

Wet hydrogen peroxide catalytic oxidation (WHPCO) of organic waste in agro-food and industrial streams

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This review discusses the use of iron- or copper-based solid catalysts in the wet oxidation using H_2O_2 as oxidant of organic molecules present in agro-food and industrial waste aqueous streams. After an introduction on the advantages and limits of using wet hydrogen peroxide catalytic oxidation (WHPCO) as opposite to wet air catalytic oxidation (WACO), the contribution shortly analyses recent results in the field in order to evidence new trends and open issues. More specific examples discussed regard the performances of Fe/zeolite and Fe-containing pillared clays in the oxidation of selected molecules (*p*-coumaric acid, propionic acid) of relevance for the treatment of organic waste from agro-food production (with reference especially to olive oil milling wastewater). The application of WHPCO in the treatment of complex effluents from electronic industry is also shortly discussed.

1. Introduction

Water and wastewater treatment has become a major social, technological, economical, and political problem. Different factors contributed in determining this issue such as overexploitation of available water, changed and depleted natural vegetation, reduced water infiltration into the soil and increased surface water run-off, and finally not-least pollution. As a consequence, there is an increasing social pressure towards a sustainable use of water and a renewed interest in improving existing technologies for water treatment [1,2].

Current levels of removal of the pollutants from water which can be achieved using the conventional water treatment technologies are often not more sufficient, especially when waste water streams contain significant amounts of hardly biodegradable chemicals or even compounds having phytotoxic effect on the micro-organisms responsible for biological degradation of the organic waste. An example is the presence of polyphenolic compounds often present in several water streams from agro-food productions (for example, in milling wastewater from olive oil production, in brewery and wine distillery wastewater). In these cases, it is useful to add a pre-treatment stage aimed to remove phytotoxicity and improve biodegradability before to send the wastewater to the biological unit [3]. The integration between chemical and biological oxidation allows to design more effective and economical processes [4].

Water consumption in industry has also increased considerably in the last decade and at the same time the cost of industrial water has increased exponentially in several areas. In several industries large amounts of water are used in cleaning and process applications and thus recycling this water can be an opportunity to

combine a reduction in the costs of industrial water with improved control of water management and a better environmental impact on natural resources [5–7]. For example, the electronic industry uses large amounts of rinse water for the production of printed circuit boards (PCBs) and semiconductors. It was shown also on a pilot plant scale that a water recycling process requires to combine an advanced oxidation step to a biological unit (biological granular activated carbon: BGAC) and a reverse osmosis (RO) membrane unit to reach the required levels of water purification necessary to recycle rinse water (TOC values lower than 0.20 mg/L) [8]. Such low TOC values could not be achieved when both oxidation and BGAC filtration were not used prior to the reverse osmosis step.

There are several other areas in which advanced oxidation processes (AOPs), although in principle more costly than conventional water treatment trains (sometimes up to 10 times more costly) [9], can be preferable in terms of combined techno-economical and environmental assessment. Example, include the destruction of organic compounds in groundwater, landfill leachate, biosolids, municipal water and wastewater systems, and industrial rinse waters [10–12].

Therefore, there are several incentives to develop novel AOPs. The use of catalysts in several cases improve the performances and lower the costs of these technologies by (i) increasing the reaction rates, (ii) allowing the use of more compact reactors and milder conditions for operations, (iii) allowing a better finishing (better decolourization, elimination of harmful byproducts in traces, etc.) and improved efficiency in pollutants removal, and often also (iv) improving the selective use of the oxidizing agents in converting the target chemicals. In fact, usually several compounds are present in the real wastewater, but when AOPs are used to pre-treat the wastewater before a biological unit, it is

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necessary to have a selective elimination of only the target chemicals (hardly biodegradable, inhibitor or ecotoxic compounds), in order to limit the costs of the pre-treatment [2,13–15]. Catalytic AOPs find application in various areas, for example in the treatment of wastewater from (i) dyeing and printing [16–18], (ii) Kraft-pulp bleaching [15,19,20], (iii) petrochemical industry [21], (iv) olive milling [22], (v) H-acid manufacturing process [23] and (vi) wood pyrolysis and cooking plant [24], although the commercial processes are still limited [12].

There are basically three main types of AOPs, depending on the type of oxidant (oxygen, hydrogen peroxide and ozone), in addition, a fourth type is represented by photocatalytic processes. However, the number of AOPs is higher, because there are several possible combinations, such as the use of both H_2O_2 and O_2 or O_3 , H_2O_2 /light, etc. [25]. Notwithstanding the significant differences in various AOPs, the common aspect is the fact that hydroxyl radicals are the common reacting species (although not the only one). OH radicals are extraordinarily reactive species, they attack the most part of organic molecules with rate constants usually in the order of 10^6 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ [26]. Hydroxyl radicals, due to their high reactivity, can react with almost all types of organic and inorganic chemicals.

The different AOPs may be thus viewed as different ways in which hydroxyl radicals can be generated from the different reaction sources (H_2O , O_2 , H_2O_2 , O_3). The rate of generation of these reactive species (as well as of other radical species such as HO_2^\bullet which are often in equilibrium with OH^\bullet and other reactive species in solution) is the critical factor which determines both the reaction conditions to be used and the type of feed that can be treated. In fact, photocatalytic processes are very interesting water treatment techniques, but limited in the application to feeds containing relatively low concentrations of organic substances (typically lower than 100 mg C/L). Treating more concentrated streams need to combine photocatalytic methods to other AOPs, for example with H_2O_2 and iron salts (the so-called photo-Fenton processes [27–29]).

Ozonation is also an extensively used AOP, but the limited solubility of ozone in water makes it applicable essentially to diluted solutions. Also in this case, the ozone effect may be enhanced by combining it with H_2O_2 [30,31]. For medium-high concentration of organic pollutants in water, as often encountered in several agro-food or industrial streams, wet air or wet hydrogen peroxide oxidations are the preferable solutions in the largest number of practical cases. Both technologies can be promoted significantly by the use of solid catalysts, which are typically preferable to homogeneous catalysts (although much less investigated in literature), due to the lower contamination of the purified water from the catalyst itself, a critical factor in several applications. We will focus discussion on the following sections on the use of solid catalysts for the

wet hydrogen peroxide catalytic oxidation (WHPCO), after a short comparison of the general pro/cons of WHPCO versus the wet air catalytic oxidation (WACO).

2. A comparison of WHPCO versus WACO technologies

WACO processes have been applied to treat various industrial streams such as the wastewater from bleaching operation of Kraft wood pulp [32], the desizing of wastewater from the textile industry [33] and the removal of toxicity of olive-related wastewater [34]. Examples of commercial processes [12] are (i) that proposed by Lenntech (<http://www.lenntech.com/cwao.htm>) for industrial waste water streams having chemical oxygen demands (COD) in the 10,000–100,000 mg C/l range, (ii) the NS-LC (Nippon Shokubai's; <http://www.shokubai.co.jp>) process using Pt–Pd/TiO₂–ZrO₂ honeycomb catalyst, and (iii) the Osaka Gas CWO process [35] (<http://www.osakagas.co.jp>) also based on a mixture of precious and base metals on titania or titania–zirconia carriers (honeycomb or spheres). These processes are proposed for treating various kinds of industrial wastewater, domestic wastewater and sludge.

Also WHPCO process has been proposed for a variety of agro-food and industrial effluents: (i) removal of dyestuffs from textile [36], (ii) treat sewage sludge [37], (iii) purify wastewater from pharmaceutical and chemical production, dumping site, or from cellulose production [38] and (iv) pre-treat water streams from food-processing industries (olive oil mills, distilleries, sugar refineries, coffee production, tanneries, etc.) [39]. Examples of commercial processes are the (i) OXY-PURE of Delta Umwelttechnik (<http://www.delta-ut.de>) to eliminate cyanide, phenols and other organic species from heavily organic-loaded and turbid wastewaters [40] and (ii) the US Peroxide processes (<http://H2O2.com>) for various environmental and industrial applications. There are no commercial WHPCO processes using solid catalysts.

Recent advances have been reported in using “bio-inspired” catalysts for the oxidation of waste in solution using H_2O_2 , and in particular the oxidation of chlorophenols using iron tetrasulfophthalocyanine catalysts [41]. Phthalocyanines are industrial dyes and therefore their cost is supposed to be low, although it is significantly higher than that of some of the very cheap solid catalysts (few € per kg) discussed in the following sections (for example, iron-based clays). In addition, using homogeneous catalyst the problem of recovery has a market incidence on the overall cost of the technology. The iron-phthalocyanines can be linked to organic copolymers [41d] in order to improve recovery, but this further increases the catalyst cost. The results which have been reported indicate that further effort is

necessary for using these catalysts, even considering that chlorohydrocarbons are recalcitrant pollutants. 2,4,6-Trichlorophenol (TCP) is mineralized to CO₂ only with 11% yield and the byproducts are toxic chemicals such as C4-diacids (for example, chloro-maleic acid) [41e]. Present data indicate that solid catalysts are preferable with respect to these “bioinspired” catalysts.

There are several manuscripts in the literature which have compared pro/cons of AOPs methods, for example in the degradation of chlorophenols [42], landfill leachate [30], remediation of underground contaminated water [43], destruction of 2,4-dinitrophenol [44] and atrazine [45], for reactive dye wastewater [36,46], industrial wastewater cleaning from cyanides [47], treatment of olive oil milling wastewater [48a] and other industrial waste water streams [48b]. However, no clear indication can be derived about the comparison of WACO and WHPCO methods. It should be also commented that generally comparison of the AOPs technologies is mainly made in terms of efficiency of removal, while a more correct comparison should take account of several parameters, such as (i) safety of operations, (ii) manageability and applicability to the specific operations (for example, when small volume effluents dispersed over a wide territory should be used, may be preferable to transport a water treatment unit instead that to collect all wastewater in a single central treatment unit), (iii) technical effectiveness using real streams, (iv) absence of necessity of post-treatments (to eliminate some residual compound, even in traces, or metal ions), (v) secondary pollution prevention, (vi) minimal toxicity of emissions, (vii) minimal corrosion, plugging, sensitive process-control parameters, and other operating difficulties, and not least (viii) cost. These parameters are often not considered or only in part, and therefore reliable conclusions about the comparison of WACO and WHPCO technologies cannot be drawn from literature data, neither often about their eco-technoeconomical comparison with alternative AOPs methods. However, it is useful to make some general consideration about the specific comparison between WACO and WHPCO technologies.

