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Catalytic processes for the purification of drinking water and industrial effluents

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Abstract

Catalytic liquid-phase hydrogenation of aqueous nitrate solutions is presented as a potential, advanced treatment technology for the removal of excessive quantities of nitrate ions from polluted drinking water streams. Catalysts are briefly reviewed first, followed by mechanistic speculations and kinetics that have been proposed for the liquid-phase nitrate reduction. Subsequently, a novel process scheme consisting of integrated ion-exchange and catalytic denitrification steps is discussed.

This paper reviews also the developments in the field of catalytic wet-air oxidation (CWAO). 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, 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 reported.

Keywords: Catalytic denitrification; Catalytic wet-air oxidation; Detoxification; Drinking water purification; Heterogeneous catalysis; Industrial effluents; Integrated process; Nitrate removal; Wastewater treatment

1. Catalytic treatment of drinking water

Groundwater pollution by nitrates, which are perhaps the most ubiquitous of all groundwater contaminants, is a widespread problem in many locations in the world. Man-made or man-induced sources of nitrogen introduction into the subsurface environment include agricultural fertilizers, septic tank systems, and animal waste disposal. A number of hydrogeological factors and agricultural practices like precipitation/runoff, irrigation, soil type, and depth and geological features, such as karst areas, denitrification, fertilizing intensity, crop types, and land usage influence the concentration of nitrates in groundwater at specific locations. Canter [1] and Sell et al. [2] provide statistical data, which represent the extent of drinking water contamination by nitrates in United States and European countries. It is reported by the first author that for some locations nitrate concentration in water has been found to be at risky levels up to 200 $\mathrm{mg\,l^{-1}}$. Since this value is excessively above the maximum admissible concentration (i.e., 50 $\mathrm{mg\,l^{-1}}$) set by the European Drinking Water Directive, the nitrate content in such streams should be necessarily reduced in order to avoid health risk. The toxicity of nitrates to humans is due to the body's reduction of nitrate to nitrite. The role of the latter as a precursor of to clinical cyanosis (blue baby syndrome) and carcinogenic nitrosamines as well as to other *N*-nitroso compounds is firmly established [1].

Removal of nitrates from drinking water is an important and developing area of research. Although technology in this area is developing, there is still a need to further optimize the current treatment

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techniques and develop the emerging processes for nitrate remediation. In a review paper of Kapoor and Viraraghavan [3], the present state-of-the-art of treatment methods for the removal of excessive quantities of nitrate ions from drinking water is discussed, and various treatment options are compared in terms of their effectiveness, ease of operation, and cost. Physicochemical methods allow effective removal of nitrate ions from contaminated groundwater by concentrating them in a secondary waste stream. Among these methods, the capital and operating costs are the lowest for the ion-exchange process; nevertheless, it is very difficult and costly to dispose of large quantities of spent regenerant brine in noncoastal locations where natural evaporation is impossible. The most promising techniques for nitrate removal, without any occurrence of wastewater, are biological digestion and catalytic denitrification by using noble metal catalysts [3]. Biological denitrification processes (either heterotrophic or autotrophic) are known to have great potential for the treatment of municipal and industrial wastewater streams. The main reasons for the slow transfer of technology to drinking water purification are concerns over possible bacterial contamination of treated water, the presence of residual organics in treated water, and the possible increase in chlorine demand of purified water. The reduction of aqueous nitrate solutions by using hydrogen over a solid catalyst, first described by Vorlop et al. [4–7], offers an alternative and economically advantageous process to biological treatment as a means of purifying drinking water streams. In this process, nitrates are selectively converted by means of hydrogen via intermediates to nitrogen in a two- or three-phase reactor operating under mild reaction conditions (e.g., $T = 278$–$298\,K$, $p(H_2)$ up to 7 bar [2]). To maintain electroneutrality of the aqueous phase, nitrates are replaced by hydroxide ions. Supported Pd–Cu, Pd–Sn, Pd–In and Pt–Cu bimetallic catalysts exhibit high activity for nitrate reduction and chemical resistance, but still inadequate selectivity toward nitrogen production. The main drawback of these solids is formation of the side product, ammonia, which is undesirable in drinking water. Since catalytic liquid-phase hydrogenation of aqueous nitrate solutions is in a stage of development, it is obvious that more kinetic and mechanistic studies are needed in order to develop an effective catalytic process for purifying drinking water streams.

