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Catalytic wet-air oxidation processes: A review

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Abstract

Environmental catalysis usually refers to end-of-the-pipe treatment processes that reduce the emissions of hazardous pollutants. Abatement of pollutants in aqueous streams by means of heterogeneous catalysts is an example of such process. This paper reviews the developments in the field of catalytic wet-air oxidation (CWAO). Catalysts are reviewed first, followed by mechanistic speculations and kinetics that have been proposed for the CWAO process. The process is discussed more in detail only in those cases where it is already commercialised or at least foreseen to be in the near future. Particular attention was given to the heterogeneously catalyzed wet-air oxidation of real industrial wastewaters (such as Kraft bleach plant effluents) in batch and continuous-flow oxidation reactors. Finally, the considerable potential of the CWAO process to ultimately destroy organic pollutants in industrial effluents and detoxify them by using novel titania-supported Ru catalysts is presented.

Keywords: Catalytic wet-air oxidation; Detoxification; Heterogeneous catalysis; Industrial effluents; Wastewater treatment

1. Introduction

An immense array of organic compounds are currently widely used, and many of these are potent contaminants when they are released into freshwater ecosystems. In a great majority of industrial processes water is used as a solvent, reaction or transport medium, therefore it is not surprising that many efforts in the last two decades have been made for the abatement of pollutants from industrial aqueous waste streams. Industrial plants generate increasing amounts of wastewater, contaminated with toxic and hazardous organic compounds, which cause severe problems for the environment. Wastewaters produced in many industrial processes often contain organic compounds that are toxic and not amenable to direct biological treatment. These industrial wastewaters must be treated in order to meet the specifications for discharge or for recycling in the process. The incapability of conventional methods to effectively remove many organic pollutants has made it evident that new, compact and more efficient systems are needed.

Among them, the wet-air or thermal liquid-phase oxidation (WAO) process, in which the generation of active oxygen species, such as hydroxyl radicals, takes place at high temperatures and pressures, is known to have a great potential for the treatment of effluents containing a high content of organic matter (chemical oxygen demand (COD) 10–100 g/l), or toxic contaminants for which direct biological purification is unfeasible [1]. The WAO process has well-known capacities for breaking down biologically refractory compounds to simpler, easily treated materials before they are released into the environment. In general, this aqueous phase flameless combustion process takes place at high reaction temperatures (473–593 K) and pressures (20–200 bar) by means of active oxygen species, such as hydroxyl radicals. Residence times of the liquid-phase in a three-phase reactor may range from 15 to 120 min, and the extent of COD removal may typically be about 75–90% [2]. In WAO processes, the organic contaminants dissolved in water are either partially degraded by means of an oxidizing agent into biodegradable intermediates or mineralised into innocuous inorganic compounds such as CO_2, H_2O and inorganic salts, which remain in the aqueous phase. Sulphur is converted to sulphate, halogens to halides and phosphorus to phosphates. Organic nitrogen may produce ammonia, nitrate and nitrogen. In contrast to other thermal processes, WAO produces no NO_x, SO_2, HCl, dioxins, furans, fly ash, *etc.* [2]. One of the main drawbacks of the WAO process is its

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inability to achieve complete mineralization of organics, since some low molecular weight oxygenated compounds (especially acetic and propionic acids as well as methanol, ethanol, and acetaldehyde), originally present in a wastewater or accumulated in the liquid-phase during the oxidation process, are resistant to further transformation to carbon dioxide. For example, removal of acetic acid is usually negligible at temperatures lower than 573 K [1]. Furthermore, organic nitrogen compounds are mostly transformed to ammonia, which is also stable at WAO operating conditions. Hence, the WAO process is considered as a pretreatment step of wastewaters, which requires additional treatment, typically in a conventional biological treatment plant.

The origins of WAO can be traced to the Strehlenert Process of wood technology patented in 1911 and to the zinc sulphide oxidation process of hydrometallurgy patented in 1927 [3]. The majority of WAO research development took place in the United States about 50 years ago, resulting in the construction of several large WAO plants for the treatment of municipal wastewater sludge by the Zimpro Company in the early 1960s [4]. Nowadays, over 400 WAO plants are in operation worldwide to treat preferentially wastewaters from petrochemical, chemical and pharmaceutical industries as well as residual sludge from biological treatment plants. Nevertheless, the WAO process may be prohibitively expensive when used to achieve deep oxidation of all organic material to carbon dioxide. Consequently, it is considered one of the most promising and simplest techniques for partial oxidation of parent pollutants into more biologically amenable intermediates. The efficiency of aqueous phase oxidation (WAO) can be improved considerably by the use of catalysts, either in the form of solids or as homogeneous catalysts.

The development of new catalysts during the last two decades has introduced more environmentally acceptable processes into the production. The industrial solid catalysts that once played a major role in bulk chemicals manufacture are nowadays distributed among the industrial sectors, so that about 25% of produced catalysts are used in chemical industry, 40% in petroleum industry, 30% in environmental protection, and 5% in the production of pharmaceuticals [5]. Environmental catalysis accounts for (i) waste minimization by providing alternative catalytic synthesis of important compounds without the formation of environmentally unacceptable by-products, and (ii) emission reduction by means of decomposing environmentally unacceptable compounds by using catalysts. The waste minimization is linked with the reaction(s) selectivity and therefore proper choice of the catalyst plays a decisive role. Emission reduction usually refers to end-of-the-pipe treatment processes where the selectivity of the catalyst is not an important issue. Because it is almost impossible to transform the raw materials into the desired products without any by-product(s), one must account for the necessity to furnish the production process with an end-of-the-pipe treatment unit. Only such production can then be considered benign and harmless for the environment.

Interest in innovative methods of wastewater treatment based on catalytic oxidation has been growing rapidly, as this technique has been confirmed as a powerful method of purifying wastewaters in numerous studies in the open literature. Compared to conventional wet-air oxidation, catalytic wet-air oxidation (CWAO) has lower energy requirements. Due to the presence of a catalyst much higher oxidation rates are achieved and consequently, one can use less severe reaction conditions to reduce chemical oxygen demand to the same degree as in the case of noncatalytic process. In the CWAO process, organics are oxidized to innocuous inorganic compounds such as CO_2, H_2O and heteroatom dissolved ions at much lower temperatures and pressures than in uncatalyzed thermal processes. Depending on the type and amount of organic compounds dissolved in wastewater, the process can be designed either to reduce their concentration or ultimately destroy them. In the former case, the intermediate products formed during the oxidation must be biodegradable. For reactions necessitating a solid catalyst and involving both relatively volatile (oxygen) and nonvolatile reactants (pollutant in wastewater stream), three-phase reactors are required. Pintar and Levec [6], who investigated catalytic liquid-phase phenol oxidation in a variety of reactor systems, have reported that oxidative coupling reactions, which contribute significantly to rapid catalyst deactivation via coke deposition on the surface of catalyst particles, are enhanced in the bulk liquid-phase. Consequently, in a reactor with a high liquid-to-catalyst volumetric ratio (such as slurry and bubble column fixed-bed reactors), wastewaters containing pollutants that tend to polymerize (*e.g.*, aromatic compounds) should not be treated. Furthermore, the key points to be solved are stability of heterogeneous catalysts and recycling of homogeneous catalysts.

The development of commercial CWAO processes started as early as the mid-fifties in the United States [7]. Several Japanese companies developed CWAO technologies relying on heterogeneous catalysts based on precious metals deposited on titania or titania-zirconia oxides. In Europe, on the other hand, the focus was more on homogeneous CWAO. Several homogeneously catalyzed wet-air oxidation processes based on this concept (*e.g.*, Ciba-Geigy, LOPROX, WPO, ORCAN and ATHOS processes) have been developed in the last two decades [2]. Soluble transition metal catalysts based on iron or copper salts are now being applied in several commercial wet-air oxidation plants, which are operating successfully to treat industrial effluents and sludge. Homogeneous transition metal catalysts, however, need to be separated from the treated wastewater stream and recycled to the reactor inlet or discarded. Therefore, their use has to be evaluated in the early process design stage according to the existing discharge regulations either in the liquid or solid phases.

2. Heterogeneous catalytic wet-air oxidation processes

2.1. Catalysts

As reported above, the WAO process is carried out at high temperatures and pressures. Under such extreme conditions, most materials for construction are susceptible to stress corrosion cracking when chloride ions are present in the waste stream. Consequently, this resulted in a need to discover catalysts which would allow to substantially lower the reaction temperature, the pressure and the residence time of the liquid-phase in an oxidation reactor. Another major benefit of using catalysts in the WAO process is their ability to oxidize refractory acetic acid and ammonia at much lower temperatures than if the process is conducted in the absence of catalysts. However, several crucial issues have to be solved concerning the stability of heterogeneous oxidation catalysts at hydrothermal operating conditions: (i) leaching and sintering of the active ingredient material; (ii) loss of surface area of the supporting material; (iii) possible poisoning of the active sites by carbon monoxide evolution; (iv) deposition of organic or inorganic compounds (coking) on the catalyst surface. Dissolution of active ingredient material can be controlled to a large extent by appropriate choice of catalytic metal or metal oxide phase and by pH control during CWAO. In this respect, various heterogeneous catalysts have been synthesized and tested in the last decades, based either on metal oxides or supported precious metals [6,8–93]. Mixtures of metal oxides of Cu, Zn, Co, Mn and Bi are reported to exhibit good activity, but leaching of these catalysts has been detected [36,44,49]. On the contrary, heterogeneous catalysts based on precious metals deposited on stable supports are less prone to active ingredient leaching [28,45,48,73–76]. Furthermore, noble metal catalysts are generally found to be more effective than metal oxide catalysts for oxidizing acetic acid, while with both noble metal and metal oxide catalysts the rate of total oxidation is significantly higher than that of the uncatalyzed reaction [1,44,46,73,75,77,90]. The same parameters as described above are also important for controlling the hydrothermal stability of the catalyst carrier. Oxides of Al, Hf, Zr, and Ti are known to be stable and should be used as catalyst supports [78]. Additional information about studies performed in the field of CWAO is available in recent review papers [1,2,94–99].

The catalysts that have exhibited a reasonably long lifetime consist of rather expensive metals, which is a drawback for any end-of-the-pipe treatment process. It is unlikely that one type of catalyst can be successfully used for treating many varieties of aqueous waste streams, therefore many different catalyst systems are needed. Researchers should look for systems with less expensive but catalytically active compounds, *e.g.* manganese or copper, and decrease their solubility by incorporating them in a lattice of catalyst support to accomplish the task [52,54].