Wet air oxidation process (WAO), notwithstanding the name, operates typically under oxygen pressure (5–200 bar) (using air around four times higher pressure is necessary) and at elevated temperatures (125–320 °C). Residence times ranges from 15 to 120 min, but often longer times are necessary for high organics loading or high levels of chemical oxygen demand (COD) removal (typically ranging between 75 and 90%). In contrast to supercritical water oxidation (SCWO), a complete mineralization of the waste stream is often impossible by WAO, since some low molecular weight oxygenated compounds (especially acetic and propionic acids, methanol, ethanol, and acetaldehyde) are resistant to oxidation. For instance, removal of acetic acid is usually minimal at temperatures lower than 300 °C. Organic

nitrogen compounds are easily transformed into ammonia, which is also very stable in WAO conditions. Therefore, WAO is a pre-treatment of liquid wastes which requires additional treatment of the liquid and gas streams. Over hundred plants are in operation today, mostly to treat waste streams from petrochemical, chemical and pharmaceutical industries as well as residual sludge from wastewater treatment [12]. The use of catalysts (WACO) allows to use milder reaction conditions [49], but especially to promote conversion of the reaction intermediates (for example, acetic acid [50] and ammonia [13]) which are very difficult to convert in the absence of catalysts, as mentioned above.

Figure 1(a) reports a simplified flow diagram of a WACO process which consists mainly of a high-pressure pump, an air or oxygen compressor, a heat-exchanger, a high-pressure (fixed bed) reactor and a downstream separator. The simplest reactor design is usually a cocurrent vertical bubble column with a height-to-diameter ratio in the range of 5–20 [51]. A catalytic unit for the treatment of the off-gas is also typically necessary.

There are two main drawbacks of the WACO technology, besides the general issue of leaching of metals and catalyst deactivation common to all multiphase processes using solid catalysts: (i) the cost of using high temperatures/pressures which makes quite energy consuming the process (the oxidation of organics is an exothermic reaction, but only in part the heat of reaction can be recovered, especially if a batch type autoclave reactor is used), and (ii) the cost of the reactor (it is necessary to use special materials such as titanium for the autoclave reactor, because there are often severe problems of corrosion related to the formation of high concentration of low molecular weight acids as products of reaction; in addition, often the real streams to be treated contain large amounts of ions such as chlorine which may be oxidized under the conditions of wet oxidation, making very corrosive the reaction medium). In addition, the use of high pressure reactors makes necessary to employ specialized personnel and use all the typical safety procedures for high pressure autoclave apparatus which further increase the costs. Although possible, the technology can be moved with difficulty from place to place due to safety related aspects. Additional issues are related to the treatment of discharged gaseous emissions containing NO_x, CO, VOC and smelling odors.

WHPCO operates at temperatures in the 20–80 °C range and atmospheric pressure. Therefore, there is no need for special autoclave reactors and conventional stainless steel reactors or even basins may be usually suitable. Formation of foams and smelling odors is also a much less critical problem than in WACO operations. Safety problems are only related to storage of H₂O₂, although this is not a very critical issue (but special handling precautions are required). Technology may be

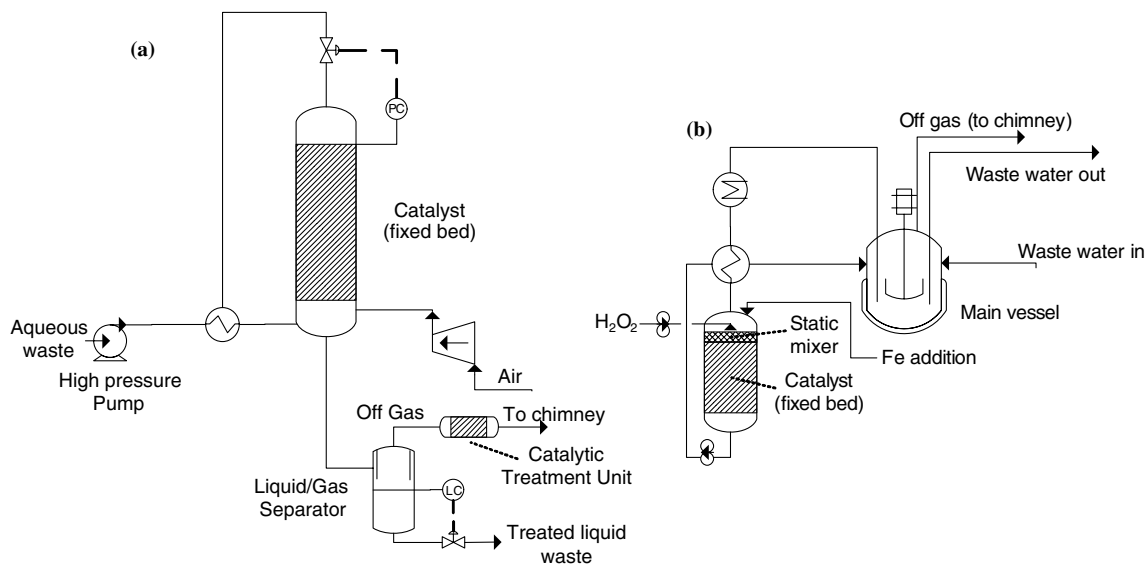


Figure 1. Simplified flow diagrams of WACO (a) and WHPCO (b) processes.

movable from site to site and do not require highly specialized personal. On the other hand, H_2O_2 cost is higher than that of air. However, as mentioned above, often O_2 is required to avoid too high pressure or long reaction times. Oxygen needs to be stored under pressure or low temperatures, and the selling cost is not negligible. In addition, H_2O_2 cost was progressively decreasing over the last decade, and therefore there are increasing incentives to expand its use in environment protection applications [52].

Figure 1(b) reports a simplified flow diagram of the WHPCO technology proposed by Centi *et al.* [53] for the treatment of olive oil milling waste water using Fe-ZSM-5 solid catalysts. H_2O_2 is added progressively at the top of a fixed bed catalytic reactor (before a static mixer), in order to maximize its local concentration. The reactor operates in the 50–70 °C temperature range and atmospheric pressure. Conventional atmospheric pressure reactors may be used, because corrosion characteristics of the feed and reaction products/conditions are not severe. An iron solution is added on the top of the reactor to maintain catalyst activity constant. The feed solution is recirculated to and from a tank in order to have good turbulence in the catalyst bed, but also to guarantee the necessary total residence time to obtain the required level of removal of phytotoxic chemicals (for good removal of phytotoxicity, but TOC removals lower than about 30% a residence time of 15–30 min is required). The heat of reaction produced in the oxidation is able to maintain autothermic operation.

Based on these considerations, it is possible to conclude that WHPCO technology would be preferable over WACO option for the following situations, where capital costs are predominant over running costs:

- pre-treatment of the streams before to send to biological units which require the selective conversion of hardly biodegradable or toxic chemicals, but low levels of TOC (total organic carbon) removal – less than 30% (for example, in the pre-treatment of streams from agro-food industry),
- treatment of wastewater having a medium-low content in organics (1–30 g C/L of TOC), and low volumes of effluents (1–100 m³/day).

Figure 2 reports a comparison of the two wet oxidation methods in the treatment of high concentrations of Basilen Brilliant Blue P-3R, a reactive dye often found in the textile dyeing wastewater [54]. At 200 °C WAO is not very effective in treating this stream. Even adding

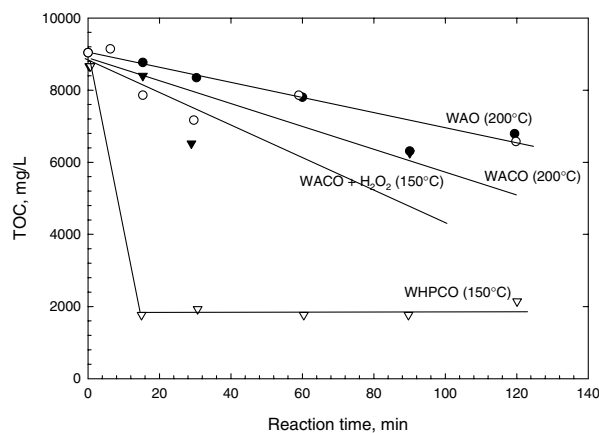


Figure 2. Wet oxidation of reactive blue (Basilen Brilliant Blue P-3R) at pH 8.8 (temperature, see legend): WAO: wet air oxidation (O_2 , 115% of the stoichiometric for total oxidation); WACO: wet air oxidation in the presence of Cu^{2+} ions as the catalyst (200 mg/L); WACO + H_2O_2 (as WACO, but plus H_2O_2 —10% of the stoichiometric for total oxidation); WHPCO: as WACO, but feeding H_2O_2 instead of O_2). Elaborated from Chen *et al.* [54].

Cu^{2+} as the catalyst (one of the most common homogeneous catalysts used in WACO treatments [55]), the improvement of the rate of reaction is minimal. Adding some H_2O_2 to promote the reaction (and lowering the reaction temperature to $150\text{ }^\circ\text{C}$ in order to limit H_2O_2 decomposition), the rate of reaction also does not significantly improve. On the contrary, feeding only H_2O_2 instead of O_2 (in the amount to have in both cases a slight excess of oxidant with respect to the stoichiometric amount required for complete TOC removal) there is a very fast increase in the reaction rate. In less than 20 min almost 80% of TOC is removed and also over 90% of the color is removed. The residual TOC is due to hardly oxidizable small organic acids.

