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Recycle rinse water: problems and opportunities

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Abstract

Problems and opportunities in recycle rinse water, with specific reference to the case of rinse water in the electronics industry are reviewed. After a discussion of the characteristics of rinse water and why recycling can be an economic opportunity, lower the impact of production on natural resources and improve water management, some of the general features of the technologies for recycle rinse water are discussed with emphasis on the necessity for the development of innovative catalytic technologies for the treatment of the recycled water. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Rinse water; Water catalytic technologies; Electronics industry; Recycle water; Catalytic wet oxidation

1. Introduction

The amount of water consumption in industrialized countries is continuously increasing (it has doubled in about the last two decades) and in several countries the depletion of underground sources and/or their increasing level of contamination has become a central question. Therefore, rational use of water resources is a key issue for sustainable growth.

Water consumption in industry has also increased considerably in the last decade and at the same time the cost of industrial water, which includes its direct cost, the cost of the treatments necessary to reach the water quality required for the specific application, and/or the cost of post-treatments, has increased exponentially. 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.

Water use in industry largely depends on the specific production, but can be classified in four main categories: (i) processing, (ii) washing, (iii) cooling and (iv) duties. There are several classes of water-intensive-use industries such as (i) food and kindred products, (ii) paper and allied products, (iii) production of electronic devices, (iv) chemical, petrochemical and refining products and (v) primary metal industries. In this contribution problems and opportunities mainly related to rinse water originating from cleaning processes in the electronics industry will be discussed for the specific relevance of this topic [1–3], although most of the aspects discussed are not specific to this case only.

As background information for the discussion, some of the ideas and conclusions originating from an industrial research project on this topic supported by the European Community (contract BRPR-CT95-0034) are used, but put in a general perspective in order to highlight the open questions and outlook for this area of research.

After definition of the characteristics of the rinse water and why its recycle can be both an economic and environmental opportunity, some general aspects

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of the technologies to treat recycled rinse water are examined. The final part of the contribution deals with an analysis of the catalytic technologies for treatment of the recycled water, because the use of catalysts offers several possibilities for the improvement of current technologies, although research on this topic is only at an early stage [4].

2. Characteristics of rinse water and reasons for recycling

Rinse water originates from several steps in the manufacturing process for electronic devices. The production of printed circuit boards (PCB) can be used as an example [5,6]. Several steps of the complex process produce large volumes of rinse water, as illustrated in Fig. 1a. All streams are usually sent to a first rinse water bath for primary treatment (Fig. 1b) such as recovery of metal ions and then to a second rinse water bath from which after dilution and eventual post-treatment it is discharged. In the option of recycle, the rinse water from the second bath, after the necessary treatments, is sent to the deionization unit to reduce tap water consumption and cost of its further treatment to reach the required quality. In fact, for example, the total organic carbon (TOC) content of tap water usually ranges from 2 to 3 mg C l^{-1}, whereas the TOC limit for most applications in the electronics industry is usually four orders of magnitude lower (Fig. 2). The TOC value of rinse water from the second bath is often 2–3 times higher than that of tap water. The reduction of 99.5% of its TOC (possible with current technologies) will not allow the final limit in TOC to be reached, but the severity of treatment required in the deionization unit considerably decreases. The cost of the deionization process is the largest in the overall cost of process water for cleaning treatments in the electronics industry and thus a reduction of its cost is the critical issue for process economics. Furthermore, a considerable part of the organics contained in the rinse water are non-biodegradable or ‘recalcitrant’ chemicals (i.e. of difficult conversion) and thus their elimination before emission into surface water is necessary. This post-treatment unit is also a not-negligible part of the global cost of water management [7].

The recycle of rinse water therefore can be an economic opportunity. Ojima et al. [8] estimated the cost of water for semiconductor fabrication in Japan and concluded that in the case of water recycle the running and fixed capital costs can be reduced to about 70% of the original cost in the absence of water recycling. Similar estimations in the case of printed circuit board manufacture in Europe lead to comparable values [2]. Thus, water recycle can be not only a benefit for the environment and natural resources, but also can be an economical opportunity to decrease the cost of water management. In addition, the possibility of better control of water quality leads to better control of water management and thus to higher standards of quality in the production.

