Front. Environ. Sci. Eng. 2018, 12(1): 1
DOI 10.1007/s11783-017-0970-2

REVIEW ARTICLE

Phenolic compounds removal by wet air oxidation based processes

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HIGHLIGHTS

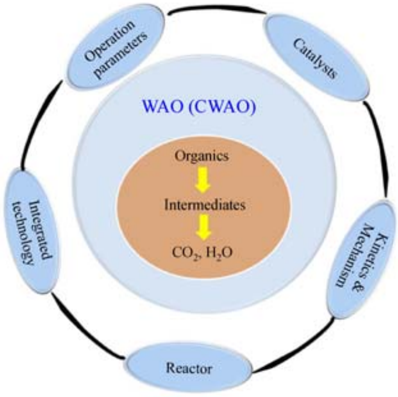
- Different reaction parameters are emphasized in the WAO process.
- Homogenous catalysts and heterogeneous catalysts are extensively discussed.
- Mechanism and kinetic of WAO are elaborated.
- Three kinds of the reactors for CWAO are compared.
- Integration of CWAO with biological degradation is discussed.

ARTICLE INFO

Article history:
Received 20 January 2017
Revised 13 March 2017
Accepted 13 April 2017
Available online 13 July 2017

Keywords:
Wet air oxidation
Catalytic wet air oxidation
Phenolic compounds
Heterogeneous catalysts
Mechanism

GRAPHIC ABSTRACT



ABSTRACT

Wet air oxidation (WAO) and catalytic wet air oxidation (CWAO) are efficient processes to degrade organic pollutants in water. In this paper, we especially reviewed the WAO and CWAO processes for phenolic compounds degradation. It provides a comprehensive introduction to the CWAO processes that could be beneficial to the scientists entering this field of research. The influence of different reaction parameters, such as temperature, oxygen pressure, pH, stirring speed are analyzed in detail; Homogenous catalysts and heterogeneous catalysts including carbon materials, transitional metal oxides and noble metals are extensively discussed, among which Cu based catalysts and Ru catalysts were shown to be the most active. Three different kinds of the reactor implemented for the CWAO (autoclave, packed bed and membrane reactors) are illustrated and compared. To enhance the degradation efficiency and reduce the cost of the CWAO process, biological degradation can be combined to develop an integrated technology.

1 Introduction

Phenolics usually include monophenols, polyphenols as well as substituted-phenols. They are extensively present in wastewater generated by petrochemical, petroleum refinery, coke-to-chemicals, leather, pharmacy, printing and dyeing industries, with concentrations ranging from 10 to 17 × 10^3 mg·L^{-1} [1–3]. Because of their toxicity and mutagenic, carcinogenic, and teratogenic effects, a discharge limit was set at 0.5 mg·L^{-1}. Concentration of phenol higher than 1 mg·L^{-1} in water can endanger the aquatic life. Environmental Protection Agency of America fixed the limit at 1 ppb for surface waters and 0.1 mg·L^{-1} (100 ppb) in nonchlorinated water. According to some water supply standards [3–5], the concentration of phenol in the chlorinated water is 1–2 μg·L^{-1}.

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[*] Special Issue—Advanced Treatment Technology for Industrial Wastewaters (Responsible Editors: Junfeng Niu & Hongbin Cao)

All phenolic compounds are constituted with benzene ring and some functional groups. Some of them are very stable and toxic, and it is a tough task to decompose them into harmless substances. Physical, chemical and biological technologies or combination of them, have been investigated to remove phenols from wastewater. For a high concentration of phenolics in wastewater, solvent extraction and activated carbon adsorption can be economical choices. However, solvent extraction often suffers from selectivity to certain phenols and part of phenols still remains in the solution. Activated carbon adsorption requires expensive and complex regeneration of the adsorbent and the obtained phenols need further treatment. Biological degradation has been proved to be the most effective and cheapest method in organics removal; however the toxicity of phenolic compounds dramatically lower the efficiency of such processes. For example, o-cresol has been found to be resistant to anaerobic degradation [5].

Chemical oxidation processes can decompose phenolics into smaller molecules which are less toxic and easier to treat or mineralized [6,7]. Among the chemical oxidation processes, advanced oxidation processes (AOPs) such as the Fenton process, ozonation, photolysis or combinations such as photo-Fenton, photocatalytic ozonation, are recommended for low concentrations of organics. Incineration process is suitable for very high concentrations of organics ($\mathrm{COD} \geqslant 100\ \mathrm{g \cdot L^{-1}}$). However, it is not encouraged anymore since recent years because it is not an eco-friendly process and other hazardous compounds might be produced upon reaction [8]. The wet air oxidation (WAO) reaction is recognized as the cleanest technique because no additive was added to cause second pollution. At reasonable temperature (175°C–320°C) and high pressure of 2.17–20.71 MPa, wastewater is kept in liquid phase and the organics are oxidized into small organic acids which are likely biodegradable [9]. Usually, this process is suitable for wide range of wastewater with initial COD between 20 and 200 $\mathrm{g \cdot L^{-1}}$ [10], therefore, it is a practical treatment option for wastes which are either too dilute to be incinerated or too concentrated for AOPs [11]. It is also recognized as a potential pretreatment before biodegradation (BOD) to detoxify hazardous pollutants and satisfy the biodegradation requirements [12]. The WAO process can be thermally self-sufficient when the COD is above 30 $\mathrm{g \cdot L^{-1}}$ [13–15], this means it is economically feasible technique for the treatment of high concentration of organics. Addition of a catalyst into the WAO system could not only reduce the reaction conditions, but also improve the mineralization of the target organics.

After laboratory scale experiments, WAO plants were first setup in the USA to treat the municipal wastewater (Zimpro Company). Until 2010, more than 400 plants of WAO have been constructed to treat the wastewater from petrochemical, chemical and pharmaceutical industries, and the sludge from biological treatment plants [13]. European companies paid much attention on the homogeneous catalytic wet air oxidation (CWAO) processes based on soluble transition metal ions, while Japanese companies were much more interested in the heterogeneous CWAO technologies based on precious metals supported on high specific surface materials. In recent years, Prof. Chenglin Sun in China developed an effective CWAO technique and applied in several industrial plants. The treating capacities of the plants are 10–30 thousand tons/year, and the operating cost is 3–4 US dollars/ton (the catalyst and the labor cost are not included). These showed a promising potential for WAO (CWAO) in practical application.

In this paper, we review the literatures on the WAO and CWAO of phenolic compounds. The influence of the different operating parameters and the type of the reactor, the reaction kinetics and mechanisms are discussed. As far as the catalyst is the most important factor upon CWAO, the performances of different heterogeneous catalysts in phenolics removal are compared. The combination of WAO/CWAO with a biological degradation step is also discussed to better evaluate its efficiency and practical application to high concentration wastewater.

2 Wet air oxidation (WAO)

The WAO process was first proposed by F. J. Zimmermann in 1944 [9]. It utilizes oxygen at elevated temperature (400–573 K) under high pressure (0.5–20 MPa) to oxide the toxic organics into CO_2 and H_2O or smaller molecule that can be handled via biodegradation [16–18]. The WAO of phenolic compounds is a mass transfer controlled process since oxygen must be transferred from the gas phase to the liquid phase to react with the organic compounds.

According to Pintar et al. [19], the rate constant (which was determined by temperature), concentration of phenolics and dissolved oxygen were closely related with the reaction rate. By enhanced the pressure of oxygen and the stirring speed at high temperature can greatly influence the mass transfer and the degree of mineralization. Besides, pH also had a strong impact on the reaction rate and the total organic carbon (TOC) or the chemical oxygen demand (COD) removal [16]. The influence of these factors will be separately discussed in the following sections.

2.1 Operating parameters

2.1.1 Temperature

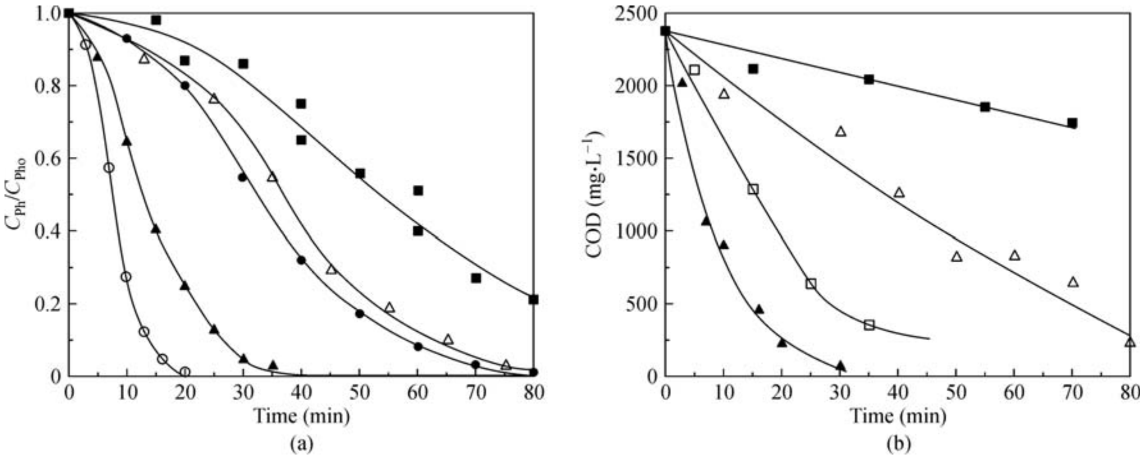
Temperature plays a very important role in the WAO process. It can affect both the reaction rate and the overall removal of COD or TOC. Even the mechanism of the reaction can be changed depending on the temperature range since different kinds of radicals can be trigged at higher temperature [20,21]. The activation energy for the WAO of phenol and its derivatives is reported to be very high because of their aromatic structure. Thus, high reaction temperatures (above 175°C) are required to overcome such high activation energy barriers.