2.2. *Oxidation kinetics*

The great majority of studies dealing with the kinetics of the CWAO process were performed by using model aqueous solutions. In a kinetic investigation of catalytic liquid-phase phenol oxidation carried out in a semi-batch slurry reactor in the presence of $CuO/ZnO/Al_2O_3$ catalyst [36,37], it has been found that homogeneous stepwise polymerization reactions are enhanced in the bulk liquid-phase due to the high liquid-to-solid volumetric ratio. The rate of phenol disappearance has been expressed on the basis of power-law kinetics as a sum of heterogeneous and homogeneous (polymerization) contributions, thus

$$(-r_{\text{PhOH}}) = k_{\text{het.}} \cdot c_{\text{PhOH}} \cdot c_{\text{O}_2}^{1/4} + k_{\text{hom.}} \cdot c_{\text{PhOH}} \cdot \sum c(P_n) \qquad (1)$$

where $k_{\text{het.}}$ is the apparent rate constant for the heterogeneous oxidation steps, and $k_{\text{hom.}}$ is the lump polymerization constant including initiation and propagation steps [36]. Experimental evidence has further confirmed that the reaction obeys a consecutive-parallel reaction pathway; 1,2 and 1,4 hydroxylated benzenes, benzoquinones, and carboxylic acids are formed during the reaction course towards carbon dioxide production. In addition, the measured reaction rate was affected by the pH value of the aqueous solution, and radical as well as inhibitor additions. Based on these facts, a heterogeneous–homogeneous free radical mechanism is proposed. The catalyst probably plays a role in the activation of both reactants, *i.e.*, phenol and oxygen. The temporal course of CO_2 formation during the catalytic phenol oxidation carried out in a slurry reactor revealed that only about one-half of the initial organic content is converted to CO_2. At the end of the oxidation run, the rest of carbon is found in the form of polyaromatic condensates strongly adsorbed on the catalyst surface, as confirmed by CHN and ^{13}C CPMAS NMR examinations. These results suggest that in a slurry reactor the degenerate branched chain mechanism prevails, which favours oligomerization and oxidative coupling reactions. The selectivity of the investigated reaction (*i.e.*, carbon dioxide formation) was markedly influenced by the liquid-to-solid volumetric ratio. In fixed-bed reactors (*e.g.*, ‘‘liquid-saturated’’, trickle-bed) this ratio is rather low; correspondingly, the propagation reactions taking place in the liquid-phase are suppressed, which leads to an almost quantitative transformation of phenol to carbon dioxide. This might be attributed to the immobilization of the catalyst in these reactor units, which markedly reduces or even prevents diffusion of radicals into the bulk liquid-phase. A thorough kinetic investigation carried out in an isothermal, differentially operated ‘‘liquid-saturated’’ fixed-bed reactor [6,42] shows that the phenol disappearance rate can be well described by the Langmuir–Hinshelwood (L–H) kinetic model. The proposed intrinsic rate expression

$$(-r_{\text{poll.}}) = \frac{k_{\text{sr,app.}} \cdot K_{\text{poll.}} \cdot K_{\text{O}_2}^{1/2} \cdot c_{\text{poll.}} \cdot c_{\text{O}_2}^{1/2}}{(1 + K_{\text{poll.}} \cdot c_{\text{poll.}}) \cdot (1 + K_{\text{O}_2}^{1/2} \cdot c_{\text{O}_2}^{1/2})} \qquad (2)$$

accounts for the model pollutant (poll.) as well as dissociative oxygen adsorption processes on different types of active sites. The adsorption–desorption steps of reactants were determined to be fast and thus at equilibrium. Additional investigations of structure–reactivity relationships have confirmed that the activation of the reactants on the catalyst surface occurs via a stepwise oxidation mechanism. On the basis of experimental results, it is concluded that the disappearance rate of phenol and substituted derivatives is dependent on: (1) precursor surface complex formation, and (2) subsequent homolytic electron transfer rate, the step in which phenoxy radicals are produced. The hydroxyl hydrogen radical abstraction from surface phenol complexes, which occurs directly by valence band holes, or indirectly by trapped holes at the particle surface, was found to be the rate-controlling step. In the reaction system investigated, oxygen acts as a primary scavenger of electrons in the conduction band. The observed reaction order of 1/2 with respect to oxygen is consistent with oxygen being activated to form surface bound O^- and hydroxyl radicals. These species react further with phenoxy species adsorbed on adjacent surface sites, thus enabling total oxidation of the parent molecule. It was also found out that the oxidation rates decrease as the Hammett σ constants of the *para* constituents increase, indicating that phenols with electron-withdrawing substituents are more resistant to oxidation than phenols with electron-donating substituents [42].

On the other hand, scrutiny of the past literature reveals that a large number of previous investigations of the catalytic wet-air oxidation process employed simulated wastewaters which consisted of a single organic compound. Information on catalytic oxidation of the multi-component mixtures of organic pollutants is very limited [1,2,95–101]. Experimental results of wet-air oxidation of high-concentration chemical wastewater (COD up to 42,800 mg/l) containing various organic acids and inorganic compounds indicated that over 50% reduction of the chemical oxygen demand concentration could be easily achieved in about an hour at $T = 473$ K and total operating pressure of 30 bar; a pronounced increase in COD removal using $CuSO_4$ over that without a catalyst was observed. However, the improvement became less appreciable with Co_2O_3 and ZnO heterogeneous catalysts [102]. Imamura et al. [103] studied wet-air oxidation of domestic wastewater in the presence of Mn/Ce and Ru/Ce catalysts. The Ru/Mn/Ce solids, which had an atomic ratio of Mn to Ce of 1/9 and contained 3 wt.% Ru, exhibited the highest activity. For example, at the reaction temperature of 473 K and oxygen partial pressure of 15 bar, about 90% of initial organic carbon content (315 mg/l) was eliminated after a 3-h run. Belkacemi et al. [104,105] investigated the removal efficiency of total organic carbon from raw high-strength alcohol-distillery waste liquors (TOC up to 22,500 mg/l) in a batch stirred autoclave over various catalysts. In the temperature and oxygen partial pressure ranges of 453–523 K and 5–25 bar, respectively, TOC conversions did not exceed 60%. The initial reaction rates were found to be of first-order with respect to TOC, and the activation energies ranged from 34 to 51 kJ/mol. The highest TOC removal was achieved with Mn/Ce oxides and Cu(II)/NaY catalysts. The catalysts were found to be very effective for short contact times, while for prolonged exposures inhibition by stable dissolved intermediates and catalyst deactivation by fouling carbonaceous materials were the prime factor responsible for the loss of catalytic activity. Zhang and Chuang [50,106] showed that an alkaline (c(TOC) = 1500 mg/l, pH 11) and an acidic (c(TOC) = 720 mg/l, pH 2.2) bleach plant effluent can be successfully treated by catalytic wet-air oxidation at 463 K under 15 bar of oxygen partial pressure in the presence of palladium supported on alumina or alumina-ceria. A 70% removal of TOC in alkaline wastewater could be achieved. When adjusting the pH of the acidic effluent by addition of variable amounts of NaOH, it was observed that the TOC removal in the wastewater decreased with increasing pH (23% TOC removal at pH 11 as compared to 64% at pH 2.2, after 3 h of reaction). Leaching of the metal was strongly dependent on the pH and was significant at the low and high pH [107]. To address these problems, Pd-Pt-Ce/Al_2O_3 catalysts were used for the treatment of combined acidic and alkaline effluents (c(TOC) = 850 mg/l, pH 8.5) [108]. No leaching of platinum and cerium was observed, but dissolution of palladium (0.14 mg/l) and aluminium (41.1 mg/l) were still detected at 443 K and after a 3-h run, which makes the use of this catalyst in continuous-flow operation questionable. The wet-air oxidation of acidic (D0) and alkaline (E1) Kraft bleach plant effluents (TOC content 665 and 1380 mg/l, respectively) was recently investigated in a batch slurry reactor in the presence of titanium or zirconium oxides, or ruthenium catalysts supported on these oxides [109]. The TOC disappearance rate was not influenced by the nature and structure of the oxides or by the acidic/basic character of the surface, but it was found to increase with the specific surface area of the oxides (see Fig. 1). With the addition

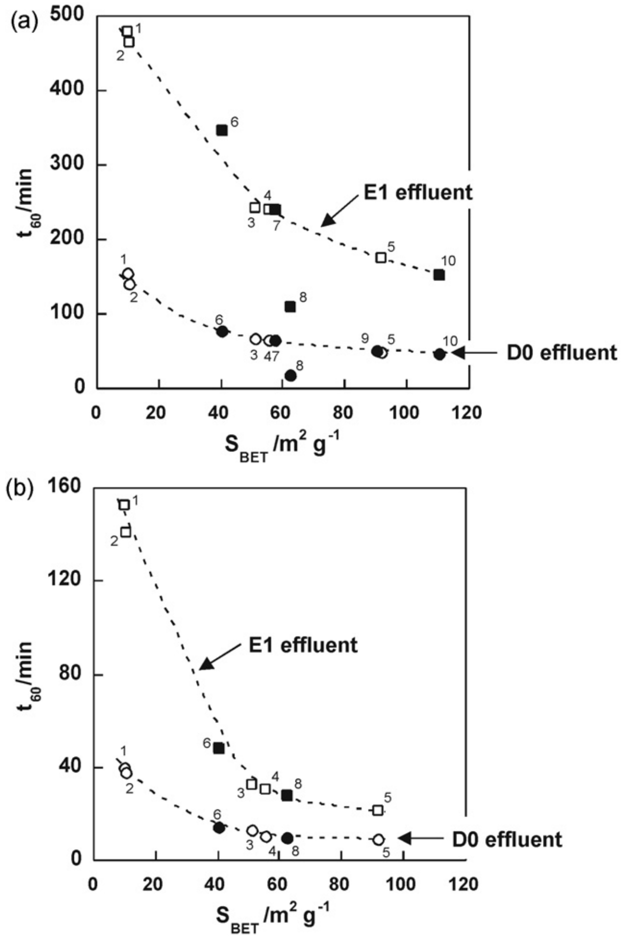


Fig. 1. Time necessary to achieve 60% abatement of TOC in effluents D0 and E1 in the presence of titania or zirconia oxides (a), or supported ruthenium catalysts (b). Supports: (1) TiO_2 AT1 (Thann and Mulhouse); (2) TiO_2 RL11A (Thann and Mulhouse); (3) TiO_2 Q500-075 (Engelhard); (4) TiO_2 P25 (Degussa); (5) TiO_2 DT51 (Thann and Mulhouse); (6) ZrO_2 EP (Degussa); (7) ZrO_2 57 [109]; (8) ZrO_2 XZ0631/1 (MEL Chemicals); (9) ZrO_2 137 (Degussa); (10) ZrO_2 110 [109]. Operating conditions: $T = 463$ K, $p(O_2) = 7.4$ bar, $c_{cat.} = 5.0$ g/l.