It is reported by Hörold et al. [7,8] that Pd hydrogenation catalysts doped by Cu represent active and selective bimetallic solids for the transformation of nitrates to nitrogen. The potential of Pd–Cu catalysts for liquid-phase nitrate hydrogenation was studied by these authors at $T = 283\,K$ in a slurry reactor sparged by pure hydrogen. For the initial nitrate concentration set to $100\,mg\,l^{-1}$, the reaction selectivity was found to be at a level of 82 mol%. This value could be further increased by carrying out the reaction at lower hydrogen concentrations over a mixture of supported Pd–Cu and Pd catalysts [7,9]. In this way, it was possible to reduce $100\,mg\,l^{-1}$ of nitrate without exceeding the European Community permitted level of ammonia in drinking water (i.e., $0.5\,mg\,l^{-1}$). Hörold et al. [8] have also proposed that the catalytic nitrate reduction, similarly to the autotrophic–chemolitotrophic denitrification with microorganisms, undergoes a stepwise transformation of the parent ion via intermediates (such as NO and N_2O) to nitrogen and ammonia. In agreement with these observations, Wärnå et al. [10], who performed measurements in a metallic monolith reactor, suggested that in the process of catalytic nitrate reduction the key intermediate on a noble metal surface might be NO. Pintar and Kajiuchi [11] studied the same reaction in the presence of various Pd–Cu bimetallic catalysts, which were prepared according to different impregnation sequences of γ-Al_2O_3 support. The results showed that the nitrate to nitrite reduction step undergoes a structure-insensitive reaction, which has been confirmed recently by Deganello et al. [12]. Furthermore, it was indicated by Pintar and Kajiuchi [11] that the overall reaction selectivity is adversely affected by the amount of nitrite ions accumulated in the liquid-phase. It is reported by Batista et al. [13] and Pintar et al. [14] that the selectivity of the reaction under consideration strongly depends on the spatial distribution of Pd and Cu metallic phases, which is confirmed by AES profiling. Among all Pd–Cu bimetallic solids tested in a semibatch slurry reactor, the highest reaction selectivity (i.e., over 90 mol% for the initial nitrate concentration equal to $200\,mg\,l^{-1}$) has been obtained for the catalyst sample in which the very first surface sublayers were enriched by palladium atoms. Similar behavior with respect to minimum nitrite accumulation was reported also for Pd–Cu bimetallic catalysts synthesized by using a sol–gel preparation procedure [15]. However, the obtained reaction selectivities were found to be as low as 60–75 mol%, which was probably caused by inappropriate textural properties of these materials. It should be mentioned that the catalytic properties of Pd–Cu catalysts were found to be sensitive to the ratio of the two metals in the catalyst [7,8,12,16]. Some years ago, new selective nitrate-reducing bimetallics, namely alumina-supported Pd–Sn and Pd–In, were introduced [17–19]. Compared to Pd–Cu catalysts, both Pd–Sn and Pd–In catalysts synthesized by a deposition–precipitation procedure, are more active and selective for nitrate removal, although opposite results were found by Strukul et al. [20] for titania- and zirconia-supported Pd–Sn catalysts. As reported by Prüsse et al. [21], another factor in improving the reaction selectivity is the use of formic acid instead of hydrogen as a reductant, which is in situ transformed to H_2 and CO_2.

Quantitative rate data concerning the catalytic liquid-phase nitrate reduction are meager. Tacke and Vorlop [22] determined the kinetics of nitrate hydrogenation over a Pd–Cu bimetallic catalyst containing 5 wt.% of Pd and 1.25 wt.% of Cu. The measurements were performed in a slurry reactor at $T = 283$ K. The initial rate kinetic data they analyzed resulted in the rate expression of power-law type. They found the reaction rate to be of 0.7 order with respect to nitrate and independent of hydrogen partial pressure provided that this pressure is greater than about 1.0 bar. It is further reported that the observed rate per unit weight of catalyst is not affected by the catalyst concentration. A detailed kinetic model of the catalytic nitrate reduction was derived by Pintar et al. [23]. The rate of nitrate disappearance has been well described by a rate equation of the Langmuir–Hinshelwood type, which accounts for both noncompetitive and equilibrium nitrate and dissociative hydrogen adsorption steps as well as an irreversible bimolecular surface process that controls the overall reaction rate. The observed kinetics in the slurry reactor is not influenced by the presence of nitrites as intermediates in the reduction toward nitrogen formation. Furthermore, the change in pH value of aqueous solution during the reaction course has a minor influence on the nitrate disappearance rate. The authors have also reported that the liquid-phase reduction of aqueous nitrate solutions over supported Pd–Cu bimetallics occurs by a heterolytic electron transfer between adsorbed reactant species on different types of active sites. It was discovered in a series of runs using various nitrate salts as sources of nitrate ions that the apparent surface reaction rate constant increases in the order $K^+ < Na^+ < Ca^{2+} < Mg^{2+} < Al^{3+}$ and changes proportionally with the ionization potential of the cations present in the aqueous solution [24]. A detailed analysis of experimental data confirmed that efficiency of the Pd–Cu bimetallic catalyst in catalytic nitrate reduction is influenced by the migration of produced hydroxide ions from the Helmholtz layer. The permanent hardness of drinking water exhibits no inhibitive impact either on the extent of nitrate removal or on reaction selectivity. On the other hand, the nitrate disappearance rate as well as the nitrogen production yield decrease appreciably in the presence of hydrogencarbonates [24].