As shown on Fig. 1, as the reaction temperature increased, the degradation of phenol and the COD removal increased. Once the reaction temperature was higher than 200°C, the phenol concentration was drastically reduced within 30 min, and so did the COD abatement. It can be deduced that there was a critical temperature between 448 K and 473 K, above which, the decomposition of the phenol and the degradation products increased sharply. Lin et al. [22] also observed this phenomenon and proposed that this phenomenon could be related to the boiling point of phenol (182°C) and that new active intermediates could be generated at higher temperature. At lower temperature, the free phenoxyperoxyl radical (PhOO·) would predominate, while O· and ·OH radicals would play a dominant role in the WAO process under supercritical conditions [20,21]. The activation energy of phenol was found to be in the range 12.4–201 kJ·mol^{-1} for the WAO reaction [18,20–23]. Shibaeva et al. [23]carried out their experiments in the range 180°C–210°C and calculated that the activation energy was 107 kJ·mol^{-1}, while Willms et al. reported an activation energy ca. 112 kJ·mol^{-1} in the temperature range of 130°C–200°C [24]. On the other hand, the activation energy calculated by Vicente et al. [25] was 67.4±9.8 kJ·mol^{-1} in the range 170°C–220°C, in agreement with the values obtained in the range 150°C–250°C reported by Pruden et al. [26], Jaulin et al. [27] and Joglekar et al. [20], respectively. Kolaczkowski et al. [18] pointed out that such differences could be attributed to the involvement of different radicals or intermediates depending on the reaction conditions. Rivas et al. [21] calculated that the activation energy for the reaction between phenol and the phenoxyperoxyl radical (PhOO·) was 47±3 kJ·mol^{-1} at low temperature, while it was 126±4 kJ·mol^{-1} at higher reaction temperature.

2.1.2 Oxygen pressure

The oxygen partial pressure can affect both the reaction kinetic and intermediates distribution upon WAO of phenols [17,18]. Because of the significant decrease of the dissolved oxygen concentration at high temperature and higher partial oxygen pressures are required to increase the concentration of oxygen in solution. The oxidation reaction was shown to be first order in oxygen and also first order with respect to the phenolic substrate during both induction and the fast reaction periods [23,26,27]. However, Willms et al. [24] showed that during the rapid reaction period, the oxidation kinetics were half order in dissolved oxygen [24,28]. The WAO of phenols involves the initial production of free radicals, which explains the induction period before the reaction really starts [20,25]. During the induction period, only little phenol and/or TOC is eliminated and this is closely related to the low concentration of free radicals at the initial stage of the reaction [24]. According to Henry's law, higher concentration or partial pressure of oxygen in the gas phase promotes the oxygen dissolution in the aqueous phase. The dissolved oxygen may react with water at elevated temperature to form free radicals [18]. Once the concentration of the free radicals reaches a critical concentration, the radicals will start participating in the phenolics oxidation. Thus, higher partial pressure of oxygen should shorten the induction period. Kolaczkowski et al. [18] found that the removal rates of phenol and COD also increased during fast reaction stage as the oxygen partial pressure increased, especially since more free radicals participated in the reaction.

Besides the effect of the oxygen pressure on the reaction rate, it also affected the distribution of the reaction



(a) (b)

Fig. 1 WAO of phenol [P_{O_2} = 0.4 MPa, C_{Phenol} = 0.01mol·L^{-1}]. (a) Evaluation of the relative concentration of phenol (C_{ph}/C_{ph0}) upon reaction at ○483K, ▲473K, ●l463K, △458K, ■448K; (b) Evaluation of the COD removal at ▲483K, □473K, △463K, ■448K [18] intermediates [17]. Increasing the oxygen partial pressure also meant higher oxygen to phenol ratio. This induced a decrease of the amount of some of the intermediates, such as the aromatic compounds, dihydroxylated phenols and the quinone-like substances [17] (Fig. 2). Under excess oxygen, more oxalic acid and carbon dioxide were generated. However, once it exceeded a critical amount, no obvious difference was observed anymore.

2.1.3 pH

The effect of the pH on the phenolic compounds degradation has been intensively studied. In general, strongly alkaline and weakly acidic conditions were shown to favor the elimination process [18,22,29]. However, Rivas et al. [21] reported that phenol had a very low reactivity with oxygen under weak alkaline solution (pH: 7–10) and a very strong acidic conditions (pH $<$ 2). Shibaeva et al. [23] figured out that phenol is converted into phenolate ion at pH$\geqslant$10 and that the reaction rate of phenolate ion with oxygen was 10^7 times faster compared to phenol. As acidic intermediates are produced upon WAO process, the pH of the solution decreases during the first stage of the reaction, before it increases again slightly as some intermediates are further decomposed into CO_2 and H_2O [17,22]. Lin et al. [22] studied the influence of the initial pH of the reaction mixture on the COD removal in the range of 150°C–300°C. When a K_2PO_4-NaCl buffer solution was added into the system to stabilize the pH of the solution, the COD removal decreased apparently compared to reaction without buffer [22].

2.1.4 Stirring speed

The WAO reaction is carried out in a heterogeneous gas-liquid system and the mass transfer between the liquid and the gas phases are crucial: i) the oxygen must be transferred from the gas phase to the gas-liquid interface; ii) the dissolved oxygen must have been transferred from gas-liquid interface to the liquid phase; iii) and finally the oxygen will react with the phenols in the bulk of the solution. Mass transfers between the liquid and the gas phases are controlled by the liquid film resistance and this resistance might be reduced by increasing the intensity of the turbulence in the liquid phase [12]. Reactors are equipped with stirrers specially designed to overcome mass transfer resistance upon increasing the rotation speed and the turbulence. Vaidya et al. [29] applied different stirring speed upon phenol oxidation at 230°C. They found that the mass transfer resistance could be overcome as the stirring speed was higher than 15 r·min^{-1}. However, Lin et al. [22] found that mass transfer resistance was still limiting the COD removal during degradation of phenol when the stirring speed was below 300 r·min^{-1}. In their experiment, the resistance could only be eliminated when the stirring speed was higher than 300 r·min^{-1}. Generally speaking, the stirring speed required to overcome any interface resistance is highly dependent on the reaction conditions and setup, such as the reactor size, the

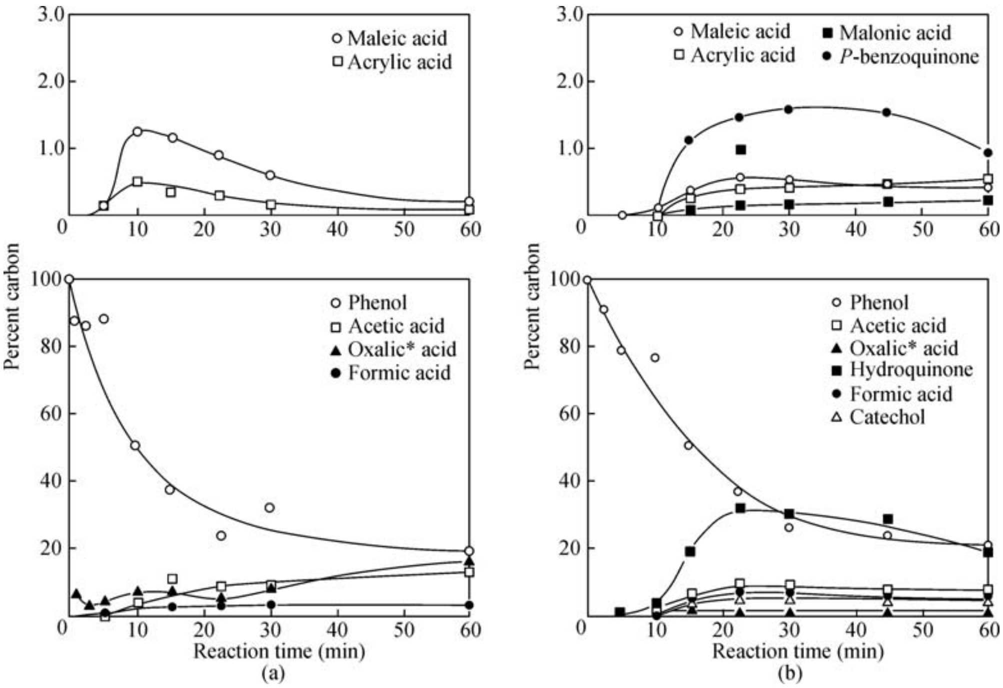


Fig. 2 Intermediates produced in the WAO of phenol at 200°C. (a) Under excess of oxygen; (b) Under excess of phenol [17]

temperature, the oxygen pressure and the concentration of substrate. The higher the temperature and the oxygen pressure, the lower the stirring speed needed to overcome the interface the resistance.

2.2 Reaction kinetics and mechanisms

The WAO of phenols was unambiguously shown to follow a free-radical mechanism. The oxidation was demonstrated to be first [18,20,27] or half order [24,28] in dissolved oxygen and also first order with respect to the phenolic substrate [25,26]. Vaidya et al. [29] demonstrated that the WAO of phenols followed a free radical mechanism by adding *t*-butanol as a free radical scavenger or trace amount of a free radical generator, i.e. hydroquinone. Experiments showed that the radical scavenger had a negative effect on the degradation of phenol, while the free radical generator enhanced the rate of oxidation of phenol [16,20,30]. It was proposed that free radicals were responsible for phenol destruction [21]. They were proposed to be generated from the bimolecular reaction between phenol and oxygen under subcritical conditions (Eq. (1)). Under supercritical conditions, free radicals such as O· and ·OH were considered to be generated via the unimolecular decomposition of O_2 (Eqs. (4-6) [31]. The activation energy of the bimolecular reaction (Eq. (1)) was obviously lower than those of reactions in Eqs. (4–6). The reaction rate between phenol and oxygen (Eq. (1), k_1) was several orders of magnitude larger than those of the unimolecular decomposition of oxygen [32,33]. The unimolecular initiated reaction mechanism was almost excluded under subcritical temperature. The reaction activation energy at lower temperature was 56 $\mathrm{kJ \cdot mol^{-1}}$, while it was 170 $\mathrm{kJ \cdot mol^{-1}}$ at higher temperature [25]. This result indicated that at higher temperature, the unimolecular decomposition reactions (Eqs. (4–6) contributed to the overall reaction significantly resulting in a higher activation energy.

$$\mathrm{Ph} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{Ph\cdot} + \mathrm{HO_2\cdot}$$

$$k_1 = 7 \times 10^{12}\exp(-150000/RT) \tag{1}$$

$$\mathrm{Ph\cdot} + \mathrm{O_2} \xrightarrow{k_2} \mathrm{PhOO\cdot}$$

$$k_2 = 1200 \tag{2}$$

$$\mathrm{PhOO\cdot} \xrightarrow{k_{-2}} \mathrm{Ph\cdot} + \mathrm{O_2} \tag{3}$$