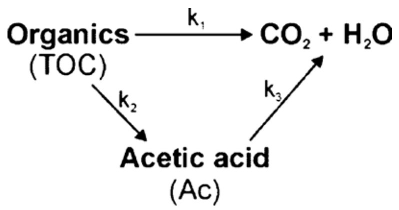


Fig. 2. Simplified triangular reaction scheme of wet-air oxidation.

of ruthenium on these supports, over 99% TOC abatement could be achieved within 6 h at conditions of $T = 463$ K and oxygen partial pressure of 8 bar. Leaching of supporting material and of active ruthenium was not observed in any of the runs.

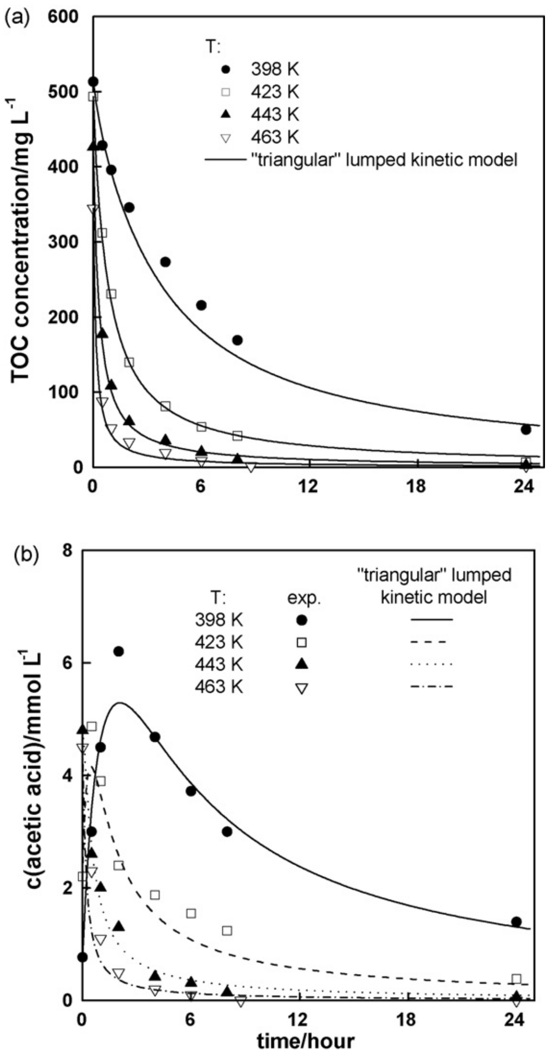


Fig. 3. TOC concentration as a function of time obtained during the catalytic wet-air oxidation of D0-I bleach plant effluent (a) and concentration–time profiles of intermediate acetic acid in effluent D0-I (b) measured in the slurry reactor at different temperatures in the presence of a Ru(3 wt.%)/TiO_2 catalyst. Operating conditions: $p(O_2) = 7.4$ bar, $c_{cat.} = 5.0$ g/l. Adopted from ref. [111].

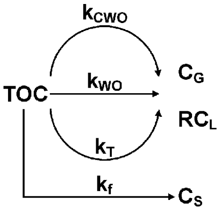
Kinetic models that solely predict the disappearance rate of pure compounds are useful for understanding of reaction mechanisms; however, they are not sufficient for the design purposes. What is needed is a tool capable of predicting complete conversion of all organic species present in a wastewater, regardless of whether they are originally present or formed as intermediate products. Therefore, the rate law has to be expressed by means of a lumped parameter such as total organic carbon (TOC), which accounts for all organic species present in a wastewater, or chemical oxygen demand (COD), which also takes into account oxidizable inorganics. For non-catalytic oxidation Li et al. [110] proposed a generalized lumped kinetic model which is based on a simplified reaction scheme with acetic acid as the rate-limiting reactant, as shown in Fig. 2. Here, the rates of all steps are of the first-order. Very recently, the overall kinetics of TOC removal from Kraft bleach plant effluents in the presence of Ru/TiO_2 catalyst was well described by a simplified lumped kinetic model [111], assuming second-order kinetics for all reaction steps in the triangular reaction scheme (Fig. 2). This model, presented by the set of two differential equations, is:

$$\frac{d[TOC - 2\cdot Ac]}{dt} = -k_1\cdot[TOC - 2\cdot Ac]^2 - k_2\cdot[TOC - 2\cdot Ac]^2 \tag{3}$$

$$\frac{d[Ac]}{dt} = 0.5\cdot k_2\cdot[TOC - 2\cdot Ac]^2 - k_3\cdot[Ac]^2 \tag{4}$$

with $[TOC] = [TOC]_0$; $[Ac] = [Ac]_0$ at $t = 0$, where the brackets stand for the concentration of TOC and acetic acid (Ac), respectively. It is illustrated in Fig. 3 that the model and its calculated parameters successfully predicted the time course and distribution of carbon lumps involved in the reactions, since satisfactory agreement between the measured and the predicted values was obtained for both the bleach plant effluent and the intermediate acetic acid. It is interesting to note that the second-order rate law is in agreement with the lumped kinetics found by Đonlagić and Levec [112] for WAO of an azo dye compound in a batch reactor.

Belkacemi et al. [104] proposed an inhibition–deactivation reaction scheme for the catalytic removal of TOC from raw high-strength alcohol distillery waste liquors:



The kinetic model involving the rates for three carbon lumps, namely carbon in liquid (TOC), carbon deposited on solid catalyst (c_S), and carbon in the gas-phase (c_G), consists of the following set of equations:

$$-\frac{d[TOC]}{dt} = k_T[TOC]\tau + k_{WO}[TOC]\tau + m_{cat}k_{CWO}[O_2]^{0.45}[TOC]\left(1 - \frac{c_S}{c_{S\infty}}\right) \tag{5}$$

$$-\frac{dc_S}{dt} = k_f c_{S\infty}[TOC]\left(1 - \frac{c_S}{c_{S\infty}}\right) \tag{6}$$

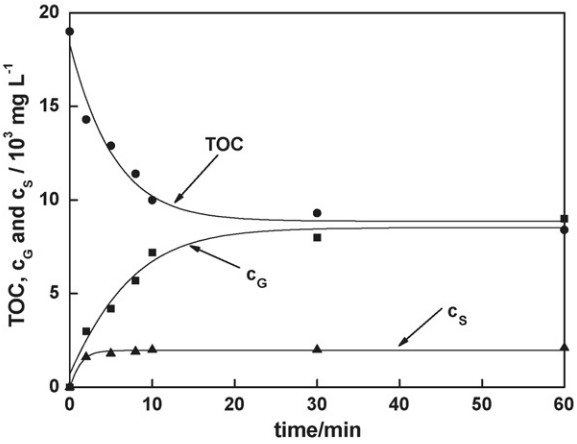


Fig. 4. Experimental and predicted concentration profiles for combined thermolysis, non-catalytic, and catalytic wet-air oxidation of high-strength alcohol distillery liquor over a MnO_2/CeO_2 catalyst. Adopted from ref. [104].

with

$$[\mathrm{TOC}]_0 = [\mathrm{TOC}] + c_\mathrm{G} + c_\mathrm{S};$$
$$[\mathrm{TOC}] = [\mathrm{TOC}]_0, c_\mathrm{G} = c_\mathrm{S} = 0, \quad \mathrm{at}\, t = 0.$$

In Eq. (5) k_T, k_WO, and k_CWO are the rate constants for thermolysis, homogeneous oxidation, and catalytic oxidation, respectively, whereas τ represents a simple inhibition function expressed as

$$\tau = 1 - \frac{[\mathrm{TOC}]_\infty}{[\mathrm{TOC}]}. \tag{7}$$

In the above expression $[\mathrm{TOC}]_\infty$ is the asymptotic residual organic carbon ($\mathrm{RC_L}$), which cannot be oxidized further. Agreement between the experimental data for combined thermolysis, non-catalytic, and catalytic WAO and the model prediction is shown in Fig. 4. One can conclude from this plot that the oxidation progress is terminated once the catalyst is deactivated due to the adsorption of carbonaceous intermediates on its surface.

Very recently, the application of stochastic methods (simulated annealing) to non-linear multi-parameter optimization that represents a competitive alternative to the classical gradient-based estimation techniques (*e.g.*, Levenberg–Marquardt algorithm), has been successfully employed to derive a global kinetic model of liquid-phase phenol oxidation conducted over active carbon in the trickle-bed reactor [113]. However, for the practical design purposes one should use the lump kinetic approach based on a triangular reaction scheme, such as depicted in Fig. 2. It is believed that the rate laws can be mostly expressed by a simple power function. Nevertheless, using the lumped kinetic approach may introduce other problems in the design task, due to the following facts:

- Systems with some degree of back-mixing may have to be lumped with a different rate expression than systems with plug-flow behaviour [114].
- In many cases lumped kinetics is in the power-law form, with the exponent for a CSTR being lower than that for a plug-flow reactor [115].
- Behaviour of the reaction mixture is always governed by the most refractory fraction of the feed in the case of plug-flow reactor, while this is not the case with CSTR [115].