The various steps in the manufacture of components in the electronics industry which give rise to rinse water can be classified as follows:

- Cleaning: Removal of oil, grease, cooling fluids and other contaminants generated by mechanical shaping. The relative water solutions contain surfactants, inorganic salts and various additives. Major components are inorganic acids or alkali hydroxide, surfactants, corrosion inhibitor, complexing agents, phosphates, silicates, borates, etc.
- Etching: Removal of parts of the products. Major components are acid aqueous solutions containing various additives such as brighteners, corrosion inhibitor, etc.
- Layer deposition/removal: Complete or partial (residual parts) elimination of the layers produced by galvanic, lacquering and wet or dry coating (CVD, spinning) techniques. Major components are complexing agents, organic solvents and developers, wetting agents, brighteners, corrosion inhibitor, organic stripping agents, lacquer residue, polymers, etc.

The rinse water in electronics industry thus usually contains several classes of chemicals such as (i) organic acids (methane sulfonic acid, *p*-toluensulfonic, formic, acetic and citric acids, etc.), (ii) organic bases (triethanolamine, thiourea, amines, etc.), (iii) surfactants (polyglycol ether, alkyl benzene and alkane sulfonates, α-sulfo fatty acid esters, soap, fatty alcohol polyglycol ether, ethoxylated fatty amines, etc.), (iv) organic solvents and developers (alcohols, resorcinol, γ-butirrolactone, formaldehyde, ketones, etc.), (v) inorganic chemicals such as acids (HNO_3, H_2SO_4, HBF_4, HCl, etc.), salts (K-citrate, NaF, NH_4Cl, etc.), metals (Cu, Sn, Ni, Pb, etc.), etc., and (vi) complexing