Debellefontaine *et al.* [56] also found comparable results in comparing WACO and WHPCO technologies in the treatment of industrial wastes. Therefore, although not extensive data are available on the comparison between WACO and WHPCO technologies under practical relevant cases, the published results confirm above conclusions. However, it should be taken into account that the nature of the organic to convert is also important for the choice of the right technology. For example, at $150\text{ }^\circ\text{C}$ using the WHPCO approach [54] over 90% of TOC is eliminated in the case of reactive red (Procion Red PX-4B), while 77% of TOC in 30 min using Basilen Brilliant Blue P-3R. Figure 3 compares the order to reactivity of some organic compounds in WAO ($260\text{ }^\circ\text{C}$, $p_{\text{O}_2} = 20\text{ bar}$, $\tau = 1\text{ h}$) and WHPCO ($120\text{ }^\circ\text{C}$, $\tau = 1\text{ h}$), according to the reactivity order reported by Debellefontaine *et al.* [56]. The reaction conditions and the use of a catalyst (as well as the type of catalyst) can strongly influence this order of reactivity, but nevertheless figure 3 evidences the great dependence of the performances on the nature of the organic compounds, including, for example, the presence and position of a substituent on the aromatic ring. Therefore, depending on the type of stream to be used, opposite conclusions are possible about the preferable use of WACO and WHPCO technologies.

It is useful also to note that an integration of the two technologies may be useful in some cases, because reaction products which may be difficult to convert in one case, can be easier converted in the other case, because the two reaction mechanisms and pathways of transformation are different. For example, acetic acid is a quite refractory chemical to be converted by wet air oxidation (WAO) (temperature above $250\text{ }^\circ\text{C}$ are requested) and is one of the main byproducts in the conversion of the largest part of chemicals, as mentioned before. On the contrary, acetic acid can be converted under relatively mild conditions by WHPCO [57]. Figure 4 reports some results obtained in the conversion of propionic acid using a Fe-ZSM-5 catalyst. Formic and acetic acid are the two main reaction products. Although acetic acid shows a rate of reaction lower than that of propionic and formic acids, it can be fully

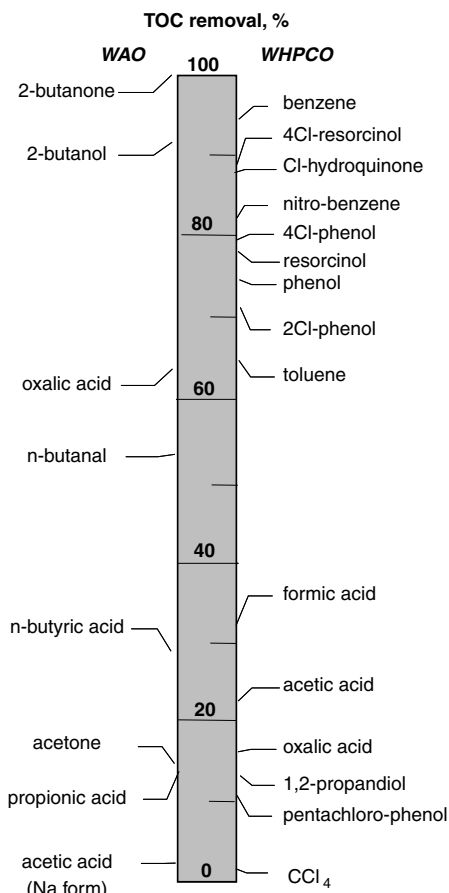


Figure 3. Degree of oxidation of some organic compounds in WAO ($260\text{ }^\circ\text{C}$, $p_{\text{O}_2} = 20\text{ bar}$, $\tau = 1\text{ h}$) and WHPCO ($120\text{ }^\circ\text{C}$, $\tau = 1\text{ h}$). Elaborated from Debellefontaine *et al.* [56].

converted at $50\text{ }^\circ\text{C}$ after around 2–3 h of time on stream. The rate of acetic acid conversion can be further improved by adding some Pt to the catalyst, but this also increases the rate of H_2O_2 decomposition. Therefore, while acetic acid formation is lower after about 1 h of reaction, the residual acetic acid is slightly higher after 3 h of reaction. On the other hand, oxalic acid is the main product formed in the WHPCO reaction [53] (especially in the conversion of substituted aromatic compounds), and is quite resistant to further conversion. Oxalic acid may be instead readily oxidized to CO_2 and water under very mild conditions ($50\text{--}80\text{ }^\circ\text{C}$, atmospheric pressure) by wet air oxidation using a Pt/ Al_2O_3 catalyst [58] or Pt/C catalyst [59].

3. Perspectives in using Solid Catalysts for the Wet Hydrogen Peroxide Oxidation

Hydrogen peroxide is a clean and powerful oxidant, but the generation of hydroxyl radicals from it (see Section 1) requires either UV radiation or a catalyst. The ability of transition metals such as iron and copper to catalyze this reaction was discovered more than

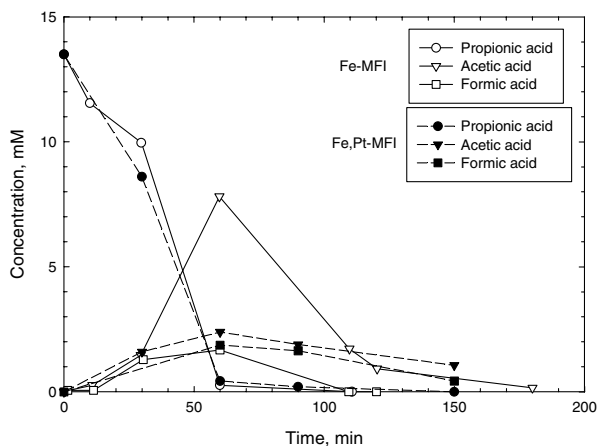
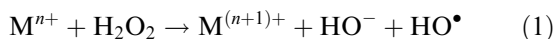


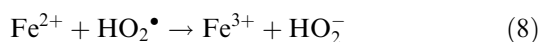
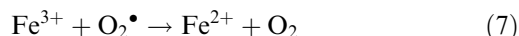
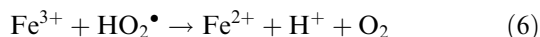
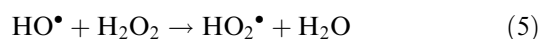
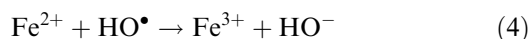
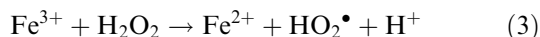
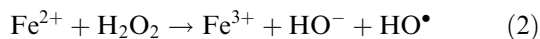
Figure 4. Conversion of propionic acid and of the products of reaction as a function of time on stream during the WHPCO reaction at 50 °C. Fe-MFI catalyst (prepared by ion exchange, 3.2% Fe) and Fe,Pt-MFI catalyst (same preparation as Fe-MFI, but containing 0.3% Pt). Experimental conditions: $H_2O_2/C_3H_6O_2 = 7$ (with respect to stoichiometric ratio), H_2O_2 addition rate: 5.0 mmol/l/min.

hundred years ago by Fenton studying the oxidation of tartaric acid [60], but only about 40 years later Haber and Weiss [61] discovered that the effective oxidative agent in the Fenton reaction was the hydroxyl radical. The Fenton reaction can be outlined as follows:



where M is a transition metal as Fe or Cu.

In the absence of light and complexing ligands other than water, the most accepted mechanism of H_2O_2 decomposition in acid homogeneous aqueous solution, involves the formation of hydroxyperoxyl (HO_2^\bullet/O_2^-) and hydroxyl radicals HO^\bullet [62]. The HO^\bullet radical once in solution attacks almost every organic compound. The metal regeneration can follow different paths. For Fe^{2+} , the most accepted scheme is described in the following equations [63]:



This sequence of reactions evidences that the Fenton reaction depends not only on H_2O_2 concentration and iron added, but considerably also on the pH value. The pH of operations should be strictly controlled around pH = 3.5, because the rate of reaction passes through a sharp maximum around this value. In addition, if the pH

is too high the iron precipitate in $Fe(OH)_3$ and will decompose the H_2O_2 to water and oxygen. A further significant drawback of the use of homogenous iron salts for the WHPCO reaction (besides to the issue of their precipitation in the outlet stream) is that often several of the compounds present in solution in real feeds and the products of reaction (for example, oxalic acid) make complexes with the iron ions, inhibiting their activity and catalyzing side decomposition of H_2O_2 . Therefore, efficiency in the use of H_2O_2 will be low and the reaction rate may become also quite low. In fact, to limit these adverse effects usually there is a progressive dosage of both H_2O_2 and iron sources (usually $FeSO_4$) during the reaction.

The use of solid catalysts, in principle, can eliminate or reduce these drawbacks by:

- (i) enhancing the reaction rate (the adsorption of the organic molecules on the solid can enhance their reactivity, but in addition the local concentration of radical species near to the catalyst surface can be higher — the concentration of radical species is a determining factor for the performances in these reactions. As observed for catalytic ozonation [31], in these reactions the hydrophobic/hydrophilic character of the solid catalyst can create local enhancements of the concentration profiles resulting in a marked increase in the reaction rates);
- (ii) modifying local effective pH (local pH inside the pore structure of microporous materials can be different from that of the bulk solution) and preventing precipitation of iron-(hydr)oxide (due to the electrostatic field inside zeolite channels, for example);
- (iii) protecting active sites (iron or copper ions) from the complexation and deactivation (if, for example, sites are located inside zeolite channels and are not accessible from larger molecules in solution);
- (iv) providing opportunities to have a selective attack on target molecules (therefore, enhancing the selective use of H_2O_2). This last opportunity was not yet explored in literature, but it is of clear fundamental importance when only specific compounds should be selectively removed. An example is the removal of phytotoxic polyphenols from agro-food wastewater streams. The concentration of these compounds is typically around 1% and should be reduced to less than 30 ppm, while other compounds should be preferably not converted in order to reduce H_2O_2 consumption.