In other words, the lumped oxidation kinetics obtained in reactors with different Residence Time Distributions (RTDs) are not identical. Precaution is thus needed when predicting the performance of a reactor from the kinetics that is obtained from a reactor with a different RTD. For example, it was observed that there exists a difference between the lumped oxidation kinetics obtained in the batch (or plug-flow) reactor on the one hand, and CSTR on the other. This was illustrated by the TOC disappearance rate equations obtained in these two reactor systems for the WAO of an azo dye Orange II [112]: in the batch reactor, the TOC disappearance rate is found proportional to the square of TOC concentration, whereas in CSTR it is linearly dependent. If we now wish to predict the behaviour of CSTR by means of the TOC lumped kinetics obtained in the batch reactor (Fig. 5), we might be surprised because we cannot match the data either with the so called early or late lumping approach [112,116]. On the other hand, we can see in Fig. 5 that the decay of dye concentration can be well predicted because the rate equation for the dye disappearance represents the intrinsic rate. Different lumped kinetic behaviours in the batch and CSTR systems result in a drastic difference in the predicted value of the reactor volume. To conclude: in principle, one may be able to predict the CSTR behaviour by means of exact (proper) lumping [117]

$$\frac{c_\mathrm{TOC}}{c_\mathrm{TOC,0}} = \int_0^\infty \exp(\widehat{K}t)E(t)\,\mathrm{d}t \tag{8}$$

if we know the lumped rate constant matrix $\widehat{K}$, which can hardly be imagined. The same as described above for non-catalytic wet-air oxidation could be observed in the CWAO process, especially during the destructive treatment of real effluents in which organic compounds undergo both non-catalyzed and heterogeneously catalyzed oxidation routes [111].

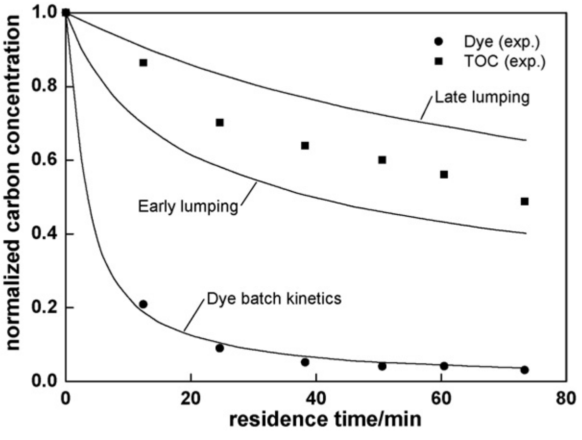


Fig. 5. Predicted *vs.* experimental dye and TOC data from CSTR operated at $T = 513$ K and 10 bar of oxygen partial pressure. Adopted from ref. [112].

It is of practical interest to achieve better understanding of the kinetic behaviour of lumps that may undergo wet-air oxidation in reactors with different residence time distributions. One should bear in mind that wet-air oxidation reactors operate in a broad spectrum of Peclet numbers—the system may approach a completely mixed flow on the one hand, when high oxygen transfer rates are needed, or plug-flow on the other hand when the system calls for moderate/low oxygen transfer rates. Information on the kinetic behaviour of key lumps, which frequently dictate the overall TOC reduction, in different two- and three-phase reactor arrangements seems to be of high importance.

2.3. Oxidation processes

It seems that Katzer et al. [118] were the first who evaluated the catalytic liquid-phase oxidation as a potential wastewater treatment technology and offered a process scheme. They have demonstrated that catalytic wet-air oxidation may not be economically attractive for low concentrations of organics because of the energy required to heat up the wastewater stream. High organic concentrations in wastewaters provide enough heat, so that the process is thermally self-sufficient; in this case the process becomes economically feasible. Farha et al. [119] have elaborated experimentally in great detail the possibility of using catalytic oxidation in advanced waste treatment facilities. Their process design and economic evaluations have indicated that the process is economically sound. They have also found out that organics removal in the two reactor systems, bubble column fixed bed and trickle bed, are comparable despite somewhat different mass transfer conditions. Fig. 6 illustrates a simplified process scheme for the catalytic liquid-phase oxidation of organics in wastewaters employing a trickle-bed reactor. Pre-filtered wastewater is pumped to operating pressure, and brought to the reactor operating temperature by a feed/effluent heat exchanger. A compressed air/oxygen stream at stoichiometric excess is fed contemporaneously to the top of the trickle bed reactor. Since energy costs preclude vaporization, the reactor must operate at a pressure above the vapour pressure of water. The treated reactor effluent may be suitable for surface discharge. In the case of a waste stream containing relatively low concentrations of organic contaminants, a step in which the organics are preconcentrated may be required. The CALIPHOX process invented by our group, which uses an activated carbon adsorption-preconcentration step, is shown schematically in Fig. 7 [94]. The active carbon bed, after being saturated with organics, is regenerated by routing hot water at temperatures up to 453 K and elevated pressure through the adsorber. Under these conditions, most of the organics are desorbed and subsequently oxidized over the catalyst in a trickle-bed reactor [120]. For optimal effect, one or the other of the processes depicted in Figs. 6 and 7 should be applied at the source of wastewater production in an industrial plant. Both processes can be designed either to oxidize completely the organic compounds dissolved in water or merely to reduce their concentration and convert them into biologically more amenable products. Similarly to the CALIPHOX process, a two-step adsorption–desorption process for treatment of aqueous phenolic effluents was recently proposed by Polaert et al. [121]. This process is based on the use of activated carbon as an adsorbent in the first step and as an oxidation catalyst in the second step, in a single bi-functional reactor. The main advantage of this process is in the regeneration–oxidation step, for which only a small quantity of liquid has to be heated and pressurized, thus reducing heat consumption. The two-step adsorption–oxidation process appears to offer good potentials for treating moderate flow rates of wastewater, especially when the effluent is dilute [121].

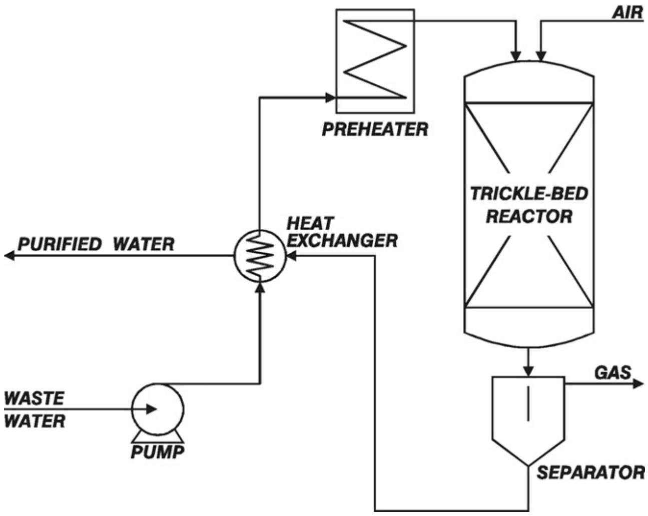


Fig. 6. Schematic drawing of a simple process for catalytic wet-air oxidation.

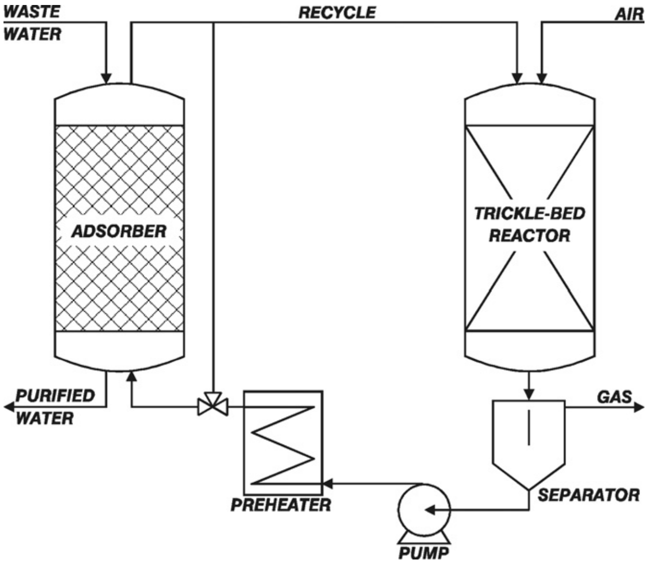


Fig. 7. Schematic drawing of the CALIPHOX process for catalytic liquid-phase oxidation of organic pollutants with an adsorber unit for preconcentration.

Several catalytic wet-air oxidation systems were commercialized in the mid-eighties in Japan. They are all based on heterogeneous catalysts containing precious metals deposited on titania or titania-zirconia carriers. Compared to conventional WAO units, these processes are able to oxidize two recalcitrant compounds, *i.e.*, acetic acid and ammonia. Therefore, the treated water can be discharged directly into an open body of water or reused as process water. The NS-LC process [122], which operates at $T = 493$ K, $P_{\text{tot.}} = 40$ bar and $\text{SV} = 2\ \text{h}^{-1}$, involves a Pt-Pd/$TiO_2$-$ZrO_2$ honeycomb catalyst. The slug flow established in vertical monolith channels significantly improves mass transfer [123,124] and prevents solids deposition. At these conditions, the extent of oxidation of compounds such as phenol, formaldehyde, acetic acid, glucose, *etc.*, reaches or exceeds 99% [122]. The Osaka Gas CWAO process [125–127] uses a catalyst composed of a mixture of precious and base metals on titania or titania-zirconia carriers (honeycomb or spheres). The catalyst life time is reported to be over 8 years. This process has been demonstrated to efficiently treat a variety of municipal waste streams and industrial wastewaters. By means of the Kurita process, ammonia can be selectively oxidized into N_2 and N_2O by the NO_2^- ion at lower temperatures than in the presence of oxygen. The reaction is carried out at $T = 443$ K in the presence of a supported platinum catalyst.

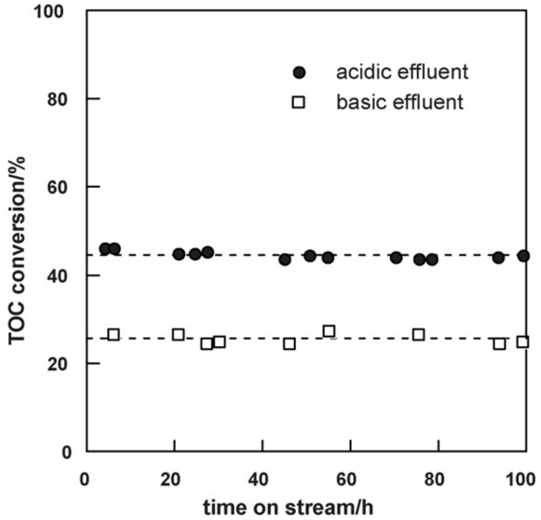


Fig. 8. TOC conversion as a function of time on stream, obtained during the oxidation of bleach plant effluents in the trickle-bed reactor packed with TiO_2 extrudates. $T = 463$ K, $P_{\text{tot.}} = 55$ bar, $\Phi_{\text{vol.,L}} = 1.0$ ml/min, $m_{\text{cat.}} = 12.3$ g. Adopted from ref. [134].