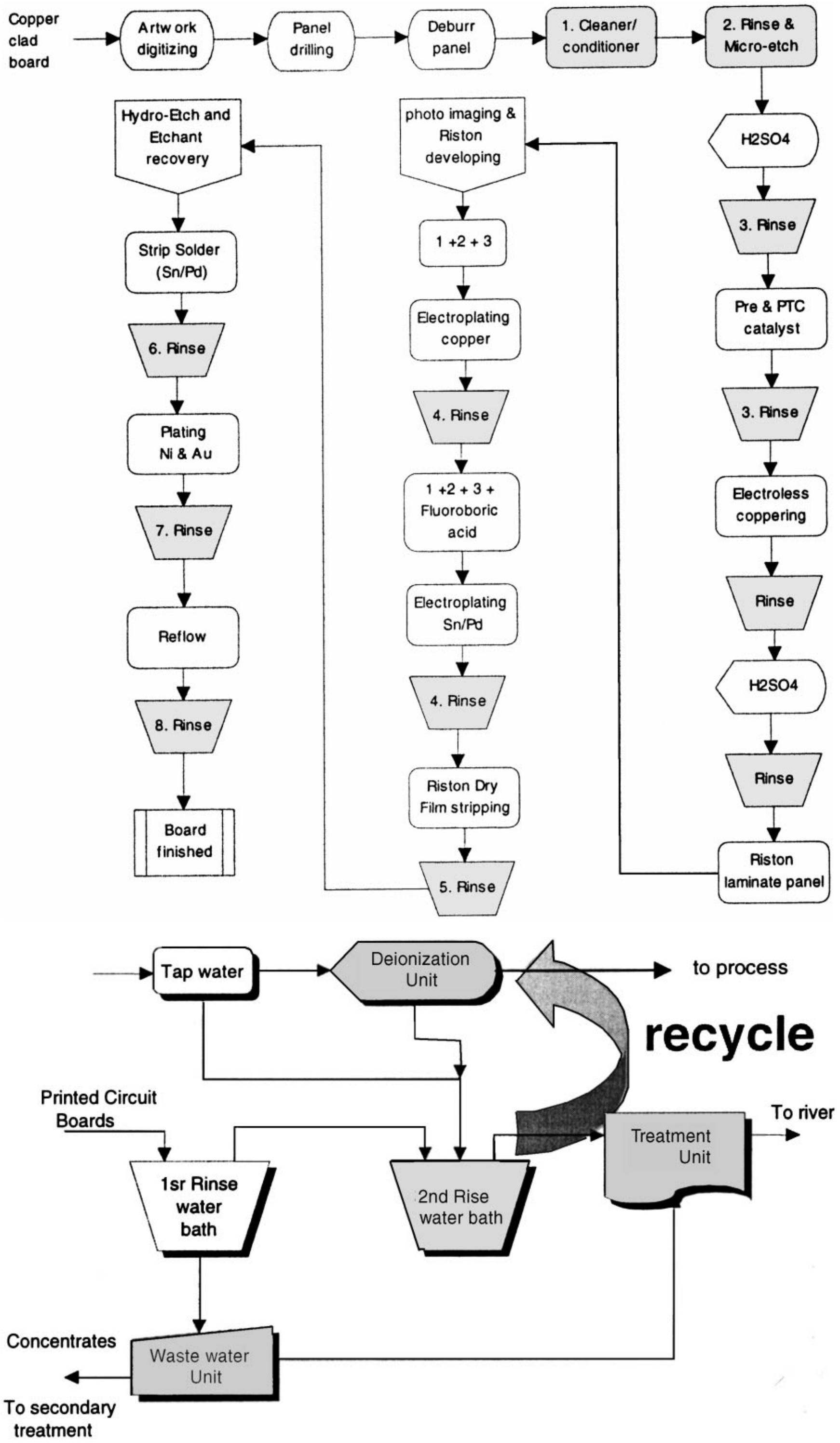

Fig. 1. (a) Flow sheet of the various steps in the production of printed circuit boards; the steps of generation of rinse water are highlighted. (b) Overall general scheme of water management in the electronics industry.

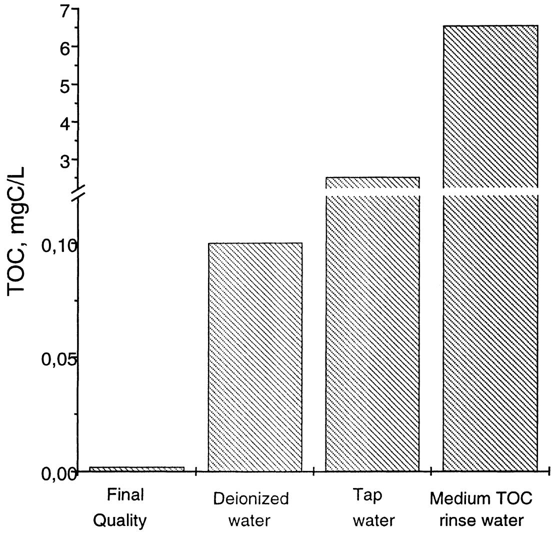

Fig. 2. Total organic carbon (TOC) for different steps in water management in the electronics industry.

and wetting agents (cyanides, tartrate, polyethylene oxide), etc. The composition is thus quite complex with several classes of compounds with different chemical properties. Furthermore, the composition may change with time depending on the specific type of production. In addition several of the chemicals present in the rinse water are non-biodegradable or ‘recalcitrant’.

3. General features of technologies to recycle rinse water

Water is a relatively cheap commodity and thus the cost/benefit analysis in a technico-economical evaluation is a key parameter for the selection of the possible technologies. In this respect, the energy process cost is a fundamental component of the overall process economics and thus differently from the normal approaches used to develop chemical processes (reaction conditions are selected to give the best results), the technologies for water treatment should be adapted to operate at the conditions of the water stream (temperature, pH, concentration of contaminants, etc.). Temperature, in particular, is a critical aspect, and since the rinse water in the electronics industry is usually available at room temperature, the technologies for water treatment must preferably operate at this temperature. When organic concentration is high, the heat of reaction released from the oxidation can be used to operate the reaction autothermally (Fig. 3a) and high temperature operations are possible [9]. A relationship exists between concentration of organics in solution and temperature at which the technology can operate autothermally. This relationship is outlined in Fig. 3b, although it must be considered only indicative, because the specific value of minimum temperature of autothermic operations depends on various factors such as the conversion of the organics, efficiency of heat recovery, loss of heat of the reactor, etc.

Outlined in Fig. 3b are also different advanced oxidation processes (AOP) which correspond to the different ranges of temperatures of operation. If autothermic operations are possible, increasing the operating temperature makes possible less costly oxidants and/or technologies with thus a reduction in both the running and fixed costs (Fig. 3c). Otherwise, the cost of energy to heat the water stream to the temperature of operation may be higher than the economic advantages in using cheaper oxidants.

In the selection of the possible technologies to recycle rinse water, the concentration of organics in solution is thus a key parameter. However, the composition of rinse water is often very complex as indicated in the previous section. Furthermore, the composition and flow rates are often not constant and may change significantly during operation. Thus a fundamental aspect of the water treatment technology is also its flexibility in terms of both handling a large variety of chemicals with different and contrasting characteristics (Section 2) and adapting to variable loadings and flow conditions.