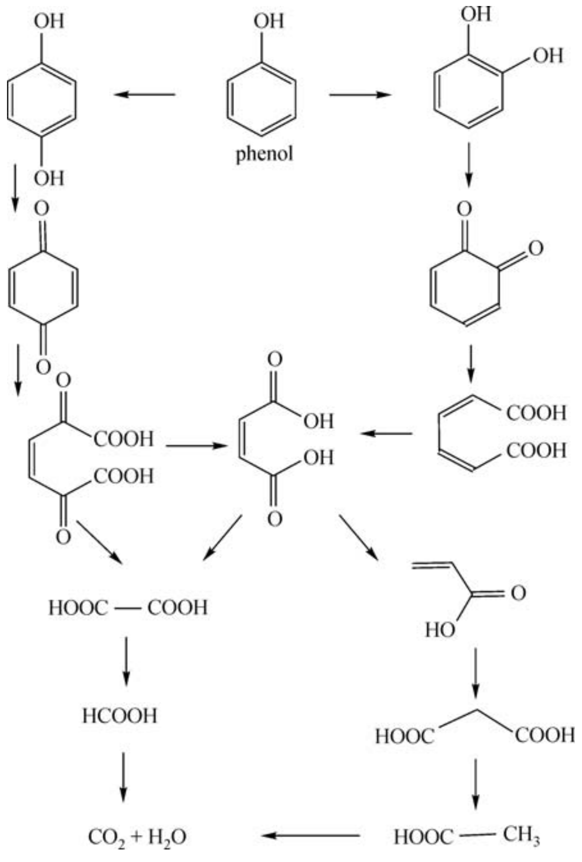


Fig. 3 Reaction pathway of phenol [17]

$$O_2 \xrightarrow{k_{O_2}} 2O\cdot \tag{4}$$

$$RH \xrightarrow{k_{RH}} R\cdot + H\cdot \tag{5}$$

$$H_2O \xrightarrow{k_{H_2O}} \cdot OH + H\cdot \tag{6}$$

Devlin et al. [17] proposed a reaction pathway for the oxidation of phenol with the dissolved oxygen (Fig. 3). It was demonstrated that phenol was initially degraded into hydroquinone and catechol. Then, hydroquinones were oxidized to benzoquinones. Finally, small organic acids such as oxalic acid, acetic acid, succinic acid, malonic acid, maleic acid and fumaric acid were formed (Table 1). More complex phenolic substrate followed the same pathway after abstraction of the functional groups on the aromatic ring [17,20,34].

The effect of the functional group on the reaction kinetics was also studied [20]. Nine different substituted phenols were investigated. Both the position and the type of functional group impacted on the conversion and the TOC abatement. In line with the free-radical mechanism of the reaction, the electrophilic groups accelerated the reaction; The high electron donating ability of the functional group benefited the reaction rate. Groups such as -OCH_3, -OC_2H_5, -CH_3 in ortho/para position of the phenolic hydroxyl group stabilized the hyperconjugation. Moreover, some groups in ortho position had to some extent a steric hindrance to the stabilization. The p-substituted phenols showed higher reactively compared to the *o*-substituted phenols in some cases.

3 Catalytic wet air oxidation

To achieve a complete oxidation of the organic pollutants to carbon dioxide via WAO, high reaction temperature and pressure are often required. Indeed, only at temperature higher than 200°C and oxygen partial pressure above 0.4 MPa, remarkable TOC or COD removal can be achieved. Moreover, the WAO of phenols usually produce acidic intermediates, resulting in low TOC removal as well. This is possibly a limitation to the application of the WAO technology. However, the addition of a catalyst can help to solve this problem, and it is then referred to as the catalytic wet air oxidation (CWAO). The development of new catalysts in the CWAO in the last two decades has considerably improved its efficiency. Catalysts might be either in the form of homogeneous or solid catalysts [13,35]. Among the homogeneous catalysts, one might have Cu^{2+}, Fe^{2+} and other soluble transition metal ions [36]. The other catalysts are heterogeneous catalysts, such as carbon materials, metals (Co [36], Cu [37], Fe [38], Ru [39], Pt [40], metal oxides (MnO_2, TiO_2, γ-Al_2O_3, α-Fe_2O_3, CuO and CeO_2) [41–44] or metal oxide supported noble metals [45]. It was reported that the reaction mechanisms are significantly different whether the catalyst is homogenous or heterogeneous [30]. The homogenous catalytic process obeys a free radical path, while the heterogeneous catalytic process mostly follows a surface controlled "Langmuir-Hinshelwood (L-H)" type of mechanism. Both homogenous and heterogeneous catalytic reactions may occur simultaneously when the metal ions are leached into the solution from the heterogeneous catalyst [30].

In a semi-batch slurry reactor (autoclave reactor) [13], the high ratio of liquid to solid could lead to the polymerization reaction, and the kinetic model of phenol degradation could be described by Eq. (7), while in a fix-bed reactor (trickle-bed), it was "liquid saturated" and the kinetic model would be described by the Langmuir-Hinshelwood (L-H) kinetic model (Eq. (8)).

$$-r_{\mathrm{PhOH}} = k_{het} \times c_{\mathrm{PhOH}} \times c_{\mathrm{O_2}}^{1/4} + k_{\mathrm{hom}} \times c_{\mathrm{PhOH}} \times \sum c(\mathrm{P_n}) \tag{7}$$

$$-r_{\mathrm{poll}} = \frac{k_{\mathrm{sr,app}} \times K_{\mathrm{poll}} \times K_{\mathrm{O_2}}^{1/2} \times c_{\mathrm{poll}} \times c_{\mathrm{O_2}}^{1/2}}{(1 + K_{\mathrm{poll}} \times c_{\mathrm{poll}}) \times (1 + K_{\mathrm{O_2}}^{1/2} \times c_{\mathrm{O_2}}^{1/2})} \tag{8}$$

where, k_{het}: Apparent rate constant for the heterogeneous oxidation steps; k_{hom}: The lump polymerization constant; $k_{\mathrm{sr,app}}$: Apparent rate constant for the surface oxidation steps; K_{poll}: Adsorption equilibrium constant of pollutants; $K_{\mathrm{O_2}}$: Adsorption equilibrium constant of oxygen.

Thus, besides the operating parameters such as the

Table 1 Most common intermediates in the WAO of phenolic compounds [34]

substrate	reaction condition	phenol/TOC removal/%	intermediates
o-cresol	265°C, 2 bar	95/76	oxalic acid, acetic acid, succinic acid, malonic acid, maleic acid, fumaric acid, 4-hydroxybenzoic acid, hydroquinone, *p*-benzoquinone, phenol.
	265°C, 9 bar	100/85	
phenol	265°C, 2 bar	26/14	oxalic acid, acetic acid, succinic acid, malonic acid, maleic acid, formic acid, fumaric acid, 4-hydroxybenzoic acid, 2-hydroxybenzoic acid, hydroquinone, *p*-benzoquinone.
	265°C, 9 bar	90/73	
o-chlorophenol	265°C, 2 bar	97/81	oxalic acid, acetic acid, succinic acid, malonic acid, phenol, HCl.
	265°C, 9 bar	99/86	

temperature, the dissolved oxygen, the pH and the stirring speed, the type of reactors also affect the organics removal in the CWAO. As these operating parameters are already discussed in detail in the section of WAO, only the impact of catalysts formulation and the type of reactors are reviewed in CWAO. For more information about the reaction kinetics in CWAO, Janez Levec gave a detailed review in his paper [13].

3.1 Homogenous catalysis

The homogenous catalytic reaction was shown to be prompted by various transition-metal ions which may interact with dissolved molecular oxygen to produce free radical species. Transition metal ions such as Cu^{2+}, Fe^{2+}, Zn^{2+} and Mn^{2+} were widely used as homogenous catalysts in the CWAO. Metal ions must be shifting between two or more oxidation states to promote the reaction. The performances of the homogeneous catalysts are closely related to the redox potential of transition metal ion. Arena et al. [30] proposed that the redox potential of several of transition metal ions varies as follows:

$E_{Cu^{2+}/Cu^{+}} = 0.171$ eV, $E_{Fe^{3+}/Fe^{2+}} = 0.771$ eV, $E_{MnO_2/Mn^{2+}} = 1.229$ eV at 25°C and pH = 1. They further investigated the activity and the selectivity of Cu^{2+}, Fe^{3+} and Mn^{2+} in the CWAO of phenol at 150°C under 0.9 MPa of oxygen pressure and demonstrated that the activity varied in the order was $Cu^{2+} > Fe^{3+} > Mn^{2+}$ [30], which was in accordance with their redox potential order. Cu^{2+}, with the lowest redox potential, was the most active homogenous catalyst. Fu et al. [36] compared the activity of several homogenous catalysts in the CWAO of a phenol and nitrobenzene containing wastewater. The performances varied as follows: $Cu^{2+} > Ni^{2+} > Co^{2+} > Ce^{2+} > Fe^{3+}$, which is also in agreement with the previous results, i.e. the lower the redox potential, the easier the reduction of the transition metal ion back to its initial oxidation state to undergo a new cycle [30].

Although the addition of homogeneous catalysts can significantly enhance the degradation of phenols into less toxic organics at lower temperature, the mineralization was still very low. In addition, homogeneous catalysts precipitate under alkaline conditions [30,46], generating a secondary pollution. Finally, the removal of the homogeneous catalyst from the solution requires more investments and complex operations. In turn, heterogeneous catalysts can overcome such shortages of homogenous catalysts. Nowadays, less attention is probably being paid to homogenous catalysts.

3.2 Heterogeneous catalysis

CWAO using heterogeneous catalysts is a three-phase reaction. Carbon materials, transition metal oxides or supported noble metals have been extensively studied. Hundreds of papers on the application of heterogeneous catalysts in the CWAO have been published. In the following, we will focus on the removal of phenolics and summarize the performances which have been achieved.

3.2.1 Carbon materials

Considering their stability in acidic/basic media and the absence of metal leaching phenomenon [47,48], carbon materials was widely recognized as appropriate catalysts in the CWAO. Bare activated carbons (AC) were primarily used in the CWAO of phenol by Baricot et al. [49]. Due to their high porosity and electron transfer capabilities, AC exhibited good performances in phenol elimination by adsorption and oxidation. However, they exhibited poor performances in TOC and/or COD abatement. Moreover, they are likely to burn under oxygen at high temperature [50,51]. A lot of attention has been paid to the surface and/or structure modifications, by introducing surface functional groups of doping with heteroatoms, to enhance the activity. Carbon nanofibers (CNFs) [47], carbon nanotubes (CNTs) [52], graphite and multi-walled carbon nanotubes (MWCNTs) [53,54] could be modified by the introduction of nitrogen or by acidic treatment to redistribute the surface electrons and adjust their characteristics, and finally improve their performances in the CWAO of organic pollutants. MWCNTs functionalized with carboxylic groups were tested at 155°C and 2.5 MPa. A solution containing 1000 $mg \cdot L^{-1}$ of phenol was completely degraded in 90 min in the presence of 0.4 $g \cdot L^{-1}$ of catalyst [55]. Wang et al. [56] compared the performances of MWCNTs, CNFs and graphite treated by HNO_3-H_2SO_4 (Fig. 4) in the removal of phenol. All of them exhibited

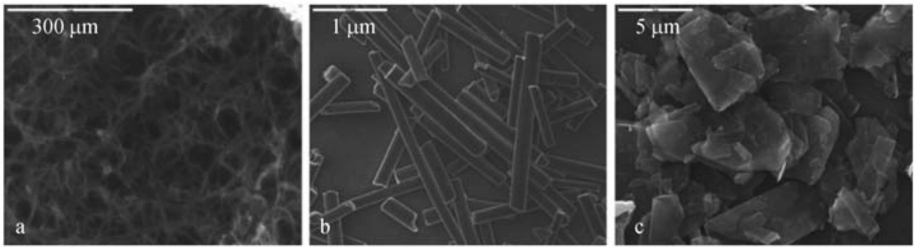


Fig. 4 SEM images of the functionalized MWCNTs (a), CNFs (b) and graphite (c) [56]

excellent activity in total conversion of phenol; however, functionalized MWCNTs showed higher TOC abatement (75%) than CNFs (60%) and graphite (40%).

