaCl₂ + CeCl₃) and (b) trihydrate of CaCl₂ with CeCl₃ catalyst after reaction.



Fig. 10 The removal rate of phenol as a function of reaction time reacting at 150 °C in CaCl₂·3H₂O medium under the catalysis of CeCl₃ catalyst with different amounts of $H_2PO_4^{2-}$ as the •OH radical scavenger. Reaction conditions: 0.01 mol of CeCl₃ catalyst, 1.5 mol of CaCl₂ and 80 mL of phenol solution (30 g L⁻¹).



Fig. 11 The proposed synergistic catalytic oxidation degradation mechanism of phenol.

that the catalytic oxidation of phenol in $CaCl_2 \cdot 3H_2O$ medium was indeed dominated by •OH radicals.

Based on the above-mentioned results, a synergistic catalytic oxidation degradation mechanism of phenol by [•OH/Ce⁴⁺] was reasonably proposed. The •OH radicals were formed by the Ce³⁺ species donating an electron to O_2 and the H^+ ion, leading to the production of •OH radicals. The intermediate Ce⁴⁺ species would act as an oxidant cooperatively with •OH radicals, simultaneously completing the catalytic cycle to give the initial Ce^{3+} oxidation state. As shown in Fig. 11, phenol was firstly oxidized to hydroquinone and further to para-benzoquinone. Secondly, the open-ring process of para-benzoquinone occurred to form a transition state. Thirdly, the transition state was thermodynamically unstable, from which two molecules of CO₂ would be eliminated generating a molecule of maleic acid. Subsequently, oxalic acid and acetic acid were formed by cleavage of the C=C bond in maleic acid. Finally, oxalic acid and acetic acid were further mineralized to CO2 and H2O.

4. Conclusions

An improved CWAO process is proposed by using CaCl₂ with three crystal waters as the reaction medium, which allows the CWAO process to be operated at high temperature but atmospheric pressure, which is of high significance for the practical application. Using atmospheric air as an oxidant at 150 °C, more than 92% phenol removal rate and 85% COD removal rate can be achieved when using CeCl3 as catalyst and CaCl2·3H2O as reaction medium in continuous operation. By taking advantage of the common-ion effect, the desalination efficiency could reach up to 100% with excellent recovered NaCl quality. A mechanistic study revealed that the •OH radicals generated by the Ce3+ catalyst plays a dominant role in ring opening, CO₂ elimination, and C=C bond cleavage during the catalytic oxidative degradation of phenol. Owing to the recyclability of CaCl₂ and CeCl₃ catalysts, the energy consumption in this process is overwhelmingly the contribution to operation cost. On the other hand, oxidation reactions of organic compounds are usually exothermic, which can compensate to some extent for the energy consumed by water vaporization. The higher the COD value in wastewater, the less energy needed for vaporization, indicating that the operation cost highly depends on the COD value of wastewater. The current work not only provides a facile and high-efficiency catalytic oxidation degradation route for high salinity phenolic wastewater treatment, but also sheds light on the degradation mechanism of phenolic compounds in MSH media and provides inspiration to treat other industrial wastewaters.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The project was supported by the National Key R&D Program of China (2019YFD1100602), the National Natural Science Foundation of China (21978158), the Joint R&D Program of Zibo City & SDUT (2019ZBXC092) and the Public Welfare Category of Key R&D Programs in Shandong Province (2018GGX107003).

Notes and references

- 1 G. A. Best and J. R. Dojlido, *Chemistry of Water and Water Pollution*, Ellis Horwood, New York, 1993.
- 2 Z. Guerra-Que, H. Pérez-Vidal, G. Torres-Torres, J. C. Arévalo-Pérez, A. A. Silahua Pavón, A. Cervantes-Uribe, A. Espinosa de los Monteros and M. A. Lunagómez-Rocha, *RSC Adv.*, 2019, **9**, 8463–8479.
- 3 A. Eslami, M. Hashemi and F. Ghanbari, *J. Cleaner Prod.*, 2018, **195**, 1389–1397.
- 4 W. Mao, H. Ma and B. Wang, Chem. Eng. J., 2010, 160, 232–238.
- J. D. Muñoz Sierra, C. Lafita, C. Gabaldón, H. Spanjers and J. B. van Lier, *Bioresour. Technol.*, 2017, 234, 106–114.