The quality of the final water is also an important parameter. In several cases in the electronics industry, high quality water is required (Fig. 2) and thus a combination of technologies is necessary to reach the final level of purification. The optimal combination of technologies depends on the specific case, but a factor of increasing importance to be considered is also the ability to convert the organics to CO_2 instead of simply separating them from the main stream, because the new environmental regulations consider the global impact of production and thus organic chemicals should be converted preferably to carbon oxides.

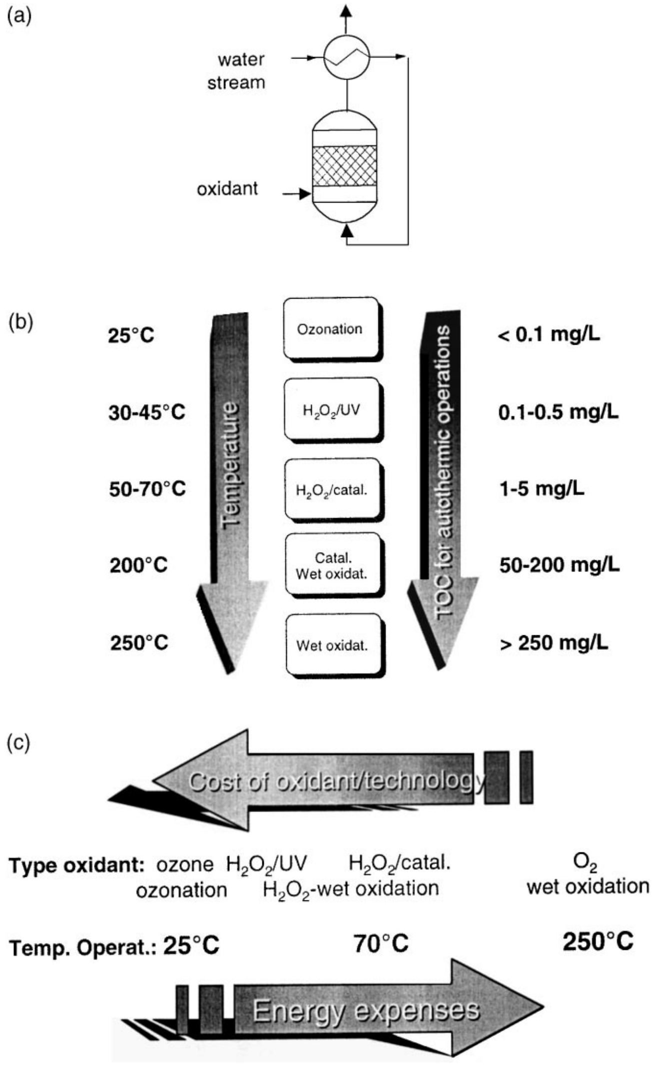

Fig. 3. (a) Scheme of the reactor for autothermic operations. (b) General relationship between temperature of operation, type of possible water treatment technology and TOC content in the inlet water stream for autothermic operations. (c) General relationship between temperature of operation, type of possible oxidant and technology for water treatment and its cost.

There are usually different possible options in combining technologies for recycling rinse water and the selection of the best method is often not straightforward. An example of two alternative solutions for the treatment of recycled rinse water for the electronic industry is discussed below and shown in Fig. 4.

The first option [8] (Fig. 4a) is composed of (i) a first column of activated carbon to remove organic impurities, (ii) a second column of weak ion-exchange resin and a third column composed of two layers, a first layer of strong-cation ion-exchange resin and a second layer of strong-anion ion-exchange resin, to remove inorganic ions, organic acids and low molecular weight ionic matter, (iii) a fourth unit of oxidation of organics by H_2O_2 in the presence of UV irradiation to activate the homolithic cleavage of hydrogen peroxide molecules forming hydroxyl radicals, (iv) a further activated carbon column to decompose residual