A further motivation in the use of solid catalysts, although also not investigated, is suggested by inspection of equations (2)–(8) which evidence the role of the redox Fe^{3+}/Fe^{2+} (or Cu^{2+}/Cu^+) cycle in the Fenton mechanism, pointing out that a stabilization of the reduced oxidation state would be preferable being Fe^{2+} (or Cu^+) ions directly involved in generating the hydroxyl radical (equation (2)). Supporting well dispersed iron or copper ions on a suitable support or

anchoring them to exchangeable sites of microporous materials it is possible to stabilize reduced oxidation states of the transition metals. Zecchina *et al.* have shown that Fe^{2+} ions are stabilized by interaction with ZSM-5 zeolite framework [64].

This difference between performances of homogeneous and heterogeneous Fenton-type catalysts is demonstrated in Figure 5a which compares the rate of reaction for homogeneous (Fe^{3+} -salt) and heterogeneous (Fe/ZSM-5) catalysts in the rate of TOC removal during *p*-cumaric acid oxidation [53]. Total Organic carbon (TOC, mg C/L) removal is a better indication that cumaric acid conversion, being the latter rate of reaction quite fast and comparable in the homogeneous and heterogeneous cases. Instead, TOC conversion clearly point out that after about 1 h of reaction (corresponding to about 5 mmol of H_2O_2 added) the

TOC conversion in the case of the homogeneous Fenton catalyst stops, in contrast to the case of the heterogeneous Fenton catalyst (Fe-ZSM-5), although the initial rate of reaction is slightly higher for the homogeneous case. This is mainly related to the complexation of iron ions in solution by the products of reaction (oxalic acid) and/or lowering of the rates of generation of Fe^{2+} ions (equations (3), (6) and (7)).

In these tests (figure 5a), the addition of H_2O_2 is made progressively to the solution in order to improve the efficiency in its use. If the efficiency in the use of H_2O_2 is constant, a linear relationship between TOC removal and amount of H_2O_2 added is expected. Instead, the progressively lowering of the slope of the curves indicates a progressive lowering of the efficiency in the use of H_2O_2 which passes from over 90–95% (initially) to less than 50% after some hours of reaction. The lower slope in the case of the homogeneous reaction with respect to heterogeneous case after about 1 h (around 5 mmol of H_2O_2 added) point out that the efficiency in the use of H_2O_2 in this case is lower.

The efficiency of use of H_2O_2 is a very critical parameter for WHPCO reaction, while often no enough attention was given to this aspect also in consideration that the solid catalyst may catalyze H_2O_2 side decomposition to water and O_2 . The efficiency in the use of H_2O_2 depends also considerably on the reaction conditions, particularly on the modality of addition of H_2O_2 and on the ratio between amount of catalyst and volume of solution, due to a competition between hydroxyl radical recombination and attack of the organic molecules. This is demonstrated by the results reported in figure 5b. The efficiency in the use of H_2O_2 to obtain the same level of TOC removal drops considerably if a too fast rate of H_2O_2 addition is used or a too low value of the ratio between catalyst amount and volume of solution are chosen. This indicates that the correct choice of experimental parameters as well as a proper reactor design are critical factors for the possibility of application of a technology of wastewater treatment with heterogeneous Fenton catalysts.

The possibility of widening the pH range in which WHPCO operations are possible by using solid catalysts is demonstrated in figure 6. For the homogeneous case, the maximum activity was observed in quite a narrow pH range. For the heterogeneous case, the catalytic behavior was less sensitive to pH and operation at pH below 2.5 or above 5.5 are still possible, unlike the homogeneous case. Therefore, the use of solid Fenton type catalysts allows to extend the range of pH values for which WHPCO processes are possible [57]. Various authors have made similar observations. Tatibouët *et al.* [65] studying the phenol oxidation over (Al,Fe) pillared clays (FAZA) clearly evidenced that the TOC abatement obtained with FAZA heterogeneous catalyst is much higher than those observed with homogeneous iron species in the same reaction conditions. The same group

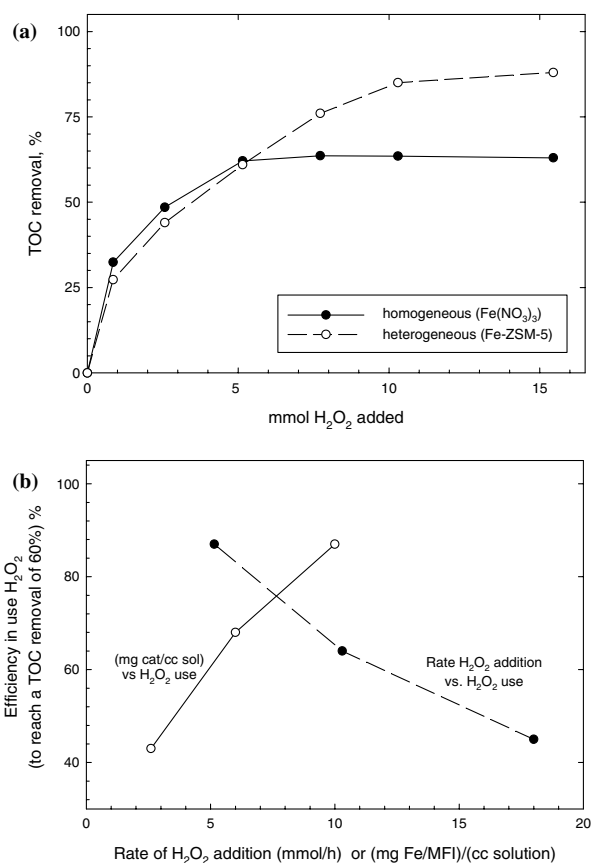


Figure 5. (a) Comparison of homogeneous ($\text{Fe}(\text{NO}_3)_3$ salt) and heterogeneous (Fe-ZSM-5) Fenton-type catalysts in the TOC removal during WHPCO of *p*-cumaric acid. Experimental conditions: 70 °C, pH = 4.8, rate of H_2O_2 addition = 5.15 mmol/h, 100 ml of *p*-cumaric acid solution (TOC initial = 330 mg C/L), 1 g Fe/ZSM-5 (1.2% Fe) or equivalent molar amount of iron ions (iron-nitrate). Elaborated from Ref. [53]. (b) Efficiency in use H_2O_2 to reach a TOC removal of 60% versus rate of H_2O_2 addition (mmol/h) and the ratio between catalyst amount and volume of solution (mg catalyst/cc solution). Experimental conditions as in figure 3 (Fe-ZSM-5 catalyst). Catalyst to solution ratio of 10 in tests at variable rate of H_2O_2 addition and rate of H_2O_2 addition of 5.15 mmol/h in tests at variable catalyst to solution ratio. Elaborated from Ref. [53].

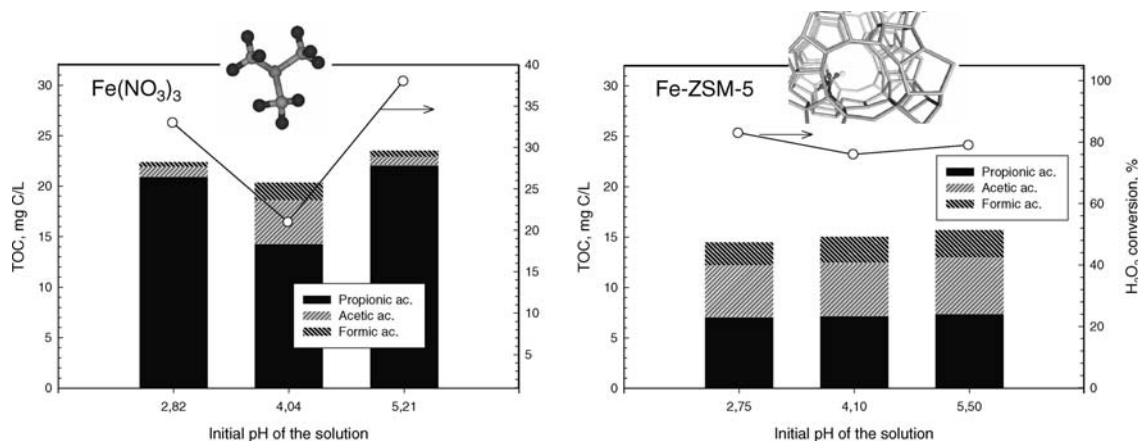


Figure 6. Effect of the pH of the initial solution on the TOC on the distribution of products and H_2O_2 conversion after 2 h at 70 °C for the homogeneous (iron-nitrate) and heterogeneous (Fe-ZSM-5) WHPCO of propionic acid. Experimental conditions: pH = 4.0, H_2O_2 /substrate = 1.5, amount of iron ions = 1.06×10^{-4} moles).

studying phenol conversion on pillared clays containing iron or copper species [66] noted the effect of pH and H_2O_2 concentration. The initial rate of reaction increases using higher molar concentrations of H_2O_2 , but not the final TOC value, i.e. the efficiency in the use of H_2O_2 decreases. In a subsequent paper [67] on the same reaction and type of catalysts, they note that the rate of H_2O_2 addition does not have a marked effect at the beginning of the reaction, but instead a negative effect at longer residence times (>1 h) due to decreased efficiency in the use of H_2O_2 . However, these authors also noted that for H_2O_2 addition rate in the 1.0×10^{-4} – 2.0×10^{-4} mol/h range, the TOC abatement could be higher than the theoretical value estimated from complete use of H_2O_2 (e.g. efficiency higher than 100%) [67]. Although further verifications are necessary, it is possible that this effect is related to the possible activation of the dissolved molecular oxygen present in the reactant solution, as already noted earlier [56]. As discussed later, contrasting results were found in literature about the possible effect of dissolved O_2 .