- 6 A. Santos, P. Yustos, A. Quintanilla and F. García-Ochoa, *Appl. Catal., B*, 2004, 53, 181–194.
- 7 P. Y. A. Santos, A. Quintanilla, S. Rodríguez and F. García-Ochoa, *Appl. Catal.*, *B*, 2002, **39**, 97–113.
- 8 G. Yang, S. Mo, B. Xing, J. Dong, X. Song, X. Liu and J. Yuan, *Environ. Pollut.*, 2020, **258**, 113687.
- 9 Z.-Y. Ding, S. N. V. K. Aki and M. A. Abraham, *Environ. Sci. Technol.*, 1995, 29, 2748–2753.
- 10 H. Tian, X. Xu, J. Qu, H. Li, Y. Hu, L. Huang, W. He and B. Li, *J. Hazard. Mater.*, 2020, **392**, 122463.
- 11 J. Li, Y. Xu, Z. Ding, A. H. Mahadi, Y. Zhao and Y.-F. Song, *Chem. Eng. J.*, 2020, **388**, 124248.
- 12 S. M. Hosseini, M. Ghiaci, S. A. Kulinich, W. Wunderlich, B. H. Monjezi, Y. Ghorbani, H. S. Ghaziaskar and A. Javaheri Koupaei, *Appl. Surf. Sci.*, 2020, **506**, 144644.
- 13 L. Zhou, H. Cao, C. Descorme and Y. Xie, Front. Environ. Sci. Eng., 2018, 12, DOI: 10.1007/s11783-017-0970-2.
- 14 E. Szabados, G. Sági, F. Somodi, B. Maróti, D. Srankó and A. Tungler, *J. Ind. Eng. Chem.*, 2017, **46**, 364–372.
- 15 K.-H. Kim and S.-K. Ihm, J. Hazard. Mater., 2011, 186, 16-34.
- 16 S. Miao, H. Zhang, S. Cui and J. Yang, *Chemosphere*, 2020, 257, 127123.
- 17 Z. Wu, A. Abramova, R. Nikonov and G. Cravotto, *Ultrason. Sonochem.*, 2020, 68, 105195.
- 18 A. J. Dos Santos, P. L. Cabot, E. Brillas and I. Sirés, Appl. Catal., B, 2020, 277, 119240.
- 19 P. Yan, J. Shen, Y. Zhou, L. Yuan, J. Kang, S. Wang and Z. Chen, *Appl. Catal.*, B, 2020, 277, 119055.
- 20 J. Kim, J. E. Lee, H. W. Lee, J.-K. Jeon, J. Song, S.-C. Jung, Y. F. Tsang and Y.-K. Park, *J. Hazard. Mater.*, 2020, **397**, 122577.
- 21 C. Ma, S. Jia, P. Yuan and Z. He, Environ. Pollut., 2020, 265, 114597.
- 22 Y. Shi, X. Wang, X. Liu, C. Ling, W. Shen and L. Zhang, *Appl. Catal.*, *B*, 2020, 277, 119229.
- 23 F. Delano, D. Duprez, J. Barbier Jr, P. Isnard and G. Blanchard, *Catal. Today*, 1996, 29, 317–322.
- 24 M. Luan, G. Jing, Y. Piao, D. Liu and L. Jin, *Arabian J. Chem.*, 2017, **10**, S769–S776.
- 25 E. Castillejos-López, A. Maroto-Valiente, D. M. Nevskaia, V. Muñoz, I. Rodríguez-Ramos and A. Guerrero-Ruiz, *Catal. Today*, 2009, 143, 355–363.

- 26 A. Pintar, J. Batista and T. Tišler, *Appl. Catal., B*, 2008, **84**, 30–41.
- 27 A. Mishra and A. Garg, J. Hazard., Toxic Radioact. Waste, 2013, 17(2), 86–89.
- 28 T. W. Leal, L. A. Lourenço, H. de L. Brandão, A. da Silva and A. A. Ulson de Souza, *J. Hazard. Mater.*, 2018, 359, 96–103.
- 29 H. Li, J. Shang, Z. Yang, W. Shen, Z. Ai and L. Zhang, *Environ. Sci. Technol.*, 2017, 51, 5685–5694.
- 30 H.-H. Emons, Electrochim. Acta, 1988, 33, 1243-1250.
- 31 N. Rodriguez Quiroz, A. M. Norton, H. Nguyen, E. Vasileiadou and D. G. Vlachos, ACS Catal., 2019, 9, 9923-9952.
- 32 J. A. Duffy and G. Leslie Wood, *J. Chem. Soc., Dalton Trans.*, 1987, 1485–1488.
- 33 J. A. Duffy and M. D. Ingram, *Inorg. Chem.*, 1978, 17, 2798–2802.
- 34 D. Zhu and Q. Zhou, Appl. Catal., B, 2020, 268, 118426.
- 35 V. Chivu, D. Gilea, N. Cioatera, G. Carja and M. Mureseanu, *Appl. Surf. Sci.*, 2020, **513**, 145853.
- 36 S. Fukuzumi, H. Kotani, Yong, M. Lee and W. Nam, J. Am. Chem. Soc., 2008, 130, 15134–15142.
- 37 B. Liu, C. Li, G. Zhang, X. Yao, S. S. C. Chuang and Z. Li, ACS Catal., 2018, 8, 10446–10456.
- 38 Z. Q. Wang, M. J. Zhang, X. B. Hu, V. P. Dravid, Z. N. Xu and G. C. Guo, *Chem. Commun.*, 2020, **56**, 403–406.
- 39 P. Gao, Y. Song, M. Hao, A. Zhu, H. Yang and S. Yang, Sep. Purif. Technol., 2018, 201, 238–243.
- 40 P. Salvador, J. Phys. Chem. C, 2007, 111, 17038-17043.
- 41 G. Ovejero, J. L. Sotelo, A. Rodríguez, C. Díaz, R. Sanz and J. García, *Ind. Eng. Chem. Res.*, 2017, 46, 6449–6455.
- 42 E. Serra-Pérez, S. Álvarez-Torrellas, V. Ismael Águeda, J. A. Delgado, G. Ovejero and J. García, *Appl. Surf. Sci.*, 2019, 473, 726–737.
- 43 S. Pirgalioğlu, Ş. Doğan and M. E. Mutseyekwa, *Water Sci. Technol.*, 2017, **76**, 2764–2775.
- 44 M. Stylidi, Appl. Catal., B, 2004, 47, 189-201.
- 45 E. Baciocchi, T. Del Giacco, F. Elisei, M. F. Gerini, M. Guerra, A. Lapi and P. Liberali, *J. Am. Chem. Soc.*, 2003, 125, 16444–16454.