Because of their high specific surface area and low cost, carbon materials were also effectively and efficiently used as supporters for CWAO catalysts. Barroso-Bogeat et al. [41] prepared a series of metal oxide catalysts (Al_2O_3, SnO_2, TiO_2, ZnO and W_2O_3) supported on AC. When metal oxides were impregnated on the surface, the S_{BET} and the pore volume were significantly reduced compared to the bare AC; except for TiO/AC which showed an increase S_{BET}. The reactivity of all these catalysts was enhanced. Fe/AC [57], Fe/CNTs and Fe/CNFs [48] were also investigated in the CWAO of phenols. All of them showed high organics removal efficiencies.

On the other hand, carbon-supported catalysts got deactivated easily because of the adsorption of polymers onto the surface and the blockage of the active sites during the reaction process. Besides, such catalysts appeared quite fragile because of the oxidation of the carbon support itself at high temperature under oxygen-rich conditions [57]. Transition metal leaching is another source of deactivation. Noble metal-loaded carbon materials also attracted lots of interest [39,40,58]. For example, Ru and Pt were impregnated on N-CNFs to prepared Ru/N-CNFs [39] and Pt/N-CNFs [40] catalysts. Both catalysts exhibited good catalytic activity and stability in the CWAO of phenol.

In summary, carbon materials are resistant to acidic and basic media, but readily deactivate upon CWAO because of the irreversible adsorption of the polymers on the surface and the blockage of the carbon porous structure [59]. Considering their low cost and high capability to dispose and stabilize metals, carbon materials are optimum catalyst's supports; however, their stability at high temperature and regenerability are still problems which still need to be solved.

3.2.2 Pillared clays materials

The pillared clay-based catalysts (PILCs) were widely applied as heterogeneous catalysts in environmental field to erase the refractory organics, due to their tunable porous structure and specific surface area [14,60–62]. The metallic hydrated polyoxocations were used as pillaring agents to provided thermally stable PILCs with high specific surface area (200–500 $m^2 \cdot g^{-1}$) [63]. The PILCs containing Al, Cu, Al-Fe or Al-Ce-Fe have been synthesized and applied in CWPO or photo-Fenton processes to degrade organics. PILC poorly performed in the degradation of phenol, while 96% of phenol can be removed by CuO/PILC at 140°C and 2 MPa [61]. Although CuO/PILC was very active in the first 2 h, the leaching of copper was very serious. Al-Fe/PILC was active in CWAO of phenol and insignificant catalyst leaching and deactivation at mild temperature (170°C) was observed [14,64]. The deposition of carboneous formation might cause the deactivation by blocking active sites and pore pathways [14,64].

3.2.3 Transition metal oxides

Transition metal oxides are widely developed in order to lower the harsh reaction conditions required for the WAO of phenols and to overcome the shortage related to the recycling of the homogeneous catalysts [42,43,65]. Cu-based catalysts exhibited interesting performances in the CWAO of organic pollutants, and thus received a widespread attention (Table 2). Cu or CuO supported on γ-Al_2O_3 [68], CeO_2 [69] and CeO_2–ZrO_2 [71] were investigated for decades. Normally, higher copper loading resulted in a higher catalytic activity. However, once the Cu loading exceeded a critic value, no further enhancement of the activity observed since the excess copper covered all the support and decreased the number of active sites [65].

Unfortunately, metal leaching was immediately recognized as a major drawback, impacting on the stability and generating a secondary pollution phenomenon [65,69,76]. Transition metal oxides were easily leached into solution under acidic and hot solution conditions [30]. The leached metal ions were then acting as homogenous catalysts and even exceeded the performances of heterogeneous catalytic system. Cu/MCM-41 catalyst was evaluated in the CWAO of phenol at 150°C and 200°C. Although more than 90% of the substrate and 90% of TOC were eliminated within 60 min, Cu leaching was severe and about 60% of the initial Cu was dissolved into the solution [65]. Both homogenous and heterogeneous catalytic reactions contributed to the high conversion of the substrates. To develop sustainable catalysts with attractive activity and resistance to leaching, bimetallic catalysts such as CuO combined with CoO, FeO, MnO or ZnO supported on γ-Al_2O_3 were explored [43]. Such bimetallic catalysts were tested for 192 h in a packed bed reactor, operated in a trickle flow regime (C_{Phenol} = 5000 $mg \cdot L^{-1}$, 2.4 h of WHSV, t = 140°C, P_{O_2} = 0.9 MPa, pH 5.9). The results demonstrated that all the catalysts undergo severe deactivation during the first 48 of operation. Afterward, the catalysts present a steady activity until the end of the test. Less than 2% of the initial Cu was leached into solution and the catalyst deactivation was remarkably hindered.

Spinel-type oxides were also developed to solve the leaching and deactivation problems [76–79]. The Zn-Fe-Al spinel phase [77,78] was explored and tested in the CWAO of phenols. Complete phenols and 90% COD were achieved under mild reaction conditions; but Fe^{2+}, Fe^{3+} and Zn^{2+} leaching were observed upon reaction. Further studies to identify suitable metal ions to stabilize the spinel phase are still necessary. A $Cu_{0.10}Zn_{0.90}Al_{1.90}Fe_{0.10}O_4$ spinel catalyst was tested in the CWAO of phenol in an

Table 2 Transition metal applied in CWAO of phenols

catalyst	reaction condition	converation of substrates/%	TOC (COD) removal/%	metal leaching	reference
Fe/AC	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{air}} = 8$ atm, $t = 400$ K, catalyst: 2.5 g, pH 3.5, reactor: trickle bed, 350 min	70	60	/	[57]
Cu(17.8%wt)/MCM-41	$C_{\mathrm{Phenol}} = 1300\ \mathrm{mg \cdot L^{-1}} P_{\mathrm{O_2}} = 2.0$ MPa, $t = 150$°C, catatlyst:1 $\mathrm{g \cdot L^{-1}}$ batch reactor, 2 h	90	50	59.8%	[65]
	$C_{\mathrm{Phenol}} = 1300\ \mathrm{mg \cdot L^{-1}}$, $t = 200$°C, $P_{\mathrm{O_2}} = 3.4$MPa, catatlyst:1 $\mathrm{g \cdot L^{-1}}$, batch reactor, 2 h	100	90	>59.8%	[65]
35%CuO-65%ZnO	$C_{\mathrm{Phenol}} = 3000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 300$ psig, $t = 403$ K, catalyst: 5 $\mathrm{g \cdot L^{-1}}$ reactor: autoclave, 1000 $\mathrm{r \cdot min^{-1}}$, 2 h	100	/	/	[42]
26%CuO-74%Cu chromite	$C_{\mathrm{Phenol}} = 3000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 300$ psig, $t = 393$ K, catalyst: 5 $\mathrm{g \cdot L^{-1}}$ reactor: autoclave, 1000 $\mathrm{r \cdot min^{-1}}$, 2 h	100	/	/	[42]
CuO-85-95%Al_2O_3	$C_{\mathrm{Phenol}} = 3000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 300$ psig, $t = 393$ K, catalyst: 5 $\mathrm{g \cdot L^{-1}}$ reactor: autoclave, 1000 $\mathrm{r \cdot min^{-1}}$, 2 h	100	/	/	[42]
10%CuO-2%ZnO- Al_2O_3	$C_{\mathrm{Phenol}} = 5000\ \mathrm{mg \cdot L^{-1}}$, $t = 140$°C, $P_{\mathrm{O_2}} = 0.9$ MPa, pH:5.9, packed bed reactor, 192 h	40	/	$Cu^{2+} \leqslant 2\%$	[43]
10%CuO-2%Fe_2O_3- Al_2O_3	$C_{\mathrm{Phenol}} = 5000\ \mathrm{mg \cdot L^{-1}}$, $t = 140$°C, $P_{\mathrm{O_2}} = 0.9$ MPa, pH:5.9, packed bed reactor, 192 h	30	/	$Cu^{2+} \leqslant 2\%$	[43]
10%CuO-2%CoO- Al_2O_3	$C_{\mathrm{Phenol}} = 5000\ \mathrm{mg \cdot L^{-1}}$, $t = 140$°C, $P_{\mathrm{O_2}} = 0.9$ MPa, pH:5.9, packed bed reactor, 192 h	25	/	$Cu^{2+} \leqslant 2\%$	[43]
10%CuO-2%MnO_2- Al_2O_3	$C_{\mathrm{Phenol}} = 5000\ \mathrm{mg \cdot L^{-1}}$, $t = 140$°C, $P_{\mathrm{O_2}} = 0.9$ MPa, pH:5.9, packed bed reactor, 192 h	20	/	$Cu^{2+} \leqslant 2\%$	[43]
10%CuO- Al_2O_3	$C_{\mathrm{Phenol}} = 5000\ \mathrm{mg \cdot L^{-1}}$, $t = 140$°C, $P_{\mathrm{O_2}} = 0.9$ MPa, pH:5.9, packed bed reactor, 192 h	25	/	$Cu^{2+} \leqslant 2\%$	[43]
42wt%CuO-47wt%ZnO-Al_2O_3	$C_{\mathrm{Phenol}} = 0.0532\ \mathrm{mol \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 5.6$ bar, catalyst: 5 $\mathrm{g \cdot L^{-1}}$ $t = 130$°C, batch reactor, 1000 $\mathrm{r \cdot min^{-1}}$, 2 h	100	90	/	[66]
$Cu_{0.10}Zn_{0.90}Al_{1.90}Fe_{0.10}O_4$	$C_{\mathrm{Phenol}} = 4.29\ \mathrm{g \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 10$ bar, $t = 150$°C, catalyst:25 $\mathrm{g \cdot L^{-1}}$, autoclave, 800 $\mathrm{r \cdot min^{-1}}$, pH: 5.9, 2 h	100	COD:95	Cu^{2+}:60 $\mathrm{mg \cdot L^{-1}}$, Fe^{2+}:4.05 $\mathrm{mg \cdot L^{-1}}$	[67]
CeO_2	$C_{\mathrm{Phenol}} = 400\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 10$ bar, catalyst: 1 $\mathrm{g \cdot L^{-1}}$, $t = 160$°C, reactor: autoclave, 3 h	90	80	/	[67]
CeO_2-TiO_2	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{air}} = 30$ bar, catalyst: 4 $\mathrm{g \cdot L^{-1}}$ $t = 150$°C, batch reactor, 2 h	/	100(COD)/77(TOC)	/	[44]
	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{air}} = 35$ bar, catalyst: 4 $\mathrm{g \cdot L^{-1}}$, $t = 140$°C, packed bed reactor, 100 h	/	91(COD)/80(TOC)	Ce^{2+}:0.2, Ti^{2+}:0.04 mg/L	
CeO_2(20wt%)/γ-Al_2O_3	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 15$ bar, catalyst: 3 $\mathrm{g \cdot L^{-1}}$ $t = 180$°C, autoclave, 2 h	100	80	/	[68]
$CuO_{0.2}$-$Ce_{0.8}O_2$, (Co-precipitation)	$C_{\mathrm{Phenol}} = 1\ \mathrm{g \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 0.73$ MPa, catalyst: 1 $\mathrm{g \cdot L^{-1}}$, $t = 150$°C, semi batch CST reactor, 1000 $\mathrm{r \cdot min^{-1}}$	100	85	Cu^{2+}:103 $\mathrm{mg \cdot L^{-1}}$	[69]