Catrinescu *et al.* [68–70] observed that (i) in the phenol oxidation with H_2O_2 over Fe-exchanged pillared beidelite the catalyst remains active even at neutral pH, while in homogeneous Fenton catalyst there is a very narrow range of activity around pH 3.0, and (ii) in the reactive yellow 84 azo dye oxidation with Fe(III)-exchanged Y zeolite there is a maximum in the efficiency in use of H_2O_2 on increasing its concentration. The activity of the Fe–Y zeolite in conditions where homogeneous iron ions are inactive was attributed to the strong electrostatic field present inside the zeolite which modifies precipitation of iron hydroxides at pH above 5.0 [69].

Due to this possibility of operation out of the typical pH range of the homogeneous case, some applications not suitable for the latter are possible for solid Fenton-type catalysts. This is demonstrated by the results reported in figure 7 which refer to the behavior of

Fe-ZSM-5 in the wet H_2O_2 oxidation of industrial wastewater from electronic industries. Wastewater from metal cleaning treatments (electronic and metal finishing industries) represents a significant problem due to the large amount of wastewater and the necessity to develop new techniques for its recycle [6,7]. The wastewater contains large amounts of hardly biodegradable and sometimes also toxic chemicals, together with large amounts of anions. The biological treatment of the wastewater may be not possible and also the use of techniques like WACO can be difficult and costly, due to the corrosive character of the medium.

Figure 7 reports an example of the performances of a Fe-ZSM-5 catalyst in the treatment by WHPCO process of an industrial stream containing nonylphenol-polyglycoether, and ethane-1,2-diol (two typical non-biodegradable components present in metal cleaning industry wastewater) as main components, around 10% H_2SO_4 (pH < 1) and various metal ions (copper and iron principally). The optimal reaction temperature is between 50 and 60 °C, because at higher temperatures the metal ions present in solution catalyze decomposition of H_2O_2 at this low pH (during the process a significant increase of the temperature of the bath is observed due to the heat of reaction). Without the presence of the solid catalyst, less than 20% of conversion is reached in the same reaction conditions, while the conversion reaches about 80% after 3 h of time on stream using the Fe-ZSM-5 catalyst. It is worthwhile to note that the reused catalyst is more active than the fresh, because part of the metal ions present in solution are ion-exchanged by the zeolite. This could be evidenced both by the faster rate in the decrease of TOC (left graph) and by the shift to lower temperature of the maximum in the peak of bath temperature associated to the release of the heat of reaction during the oxidation process. This fact evidences that metal ions coordinated to the solid are more

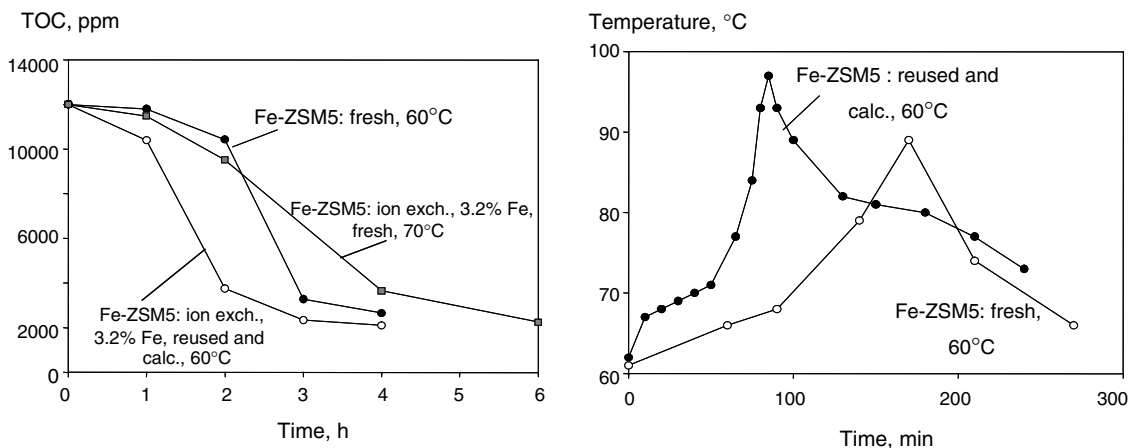


Figure 7. Performances (TOC versus time on stream, left graph, and temperature of the solution versus time on stream, right graph) of Fe-ZSM-5 catalyst in the treatment by WHPCO process of an industrial stream from electronic industry. Feed: contains nonylphenol-polyglycoether, and ethane-1,2-diol as main components, around 10% H_2SO_4 ($\text{pH} < 1$) and various metal ions (copper and iron principally).

active than those in solution for these experimental conditions.

Therefore, there are several possible benefits by using solid Fenton-type catalysts, even if a general lack of knowledge of the radical processes in solution at the liquid–solid interface should be remarked. Tatibouët *et al.* [71], studying the oxidation of phenol with H_2O_2 over carbon supported iron catalysts, have determined the concentration of hydroxyl radicals by ESR DMPO (5,5-di-Me 1-pyrroline N-oxide) spin trapping experiments and have found a relationship between hydroxyl radicals, catalytic activity and number of isolated iron species. DMPO spin trapping experiments have been extensively used to analyze the reaction mechanism in the homogeneous phase. Robert *et al.* [72a] have used this technique to identify the intermediates in the non-catalytic wet air oxidation of cellulose demonstrating that hydroxyl radicals (HO^\bullet) and H_2O_2 play the role of intermediates in the initial phase of the oxidation reactions. Sun *et al.* [72b] analyzed with this technique the generation efficiency of hydroxyl radicals in both a homogeneous (H_2O_2) and heterogeneous (TiO_2) system. The solid decreases the generation efficiency from 33 to 28%, because favors the quenching of the radicals. The origin of the hydroxyl radical in the Fenton reaction was analyzed by Lloyd *et al.* [72c], that noted that the trapped hydroxyl radical was derived exclusively from hydrogen peroxide and that no exchange of oxygen atoms between H_2O_2 and solvent water occurs. The ESR spin-trapping method was applied to the (i) study of active oxygen radicals from photoexcited semiconductors in aqueous H_2O_2 solutions [72d], (ii) quantitative correlation between radical concentrations and rate of reaction in UV- H_2O_2 process for organic pollutants conversion [72e] and (iii) comparative analysis of the rate of decomposition of H_2O_2 and atrazine by $\text{Fe(III)/H}_2\text{O}_2$, $\text{Cu(II)/H}_2\text{O}_2$, and $\text{Fe(III)/Cu(II)/H}_2\text{O}_2$ [72f].

The latter study demonstrated that the mechanism is initiated by the formation of two Fe(III) -peroxy complexes at $\text{pH} < 3.5$ followed by their slow decomposition into Fe(II) and HO_2/O_2 . The formation of intermediates (complexes, cupryl ion) has also been postulated for the catalytic decomposition of H_2O_2 by Cu(II) . Depending on the experimental conditions (nature and concentrations of the organic solutes, pH), the degradation of the organic compounds might be attributed to the hydroxyl radical or to other species like the cupryl ion (Cu(III)). Production of Cu(III) by reaction of OH with Cu(II) has also been demonstrated by pulse radiolysis experiments. Kinetic data indicate that the rate of decomposition of H_2O_2 and the rate of oxidation of organic compounds are faster with $\text{Fe(III)/H}_2\text{O}_2$ than with $\text{Cu(II)/H}_2\text{O}_2$ and that Cu(II) can improve the efficiency of the $\text{Fe(III)/H}_2\text{O}_2$ process. In the absence of organic solutes, experimental results have shown that the rate of decomposition of H_2O_2 is faster with Fe(III) than with Cu(II) . The initial rate of decomposition of H_2O_2 by Fe(III) can be described by a pseudo first-order kinetic law with respect to H_2O_2 , and dissolved oxygen has no effect on the rate of decomposition. For the $\text{Cu(II)/H}_2\text{O}_2$ system, data evidence that the decomposition of H_2O_2 by Cu(II) goes through the formation of an intermediate (probably a Cu(II) -hydroperoxy complex). Furthermore, the rate of decomposition of H_2O_2 by Cu(II) does not follow a first-order kinetic law and is affected by the concentration of dissolved oxygen. When atrazine is present in solution, the relative rates of decomposition of the organic solutes by $\text{Fe(III)/H}_2\text{O}_2$, $\text{Fe(II)/H}_2\text{O}_2$ and $\text{Cu(II)/H}_2\text{O}_2$ were identical and could be described by competitive kinetics. The data suggest that the oxidation of the organic solutes by the three systems can be attributed to a unique oxidant species, the hydroxyl radical.

The rate of oxidation of atrazine by $\text{Cu(II)/H}_2\text{O}_2$ was found to be much slower than by $\text{Fe(III)/H}_2\text{O}_2$, to be

dependent on the concentration of reactants ($[\text{Cu(II)}]_n$, $[\text{H}_2\text{O}_2]$) and to decrease in the presence of dissolved oxygen, in agreement with the slower rate of production of OH radicals by $\text{Cu(II)}/\text{H}_2\text{O}_2$ with respect to $\text{Fe(III)}/\text{H}_2\text{O}_2$. A fraction of Cu(I) may be oxidized by dissolved oxygen and this reaction, which competes with the reaction of Cu(I) with H_2O_2 , may also decrease the rate of formation of hydroxyl radicals. For the $\text{Fe(III)}/\text{Cu(II)}/\text{H}_2\text{O}_2$ system, experimental data show that the addition of Cu(II) increases the rate of decomposition of H_2O_2 and atrazine by $\text{Fe(III)}/\text{H}_2\text{O}_2$ and that these increases in the reaction rates depend on the concentration of dissolved oxygen. This catalytic effect of Cu(II) has been attributed to a fast regeneration of Fe(II) (which is the major source of OH radical) by the reaction of Cu(I) with Fe(III) . Since this reaction competes with oxidation of Cu(I) by O_2 and H_2O_2 , the catalytic properties of Fe(III) and Cu(II) mixtures will depend on the experimental conditions, such as the relative concentration of reactants and the presence/amount of dissolved oxygen.