So far, characterization data for nitrate and nitrite reducing catalysts are scarce. Pd–Cu bimetallic catalysts were examined by means of different techniques, such as SEM, XRD, TEM, EDX, AES, EXAFS, TPR, XPS, AFM and H_2 chemisorption [12–15,25,26]. Characterization was mainly done in order to get information about the nature, distribution and size of metal crystallites. Strong evidence was obtained for an intimate interaction between Pd and Cu, which was interpreted as a strong hint for the formation of an alloy. Recently, Pd–Sn catalysts were examined by means of chemisorption, FTIR and ^{119}Sn-Mössbauer spectroscopy [27]. Both Pd–Sn ensembles and pure Pd ensembles were identified in these catalysts.

The process of catalytic nitrate reduction has been studied so far mostly in batch reactors. Few investigations were published on the reduction of nitrates in continuous-flow reactors. Sell et al. [2] carried out the catalytic nitrate reduction in pilot fixed-bed and expanded-bed reactors. The units operated at a temperature of ground water and total pressures up to 6 bar over an alumina-supported Pd–Cu bimetallic catalyst containing 2.0 wt.% of Pd and 0.5 wt.% of Cu metallic phases. Hydrogen was used as a reducing agent and predissolved in the liquid-phase prior to entering into the denitrification reactor; due to the elevated operating pressure, single-phase flow was established in the catalytic bed. With an expanded-bed reactor, rates of nitrate reduction of up to 2.5 g kg^{-1} catalyst per hour were achieved. On the other hand, the nitrate disappearance rate measured in the “liquid-full” fixed-bed reactor was lower by about five times, which is attributed to mass-transfer limitations. It is furthermore reported by Sell et al. [2] that neither any accumulation of intermediate nitrites nor the formation of ammonium ions has been observed. Recently, catalytic nitrate reduction was investigated in isothermal fixed-bed reactors at $T = 298\,\mathrm{K}$ and atmospheric pressure [28]. Experiments carried out in a bubble-column fixed-bed reactor in the presence of distilled water as a reaction medium, demonstrate that nitrates can be efficiently removed from the liquid-phase, and that the maximum contaminant level for ammonium ions in drinking water is not exceeded. The measured conversions are considerably influenced by the variation of volumetric flow rate of either the gas- or liquid-phase. The order of magnitude analysis of apparent rate constant and mass transfer coefficients confirms that the observed reaction rate is governed by the mass transfer of hydrogen from the gas- into the bulk liquid-phase. Due to shorter mean residence times, lower nitrate conversions are measured in a trickle-bed reactor. At the given reaction conditions, catalyst particles were directly exposed to the gas-phase in this reactor system, which drastically enhanced ammonia production. When drinking water is used as a reaction medium instead of distilled water, the nitrate disappearance rate as well as reaction selectivity decrease appreciably, which is attributed to the presence of dissolved ionic species. Additionally, nitrite was detected in the reactor effluent at levels higher than the maximum admissible concentration (i.e., $0.02\,\mathrm{mg\,l^{-1}}$). These observations indicate that by using up-to-date bimetallic catalysts, the direct treatment of contaminated drinking water with higher amount of hydrogencarbonates seems to be unfeasible [28]. In order to decrease or avoid the formation of ammonium ions, other strategies were also tested, e.g., the use of hydrogels of polyvinyl alcohol [29], membranes [16,20,30], structured membranes [31], hollow fibers [32] or cloths [33]. Another approach was the use of metal-doped acidic ion exchangers to generate an acidic environment around the active sites [34]. Most of these efforts were more or less successful, but a real technological breakthrough appeared by the invention of an integrated process [35–37], which efficiently combines a conventional single-bed ion-exchange unit with a catalytic denitrification reactor in such a way that drawbacks of each separate technique are effectively eliminated, i.e. (i) the production of secondary waste stream containing high concentrations of nitrate, sulfate and chloride ions; (ii) the contamination of purified water with the produced ammonium ions. A schematic layout of the combined process is illustrated in Fig. 1. The nitrate concentration in water treated by the ion-exchange step, should not exceed $50\,\mathrm{mg\,l^{-1}}$. The ion-exchange step makes use of a packed-bed of anion resin in a chloride form. Feedwater anions, including nitrate, are exchanged for chloride on a strong-base anion resin, which is nitrate-selective. The nitrate-free effluent is blended with a pre-determined fraction of bypass raw water to produce water of acceptable nitrate concentration. Immediately prior to nitrate breakthrough, the column exhaustion is terminated, and the resin is regenerated in a closed circuit with a sodium chloride solution; the latter contains $5–10\,\mathrm{g\,l^{-1}}$ of NaCl, which is lower by an order of magnitude in comparison to conventional ion-exchange. The nitrate-rich regenerant passes through a two- or three-phase upflow reactor, packed with a proprietary Pd–Cu/γ-Al_2O_3 bimetallic catalyst, where nitrate is converted by means of dissolved hydrogen to nitrogen, with ammonia as a side product. The fixed-bed reactor operates at ambient temperature and atmospheric pressure. The pH value of the liquid-phase is kept constant at a value of 5.0 by adding HCl to the NaCl solution. The regenerant continues to be recirculated through the ion-exchange column and the denitrification reactor, until the ion-exchanger has reached a sufficient chloride loading. The integrated process results in about 95% reduction of waste brine, which is a considerable improvement on conventional ion-exchange. Accumulation of sulfate in the closed regeneration circuit does not affect the nitrate capacity of the resin. Since the denitrification process does not take place in direct contact with the groundwater, there is no risk of the nitrite and ammonia production affecting the water quality; so the production of reliable drinking water is possible without the need of extensive post-treatment. The use of HCl as a reagent for pH control has the advantage that no makeup of the regenerant with NaCl is required, since the stoichiometric required amount of chloride ions for the subsequent regeneration cycle is simultaneously introduced into the system via the neutralization of hydroxide ions produced during the liquid-phase nitrate reduction.