(*Continued*)

catalyst	reaction condition	converation of substrates/%	TOC (COD) removal/%	metal leaching	reference
CuO-CeO_2(so-gel)	$C_{\mathrm{Phenol}} = 1\ \mathrm{g \cdot L^{-1}}$, $t = 150°\mathrm{C}$, $P_{\mathrm{O_2}} = 0.73$ MPa, catalyst: $1\ \mathrm{g \cdot L^{-1}}$, semi batch CST reactor, $1000\ \mathrm{r \cdot min^{-1}}$	100	90	Cu^{2+}:5.7 $\mathrm{mg \cdot L^{-1}}$, Ce:30 $\mathrm{mg \cdot L^{-1}}$	[69]
$Ce_{0.80}Zr_{0.20}O_2$	$C_{\mathrm{Phenol}} = 650\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 2$ MPa, catalyst:1 $\mathrm{g \cdot L^{-1}}$, $t = 160°\mathrm{C}$, autoclave, 2 h	98.2	85.2	$\leqslant 0.05\ \mathrm{mg \cdot L^{-1}}$	[70]
CuO(wt5%)/CeO_2–ZrO_2	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 10$ bar, catalyst: $9\ \mathrm{g \cdot L^{-1}}$ $t = 160°\mathrm{C}$, reactor: autoclave, $800\ \mathrm{r \cdot min^{-1}}$, 3 h	100	/	/	[71]
Cu-CeO_2/γ-Al_2O_3	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 1.5$ MPa, catalyst: $3\ \mathrm{g \cdot L^{-1}}$, $t = 180°\mathrm{C}$, autoclave, 4 h	100	COD removal:95	/	[67]
Mn-CeO_2/γ-Al_2O_3	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 1.5$ MPa, catalyst: $3\ \mathrm{g \cdot L^{-1}}$, $t = 180°\mathrm{C}$, autoclave, 4 h	55	COD removal:45	/	
Ni(20wt%)/CeO_2–ZrO_2	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 1$ atm, catalyst: $9\ \mathrm{g \cdot L^{-1}}$, $t = 160°\mathrm{C}$, autoclave, $800\ \mathrm{r \cdot min^{-1}}$, 3 h	57.8	/	/	[72]
Mn(21.4wt%)CeO_x	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, catalyst:5 $\mathrm{g \cdot L^{-1}}$, $t = 110°\mathrm{C}$, $P_{\mathrm{O_2}} = 9$ bar, autoclave, 800 $\mathrm{r \cdot min^{-1}}$, 3 h	100	95	$\leqslant 1\ \mathrm{mg \cdot L^{-1}}$	[73]
$Mn_{0.6}Ce_{0.4}O_2$	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 5$ bar, catalyst: $5\ \mathrm{g \cdot L^{-1}}$ $t = 110°\mathrm{C}$, autoclave, $900\ \mathrm{r \cdot min^{-1}}$	95	94	/	[74]
$Ce_{0.75}Zr_{0.25}O_2$	$C_{\mathrm{Phenol}} = 3000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 5$ bar, catalyst: $3.8\ \mathrm{g \cdot L^{-1}}$ $t = 140°\mathrm{C}$, autoclave, $800\ \mathrm{r \cdot min^{-1}}$, 7 h	40.2	52.4	/	[75]
$Ce_{0.5}Mn_{0.5}O_2$	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, $P_{\mathrm{O_2}} = 5$ bar, catalyst: $3.8\ \mathrm{g \cdot L^{-1}}$ $t = 140°\mathrm{C}$, autoclave, $800\ \mathrm{r \cdot min^{-1}}$, 7 h	96.5	26.8	/	
γ-Al_2O_3/Ce–Mn	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, P_{total}: 3.5–4.5 bar, $V_{\mathrm{O_2}} = 60\ \mathrm{mL \cdot min^{-1}}$, $t = 140°\mathrm{C}$, membrane autoclave, 7 h	92.4	53.6	/	
γ-Al_2O_3/Ce–Zr	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg \cdot L^{-1}}$, P_{total}: 3.5–4.5 bar, $V_{\mathrm{O_2}} = 60\ \mathrm{mL \cdot min^{-1}}$, $t = 140°\mathrm{C}$, membrane autoclave, 7 h	43.7	75.4	/	

autoclave reactor [76]. The phenol was completely degraded in the reaction and 95% COD removal were achieved during successive tests at 170°C [76]. Compared to the supported copper catalysts, the spinel copper oxide was very stable against leaching and showed high activity. Spinel phases of Cu and Cu-Ni were also alternatively tested in trickle bed and autoclave reactor. Both of them showed higher activity and no leaching were ever detected in solution even after 15 days of operation in a trickle bed reaction. In the autoclave, Cu spinel deactivated, but the Cu-Ni spinel catalysts was demonstrated to be stable. The Cu-Ni spinel phase prevented the production of polymers [79].

The catalyst preparation method also played an important role in determining the characteristics of the catalysts [69,77]. The Zn-Al-Fe spinel phase prepared by hydrothermal showed a higher specific surface and higher performances in the CWAO compared to the catalysts synthesized by co-precipitation method [77]. Hocevar et al. [69] compared the activity and selectivity of $Ce_{1-x}CuO_xO_{1-d}$ catalysts prepared by co-precipitation (Co-pre) and sol-gel (S-G) methods. XRD and BET results demonstrated that there were significant differences in the structure and the specific surface areas. The specific surface areas of catalysts prepared by S-G method were substantially higher compared to the Co-pre method. The activities and selectivities to CO_2 of the S-G samples were about 4 times and 25% higher than the Co-pre catalysts, respectively. Moreover, Cu^{2+} leaching from the S-G samples (5.7 $mg \cdot L^{-1}$) was much lower compared with the Co-Pre samples (103 $mg \cdot L^{-1}$).

In recent years, CeO_2 based catalysts have attracted a lot of attention in the CWAO of organics, because of its high specific surface area and high oxygen storage capacity (OSC) [80,81]. Considering the low solubility of oxygen in water, the rate of O_2 transferring from the gas phase toward the catalyst has a decisive impact on the whole oxidation process. The role of the ceria support would facilitate this process because of its high OSC. CeO_2 and CeO_2 supported materials were investigated in an autoclave reactor (Fig. 5). Among all the catalysts, $CeO_2/\gamma\text{-}Al_2O_3$ was found to be the most active [82]. The Lewis acidic sites on the $\gamma\text{-}Al_2O_3$ support were proposed to be able to activate the electronic doublet of the oxygen atom of the hydroxyl group of phenol, and thus enhance the ortho-oxidation [83]. However, the stability of pure CeO_2 was poor since high OSC favored the para-oxidation of phenol, producing p-benzoquinone and subsequently polymeric products. The accumulation of such adsorbed carbon species led to severe negative effects on its activity and physical structure [83]. Thus, CeO_2-based compounds such as $CeO_2\text{-}ZrO_2$ [70] and $CeO_2\text{-}MnO_x$ [84,85] were developed to overcome this problem. The addition of ZrO_2 could remarkable enhance the activity and stability of CeO_2, with high TOC removal and no leaching. The carbonaceous deposits on the surface could be easily removed by calcination [70]. The structure, surface and catalytic properties of $CeO_2\text{-}MnO_x$ have been broadly examined in the removal of refractory organic pollutants. It was recognized that the introduction of Mn into CeO_2-based catalysts could improve the stability and redox activity of CeO_2, resulting in a perfect elimination and mineralization of the substrates [73,84,85].

Generally, metal leaching and polymer deposits were identified as the main reasons for the deactivation of transition metal oxide catalysts upon CWAO [30,73,84–86]. As the metal ions were leached into the solution, both homogenous and heterogeneous combined to the elimination of the substrates [30]. The homogenous reaction occurred via a radical-chain mechanism; while a Langmuir-Hinshelwood (L-H) mechanism was involved upon heterogeneous catalysts. The later one was shown to be remarkably influenced by the specific surface of the catalyst, since the first reaction step consists in the adsorption of the substrate on the catalyst surface [73,85,86]. Exploring new kinds of catalysts to solve

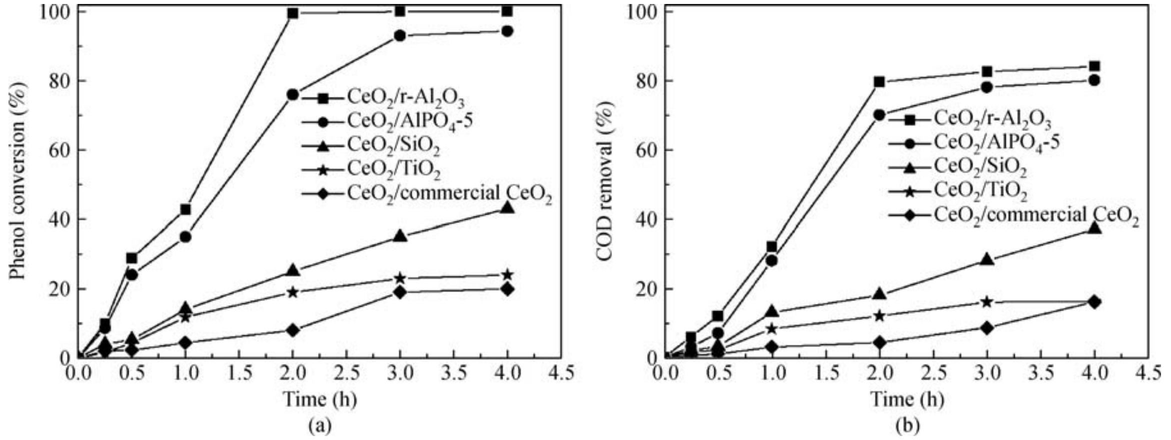


Fig. 5 Performances of CeO_2 and CeO_2 supported catalysts in the CWAO of phenol; (a) Conversion of phenol; (b) COD removal. [T:180°C, cat: 3.0 $g \cdot L^{-1}$, P_{O_2}: 1.5 MPa, Ce: 20 wt%, C_{Phenol}:1000 $mg \cdot L^{-1}$] [82]

such deactivation and secondary pollution limitations is a promising prospect.