Although it is out of the scope of this work to discuss more in detail the mechanism of radical formation and the reaction network in the homogeneous phase, this short discussion evidences that detailed information are available on these aspects. It is also shown that the presence of solids has a marked influence on the concentration of radical species. The adsorption of reactants on the solid and the different properties of iron or copper ions (or species) anchored on solid matrices (with respect to the same ions in solution) indicate that the conclusions valid for the homogeneous Fenton reaction may be not applicable to solid Fenton-type catalysts. However, information in literature on the radical mechanisms in the presence of solid Fenton-type catalysts are very limited. There is thus a need of better knowledge of the radical processes in solution at the liquid-solid interface. Also knowledge on the mass/heat diffusion aspects inside microporous materials during these fast radical-type reactions are quite limited. This is a completely open research area.

There are several other aspects which were scarcely considered in literature regarding WHPCO reaction. Oxygen forms during the reactions (equations (6) and (7), plus from the direct H_2O_2 decomposition to water and oxygen) in amounts which may exceed its solubility. A gas cap may form on the catalyst surface (especially in micropores) in these conditions (depending on the hydrophobic character of the catalyst). Therefore, intra-particle mass diffusion can be significantly altered.

Another aspect scarcely considered regards the strong adsorption of several of the reactants or reaction products (acids, in particular) which can, from one side block surface reactivity by fouling, but also can alter the character of the surface by modifying the rate of adsorption/desorption of the various anionic and radical species indicated in equations (2)–(8) (and other deriving from interaction of these species with the organic

molecules). A modification of the catalyst surface charge due to chemisorption of anions/cations determines a change in the double layer at the solid/liquid interface and as a consequence the relative diffusion rates of charged, radical and ionic substances may be differently influenced from this phenomenon. In principle it is possible to tune and optimize the sequence of reactions and improve performances using this concept (to avoid, for example, some of the reactions leading to a decrease in the radical concentration), but no attempts were made in the literature to understand and use this concept in WHPCO reactions.

In conclusion, it is evident that a solid catalyst is not only a way to have on a separate phase the active catalytic centers for the WHPCO reaction to allow an easier recovery of the catalyst after the reaction and lower contamination of the effluents (this is the mostly used motivation), but the use of solid catalysts can significantly alter all the relative rates of the sequence of radical reactions (generation of radical species, propagation, termination) and therefore it is a great opportunity to tune and improve the reaction performances. Solid Fenton-type catalysts may offer much more potentials to improve performances in WHPCO process than usually considered up to now, but the lack of fundamental knowledge on the involved chemistry has not really allowed to make a rational design of the catalyst. Instead, most of the investigations have been mainly centered on the testing of a series of catalysts (mostly on simple model reactions) and the evaluation of the effect of reaction performances.

4. An overview of the use of solid catalysts in wet hydrogen peroxide oxidation

Fajerberg and Debellefontaine [73] were the first reporting the use of iron-exchanged zeolites (Fe-ZSM-5) for the WHPCO reaction, studying the behavior in the conversion of phenol as model compound. The performances of some other transition metals exchanged in the zeolite (Cu^{2+} and Mn^{2+}) were also cited. Both phenol degradation and the leaching-off of Fe(III) ions in the solution were found to depend strongly on the pH; an optimum value exists around $\text{pH} = 3.5$, as for the homogeneous case. The optimal reaction temperature was 90°C . The catalyst can be reused three times without or with recalcination between the runs.

Pulgarin *et al.* [74] reported earlier the use of Fe-ZSM-5 and H_2O_2 , but in relation to the photocatalytic conversion of industrial pollutants (4-nitrophenol), the so called photo-Fenton process which uses UV light irradiation to promote H_2O_2 homolytic splitting, but in the presence of iron ions instead that only using UV radiation as in the $\text{UV}/\text{H}_2\text{O}_2$ process. There is a large interest in the literature on the photo-Fenton process which appear rather interesting in many applications,

for example in the treatment of (i) dyeing and printing effluents [75], (ii) oil milling wastewater [76], (iii) elimination of explosives [77], (iv) oily wastewater from lubricant production [78], (v) biorecaltritant dye precursors present in industrial wastewater [79a,b], (vi) water contaminated by pesticides [80] and (vii) purification of waste water from textile activities [79c]. It should be noted that notwithstanding the analogies between Fenton and photo-Fenton processes, the reaction mechanisms are different [81] as well as the influence of the reaction conditions. Therefore, data on photo-Fenton reaction may be not translated to the Fenton process especially in the presence of solid catalysts.

After the work of Pulgarin *et al.* [74] and Fajerberg and Debellefontaine [73] other authors have investigated the use of Fe-ZSM-5 (or analogous systems) catalysts. Centi *et al.* [53,57] have analyzed the performances of Fe/ZSM5 catalysts prepared by ion-exchange and the effect of the reaction conditions (20–70 °C temperature range) on the conversion of diluted formic, acetic and propionic acid solutions [53] and of *p*-cumaric acid aqueous solutions [57], the latter as a model compound representing phytotoxic phenols present in wastewater from agro-industrial processes. Data showed that although the heterogeneous catalysts have a higher reactivity and a reduced dependence on the pH of the solution in comparison to the homogeneous Fe³⁺ catalysts, they also have a higher rate for the side reaction of hydrogen peroxide decomposition to water and oxygen. However, this effect considerably depends on the reaction conditions and rate of H₂O₂ addition which should be optimized to limit hydrogen peroxide decomposition. Leaching tests indicate that the activity of the heterogeneous catalyst is not due to leached iron ions, although a small amount of iron was found in the aqueous solution. The amount of leached iron could be related to the amount of oxalic acid in solution, as shown in figure 8. Therefore, probably the leaching of iron is a process secondary to the catalytic reaction and related to the amount of oxalic acid which forms

(therefore, depending on the reaction conditions, besides to catalyst characteristics), differently from what observed for some copper-based catalysts for which the leaching of the metal is the first step of the process (therefore, occurring in the homogeneous phase). This indication further strengthens the concept that solid Fe-based Fenton-type catalysts are truly heterogeneous systems, although part of the iron may go to solution.

Sotelo *et al.* [82] have compared in the catalytic wet peroxide oxidation of diluted aqueous solutions of phenol zeolitic materials exchanged with ions such as Fe and Cu and zeolitic samples having analogous structure (Fe-TS-1), but synthesized by isomorphous substitution of Si atoms by Fe and Ti into the MFI zeolitic framework through hydrothermal synthesis of wetness-impregnated Fe₂O₃-TiO₂-SiO₂ xerogels. The latter material showed a complete phenol removal and TOC reduction of about 68% at 100 °C and atmospheric pressure, with a low leaching of Fe species as compared to Fe-exchanged zeolitic materials. Perovskites of the type LaTi_{0.45}Cu_{0.55}O₃ were also tested, showing Cu leaching of 22%, with a TOC conversion of 93% and total phenol removal.

Crowther and Larachi [83] have studied catalysts prepared by supporting iron(III) ions on silica-based mesoporous materials (MCM-41 and HMS-types). These materials were tested for the WHPCO of aqueous phenol in a batch slurry reactor operating at atmospheric pressure and a temperature of 80 °C. For all materials, in the first run, the conversion of phenol was total and rapid (less than 15 min), and the removal of total pollution plateaued between 55 and 85% in 180 min with mineralization selectivities of ca. 95%. The materials underwent leaching of the iron, from 6% to total. Therefore, activity in 2nd runs was lower.

Catrinescu *et al.* [84] have analyzed the catalytic performance of an Fe-exchanged, ultra-stable Y zeolite (Fe-USY) (prepared by ion-exchange) for the wet H₂O₂ oxidation of an azo dye (Reactive Yellow 84 – C.I. RY84) used in the textile finishing industry. Results indicated almost total decolorization and a relevant reduction of COD and total organic carbon, without significant leaching of Fe ions. Using the Fe-USY catalyst, it was possible to extend the range of pH for which Fenton-type oxidation could occur with no iron hydroxide sludge formed, confirming the results shown in figure 6.

Fajerberg *et al.* [85] have analyzed the effect of the reaction conditions on the performances of Fe-ZSM-5 catalysts for phenol elimination by H₂O₂. Using a H₂O₂ stoichiometric ratio equal to 1.5 avoids accumulation of any quinone-like byproducts. Under these conditions, the catalytic system H₂O₂/Fe-ZSM-5 allows a total elimination of phenol and a significant TOC removal (50%) without leaching-off more than 1 ppm of Fe(III) ions. At the end of the reaction period, only carboxylic acids (maleic, fumaric, oxalic, acetic acids) accumulate.

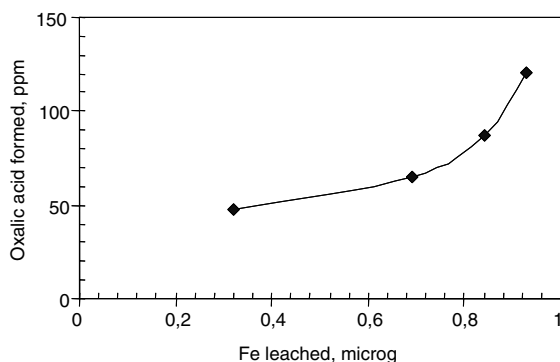


Figure 8. Relationship observed between amount of leached iron and amount of oxalic acid formed in experiments of *p*-cumaric acid conversion with H₂O₂ on different Fe-ZSM-5 catalysts.

The pH of the reaction has also a marked effect [85b]. An optimum value exists at pH 5, while lower pHs are necessary for the maximum activity in the homogeneous systems (around pH = 3.5, as commented before). At higher pH, the system becomes less effective. At lower pH, a significant leaching-off will induce homogeneous catalysis and the degradation of the catalyst.

A second class of materials studied in the WHPCO reaction is that of clays containing iron and/or copper. Barrault *et al.* [65–67,86] have extensively investigated these catalysts. (Al–Cu)-pillared clays were prepared from a crude bentonite sample either by ion exchange or by intercalation. The addition of copper largely promoted catalyst activity in phenol oxidation, but part of the copper dissolves in the reaction medium. However, tests showed that leached copper does not contribute significantly to catalyst activity. The catalyst could be recycled at least five times. Tests were made at room temperature.