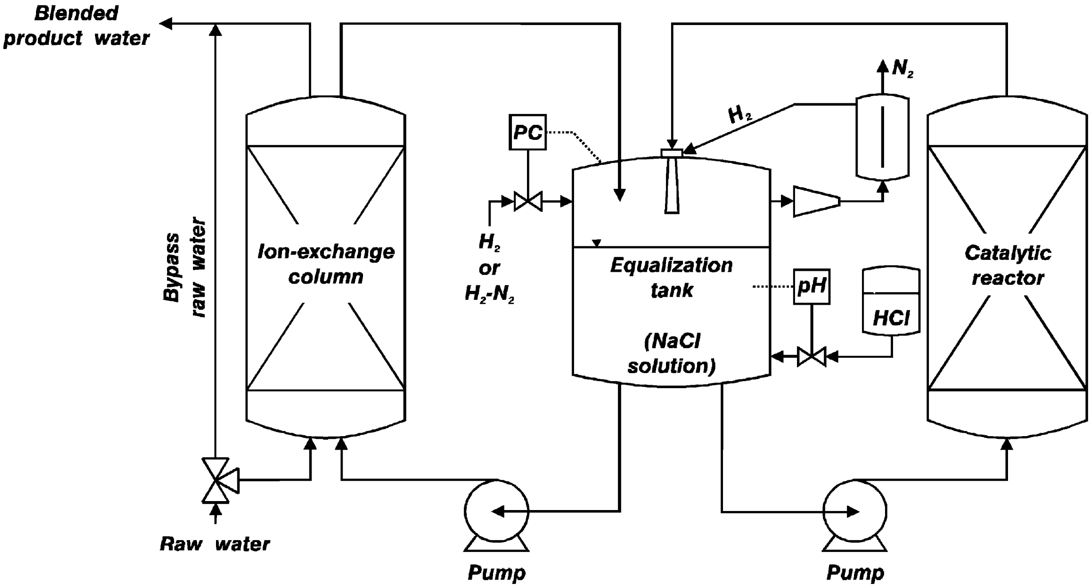

Fig. 1. Combined ion-exchange/catalytic denitrification process for nitrate removal.

2. Catalytic treatment of wastewaters

Immense arrays of organic compounds are currently widely used, and many of these are potent contaminants when they are released into freshwater ecosystems. Industrial plants generate increasing amounts of wastewater, contaminated with toxic and hazardous organic compounds, which cause severe problems to 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, before they meet the specifications for discharge or for recycling in the process. Therefore, development of efficient wastewater treatment technologies has become a major concern throughout the world and has received considerable attention.