3.2.4 Noble metals

Supported noble metal catalysts were shown to be very effective and resistant toward leaching. As such, they are probably the most promising heterogeneous CWAO catalysts. Some of the noble metal catalysts applied in the CWAO of phenolic compounds is listed in Table 3.

Ru or Ru and Ce supported on γ-Al_2O_3 (0.3 wt% Ru) were obtained by thermolysis of $Ru_3(CO)_{12}$. Such catalysts exhibited high activity in the CWAO of wastewater with initial COD as high as 200,000 $mg \cdot L^{-1}$ [95]. The performances of the catalysts were obviously affected by the pretreatment method and the support (Fig. 6). The results indicated that the Ru-Ce/γ-Al_2O_3 catalyst reduced in H_2 was the most active catalyst since CeO_2 could improve the dispersion of Ru on the surface and also promote the interaction with γ-Al_2O_3. The Ru-Ce/γ-Al_2O_3 catalyst also demonstrated good thermal stability. Rarely any carbonaceous deposit was evidenced on the catalyst surface and no metal leaching were ever detected [95].

Carbon materials [39], TiO_2 [45], ZrO_2 [90] and CeO_2 [88,89] were often chosen as supports for noble metals. In batch reactors, it was observed that the substrates were mostly eliminated from the solution by polymerization or degradation into intermediates. Ru supported on ZrO_2-CeO_2 attracted a lot of attention because of its high activity [89,91,97]. The performances of 3%Ru/ZrO_2-CeO_2, 3% Ru/ZrO_2 and 3%Ru/CeO_2 were studied in the CWAO of 2-chlorophenol [97]. It was obvious that the 3%Ru/ZrO_2-CeO_2 catalyst showed much higher activity than 3%Ru/ZrO_2 and 3%Ru/CeO_2. It exhibited high activity even at low temperature of 393 K and 3 MPa. The activities of fresh and used Ru/ZrO_2-CeO_2 catalysts were also compared in a packed-bubble column reactor [91]. After 100 h reaction, the leaching of the active species was very limited. The structure of the catalyst and the active phase did not change much, although carbonaceous deposits were detected. These deposits can be easily removed at 300°C. This showed that ZrO_2-CeO_2 appeared as a promising support in the CWAO of persistent organics.

Besides Ru, supported Pt catalysts also have received considerable attention for phenol oxidation. Pt/ZrO_2, Pt/TiO_2, Pt/TiO_2-CeO_2, Pt/ZrO_2-CeO_2 and Pt/Ce-γAl_2O_3 [87,89,92] were extensively investigated in the CWAO of organics. Pt catalysts exhibit good activities in phenolics degradation and mineralization. Martín-Hernández et al. [92] compared the catalytic activities of Ru/TiO_2, Ru/ZrO_2, Pt/TiO_2 and Pt/ZrO_2 in the CWAO of 2-cholophenol. The Ru-based catalyst was much more active than their Pt counterparts in the CWAO of phenol and aniline. This was in accordance with the results achieved by Imamura et al. [88] demonstrating that Ru $\geqslant$ Pt > Rh. Considering the prices of the active metal and their performances, Ru-based catalysts are recommend for the CWAO of organics.

3.2.5 Reactor

Since the mixing of the reactants with the catalyst is different depending on the reactor, different degradation efficiencies might be expected [16]. Even in the same kind of reactor, the material and the geometry of the reactor were found to have an important impact on the free radical termination steps. For example, metal surfaces are likely to consume the free radicals and thus hinder the reaction [18]. Moreover, the non-catalytic or the homogeneous catalytic wet air oxidation, are two-phase reactions between the gas and the liquid phase and the mass transfer of oxygen from the gas phase to the liquid phase is a crucial step. The heterogeneous process is a three phase reaction and the mass transfer resistances are even more complex.

Batch, packed-bed [44], trickle bed [59] and packed-bubble column reactors [91] have been compared. In a batch reactor, ca.100% COD and 77% TOC removals were obtained upon phenol oxidation over a CeO_2-TiO_2 catalyst at 150°Cfor 120 min; while in the packed-bed reactor, over 91% COD and 80% TOC were removed at 140°C only. Upon long-term operation, TOC removal decreased remarkably in the autoclave because polymers were formed and deposited on the active site of the catalyst; while TOC abatement did not change much in the packed-bed reactor [44]. The CWAO of phenolics over an AC catalyst was tested in a batch reactor and a trickle bed reactor at the same temperature and oxygen pressure. The initial elimination rate of phenol in the batch reactor was much faster than that in the trickle- bed. However, the reaction slowed down, and the final mineralization degree in the batch reactor was much lower than in the trickle bed reactor. This could be attributed to the generation of condensation polymers in the batch reactor which progressively led to the deactivation of the catalyst [59]. Catalytic oxidation of 4-hydroxybenzoic acid on AC performed in an autoclave and a fixed-bed reactor also proved that the production of small carboxylic acids and carbon dioxide in the trickle bed reactor was obviously higher than in the autoclave. The higher reaction rate in the autoclave at the beginning was due to the generation of more polymers. This was attributed to the higher catalyst to substrate ratio in the trickle bed reactor. AC performed well in the degradation of aromatic compounds, with up to 70% mineralization and 80% organic removal [98].

CWAO performed in membrane reactors also attracted some attention [75,99]. CWAO of phenol over Pt/Ce-Zr in a common autoclave, an autoclave reactor equipped with a membrane diffuser and a membrane reactor (Fig. 8) were compared under the same reaction condition [75]. As mentioned above, unwanted carbonaceous deposits deactivated the catalyst in the autoclave. The membrane

Table 3 Noble metal application in CWAO of phenols

catalyst	reaction condition	conversation of substrates/%	removal of TOC(COD)/%	reference
(1%–3%)Ru/(0–6.8%)N-CNFs	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg{\cdot}L^{-1}}$, $t = 140°\mathrm{C}$, $P_{\mathrm{air}} = 10$ bar, catalyst: $1.67\ \mathrm{g{\cdot}L^{-1}}$, 1 h, autoclave, $1200\ \mathrm{r{\cdot}min^{-1}}$	93	84.7	[39]
Ru(1.5wt%)/ C	$\mathrm{COD_{Phenol}} = 5\ \mathrm{g{\cdot}L^{-1}}$, $P_{\mathrm{O_2}} = 2$ MPa, catalyst: $4\ \mathrm{g{\cdot}L^{-1}}$, autoclave, $t = 160°\mathrm{C}$, 3 h	85	13	[58]
Ru(1.5wt%)-$\mathrm{CeO_2}$(5.5wt%)/C	$C_{\mathrm{Phenol}} = 5\ \mathrm{g{\cdot}L^{-1}}$ of COD, $P_{\mathrm{O_2}} = 2$ MPa, catalyst: $4\ \mathrm{g{\cdot}L^{-1}}$, autoclave, $t = 160°\mathrm{C}$, 3 h	99.5	19	
Pt/$\mathrm{TiO_2}$-$\mathrm{CeO_2}$	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg{\cdot}L^{-1}}$, $P_{\mathrm{O_2}} = 10$ bar, catalyst: $1\ \mathrm{g{\cdot}L^{-1}}$, $t = 160°\mathrm{C}$, batch reactor, $1000\ \mathrm{r{\cdot}min^{-1}}$, 2 h	96	96	[87]
$\mathrm{Ce_{0.75}Zr_{0.25}O_2}$/Pt(1.6wt%)	$C_{\mathrm{Phenol}} = 3000$ mg/L, $P_{\mathrm{O_2}} = 5$ bar, catalyst: $3.8\ \mathrm{g{\cdot}L^{-1}}$ $t = 140°\mathrm{C}$, autoclave, $800\ \mathrm{r{\cdot}min^{-1}}$, 5 h	96.1	77.8	[75]
Pt/$\mathrm{TiO_2}$	$C_{\mathrm{Phenol}} = 1000\ \mathrm{mg{\cdot}L^{-1}}$, $P_{\mathrm{O_2}} = 10$ bar, catalyst: $1\ \mathrm{g{\cdot}L^{-1}}$, $t = 160°\mathrm{C}$, batch reactor, $1000\ \mathrm{r{\cdot}min^{-1}}$, 2 h	85	77	[87]
Ru(5%)/$\mathrm{CeO_2}$	$\mathrm{TOC_{Phenol}} = 2000\ \mathrm{mg{\cdot}L^{-1}}$, $P_{\mathrm{O_2}} = 10$ bar, catalyst: 12 mmol, pH = 5.4, $t = 200°\mathrm{C}$, batch reactor, $1000\ \mathrm{r{\cdot}min^{-1}}$, 1 h	/	94.8	[88]
Ru(5%)/$\mathrm{TiO_2}$-$\mathrm{CeO_2}$	$C_{\mathrm{Phenol}} = 2.098\ \mathrm{g{\cdot}L^{-1}}$, $P_{\mathrm{O_2}} = 20$ bar, catalyst: $4\ \mathrm{g{\cdot}L^{-1}}$, pH = 5.4, $t = 160°\mathrm{C}$, batch reactor, $1000\ \mathrm{r{\cdot}min^{-1}}$, 1 h	99.5	35	[45]
Pt(5%)/$\mathrm{TiO_2}$-$\mathrm{CeO_2}$	$C_{\mathrm{Phenol}} = 2.098\ \mathrm{g{\cdot}L^{-1}}$, $P_{\mathrm{O_2}} = 20$ bar, catalyst: $4\ \mathrm{g{\cdot}L^{-1}}$, pH = 5.4, $t = 160°\mathrm{C}$, batch reactor, $1000\ \mathrm{r{\cdot}min^{-1}}$, 3 h	100	87	[45]
Ru/$\mathrm{ZrO_2}$-$\mathrm{CeO_2}$	$C_{\mathrm{Phenol}} = 2.098\ \mathrm{g{\cdot}L^{-1}}$, $P_{\mathrm{O_2}} = 20$ bar, catalyst: $4\ \mathrm{g{\cdot}L^{-1}}$, $t = 160°\mathrm{C}$, batch reactor, $1000\ \mathrm{r{\cdot}min^{-1}}$, 3 h	98	80	[89]
Pt(1%)/$\mathrm{ZrO_2}$-$\mathrm{CeO_2}$	$C_{\mathrm{Phenol}} = 2.098\ \mathrm{g{\cdot}L^{-1}}$, $P_{\mathrm{O_2}} = 20$ bar, catalyst: $4\ \mathrm{g{\cdot}L^{-1}}$, $t = 160°\mathrm{C}$, batch reactor, $1000\ \mathrm{r{\cdot}min^{-1}}$, 3 h	90	60	[89]
Ru/$\mathrm{ZrO_2}$	$C_{\mathrm{Pentachlorophenol}} = 2000\ \mathrm{mg{\cdot}L^{-1}}$, $P_{\mathrm{O_2}} = 10$ bar, catalyst: $1\ \mathrm{g{\cdot}L^{-1}}$, $t = 180°\mathrm{C}$, batch reactor, $600\ \mathrm{r{\cdot}min^{-1}}$, 90 min	92	/	[90]
Ru/$\mathrm{ZrSiO_2}$	$C_{\mathrm{Pentachlorophenol}} = 2000\ \mathrm{mg{\cdot}L^{-1}}$, $P_{\mathrm{O_2}} = 10$ bar, catalyst: $1\ \mathrm{g{\cdot}L^{-1}}$, $t = 180°\mathrm{C}$, batch reactor, $600\ \mathrm{r{\cdot}min^{-1}}$, 90 min	100	30	[90]
Ru(3wt%)/$\mathrm{ZrO_2}$-$\mathrm{CeO_2}$	$C_{\mathrm{phenol}} = 2100\ \mathrm{mg{\cdot}L^{-1}}$, $\mu_{\mathrm{L}} = 0.5\ \mathrm{mL{\cdot}min^{-1}}$,$\mu_{\mathrm{O_2}} = 80\ \mathrm{mL{\cdot}min^{-1}}$, $t = 140°\mathrm{C}$, $P_{\mathrm{air}} = 4$ MPa, packed-bubble column reactor, 100 h	100	100	[91]