Mixed (Al–Fe) pillared clays (called FAZA) were found to be rather efficient in the WHPCO reaction of aqueous solution of phenol [65–67]. In mild reaction conditions (70 °C, atmospheric pressure, reaction time about 2 h), about 80% of the initial amount of phenol is mineralized. The catalyst leaching remains very low, even after three cycles of reaction and represents less than 0.2% of the total amount of the iron contained in the catalyst. The low leaching (compared to Fe-zeolite catalysts) and good catalytic activity show that the FAZA catalyst is a promising catalyst. The (Al–Fe) pillared clay could be recycled and used several times, and its preparation is relatively simple. The same authors investigated also the nature of iron species active in the reaction [67]. This aspect will be discussed more in detail later.

Catrinescu *et al.* [68] have studied similar Fe-exchanged Al-pillared clays, but derived from synthetic beidellite. The wet hydrogen peroxide oxidation of phenolic aqueous wastes was also investigated. The results indicate that the use of this catalyst allows a total elimination of phenol and a significant removal of chemical oxygen demand, without significant leaching of Fe ions. It was also observed that by using this catalyst, it is possible to extend the range of pH values for which Fenton-type oxidations can occur, according to previous indications commented regarding Fe-zeolite catalysts.

Other similar systems reported in the literature were Al–Fe-pillared montmorillonite also in phenol oxidation [87], Al–Cu pillared clays (prepared by direct introduction of Al–Cu pillaring solution into a diluted bentonite suspension) for the catalytic wet hydrogen peroxide oxidation of reactive black 5 dye (complete removal could be achieved within 20 min at atmospheric pressure and 80 °C) [88], and Al–Fe pillared clay catalyst (in the form of extrudates) for phenol oxidation [89]. The latter authors investigated also the kinetics of the reaction.

Other solid catalyst investigated for the WHPCO reaction were iron-hydroxide (FeOOH) or goethite ([FeO(OH)], an iron oxide mineral) for the degradation of aromatic derivatives [90] and linear alkylbenzene sulphonic acid [91], structured silica fabrics (woven prepared from aluminoborosilicate fibers) exchanged with Fe-ions [92], polyacrylonitrile (PAN) fibrous catalyst (modified to introduce chelating functional groups onto the fiber surface) exchanged with iron and other transition metal ions [93], LaTi_{1-x}Cu_xO₃ perovskites for the oxidation of aqueous solutions of phenol [94], Cu/Al₂O₃ catalyst for the treatment of dyehouse effluents [95], copper-exchanged NaY zeolites for the destruction of low molecular weight carboxylic acids such as acetic, glyoxalic, and oxalic acids [96], Fe-exchanged Y zeolite for the conversion of the azo dye *Procion Marine H-EXL* [69] and CuCeO_x catalysts (again in the oxidation of phenol) [97]. A comment is useful about the latter catalyst which shows a good relationship between amount of copper leached to solution and catalytic activity, indicating that this catalyst is not a proper heterogeneous catalyst, but acts essentially as a reservoir for copper ions which are active in the homogeneous phase.

Noble metals based catalysts have been also reported for the reaction (Pd–Pt/Al₂O₃ bimetallic catalysts), but for the motivation of *in-situ* generation of H₂O₂ from H₂ and O₂ [98]. The application regards the wet oxidation of reactive dyes in the presence of 1% H₂ together with excess oxygen. Palladium acts as a promoter to spillover the adsorbed H₂ onto the surface of the oxidized Pt surface, and thereby the reducibility of the Pt increased greatly. The organic dye adsorbs on the reduced Pt surface in competition with excess oxygen. Very high activities were observed due to the combined effects of the faster redox cycle resulting from the increased reducibility of the Pt surface and the additional oxidation of the reactive dyes with hydroxyl radicals.

In-situ synthesis of H₂O₂ (or hydroxyl radicals) from H₂/O₂ is a very interesting opportunity, because the cost of production of H₂O₂ may be reduced to a half of the commercial H₂O₂ cost [99], therefore considerably widening the field of application of WHPCO technology. However, if the motivation is only to generate H₂O₂, it is preferable to have two integrated stages (a first stage of generation of H₂O₂ solution from H₂/O₂ and a second in which the solution produced in the first step is directly used for the WHPCO process), because this would allow a better optimization of each stage of the reaction. The results of Lee *et al.* [98] suggest that the organic dye mineralization is a parallel process to H₂O₂ synthesis, and not a consecutive one. Therefore, an *in-situ* production of H₂O₂ is necessary. However, data are not very conclusive about this question and there are no indications on the effectiveness in using H₂. This is an aspect which deserves further studies.

It should be noted, however, that combining noble and non-noble metals can be interesting also to synergistically promote the performances (see figure 4).

In conclusion, due to the quite different reaction conditions utilized, and sometimes incomplete results about stability and separation of the contributions between homogeneous and heterogeneous reactions, it is not possible to make a clear ranking between the proposed catalysts. However, Al-Fe-pillared clays seem the more promising between all the series of catalysts investigated. It should be remarked, however, that in the largest part of the studies, only simple model molecules have been chosen. We should remark that even if phenol has been the most extensively used model molecule, its very easy decomposition does not provide useful indications about the true performances with more relevant waste water streams containing hardly biodegradable chemicals. A further general comment regards the usual absence of good indications about the selectivity in the use of H_2O_2 which is the critical factor of the process. Ranking of the catalysts should be made with reference to this parameter instead that to the possible level of mineralization. The rate of mineralization is very dependent on the reaction conditions, reactor characteristics and other catalyst properties than only its intrinsic reactivity. Data on the formation of byproducts, and biodegradability and/or toxicity of the effluents are also quite limited [69,70], but clearly of critical relevance for applications and for the evaluation of the catalysts (often the rate of reaction is not relevant, but instead the rate of improvement of BOD_5 or reduction of the biotoxicity).

5. Differences between copper and iron as the active element

As mentioned before in comparing the differences in the radical mechanism and reactivity of iron and copper Fenton homogeneous catalysts, iron ions show better performances than copper ions, mainly due to the faster rate of oxidation by O_2 of Cu(I) with respect to Fe(II). The latter two are the effective species generating the hydroxyl radicals by reaction with H_2O_2 , although they form *in situ* by reduction of Cu(II) and Fe(III), respectively (see the Fenton cycle outlined in equations (2)–(8)). The oxidation of these Cu(I) and Fe(II) species by O_2 (competitive to their reaction with H_2O_2) decreases their steady-state concentration, although various factors (including reactor mixing and design, and the reaction conditions) determine the effective competitive inhibition. Limited information are available to analyze whether or not the same is valid also for solid Fenton-type catalysts, due to the lack of specific data and the more difficult analysis of solid catalysts, where both various species may be present and the reactivity of surface ions is strongly dependent on the oxide or zeolite local structure.

Various authors have studied copper-based solid Fenton-type catalysts. Gabelica *et al.* [100] have studied a series of MFI-type metasilicates (M = Al, Ga, Zn, Cu or their admixtures) in the wet peroxide oxidation of phenol. The best results were obtained with a (Cu,Zn,Al)-MFI system, although the performances (about 60% TOC removal in 4 h, and part of this related to adsorption) indicate low performances of these samples. A fraction of copper was solubilized, but homogeneous copper ions were suggested to have negligible role. Pillared clays containing iron (FAZA) or copper (CAZA) species were studied for the catalytic wet peroxide oxidation of phenol by Tatibouët *et al.* [66]. They found that CAZA shows an initial rate of phenol conversion about 12 times lower than that of FAZA, although the activity is only about half on an active metal weight basis. This is in agreement with the homogeneous order of reactivity. In CAZA the amount of copper ions which can be pillared between the clay sheets is around 0.7 wt.% versus about 5 wt.% for iron. Different copper species form for higher Cu loadings. As a consequence of these two aspects (lower amount of copper and intrinsic reactivity), the performances of the Cu-containing clays are markedly worsen than those of the Fe-containing clays. Cu-Fe-pillared clays were not investigated, although in principle they can be promising. As mentioned before regarding the homogeneous Fenton reaction, a synergetic effect between iron and copper ions may be expected. Both CAZA and FAZA show some leaching of copper or iron, respectively, although limited (less than 1% of the initial content) at room temperature. The leaching increases at higher temperatures.

$CuCeO_x$ catalysts were studied by Arena *et al.* [97] in the oxidation of phenol. A linear relationship between amount of copper leached to solution and catalytic activity was observed, indicating that in this case the activity is mainly associated to the copper ions in the homogeneous phase.

Cu^{2+} -NaY catalysts were studied by Levesque *et al.* [101] in the oxidation of acetic acid by H_2O_2 . Although the catalyst is less active than homogeneous Cu^{2+} ions in the same amount, the authors attributed the performances to copper ions exchanged in the zeolite. Leaching of copper was observed (copper concentration in the solution ranges from few to up to 35 ppm).

Al-Cu pillared clays were studied by Kim and Lee [102] in the wet peroxide oxidation of reactive dyes (black 5, blue 19, red 198). Very good results were obtained with complete TOC removal (as well as color removal) in about half an hour (atmospheric pressure, 80 °C), including in tests using real dyehouse effluents. No detectable Cu leaching was cited, although no data have been reported. The copper content in these samples is up to 2.5 wt.%. Therefore, significantly higher than the limit of about 0.7% indicated by Tatibouët *et al.* [66]. These samples were prepared by pillaring of

bentonite at 40 °C and ESR characterization data suggested that copper was grafted on the alumina pillars (but data were not provided).