Relatively few investigations have been published concerning catalytic liquid-phase oxidation of organic compounds in continuous-flow trickle-bed reactors. Experimental data, description of mass-transfer processes and reaction courses, as well as reactor simulation activities, which are required for successful commercial exploitation, have so far been presented only for model pollutants such as formic acid, acetic acid, succinic acid, cyclohexanol, cyanide and phenol [20,46,51,81,93,128–133]. Béziat et al. [128], who conducted the catalytic oxidation of aqueous solutions of acetic and succinic acid in a trickle-bed reactor, demonstrated that titania-supported ruthenium catalysts exhibited excellent chemical resistance in a wide range of operating conditions. Pintar et al. investigated catalytic wet-air oxidation of two acidic (D0) and alkaline (E1) bleach plant effluents from a softwood Kraft pulp mill (TOC content 1138 and 1331 mg/l, respectively) in an isothermal, concurrent downflow trickle-bed reactor at $T = 463$ K and oxygen partial pressure of 8 bar [134]. The reactor, packed with TiO_2 extrudates (Degussa, P-25 type, $S_{\text{BET}} = 51\ \text{m}^2/\text{g}$) or a titania-supported ruthenium catalyst, was operated in a low-interaction (LIR) trickle-flow regime either in continuous-flow or batch-recycle mode. The oxygen source in these experiments was pure and compressed air. The residence time of the liquid-phase in the catalytic bed was 0.6 min. In the off-gas, no carbon monoxide or chlorine-containing products were detected in any of the runs. When the catalytic bed was composed of TiO_2 particles, moderate abatement of organic compounds from the bleach plant effluents was observed. TOC conversions up to 45% and 26%, respectively, were measured in the reactor outlet (Fig. 8). By means of HPLC, acetic, acrylic, adipic, glutaric, maleic and succinic acids were detected in the liquid-phase after the oxidation of D0 and E1 effluents over the bare titanium dioxide support. Accumulation of these intermediates, especially acetic acid, was favoured during the oxidation of the E1 bleach plant effluent, *i.e.*, at higher pH values of the reaction medium. The removal of parent organic material and intermediate compounds was further enhanced by the deposition of metallic ruthenium (3 wt.%) on the titanium oxide support. In that case, the once-through oxidation produced decolorized outlet streams with deep TOC conversions as high as 89 and 88%, respectively. These values further increased to 98 and 95%, respectively, by running the trickle-bed reactor in the batch-recycle mode of operation (Fig. 9). This demonstrates that at given operating conditions ultimate destruction of parent and intermediate organic compounds and their mineralization to carbon dioxide can be achieved. The residual carbon content in treated bleach plant effluents was found in the form of acetic acid as a deep mineralization entity, which suggests that the employed Ru/TiO_2 catalyst was active also for C–C bond cleavage. The water treated in this process is of high quality, almost free of organics and with a low content

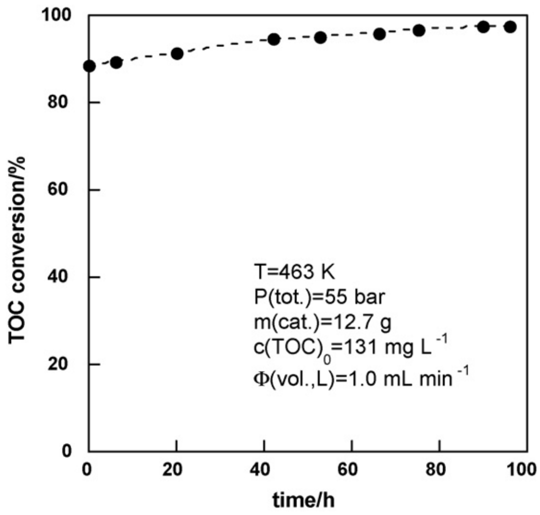


Fig. 9. TOC conversion as a function of time, obtained during the oxidation of a D0 bleach plant effluent in the batch-recycle reactor packed with a Ru(3 wt.%)/TiO_2 catalyst. Adopted from ref. [134].

of nitrates (<50 mg/l). Due to its pH value being in the range of 6–9, it can be fully recycled. No leaching of Ru and/or Ti from the employed solids to hot wet-air oxidation solutions was detected by ICP-AES analysis to the detection limits of 0.2 and 0.1 mg/l, respectively. Therefore, no homogeneously catalyzed oxidation of parent and partially oxidized organic compounds by dissolved metals took place in the trickle-bed reactor. The presence of sodium chloride and other salts in the feed solutions exhibited no measurable effect on the life period of the Ru/TiO_2 catalyst. After the TiO_2 support and Ru/TiO_2 catalyst were used in the trickle-bed reactor at $T = 463$ K for 100 h under oxidative reaction conditions, no detectable change in phase composition was found by means of XRD analysis. No agglomeration of ruthenium clusters represents a significant factor accounting for the long-term stability of the Ru/TiO_2 catalyst. Furthermore, low amounts of carbon (0.05–0.2 wt.%) were found on the surface of used solids. This provides strong evidence that catalyst fouling by carbonaceous deposits, which could take place in parallel with oxidation reactions, was avoided at the employed reaction conditions. During the wet-air oxidation of D0 and E1 effluents, no sulphur or phosphorus salts were deposited on the surface of catalyst particles. These salts could make access of the liquid-dissolved compounds to the catalyst active sites more difficult. To conclude, successful development of a titania-supported ruthenium catalyst which exhibits both high activity for TOC removal from the bleach plant effluents and long life period represents a significant breakthrough and makes it possible to meet the increasing demands in the chemical manufacturing industries to use closed-loop operation by recycling and reusing waters.

Table 1
The Hatta numbers for some organic compounds for low and high strength wastewater cases

Organic compound	COD = 10 g/l		COD = 100 g/l	
	c[a] (mol/l)	Ha^2	c[b] (mol/l)	Ha^2
Acetic acid	0.156	0.0002	1.563	0.003
n-Butanol	0.052	0.091	0.521	0.912
p-Chlorophenol	0.048	17.59	0.481	175.91
o-Cresol	0.037	0.891	0.368	8.91
Formic acid	0.625	0.011	6.250	0.107
Oxalic acid	0.313	0.0097	3.125	0.097
Propionic acid	0.089	29.09	0.893	290.87
Phenol	0.045	22.70	0.446	226.96

$T = 553$ K, $D_{\mathrm{oxy}} = 4.638 \times 10^{-8}$ m^2/s, $k_{\mathrm{l}} = 1.538 \times 10^{-5}$ m/s.
[a] Compound concentrations match the COD value of 10 g/l.
[b] Compound concentrations match the COD value of 100 g/l.

Due to the facts that in some cases considerable quantities of organic pollutants in industrial wastewaters can be totally or partially oxidized by means of non-catalytic WAO, and that recalcitrant intermediates are formed during the oxidative destruction of parent organic compounds, which requires an efficient catalyst in order to obtain sufficiently high TOC conversion in a later stage of the reaction course, it might be interesting to look for a possibility of efficiently combining WAO and CWAO processes. There are two factors that are considered of primary importance for the successful development and operation of any WAO process: (i) efficient transport of the gaseous reactant (oxygen) across the gas–liquid interface, and (ii) the intrinsic reaction kinetics. The high demand of oxygen is best illustrated by comparing the equilibrium concentration of oxygen in pure water that can be attained at temperatures and pressures used in WAO with a typical chemical oxygen demand of an aqueous medium treated by WAO: the equilibrium concentration is below 1 g/l, while the typical COD is in the range between 30 and 100 g/l. Thus, an efficient WAO system has to constantly maintain an oxygen flux up to at least 30 times the equilibrium concentration. To design such gas–liquid reactors, one must know whether the oxidation would occur in the bulk liquid-phase ($Ha^2 \ll 1$), which necessitates a large volume of liquid, or completely in the boundary layer ($Ha^2 \gg 1$), which calls for contacting devices that provide for a large interfacial area. The Hatta (*Ha*) number is defined as a ratio of the characteristic time for the gas–liquid mass transfer and that for the liquid-phase reaction. For the reactions whose rate equation can be written as

$$r_{\mathrm{org}} = k \cdot c_{\mathrm{org}}^{m} \cdot c_{\mathrm{oxy}}^{n} \tag{9}$$

the Hatta number is given in the following form [135]

$$Ha = \frac{\sqrt{(2/(n+1)) \cdot k \cdot c_{\mathrm{org}}^{m} \cdot c_{\mathrm{oxy}}^{n-1} \cdot D_{\mathrm{oxy}}}}{k_{\mathrm{l}}} \tag{10}$$

where k_{l} stands for liquid-side mass transfer coefficient. Wet-air oxidation reactions are considered to be medium rate gas–liquid reactions ($0.01 < Ha^2 < 10$) requiring long residence times for the liquid-phase. The Hatta numbers for a few organic compounds are listed in Table 1. The unique feature of the WAO reactor design lies in the fact that the *Ha* number changes in the direction of flow due to a decrease in the concentration of organics and due to the formation of more refractory compounds, such as aliphatic acids with several orders of magnitude lower rate constants. Consequently, the wet-air oxidation reactor has to be practically custom designed and optimized for a specific stream. When searching for an optimal reactor size, which is strongly dictated by the new, very expensive corrosion resistant materials, one must take into account proper balance between intensive back-mixing and plug-flow behaviour [136]. A bisectional reactor, which efficiently combines WAO and CWAO steps in a single unit, is schematically illustrated in Fig. 10. Fresh aqueous waste and oxygen containing gas are fed into the bottom section, which contains lateral baffles or static mixers that assure an uniform energy dissipation along the entire bottom section of the reactor. In order to avoid an oxygen depleting zone, intensive mixing is needed in this section, since fresh wastewater usually contains bulky molecules which are more prone to oxidation. Downstream more and more refractory compounds (*i.e.*, low molecular weight carboxylic acids) are formed, which should be oxidized catalytically in the upper section, in which a low degree of back mixing (plug-flow) is maintained. Therefore, a separator located between the two sections permits free transfer of mass but only limited transfer of momentum of the up-flowing gas–liquid mixture. The gas-phase leaving the bottom section of the reactor is not recycled;

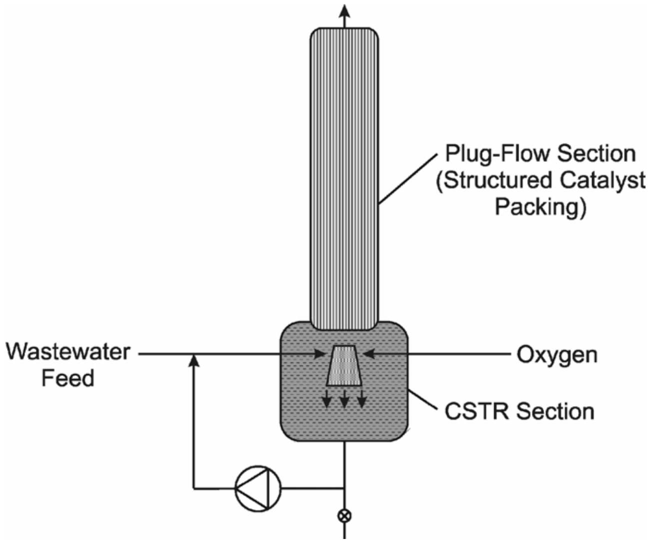


Fig. 10. Schematic drawing of a bisectional WAO/CWAO reactor unit [136].

it enters through the separator directly into the upper section together with the liquid-phase.