(*Continued*)

catalyst	reaction condition	conversation of substrates/%	removal of TOC(COD)/%	reference
Ru(3wt%)/TiO_2	$C_{\text{p-nitrophenol}} = 5000\ \text{mg}\cdot\text{L}^{-1}$, $t = 180°\text{C}$, $P_{O_2} = 7.6$ bar, catalyst: $3.6\ \text{g}\cdot\text{L}^{-1}$, batch reactor, $1000\ \text{r}\cdot\text{min}^{-1}$, 480 min	94	76	[92]
Ru(3wt%)/ZrO_2	$C_{\text{p-nitrophenol}} = 5000\ \text{mg}\cdot\text{L}^{-1}$, $t = 180°\text{C}$, $P_{O_2} = 7.6$ bar, catalyst: $3.6\ \text{g}\cdot\text{L}^{-1}$, batch reactor, $1000\ \text{r}\cdot\text{min}^{-1}$, 480 min	97	78	
Ru(3wt%)/TiO_2	$C_{\text{p-nitrophenol}} = 5000\ \text{mg}\cdot\text{L}^{-1}$, $C_{\text{NaCl}} = 25\ \text{g}\cdot\text{L}^{-1}$, $t = 180°\text{C}$, $P_{O_2} = 7.6$ bar, batch reactor, $1000\ \text{r}\cdot\text{min}^{-1}$, 480 min	94	76	
Pt(3wt%)/TiO_2	$C_{\text{p-nitrophenol}} = 5000\ \text{mg}\cdot\text{L}^{-1}$, $t = 180°\text{C}$, $P_{O_2} = 7.6$ bar, catalyst: $3.6\ \text{g}\cdot\text{L}^{-1}$, batch reactor, $1000\ \text{r}\cdot\text{min}^{-1}$, 480 min	98	80	
Pt(3wt%)/ZrO_2	$C_{\text{p-nitrophenol}} = 5000\ \text{mg}\cdot\text{L}^{-1}$, $t = 180°\text{C}$, $P_{O_2} = 7.6$ bar, catalyst: $3.6\ \text{g}\cdot\text{L}^{-1}$, batch reactor, $1000\ \text{r}\cdot\text{min}^{-1}$, 480 min	98	78	
$Pt_xAg_{1-x}MnO_2$/ CeO_2	$C_{\text{Phenol}} = 1000\ \text{mg}\cdot\text{L}^{-1}$, $t = 80°\text{C}$, $P_{O_2} = 0.5$ MPa, catalyst: $5\ \text{g}\cdot\text{L}^{-1}$, autoclave, 2 h	80	80(TOC)	[93]
1%Ru/5%CeO_2-Al_2O_3(impregnation)	$C_{\text{Phenol}} = 5000\ \text{mg}\cdot\text{L}^{-1}$, $\mu_L = 1\ \text{mL}\cdot\text{min}^{-1}$, $t = 80°\text{C}$, $P_{O_2} = 0.5$ MPa, $\mu_{O_2} = 0.46\ \text{L}\cdot\text{min}^{-1}$, catalyst: $7.5\ \text{g}\cdot\text{L}^{-1}$, trickle bed, $t = 140°\text{C}$, $P_{O_2} = 7$ atm, 7 h	30	30	[94]
1%Ru/5%CeO_2-Al_2O_3 (co-impregnation)	$C_{\text{Phenol}} = 5000\ \text{mg}\cdot\text{L}^{-1}$, $\mu_L = 1\ \text{mL}\cdot\text{min}^{-1}$, $t = 80°\text{C}$, $P_{O_2} = 0.5$ MPa, $\mu_{O_2} = 0.46\ \text{L}\cdot\text{min}^{-1}$, catalyst: $7.5\ \text{g}\cdot\text{L}^{-1}$, trickle bed, $t = 140°\text{C}$, $P_{O_2} = 7$ atm, 7 h	28	25.4	
1%Ru/5%CeO_2-Al_2O_3 (co-precipitation)	$C_{\text{Phenol}} = 5000\ \text{mg}\cdot\text{L}^{-1}$, $\mu_L = 1\ \text{mL}\cdot\text{min}^{-1}$, $t = 80°\text{C}$, $P_{O_2} = 0.5$ MPa, $\mu_{O_2} = 0.46\ \text{L}\cdot\text{min}^{-1}$, catalyst: $7.5\ \text{g}\cdot\text{L}^{-1}$, trickle bed, $t = 140°\text{C}$, $P_{O_2} = 7$ atm, 7 h	6	5	
Ru(0.3wt%)/γ-Al_2O_3	$C_{\text{COD}} = 200000\ \text{mg}\cdot\text{L}^{-1}$,$P_{O_2} = 3$ MPa, $\mu_{O_2} = 150\ \text{mL}\cdot\text{min}^{-1}$, catalyst: 7.5 g $\cdot\text{L}^{-1}$, packed-bed reactor, $t = 245°\text{C}$, $P_{O_2} = 7$ atm, 100 h	95	COD removal:75-80	[95]
Ru(0.3wt%)-Ce/γ-Al_2O_3	$C_{\text{COD}} = 200000\ \text{mg}\cdot\text{L}^{-1}$, $P_{O_2} = 3$ MPa, $\mu_{O_2} = 150\ \text{mL}\cdot\text{min}^{-1}$, catalyst: 7.5 g $\cdot\text{L}^{-1}$, packed-bed reactor, $t = 245°\text{C}$, $P_{O_2} = 7$ atm, 100 h		COD removal:95	
Pt-Ce(1wt%)/ Al_2O_3(H_2PtCl_6 as precursor)	$C_{\text{Phenol}} = 1000\ \text{mg}\cdot\text{L}^{-1}$, $t = 170°\text{C}$, $P_{\text{air}} = 5.05$ MPa, 2 h, catalyst: $7.5\ \text{g}\cdot\text{L}^{-1}$, autoclave, $1000\ \text{r}\cdot\text{min}^{-1}$, 3 h	100	/	[96]
Pt-Ce(1wt%)/ Al_2O_3($Pt(NH_3)_4Cl_2$ as precursor)	$C_{\text{Phenol}} = 1000\ \text{mg}\cdot\text{L}^{-1}$, $t = 170°\text{C}$, $P_{\text{air}} = 5.05$ MPa, 2 h, catalyst: $7.5\ \text{g}\cdot\text{L}^{-1}$, autoclave, $1000\ \text{r}\cdot\text{min}^{-1}$, 3 h	90	/	
γ-Al_2O_3/Ce-Zr-Pt(1.6wt%)	$C_{\text{Phenol}} = 1000\ \text{mg}\cdot\text{L}^{-1}$, P_{total}: 3.5–4.5 bar, $V_{O_2} = 60\ \text{mL}\cdot\text{min}^{-1}$, $t = 140°\text{C}$, membrane autoclave, 7 h	42.7	66.7	[75]
γ-Al_2O_3/Ce-Mn-Pt (1.6wt%)	$C_{\text{Phenol}} = 1000\ \text{mg}\cdot\text{L}^{-1}$, P_{total}: 3.5–4.5 bar, $V_{O_2} = 60\ \text{mL}\cdot\text{min}^{-1}$, $t = 140°\text{C}$, membrane autoclave, 7 h	54.5	44.4	

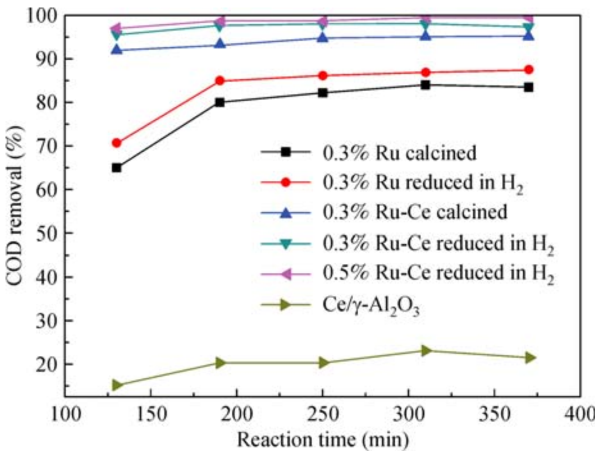


Fig. 6 Ru and Ru-Ce catalyst performances in the COD removal [initial COD: 200000 mg·L^{-1}, T: 245°C, LHSV: 1.5 h^{-1}, reaction pressure: 3.0 MPa, O_2 flowing rate: 150 mL·min^{-1}] [95]

diffuser in the autoclave changed the distribution of products and no carbonaceous acids were detected. The same was observed in the membrane reactor. Only CO_2 and carbonaceous deposits were observed in the latter two reactors. The polymers blocked the membrane surface and progressively deactivated the membrane systems. This was one of the main drawbacks of the membrane reactors which hinder their wide application in the CWAO [75].