Among them, wet-air oxidation (WAO) or thermal liquid-phase oxidation process 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^{-1}), or toxic contaminants for which direct biological purification is unfeasible [38]. 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 severe 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% [39]. In the WAO processes, the organic contaminants dissolved in water are either partially degraded by means of an oxidizing agent into biodegradable intermediates or mineralized into innocuous inorganic compounds such as CO_2, H_2O and inorganic salts, which remain in the aqueous phase. Sulfur is converted to sulfate, halogens to halides and phosphorous 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. [39]. One of the main drawbacks of the WAO process is its 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 [38]. Furthermore, organic nitrogen compounds are mostly transformed to ammonia, which is also stable in WAO operating conditions. Hence, the WAO process is considered as a pre-treatment step of wastewaters, which requires additional treatment, typically in a conventional biological treatment plant.

WAO is not a new process. Its origins can be traced to the Strehlenert process of wood technology patented in 1911 and to the zinc sulfide oxidation process of hydrometallurgy patented in 1927 [40]. The majority of the WAO research development took place in the United States about 50 years ago, which resulted into the construction of several large WAO plants for the treatment of municipal wastewater sludge by the Zimpro company in the early 1960s [41]. Nowadays, over 90 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 present to carbon dioxide. Consequently, it is considered as 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 can be largely improved by the use of catalysts, either in the form of solids or as homogeneous catalysts. Compared to conventional WAO, catalytic wet-air oxidation (CWAO) offers 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 COD 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 [42], 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 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, 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 [43]. Several Japanese companies developed CWAO technologies relying on heterogeneous catalysts based on precious metals deposited on titania or titania–zirconia oxides. On the other hand, the focus in Europe was more on homogeneous CWAO, where some processes are already commercially exploited and some of them are in various stages of development.

2.1. Heterogeneous CWAO processes

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 reaction temperature, pressure and 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 conducted typically 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) poisoning of the active sites by eventual 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 an appropriate choice of the catalytic metal or metal oxide phase and by pH control during CWAO. In this respect, various heterogeneous catalysts were synthesized and tested in the last decades, based either on metal oxides or supported precious metals [42,44–92]. Mixtures of metal oxides of Cu, Zn, Co, Mn and Bi are reported to exhibit good activity, but leaching of these catalysts was detected [72,80,85]. On the contrary, heterogeneous catalysts based on precious metals deposited on stable supports are less prone to active ingredient leaching [64,81,84,93–96]. 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 [38,80,81,93,95,97]. The same parameters as described above are also of importance to control 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 [98]. Additional information about studies performed in the field of CWAO are available in recent review papers [38,39,99–101].

This research resulted into the installation of several commercial CWAO systems especially in Japan, where three CWAO technologies have been developed since the mid-eighties. 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 [102], which operates at $T = 493\,\mathrm{K}$, $P_{\mathrm{tot.}} = 40\,\mathrm{bar}$ and $\mathrm{SV} = 2\,\mathrm{h}^{-1}$, involves a Pt–Pd/$TiO_2$–$ZrO_2$ honeycomb catalyst. Slug flow established in vertical monolith channels significantly improves mass transfer [103,104] and prevents solids deposition. In these conditions, the extent of oxidation of compounds such as phenol, formaldehyde, acetic acid, glucose, etc. reaches or exceeds 99% [102]. The Osaka Gas CWAO process [105–107] 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 larger than 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 $T = 443\,\mathrm{K}$ in the presence of supported platinum catalyst.

It seems that Katzer et al. [108] 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 CWAO may not be economically attractive for low concentrations of organics because of the energy requirement to heat up wastewater stream. High organic concentrations in wastewaters provide enough heat so that the process is thermally self-sufficient; in these cases the process becomes economically feasible. Farha et al. [109] 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 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. 2 illustrates a simplified process scheme for the catalytic liquid-phase oxidation of organics in wastewaters. Prefiltered 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 vapor 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 pre-concentrated may be required. The CALIPHOX process invented at the National Institute of Chemistry (Ljubljana, Slovenia), which uses an activated carbon adsorption–pre-concentration step, is shown schematically in Fig. 3 [99]. 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 adsorbed. Under these conditions, most of the organics are desorbed and subsequently oxidized over the catalyst in a trickle-bed reactor [110]. For optimal effect, one or other process depicted in Figs. 2 and 3 should be installed at the