2.4. Biodegradability/toxicity of CWAO treated effluents

An attractive potential alternative to complete treatment by means of chemical oxidation would be the use of an integrated chemical and biological treatment process comprising a chemical pre-treatment step to convert initially bioresistant compounds to more readily biodegradable intermediates, followed by biological oxidation of these compounds to achieve sewer or river course discharge limits. In order to use an integrated (C)WAO and biological treatment plant efficiently, the effluent from the former must be biodegradable. In the available literature, little information is provided on the biodegradability of effluents treated by means of noncatalytic or catalytic wet-air oxidation processes. WAO was found capable of improving the biodegradability of pesticide and acrylonitrile wastewaters [137,138], olive mill wastewaters [139], phenolic wastewaters [140], water-soluble polymer-containing wastewaters [141] and azo dye-containing wastewaters [142]. However, it was found that WAO decreased the biodegradability of a TNT red water effluent by introducing inhibitory effects [143]. The effect of wet-air oxidation on the aerobic biodegradability of a model wastewater containing linear alkylbenzene sulphonate (LAS) was recently investigated by Mantzavinos et al. [144]. The original LAS solution was found to be readily biodegradable in the laboratory aerobic reactors operating at low organic loadings. However, wet-air oxidation resulted in effluents that were less readily biodegradable than the original LAS, with biodegradability decreasing with the increasing degree of oxidation. This was attributed to the formation of sulphonated aromatics from partial LAS oxidation. The results of Mantzavinos et al. [144] further suggest that a combined chemical pre-oxidation and biological post-treatment process may be less effective in removing LAS than single-stage biological or chemical process. An example presenting the evolution of COD and BOD_5/COD as a function of temperature in the low-pressure catalytic wet-air oxidation LOPROX process [2] has demonstrated that this dependence increases with temperature. In other words, the biodegradability of treated effluents increases with temperature. At around 473 K, the value of the BOD_5/COD ratio is already higher than 0.5, which implies that the effluents are readily biodegradable. Đonlagić and Levec [145] have reported that the aerobic biodegradability of Orange II solutions treated by catalytic and noncatalytic oxidation processes increased with time. The results of their investigation indicate that intermediate product distribution plays a decisive role in biodegradability: the solutions treated by catalytic oxidation were found to be more amenable to aerobic biodegradation (the ratio of BOD_5/COD was found to be in the range of 0.17–0.35), simply because smaller quantities of intermediate products were formed in this process. However, Fig. 11 shows that the intermediates are differently distributed with non-catalytic and catalytic oxidation. One would expect more intermediate products amenable to biodegradation with temperature, but this was not the case with this model pollutant; maximum biodegradability was obtained at $T = 473$ K. Lower biodegradability observed at higher temperatures can probably be attributed to the presence of intermediates with either lower metabolic values or inhibitory effects. Zhu et al. [146] studied wet-air oxidation of a H-acid solution in the presence of various catalytic systems. The initial BOD_5/COD of the H-acid solution was 0.02, which indicated that it had poor biodegradability. After the 40-min treatment over a catalyst consisting of copper and cerium mixed metal oxides, this value increased to 0.3 and then with time asymptotically approached the value of 0.4, thus demonstrating that the biodegradability was improved. Santos et al. [147] investigated catalytic oxidation of phenol in aqueous solution by using bicarbonate as buffer reagent to keep the pH in the interval 7–8 over a commercial catalyst based on copper. The oxidation route obtained in this pH range was less toxic than that obtained at acid pH because dihydroxybenzenes are not formed at basic pH. All the intermediates detected were more than one order of magnitude less toxic than phenol.

Before discharging a stream exiting from a CWAO unit directly to the environment, one should assess the possible toxic

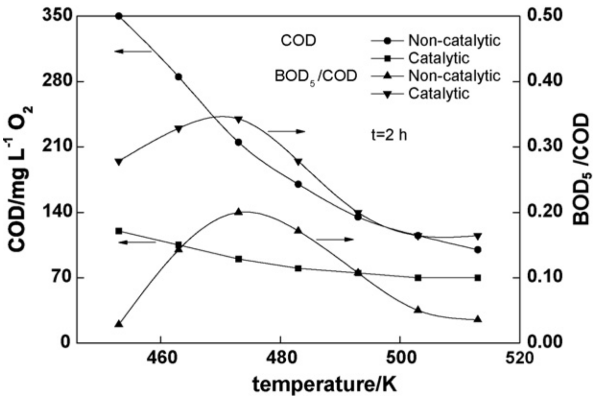


Fig. 11. COD and BOD_5/COD data obtained during the non-catalytic and catalytic treatment of a model compound Orange II. Adopted from ref. [145].

effects for an open body of water (river, lake, *etc.*). Keen and Baillod [148] studied wet-air oxidation of phenol and substituted phenols at $T = 477–533$ K and $P = 39–71$ bar. The toxicities of the starting compounds and the residual toxicity of the end-product solutions were measured with 48-h acute toxicity tests using *Daphnia magna*. The solutions of end products were all less toxic than the starting solutions by factors ranging from 10 to 120. However, the end-product solutions were somewhat more toxic than would be predicted from the known concentration of initial compound remaining in the solution of end products. Similar results are reported by Randall and Knopp [149], who showed the wet-air oxidation process to be effective in reducing toxicity to *Daphnia magna* of ten different organic pollutants. Furthermore, they indicated that the acute toxicity of end-product solutions was either because of the organic constituents present in them or from acidity, probably hydrochloric acid. In spite of the considerable research done on catalytic oxidations [1,2,94–99], there is little information available in the literature dealing with intermediate products that are responsible for the toxicity of treated wastewaters. Recently, Pintar et al. [150] performed a detailed study to provide additional information on the ability of the CWAO process to reduce the acute toxicity of industrial Kraft bleach plant effluents and to interpret the reduction in toxicity produced by the CWAO of these effluents, quantifying expected *versus* observed toxicity of the various organic products of incomplete oxidation in terms of total organic carbon concentration as a lumped parameter. The toxicities of the end-product solutions obtained by the wet-air oxidation of Kraft bleach plant effluents at $T = 463$ K in trickle-bed and batch-recycle reactors packed with either TiO_2 extrudates or the Ru(3 wt.%)/TiO_2 catalyst, were measured with 48-h and 30-min acute toxicity tests using the fresh water invertebrate *Daphnia magna* and the marine bacterium *Vibrio fischeri*, respectively. During the wet-air oxidation of D0 and E1 bleach plant effluents carried out in the presence of either TiO_2 or Ru/TiO_2 solids, various carboxylic and dicarboxylic acids were formed and their distribution played a determining role in the toxicity of end-product solutions. The solutions of end products were all more toxic to *Daphnia magna* than the starting bleach plant effluents by factors ranging from 2 to 33, which is attributed to the synergistic effects of intermediate short-chain organic acids (especially acetic acid) and inorganic salts present in these effluents. On the other hand, detoxification factors greater than unity were measured for end-product solutions treated in the presence of the Ru(3 wt.%)/TiO_2 catalyst and using *Vibrio fischeri* as a toxicity test species. Furthermore, end-product solutions were generally more toxic to *Daphnia magna* and *Vibrio fischeri* than indicated by the concentrations of total organic carbon remaining in the final solutions. Pintar et al. [150] also performed ultimate aerobic biodegradability measurements to demonstrate that bleach plant effluents treated by the CWAO process over the Ru/TiO_2 catalyst were completely biodegradable (Fig. 12). To conclude, before discharging treated wastewater streams into the environment, evaluations of the residual toxicity of solutions containing end products of catalytic wet-air oxidation should be performed that are based on actual bioassays, and not only on the potential of the process for destroying the original material entering the process. Alternatively, as bleach plant effluents treated by the CWAO process over the Ru/TiO_2 catalyst are biodegradable, an integrated CWAO and biological treatment plant would allow easy removal of the intermediate acetic acid formed in the CWAO step.

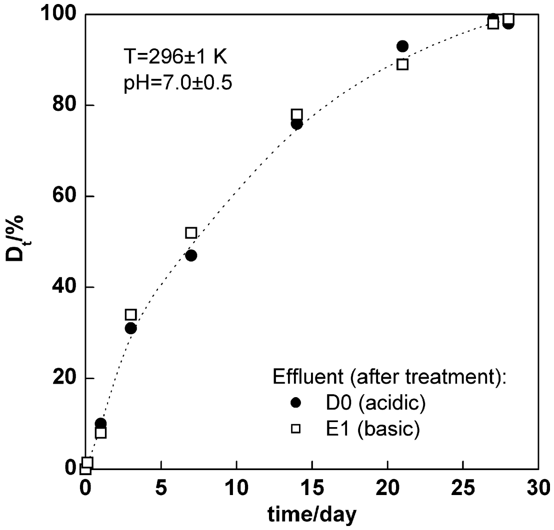


Fig. 12. Ultimate aerobic biodegradability (D_t) of end-product solutions produced by the oxidative treatment of D0 and E1 bleach plant effluents in the trickle-bed reactor packed with a Ru/TiO_2 catalyst. Adopted from ref. [150].