Therefore, copper-based solid Fenton-type could be also promising in addition to iron-based samples. In both cases, the main issue is to obtain true heterogeneous systems and to prove more effectively the absence of leaching than just analyze the amount of copper in the leachate. In fact, it is known that readsorption by the catalyst during cooling may occur. Also data on the eventual presence of an induction time could be useful. Arena *et al.* [97] in studying CuCeO_x catalysts noted the presence of an induction time indicating that leaching of copper was the starting effect for activity. On the contrary, in the case of iron-based catalysts some results pointed out that the leaching in iron-based catalyst was a secondary effect related mainly to the complexing action of reaction intermediates such as oxalic acid (see figure 8). Data are limited and therefore a general conclusion cannot be derived. However, it is important to analyze if the eventual leaching is a primary or secondary reaction (e.g. due to reactants or to the reaction products), because the strategy for designing more robust catalysts could be different (for example, if leaching is related to the formation of oxalic acid, a dopant could be searched which facilitate further conversion of this intermediate; see for example, the effect of Pt in acetic acid conversion—figure 4).

Generally speaking, more attention should be also given to understand the relationship between nature of the species present in the catalyst, rate of reaction and rate (and mechanism) of leaching. As discussed in the next section, some data are available regarding Fe-based catalysts, but few regarding Cu-based catalysts. Literature data pointed out that pillaring them between the sheets of clays improves significantly the resistance to leaching, while not markedly influences the reactivity. Ion exchange methods lead instead generally to an easy leaching during the catalytic reaction. However, in general it may be expected that the procedures for copper stabilization could be different from those used for iron. Therefore, different strategies to prepare stable Fenton-type solid catalysts should be adopted in the case of copper- and iron-based catalysts.

6. Relationship between nature of the iron species, reactivity and stability

The analysis of the relationship between nature of the iron species, reactivity and stability is a key issue in the development of Fenton-type solid catalysts for WHPCO reaction, but literature data on these aspects are limited. Often not enough attention was given to measure the metal leached during the reaction (taking into consideration also the possible readsorption of leached metal

when the temperature of the reacting solution is cooled down, and the possible change of pH during the catalytic reaction). The absence or minor reactivity of the solution after filtering the solid catalyst (e.g. checking the further conversion of the organic species after eliminating the solid catalyst), in order to prove the contribution of homogeneous leached transition metal ions, may be not an undoubtedly proof to discriminate between homogenous and heterogeneous Fenton-type reaction, because the reactivity of the organic species adsorbed on the catalyst could be different. The importance of the adsorption of the reaction/products on the catalyst, both in terms of apparent conversion and influence on the reactivity, should be considered in detail to evaluate catalyst performances.

The nature of the active species in WHPCO reaction, in terms of both activity and stability, was investigated in detail by Tatibouët *et al.* [67] for the phenol oxidation on Al-Fe-pillared clays (FAZA). ESR data indicate that iron is present as (i) isolated species (in highly distorted octahedral symmetry), probably located on the clay layer and (ii) oxide clusters. On Al-Fe pillared clay (iron introduced by ion exchange in the pillars), in addition of the preceding species, a third isolated iron species is present, probably located on the pillars as extra-framework species (also in octahedral coordination). Comparing these data with the catalytic behavior they concluded that the iron species probably located on the pillars catalyzes more efficiently the total phenol oxidation than the other iron species. The authors also reported long time (350 h) catalytic experiments in a continuous flow reactor which showed the high stability of the Al-Fe pillared clay. After these tests, the total amount of dissolved iron by the reaction being less than 5 wt.% of the iron initially contained in the catalyst.

Fe-Al-pillared clays, but derived from two natural smectites, were also studied by Ruiz-Hitzky *et al.* [103] in phenol conversion. They also indicate as the active redox centers the ions located on the pillars, but also suggested that the presence of nearby Brønsted sites are necessary to enhance the rate of Fe^{3+} reduction to Fe^{2+} . No indications were given about the stability of the iron species and their resistance to leaching.

Sotelo *et al.* [82] studying the phenol oxidation with H_2O_2 over different iron-containing zeolitic materials observed that the stability of Fe species strongly depend on the Fe environment in the zeolitic framework (structure, strength and concentration of acid sites, sitting), the synthetic route and the temperature of the treatment. The amount of leached Fe was found to range from 10% to over 90%, depending on these parameters. The more stable species are those incorporated in the zeolite framework, but the stability depends also on the presence of other T atoms.

Different conclusions were instead recently reported by Lazar *et al.* [104] studying the influence of synthesis routes on the state of Fe-species in SBA-15

mesoporous materials and the relationship with the behavior in phenol conversion with H_2O_2 . They suggested that good activity and stability of the catalysts could be obtained from catalysts containing iron mostly in the form of disordered iron oxide (hematite nanocrystals), although these authors also concluded that the possible mechanism of both reaction and leaching involves the consecutive process with transport of iron *via* embedded hematite \rightarrow ionic dispersion in the siliceous matrix \rightarrow hydrothermal dissolution.

In conclusion, some studies started to address the question of the relationship between nature of the active species, activity and stability, but more work is necessary to have a more complete and general understanding of this issue.

7. Kinetics of the WHPCO reaction

Studies on the kinetics of WHPCO reaction are limited, even though various authors have reported the effect of the reaction parameters such as temperature, concentration of the catalysts and reactants, and pH. However, no kinetic modeling has been usually reported. The only study in this direction is that reported by Guo and Al-Dahhan [89] on the catalytic wet oxidation of phenol by H_2O_2 over Al-Fe-pillared clay catalysts. The reaction network used for the kinetic modeling is reported in figure 9. They observed that the reaction takes place to a significant extent both in the liquid phase and on the catalyst surface. Two kinetic expressions to separately consider the homogeneous and heterogeneous contributions were derived. The first (homogeneous) reaction is based on a second order rate of reaction, e.g. both the primary reaction rates in the reaction scheme shown in figure 9 and the secondary reactions of the intermediate have a first order dependence on the concentration of both the organic substrate and H_2O_2 :

$$r_{\text{hom, phenol}} = k \cdot [\text{phenol}][\text{H}_2\text{O}_2] \quad (9)$$

This appears a rather oversimplification of the reaction kinetic of radical-type reactions such as the WHPCO, notwithstanding the fitting of the data. The heterogeneous reaction is instead based on a Langmuir–Hinshelwood derived mechanism:

$$r_{\text{heter, phenol}} = \frac{k \cdot [\text{phenol}] \cdot [\text{H}_2\text{O}_2]}{1 + K_1 \cdot [\text{phenol}] + K_2 \cdot [\text{B}]} \quad (10)$$

where B indicates a reaction intermediate. The overall reaction rate of phenol conversion was the following:

$$\frac{d[\text{phenol}]}{dt} = r_{\text{hom, phenol}} + r_{\text{heter, phenol}} \cdot C_{\text{cat}}^\alpha \quad (11)$$

where the term C_{cat} indicates the catalyst concentration and the exponent was found to be about 0.8 by fitting the experimental results. Equation (11) appears a rather strange kinetic expression, because a rate equation (by definition) should be independent on the concentration of the catalyst. This term is probably necessary for the fitting of the data, because the kinetic model does not consider the reaction mechanism of these radical-type reactions (including rate of generation, and termination of the hydroxyl radicals). It should be also remarked that the kinetics of homogeneous conversion of phenol with $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ [105] indicates a far more complex situation, with a zero order with respect to phenol during the major part of the reaction, while at the end of the runs this order changes due to an autocatalytic effect of phenol. Guo and Al-Dahhan [106] have also published a paper on the kinetics of wet air catalytic oxidation (WACO) of phenol using an analogous kinetic approach. In this paper the kinetic results and modeling of WACO of phenol are compared with those obtained in the WHPCO reaction cited above.

Few other data have been reported on the kinetic modeling of WHPCO reaction. The kinetics and reaction pathways for the catalytic oxidation with H_2O_2 of formaldehyde and methyl orange has been recently reported by Yang *et al.* [107]. Gregor *et al.* [108]

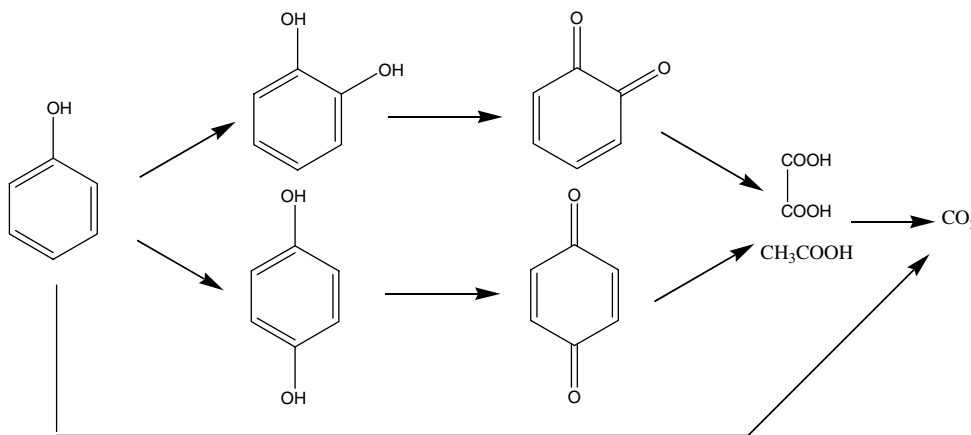


Figure 9. Reaction network used in the kinetic modelling of phenol wet oxidation by H_2O_2 over Al-Fe-pillared clays. Elaborated from Guo and Al-Dahhan [89].

analyzed the kinetics of toluenesulfonic acid (model substance for pulp and paper wastewater). However, in general a lack of detailed kinetic studies based on the reaction mechanism of the WHPCO reaction using solid Fenton-type catalysts should be remarked. Also considerations on the optimal reactor design for these reactions are limited, but experience on the wet air (catalytic) oxidation which has been studied in a more detail from this point of view [55] evidence the great relevance of a proper reactor design and of predictive modeling techniques to optimize the process.

8. Conclusions

The results on the performances of solid catalysts for WHPCO reaction indicate good perspectives for the application of this technology, but it is really necessary to make an effort in making more careful experimentations and in making a proper design of both catalysts and reactors. The latter aspect (reactor design) was not discussed in detail here, but it should be noted that a proper integrated reactor and catalyst design in these multiphase reactions are essential to achieve process intensification and reduce the costs [109].

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