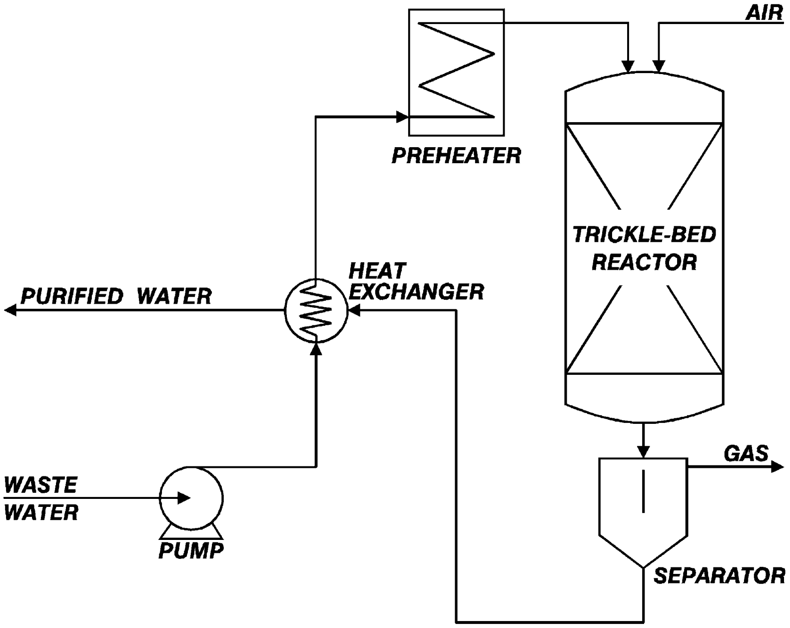

Fig. 2. Schematic drawing of a simple process for CWAO.

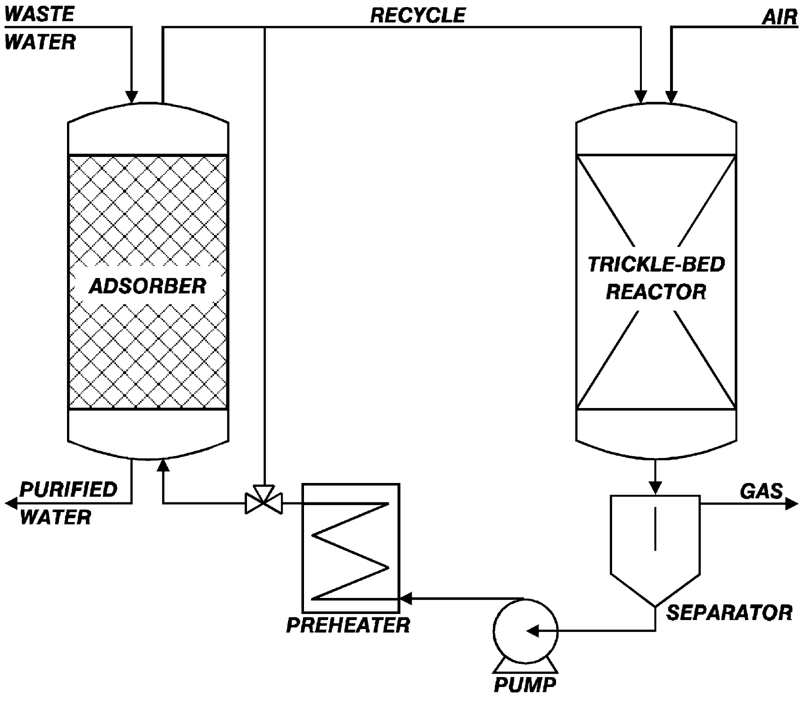

Fig. 3. Schematic drawing of the CALIPHOX process for catalytic liquid-phase oxidation of organic pollutants with an adsorber unit for pre-concentration.

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.

In France, several studies were conducted recently in order to synthesize heterogeneous precious metal catalysts for the oxidation of refractory compounds, acetic acid and ammonia, at temperatures below 473 K and total operating pressures below 40 bar [93–96,111]. These investigations supported by chemical and wastewater treatment companies led to a series of patents claiming catalysts based on supported Ru [112].