3. Conclusions

CWAO is a promising treatment technology for the abatement of organic pollutants in wastewaters. The primary goal is to convert organics into products more amenable to biological treatment; complete oxidation may be too expensive. The CWAO process has to be custom designed and must run autothermally. Due to the variety of wastewaters that have to be treated, one type of catalyst cannot fulfil all the needs. Therefore the catalyst must be tailored for each particular application and made of inexpensive materials. Oxides of Zr, Ce, and Ti may be used as stable supports. Metal oxide catalysts are very active but unstable (dissolution). In order to reduce leaching, the catalytically active compounds have to be incorporated into a lattice of catalyst support. If this is not feasible, the catalytic active phase should consist of precious metals. It would be advantageous to design a catalyst that can be employed for the treatment in single-pass reactors with a minimum lifetime over 500 h.

The triangular reaction network and the corresponding kinetics fulfil today's needs for reactor design. It might be advantageous to employ a bisectional reactor with homogeneous (non-catalytic) and heterogeneous (catalytic) sections. More experimental data are needed for high temperature and pressure for systems such as monolith/membrane reactors.

Thorough investigations with a variety of model solutions and industrial effluents are needed in order to demonstrate the capability of the CWAO process to considerably reduce toxicity, and/or improve the ultimate aerobic biodegradability of treated streams.

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References

[1] V.S. Mishra, V.V. Mahajani, J.B. Joshi, Ind. Eng. Chem. Res. 34 (1995) 2.
[2] F. Luck, Catal. Today 53 (1999) 81.
[3] R.W. Strehlenert, Swed. Patent 34,941 (1911); US Patent 1,149,420 (1915).
[4] G.S. Seiler, Sludge Manage. Ser. 17 (1987) 100.
[5] K. Kochloefl, Chem. Eng. Technol. 24 (2001) 229.
[6] A. Pintar, J. Levec, Ind. Eng. Chem. Res. 33 (1994) 3070.
[7] D.V. Moses, E.A. Smith, US Patent 2,690,425 (1954).
[8] E. Müller, K. Schwabe, Kolloid Z. 52 (1930) 163.
[9] K. Heyns, H. Paulsen, Angew. Chem. 69 (1957) 600.
[10] A. Rieche, H. Seeboth, H. Seyfarth, Brennst. Chem. 40 (1959) 194.
[11] C.E. Hamilton, J.L. Teal, J.A. Kelley, US Patent 344,280 (1969).
[12] E.O. Box, Jr., F. Farha, US Patent 3,823,088 (1974).
[13] S. Takahashi, T. Iguchi, Jpn. Kokai 74 (78) (1974) 636.
[14] T. Komabashiri, H. Yoshino, T. Ikeuchi, Jpn. Kokai 74 95 462 and 74 84 057 (1974); 75 04 859 and 75 04 860 (1975).
[15] A. Sadana, J.R. Katzer, Ind. Eng. Chem. Fundam. 13 (1974) 127.
[16] G. Baldi, S. Goto, C.-K. Chow, J.M. Smith, Ind. Eng. Chem. Proc. Des. Dev. 13 (1974) 447.
[17] A. Sadana, J.R. Katzer, J. Catal. 35 (1974) 140.
[18] A.K. Chowdhury, L.W. Ross, AIChE. Ser. Symp. Water 71 (1975) 46.
[19] B.I. Kolotusha, Ya.B. Goroghovatski, V.V. Shalya, Kinet. Katal. 16 (1975) 451.
[20] J. Levec, J.M. Smith, AIChE J. 22 (1976) 159.
[21] J. Levec, M. Herskowitz, J.M. Smith, AIChE J. 22 (1976) 919.
[22] A.I. Njiribeako, P.L. Silveston, R.R. Hudgins, Can. J. Chem. Eng. 56 (1978) 643.
[23] A.I. Njiribeako, R.R. Hudgins, P.L. Silveston, Ind. Eng. Chem. Fundam. 17 (1978) 234.
[24] H. Ohta, S. Goto, H. Teshima, Ind. Eng. Chem. Fundam. 19 (1980) 180.
[25] S. Imamura, A. Hirano, N. Kawabata, Ind. Eng. Chem. Prod. Res. Dev. 21 (1982) 570.
[26] S. Imamura, A. Doi, S. Ishida, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 75.
[27] S. Imamura, M. Nakamura, N. Kawabata, J. Yoshida, S. Ishida, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 34.
[28] S. Imamura, I. Fukuda, S. Ishida, Ind. Eng. Chem. Res. 27 (1988) 718.
[29] M.M. Ito, K. Akita, H. Inoue, Ind. Eng. Chem. Res. 28 (1989) 894.
[30] J. Levec, Appl. Catal. 63 (1990) L1.
[31] F.K. Schmidt, R.P. Kochetkova, A.F. Babikov, I.P. Shiverskaia, L.I. Shpilevskaia, C.A. Eppel, in: Proceedings of the 8th French-Soviet Meeting on Catalysis, Novossibirsk, June, (1990), p. 140.
[32] S. Kim, Y.T. Shah, R.L. Cerro, M.A. Abraham, Proc. AIChE Annual Meeting, Pittsburgh, August, (1991), p. 46.
[33] Y. Takahashi, N. Takeda, T. Aoyagi, K. Tanaka, Proc. 4th Eur. Symp. Space Environ. Control Syst., Florence, ESA SP-324, 1991, vol. 2, (1991), p. 643.
[34] T. Ishii, K. Mitsui, K. Sano, A. Inoue, Eur. Patent 431,932 (1991).
[35] A.R. Sanger, T.T.K. Lee, K.T. Chuang, in: K.J. Smith, E.C. Sanford (Eds.), Progress in Catalysis, Elsevier, 1992, p. 197.
[36] A. Pintar, J. Levec, J. Catal. 135 (1992) 345.
[37] A. Pintar, J. Levec, Chem. Eng. Sci. 47 (1992) 2395.
[38] A. Pintar, G. Berčič, J. Levec, in: G. Froment (Ed.), Proc. 8th Intern. Symp. Large Chem. Plants, Royal Flemish Soc. Eng., Antwerp, 1992, p. 333.
[39] J. Levec, Eur. Patent 04 29 750 B1 (1993).
[40] V.S. Mishra, J.B. Joshi, V.V. Mahajani, Ind. Chem. Eng. 34 (1993) 211.
[41] Y. Harada, K. Yamasaki, in: Proceedings of IDA/WRPC World Conference on Desalination Water Treatment, Yokohama, vol. 1, (1993), p. 231.
[42] A. Pintar, J. Levec, Chem. Eng. Sci. 49 (1994) 4391.
[43] A. Fortuny, C. Ferrer, C. Bengoa, J. Font, A. Fabregat, Catal. Today 24 (1995) 79.
[44] D. Mantzavinos, R. Hellenbrand, A.G. Livingston, I.S. Metcalfe, Appl. Catal. B 7 (1996) 379.
[45] D. Mantzavinos, R. Hellenbrand, A.G. Livingston, I.S. Metcalfe, Appl. Catal. B 11 (1996) 99.
[46] A. Pintar, G. Berčič, J. Levec, Chem. Eng. Sci. 52 (1997) 4143.
[47] C.A. Maugans, A. Akgerman, Water Res. 31 (1997) 3116.
[48] J. Barbier Jr., F. Delanoë, F. Jabouille, G. Blanchard, D. Duprez, J. Catal. 177 (1998) 378.
[49] A. Fortuny, J. Font, A. Fabregat, Appl. Catal. B 19 (1998) 165.
[50] Q. Zhang, K.T. Chuang, Appl. Catal. B 17 (1998) 321.
[51] A. Fortuny, C. Bengoa, J. Font, F. Castells, A. Fabregat, Catal. Today 53 (1999) 107.
[52] S. Hočevar, J. Batista, J. Levec, J. Catal. 184 (1999) 39.
[53] M. Sheintuch, Y.I. Matatov-Meytal, Catal. Today 53 (1999) 73.
[54] S. Hočevar, U. Opara Krašovec, B. Orel, A.S. Aricó, H. Kim, Appl. Catal. B 28 (2000) 113.
[55] S. Christoskova, M. Stoyanova, Water Res. 35 (2001) 2073.
[56] A. Alejandre, F. Medina, X. Rodriguez, P. Salagre, Y. Cesteros, J.E. Sueiras, Appl. Catal. B 30 (2001) 195.
[57] S.S. Lin, C.L. Chen, D.J. Chang, C.C. Chen, Water Res. 36 (2002) 3009.
[58] H.T. Gomes, J.L. Figueiredo, J.L. Faria, Ph. Serp, Ph. Kalck, J. Mol. Catal. A 182/183 (2002) 47.
[59] H.T. Gomes, J.L. Figueiredo, J.L. Faria, Catal. Today 75 (2002) 23.
[60] G. Neri, A. Pistone, C. Milone, S. Galvagno, Appl. Catal. B 38 (2002) 321.
[61] J. Barbier Jr., L. Oliviero, B. Renard, D. Duprez, Catal. Today 75 (2002) 29.
[62] P.D. Vaidya, V.V. Mahajani, Chem. Eng. J. 87 (2002) 403.
[63] S.T. Christoskova, M. Stoyanova, Water Res. 36 (2002) 2297.
[64] A.M.T. Silva, I.M. Castelo-Branco, R.M. Quinta-Ferreira, J. Levec, Chem. Eng. Sci. 58 (2003) 963.
[65] A.M.T. Silva, R.M. Quinta-Ferreira, J. Levec, Ind. Eng. Chem. Res. 42 (2003) 5099.
[66] C. Aguilar, R. García, G. Soto-Garrido, R. Arriagada, Appl. Catal. B 46 (2003) 229.
[67] M. Besson, A. Kallel, P. Gallezot, R. Zanella, C. Louis, Catal. Commun. 4 (2003) 471.
[68] D.J. Chang, I.P. Chen, M.T. Chen, S.S. Lin, Chemosphere 52 (2003) 943.
[69] S.S. Lin, D.J. Chang, C.H. Wang, C.C. Chen, Water Res. 37 (2003) 793.
[70] Q. Wu, X. Hu, P.L. Yue, Chem. Eng. Sci. 58 (2003) 923.
[71] J. Trawczyński, Carbon 41 (2003) 1515.
[72] S. Cao, G. Chen, X. Hu, P.L. Yue, Catal. Today 88 (2003) 37.
[73] D. Duprez, F. Delanoë, J. Barbier Jr., P. Isnard, G. Blanchard, Catal. Today 29 (1996) 317.
[74] P. Gallezot, S. Chaumet, A. Perrard, P. Isnard, J. Catal. 168 (1994) 104.
[75] P. Gallezot, N. Laurain, P. Isnard, Appl. Catal. B 9 (1996) L11.
[76] J.-C. Béziat, M. Besson, P. Gallezot, S. Durecu, J. Catal. 182 (1999) 129.
[77] C.R. Baillod, B.M. Faith, O. Masi, Environ. Prog. 1 (1982) 217.
[78] Z.Y. Ding, M.A. Frisch, L. Li, E.F. Gloyna, Ind. Eng. Chem. Res. 35 (1996) 3257.
[79] H.T. Gomes, J.J.M. Orfao, J.L. Figueiredo, J.L. Faria, Ind. Eng. Chem. Res. 43 (2004) 1216.
[80] M. Abecassis-Wolfovich, M.V. Landau, A. Brenner, M. Herskowitz, Ind. Eng. Chem. Res. 43 (2004) 5089.
[81] A. Cybulski, J. Trawczyski, Appl. Catal. B 47 (2004) 1.
[82] A.M.T. Silva, R.R.N. Marques, R.M. Quinta-Ferreira, Appl. Catal. B 47 (2004) 269.
[83] I.-P. Chen, S.-S. Lin, C.-H. Wang, L. Chang, J.-S. Chang, Appl. Catal. B 50 (2004) 49.