Among the reactors mentioned above, the autoclave reactor is widely recognized for its compact structure and fast initial reaction rate, which is good for handling high concentrations of organics in a short time. Fixed bed reactor is quite qualified for deep oxidation of organics and the catalyst does not easily get deactivated, although the reaction rate is slower than in an autoclave.

4 Combined CWAO and biodegradation

Total mineralization of phenols by WAO requires high temperature and high oxygen pressure, since the carbonic acids which are formed as intermediates are very refractory toward further decomposition. This implies high capital and operation costs [31]. Biological processes are accepted as a first choice process for the treatment of organic pollutants. However, biological processes are not suitable for the treatment of organics which are inhibitory, toxic or resistant to biological treatments [100]. Therefore WAO or CWAO was considered as pre-treatment step, to partly decompose the initial biological toxic organics into biodegradable intermediates, before a biodegradation treatment (BD) to complete the mineralization of the organics in an economical way.

The biodegradability of the effluent after the pre-treatment is a determining factor for the combination of WAO or CWAO with BD. The biodegradability is usually measured by the percentage of readily biodegradable COD (COD_{RB}) [101]. Once the oxygen consumption (OC) is obtained from the respirometric tests, the COD_{RB} can be calculated using the heterotrophic yield coefficient (Y_H) (Eq. (9)):

$$COD_{RB} = \frac{OC}{1 - Y_H} \tag{9}$$

Y_H represents the fraction of substrate used for the production of new biomass, which is the heterotrophic yield coefficient (Y_H = 0.71±0.02) or that can be calculated by respirometric techniques [101]. Then COD_{RB} of the CWAO or WAO effluents can be calculated according the Eq. (10).

$$\%COD_{RB} = \frac{COD_{RB}}{COD_{added}} \times 100 \tag{10}$$

The removal rates upon WAO were 24% for phenol at 265°C, 10% for *o*-cresol at 265°C and 19% for 2-chlorophenol at 215°C. In the process, the biodegradable intermediates such as fumaric, propionic, acetic, succinic and formic acids were present in minor amounts, while the bio-inhibitory intermediates such as oxalic, maleic, malonic, 4-hydroxybenzoic and 2-hydroxybenzoics, hydroquinone, p-benzoquinone, catechol and polymers

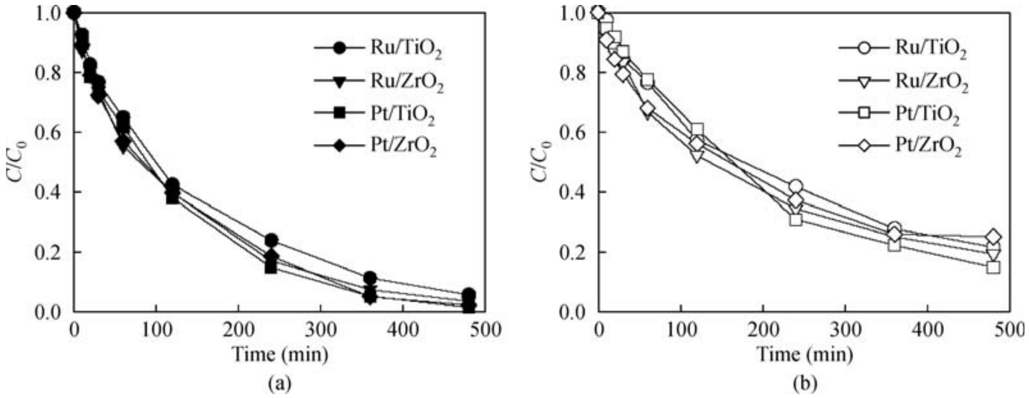
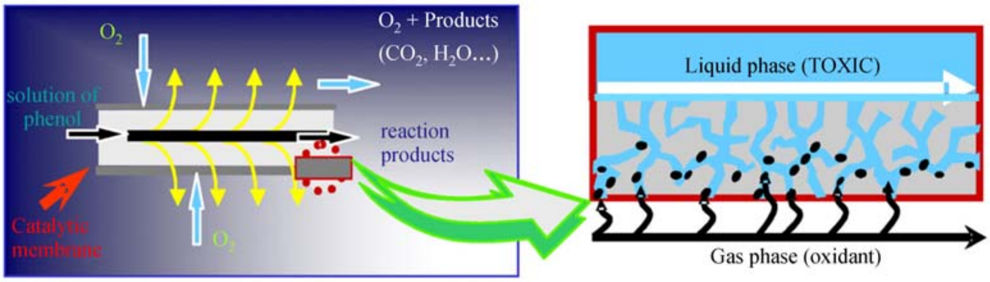
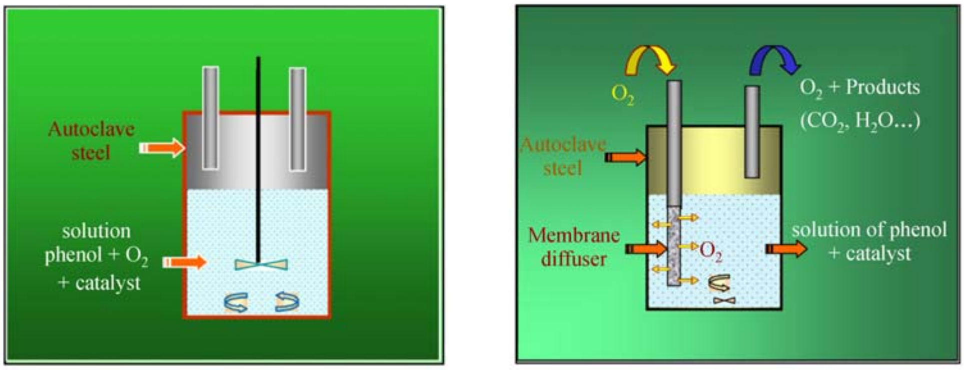


Fig. 7 (a) *p*-nitrophenol degradation; (b) TOC abatement in the CWAO using different catalysts [T:180°C, P_{O_2}:7.6 bar, cat.0.5 g·L^{-1}] [92]



(a) Concept of the catalytic membrane reactor type contactor



(b) Conventional autoclave type "slurry" reactor (c) Autoclave reactor with membrane diffuser

Fig. 8 (a) Catalytic membrane reactor; (b) autoclave reactor; (c) autoclave reactor with membrane diffuser [stirring speed: 800 $\text{r}\cdot\text{min}^{-1}$, P_{O_2}:3.5–4.5 bar] at C_{Phenol}: 1000–3000 $\text{mg}\cdot\text{L}^{-1}$, T: 140°C, catalyst: Pt/γ-Al_2O_3/Ce-Zr, cat.3.8 $\text{g}\cdot\text{L}^{-1}$ [75]

were detected in larger quantities in the effluent [102]. Martín et al. [92] used different catalysts in the CWAO of nitrophenol at 180°C and the biodegradability was enhanced by 61, 56, 64 and 60% over Ru/TiO_2, Ru/ZrO_2, Pt/TiO_2 and Pt/ZrO_2, respectively, which was remarkably better than the WAO process. The combination of CWAO with BD was also successfully tested in a pilot scale for the elimination of toxic organics, and a 98% COD removal was achieved in a AC/CWAO process combined with BD [102].

A filtration step prior to the BD treatment can improve the efficiency of the coupled technology. The larger bio-inhibitory compounds can be separated and sent back to the CWAO process to undergo further oxidation [103,104]. For example, WAO integrated with nanofiltration and biodegradation was applied to treat bio-resistant industrial wastewaters. Within 6-h residence time, 95% of TOC was removed in the biological reactor; while a residence time of 48 h was required to achieve the same goal in the absence of filtration. Without the WAO pretreatment and the nanofiltration step, only 35±13% of TOC removal was obtained by biodegradation treatment with a residence time of 48 h [103].

WAO is a promising pre-treatment compared to other technologies developed in the past decades. Moderately to highly concentrate effluents might be easily handled and the operating conditions can be tuned to adjust the biotoxicity of the intermediates. However, high costs are associated to the WAO process because of high temperature and high pressure conditions, the long running times and the special design of the reactors to improve corrosion resistance. Combination of heterogeneous catalysis and filtration can lower the temperature, the pressure and shorten the reaction times, and thus cut down the costs. Moreover, the combination of CWAO as pre-treatment with biological degradation can further improve the mineralization of the biodegradable intermediates at a lower cost.

5 Conclusions and perspectives

WAO is recognized as a green process to degrade high concentration of organics into carbon dioxide. High temperature, high pressure and strongly alkaline or weakly acidic conditions favor the elimination process. CWAO can improve the oxidation and the mineralization of the substrates under milder conditions. Among the catalysts, carbon materials appeared attractive because of their high specific surface and no leaching under acidic or alkaline conditions. However, they partly got oxidized at high temperature under oxygen. Transition metal oxides were excessively exploited and Cu-based catalysts exhibited promising performances. Bimetallic and spinel-type catalysts were developed to achieve a higher activity and stability. Supported noble metals can significantly promote the elimination of the substrates and TOC removal without obvious metal leaching. Among them, Ru exhibited the best activity in cutting the C-C bond of the phenolics into smaller carbonic acids and CO_2. The combination of CWAO with biological degradation is a suitable way to achieve good performance in COD or TOC removal in a more economical manner.

There are still several problems to be solved in the CWAO of phenols. First, the reactor is vulnerable to be corroded in the acid solution at high temperatures with excess of oxygen. Special and expensive materials may be required to manufacture a reliable reactor. Secondly, active and stable heterogeneous catalysts are still urgently needed. Carbon material oxidation, metal leaching or coverage of carbonaceous deposits should be avoided to achieve a promising catalyst for CWAO. The combination of stable supports (such as ZrO_2, TiO_2) with active metal components can be adopted to avoid these problems. Thirdly, the reaction conditions needs to be moderated, which is directly related with the operation cost and deeply depended on the performance of the catalysts.

Acknowledgements This work was financially supported by the National Science Fund for Distinguished Young Scholars (No. 51425405), Beijing Natural Science Foundation (No. 8172043) and Chinese Academy of Sciences (ZDRW-ZS-2016-5-3).

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