Scrutiny of the past literature reveals that a large number of previous investigations of the CWAO process employed simulated wastewaters, which consisted of a single organic compound. The information on catalytic oxidation of the multi-component mixtures of organic pollutants is very limited [38,39, 99–101]. Experimental results of WAO of high-concentration chemical wastewater (COD up to 42 800 mg l^{-1}) containing various organic acids and inorganic compounds indicated that over 50% reduction of the COD concentration could be easily achieved in about an hour at $T = 473$ K and total operating pressure of 30 bar. A pronounced increase in the COD removal using $CuSO_4$ over that without catalyst was observed; however, the improvement became less appreciable with Co_2O_3 and ZnO heterogeneous catalysts [113]. Imamura et al. [114] studied the WAO of a domestic wastewater in the presence of Mn/Ce and Ru/Ce catalysts. The Ru/Mn/Ce solid, 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^{-1}) was eliminated after a 3 h run. Belkacemi et al. [115,116] investigated the removal efficiency of total organic carbon from raw high-strength alcohol-distillery waste liquors (TOC up to 22 500 mg l^{-1}) in a batch stirred autoclave over various catalysts. In the temperature and oxygen partial pressure ranges 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^{-1}. 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. The kinetics of TOC, solid and gaseous carbons under the combined effects of thermolysis, WAO and solid-catalyzed WAO were described by a global inhibition–deactivation model [115]. Zhang and Chuang [86,117] showed that an alkaline (c(TOC) = 1500 mg l^{-1}, pH = 11) and an acidic (c(TOC) = 720 mg l^{-1}, pH = 2.2) bleach plant effluents can be successfully treated by CWAO at 463 K under 15 bar of oxygen partial pressure in the presence of palladium-supported on alumina or alumina-ceria. 70% removal of TOC in the alkaline wastewater could be achieved. By 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 [118]. 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^{-1}, pH = 8.5) [119]. No leaching of platinum and cerium was observed, but dissolution of palladium (0.14 mg l^{-1}) and aluminum (41.1 mg l^{-1}) 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 WAO of acidic and alkaline Kraft bleach plant effluents was recently investigated in a batch slurry reactor in the presence of titanium or zirconium oxides, or ruthenium catalysts supported on these oxides [120]. 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. With the addition 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.

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 and phenol [56,82,87,111,121]. Béziat et al. [111] 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 an excellent chemical resistance in a wide range of operating conditions. Recently, Pintar et al. [122] investigated CWAO of two acidic (D0) and alkaline (E1) bleach plant effluents from a softwood Kraft pulp mill (TOC content of 1138 and 1331 $mg\,l^{-1}$, respectively) in an isothermal, concurrent downflow trickle-bed reactor at $T = 463\,K$ and oxygen partial pressure of 8 bar. The reactor packed with TiO_2 extrudates (Degussa, P-25 type, $S_{BET} = 51\,m^2\,g^{-1}$) or 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 equal to 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 (see Fig. 4). By means of HPLC, the following acids: 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. The accumulation of these intermediates, especially acetic acid, was favored during the oxidation of 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 (see Fig. 5). This demonstrates that at the 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. Water treated in this process is of high quality, almost free of organics and

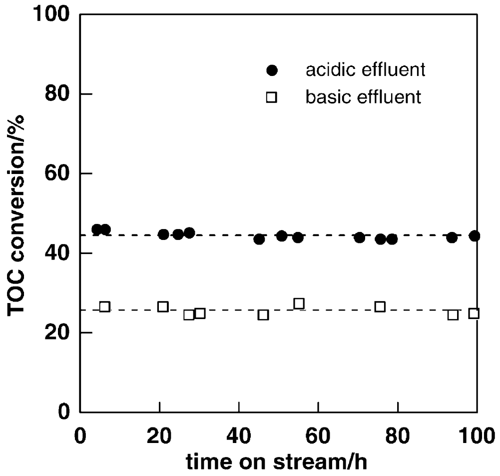

Fig. 4. TOC conversion as a function of time on stream, obtained in the trickle-bed reactor packed with TiO_2 extrudates. $T = 463\,K$, $P_{tot.} = 55$ bar, $\Phi_{vol.,L} = 1.0\,ml\,min^{-1}$, $m_{cat.} = 12.3\,g$.

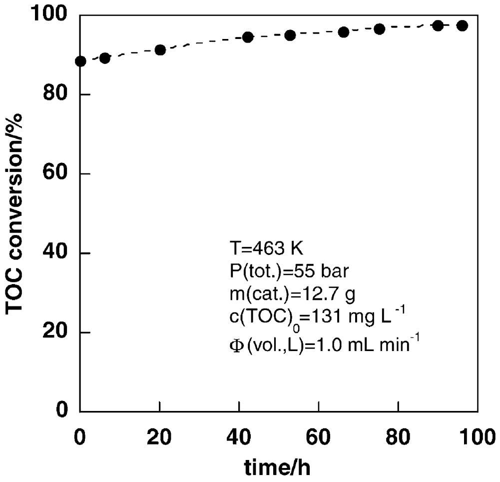

Fig. 5. TOC conversion as a function of time, obtained during the oxidation of D0 bleach plant effluent in the batch-recycle reactor packed with a Ru(3 wt.%)/TiO_2 catalyst.

with a low content of nitrates ($<$50 mg l^{-1}). Due to its pH value being in the range 6–9, it can be fully recycled. No leaching of Ru and/or Ti from the employed solids to hot WAO solutions was detected by ICP-AES analysis to the detection limits of 0.2 and 0.1 mg l^{-1}, 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 to oxidation reactions, was avoided at the employed reaction conditions. During the WAO of D0 and E1 effluents, no sulfur or phosphorus salts were deposited on the surface of catalyst particles, which could render more difficult the access of the liquid-dissolved compounds to the catalyst active sites. To conclude, successful development of 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 enables to fulfil the increasing demands in the chemical manufacturing industries to use closed-loop operation by recycling and reusing waters.