[84] H.T. Gomes, P.V. Samant, Ph. Serp, Ph. Kalck, J.L. Figueiredo, J.L. Faria, Appl. Catal. B 54 (2004) 175.
[85] B. Renard, J. Barbier Jr., D. Duprez, S. Durécu, Appl. Catal. B 55 (2005) 1.
[86] J. Garcia, H.T. Gomes, Ph. Serp, Ph. Kalck, J.L. Figueiredo, J.L. Faria, Catal. Today 102–103 (2005) 101.
[87] N. Perkas, D.P. Minh, P. Gallezot, A. Gedanken, M. Besson, Appl. Catal. B 59 (2005) 121.
[88] A. Santos, P. Yustos, A. Quintanilla, G. Ruiz, F. Garcia-Ochoa, Appl. Catal. B 61 (2005) 323.
[89] H.T. Gomes, P. Selvam, S.E. Dapurkar, J.L. Figueiredo, J.L. Faria, Micropor. Mesopor. Mater. 86 (2005) 287.
[90] J. Barbier, L. Oliviero, B. Renard, D. Duprez, Top. Catal. 33 (2005) 77.
[91] D.P. Minh, P. Gallezot, M. Besson, Appl. Catal. B 63 (2006) 68.
[92] J. Garcia, H.T. Gomes, Ph. Serp, Ph. Kalck, J.L. Figueiredo, J.L. Faria, Carbon 44 (2006) 2384.
[93] C. Milone, M. Fazio, A. Pistone, S. Galvagno, Appl. Catal. B 68 (2006) 28.
[94] J. Levec, A. Pintar, Catal. Today 24 (1995) 51.
[95] Y.I. Matatov-Meytal, M. Sheintuch, Ind. Eng. Chem. Res. 37 (1998) 309.
[96] S. Imamura, Ind. Eng. Chem. Res. 38 (1999) 1743.
[97] K. Pirkanniemi, M. Sillanpää, Chemosphere 48 (2002) 1047.
[98] A. Pintar, Catal. Today 77 (2003) 451.
[99] S.K. Bhargava, J. Tardio, J. Prasad, K. Foger, D.B. Akolekar, S.C. Grocott, Ind. Eng. Chem. Res. 45 (2006) 1221.
[100] D.B. Akolekar, S.K. Bhargava, I. Shirgoankar, J. Prasad, Appl. Catal. A 236 (2002) 255.
[101] J. Tardio, S. Bhargava, S. Eyer, M. Sumich, D.B. Akolekar, Ind. Eng. Chem. Res. 43 (2004) 847.
[102] S.H. Lin, S.J. Ho, C.L. Wu, Ind. Eng. Chem. Res. 35 (1996) 307.
[103] S. Imamura, Y. Okumura, T. Nishio, K. Utani, Y. Matsumura, Ind. Eng. Chem. Res. 37 (1998) 1136.
[104] K. Belkacemi, F. Larachi, S. Hamoudi, G. Turcotte, A. Sayari, Ind. Eng. Chem. Res. 38 (1999) 2268.
[105] K. Belkacemi, F. Larachi, S. Hamoudi, A. Sayari, Appl. Catal. A 199 (2000) 199.
[106] Q. Zhang, K.T. Chuang, Ind. Eng. Chem. Res. 37 (1998) 3343.
[107] Q. Zhang, K.T. Chuang, Can. J. Chem. Eng. 77 (1999) 399.
[108] Q. Zhang, K.T. Chuang, Environ. Sci. Technol. 33 (1999) 3641.
[109] A. Pintar, M. Besson, P. Gallezot, Appl. Catal. B 30 (2001) 123.
[110] L. Li, P. Chen, E.F. Gloyna, AIChE J. 37 (1991) 1687.
[111] A. Pintar, G. Berčič, M. Besson, P. Gallezot, Appl. Catal. B 47 (2004) 143.
[112] J. Đonlagić, J. Levec, AIChE J. 45 (1999) 2571.
[113] A. Eftaxias, J. Font, A. Fortuny, A. Fabregat, F. Stüber, Appl. Catal. B 67 (2006) 12.
[114] P. Hutchinson, D. Luss, Chem. Eng. J. 1 (1970) 129.
[115] T.C. Ho, AIChE J. 42 (1996) 214.
[116] K.B. Bischoff, in: A.J. Sapre, F.J. Krambeck (Eds.), Chemical Reactions in Complex Mixtures, Van Nostrand Reinhold, New York, 1991.
[117] J. Wei, J.C.W. Kuo, Ind. Eng. Chem. Fundam. 8 (1969) 114.
[118] J.R. Katzer, H.H. Ficke, A. Sadana, J. Water Poll. Control Fed. 48 (1976) 920.
[119] F. Farha, E.O. Box, R.O. Dunn, R.D. Kuerston, Div. Petro. Chem., ACS 23 (1978) 93.
[120] G. Berčič, A. Pintar, J. Levec, Ind. Eng. Chem. Res. 35 (1996) 4619.
[121] I. Polaert, A.M. Wilhelm, H. Delmas, Chem. Eng. Sci. 57 (2002) 1585.
[122] NS-LC Wastewater Treatment System—Catalytic Oxidation, Nippon Shokubai Technical Leaflet, 2009.
[123] V. Hatzantoniou, B. Andersson, N.-H. Schöön, Ind. Eng. Chem. Prod. Des. Dev. 25 (1986) 964.
[124] G. Berčič, A. Pintar, Chem. Eng. Sci. 52 (1997) 3709.
[125] B.H. Cooke, M.R. Taylor, Fuel 72 (1993) 305.
[126] M. Fukatawa, H. Takahashi, G. Inoue, T. Fujioka, in: Proceedings of IDA/WRPC World Conference on Desalination Water Treatment, Yokohama, vol. 1, (1993), p. 231.
[127] Y. Harada, K. Yamasaki, in: Proceedings of IDA/WRPC World Conference on Desalination Water Treatment, Yokohama, vol. 2, (1993), p. 505.
[128] J.-C. Béziat, M. Besson, P. Gallezot, S. Durecu, Ind. Eng. Chem. Res. 38 (1999) 1310.
[129] S. Goto, J.M. Smith, AIChE J. 21 (1975) 714.
[130] A. Alıcılar, M. Kömürcü, M. Gürü, Chem. Eng. Proc. 41 (2002) 525.
[131] C.B. Maugans, A. Akgerman, Water Res. 37 (2003) 319.
[132] A. Singh, K.K. Pant, K.D.P. Nigam, Chem. Eng. J. 103 (2004) 51.
[133] J. Guo, M. Al-Dahhan, Ind. Eng. Chem. Res. 44 (2005) 6634.
[134] A. Pintar, M. Besson, P. Gallezot, Appl. Catal. B 31 (2001) 275.
[135] W.-D. Deckwer, Bubble Column Reactors, Wiley, Chichester, 1992.
[136] J. Levec, EP 0 819 101 B1, European Patent Office, Munich (1998).
[137] A.R. Wilhelmi, R.B. Ely, Chem. Eng. (February) (1976) 105.
[138] V.S. Mishra, V. Padiyar, J.B. Joshi, V.V. Mahajani, J.D. Desai, Process Safety Environ Prot. 73 (1995) 243.
[139] M. Chakchouk, M. Hamdi, J.N. Foussard, H. Debellefontaine, Environ. Technol. 15 (1994) 323.
[140] S.H. Lin, T.S. Chuang, J. Environ, Sci. Health Part A-Environ. Sci. Eng. Toxic Hazard. Sub. Control 29 (1994) 547.
[141] E. Otal, D. Mantzavinos, M.V. Delgado, R. Hellenbrand, J. Lebrato, I.S. Metcalfe, A.G. Livingston, J. Chem. Technol. Biotechnol. 70 (1997) 147.
[142] J. Đonlagić, J. Levec, Appl. Catal. B 17 (1998) L1.
[143] O.J. Hao, K.K. Phull, J.M. Chen, Water Res. 28 (1994) 283.
[144] D. Mantzavinos, D.M.P. Burrows, R. Willey, G. Lo Biundo, S.F. Zhang, A.G. Livingston, I.S. Metcalfe, Water Res. 35 (2001) 3337.
[145] J. Đonlagić, J. Levec, Environ. Sci. Technol. 32 (1998) 1294.
[146] W. Zhu, Y. Bin, Z. Li, Z. Jiang, T. Yin, Water Res. 36 (2002) 1947.
[147] A. Santos, P. Yustos, A. Quintanilla, F. García-Ochoa, Appl. Catal. B 53 (2004) 181.
[148] R. Keen, C.R. Baillod, Water Res. 19 (1985) 767.
[149] T.L. Randall, P.V. Knopp, J. Water Poll. Control Fed. 52 (1980) 2117.
[150] A. Pintar, M. Besson, P. Gallezot, J. Gibert, D. Martin, Water Res. 38 (2004) 289.