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 rivercourse discharge limits. In order to use an integrated (C)WAO and biological treatment plant efficiently, the effluent from the former must be biodegradable and less toxic than the original wastewater. In the available literature, little information is available on the biodegradability and toxicity of effluents treated by means of noncatalytic or CWAO processes. WAO was found capable of improving the biodegradability of pesticide and acrylonitrile wastewaters [123,124], olive mill wastewaters [125], phenolic wastewaters [126], water-soluble polymer-containing wastewaters [127] and azo dye-containing wastewaters [128]. However, in one case [129] it was found that WAO decreased the biodegradability of a TNT red water effluent by introducing inhibitory effects. The effect of WAO on the aerobic biodegradability of a model wastewater containing linear alkylbenzene sulfonate (LAS) was recently investigated by Mantzavinos et al. [130]. The original LAS solution was found to be readily biodegradable in the laboratory aerobic reactors operating at low organic loadings. However, WAO resulted in effluents that were less readily biodegradable than the original LAS with biodegradability decreasing with increasing degree of oxidation. This was attributed to the formation of sulfonated aromatics from partial LAS oxidation. The results of Mantzavinos et al. [130] 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. Keen and Baillod [131] studied WAO of phenol and substituted phenols at $T = 477$–533 K and $P = 39$–71 bar. The toxicities of the starting compounds and 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 [132], who showed the WAO process to be effective in reducing toxicity to *D. magna* of 10 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. An example presenting the evolution of COD and BOD_5/COD as a function of temperature in the low-pressure CWAO LOPROX process [39] 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 [133] 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 0.17–0.35), simply because smaller quantities of intermediate products were formed in this process. Recently, Zhu et al. [134] studied WAO of H-acid solution in the presence of various catalytic systems. The initial BOD_5/COD of 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 asymptotically approached with time to 0.4, thus demonstrating that the biodegradability was greatly improved. In spite of the considerable research done on catalytic oxidations [38,39,99–101], there is no work in the literature available dealing with intermediate products that are responsible for toxicity of treated wastewaters. It has been demonstrated recently by Pintar et al. [120,122], who investigated liquid-phase oxidation of industrial bleach plant effluents in the presence of titania- and zirconia-supported ruthenium catalysts, that complete mineralization of parent organic compounds into carbon dioxide and acetic acid as a side product can be achieved by means of CWAO. However, scrutiny of the past literature reveals that there is no experimental evidence available that CWAO converts starting effluents into end-product solutions that are less poisonous. In this respect, Pintar et al. [135] recently 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 CWAO of these effluents, quantifying expected vs. 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 WAO of Kraft bleach plant effluents at $T = 463\,K$ in trickle-bed and batch-recycle reactors packed with either TiO_2 extrudates or Ru(3 wt.%)/TiO_2 catalyst, were measured with 48-h and 30-min acute toxicity tests using *D. magna* and *Vibrio fischeri*, respectively. During the WAO 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 *D. 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 *V. fischeri* as a toxicity test species. Furthermore, end-product solutions were generally more toxic to *D. magna* and *V. fischeri* than indicated by the concentrations of total organic carbon remaining in the final solutions. Pintar et al. [135] provide also an evidence that the CWAO displays considerable potential for the ultimate destruction of organic pollutants in industrial wastewaters and allows full recycling of water treated in this process. However, before discharging treated wastewater streams into the environment or a publicly owned treatment plant, evaluations of the residual toxicity of solutions containing end products of CWAO 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. The same evaluations, with additional biological activity tests, should be performed to efficiently run an integrated CWAO and biological treatment plant.

2.2. *Homogeneous CWAO processes*

An alternative to insoluble precious metal catalysts is the use of homogeneous transition metal catalysts, which, however, need to be separated from the treated wastewater stream and recycled to the reactor inlet or discarded. Several homogeneously catalyzed WAO processes based on this concept (e.g., Ciba-Geigy, LOPROX, WPO, ORCAN and ATHOS processes) have been developed in the last decade [39]. Soluble transition metal catalysts based on iron or copper salts are now being applied in several commercial WAO plants, which are operating successfully to treat industrial effluents and sludges. The use of the homogeneous catalyst has to be evaluated in the early process design stage according to the existing discharge regulations either in the liquid or solid phases.

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