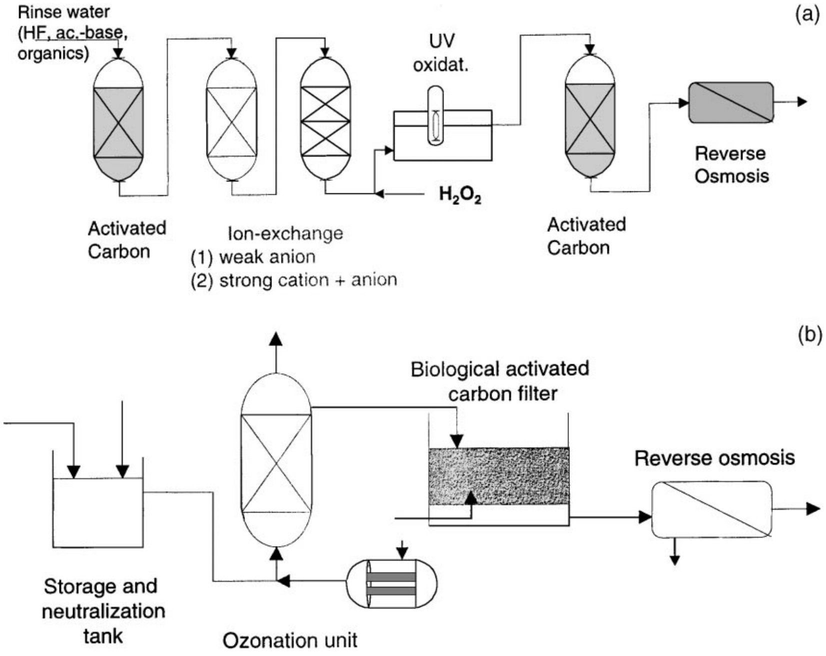

Fig. 4. Two alternative process possibilities for the treatment of the recycled rinse water in the electronics industry (see text).

H_2O_2 and adsorb organic fragments produced in the H_2O_2/UV unit, and (v) a final stage of reverse osmosis to remove traces of organics, particles, bacteria, etc.

This combination of technologies allows a good quality of the final water to be obtained, but about 50–60% of the total running cost is due to power and lamp cost for the H_2O_2/UV unit [8]. Furthermore, periodic change of the UV lamps (two medium-pressure Hg lamps in series) is quite short and periodic regeneration of the active carbon and ion-exchange units is need. Thus, duplicate columns are necessary for continuous operation which increases the fixed capital costs. In addition, only about 20–30% of initial TOC is converted to CO_2, the remainder is rejected in reverse osmosis units or remains adsorbed on active carbons and resins.

An alternative solution which allows a reduction of running and fixed capital costs, continuous operation and an increased fraction of TOC removal as CO_2 (up to about 40–50%) is shown in Fig. 4b. The first treatment (after a preliminary tank to minimize fluctuations in flow and composition and regulate pH) is catalytic ozonation with the function of removing about 20% of the initial TOC as CO_2, but especially to break large, non-biodegradable molecules. The second step is a biological activated carbon filter where the microdispersed active carbon acts as a support for the biological microorganisms, as a buffering component to minimize fluctuations and as a catalyst to eliminate any residual traces of ozone. The final stage is again nanofiltration by reverse osmosis. The largest abatement in TOC is connected to this last step (Fig. 5), but the two former steps are necessary (i) to reach the final quality of water required (the TOC removal in nanofiltration is nearly linear with the concentration) and especially (ii) to minimize fouling of the membrane, thus allowing longer continuous operation [10,11].

4. Catalytic technologies as a new opportunity

Although technologies for treating recycled rinse water are available commercially, there are limitations in terms of cost of chemicals/technology, efficiency of removal of pollutants, production of side streams, severity of operation, range of conditions for operation, etc., for which innovative solutions are required [4,12–15]. A new opportunity which can be consid-

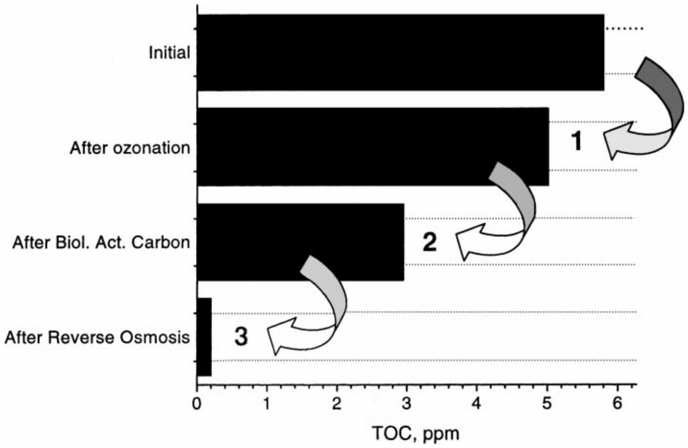

Fig. 5. Change in TOC in the various steps of the process configuration shown in Fig. 4b.

ered still at an early stage of research is the use of solid catalysts to overcome or reduce these limitations.

There are two main classes of processes for treating recycled rinse water which can be improved by the use of solid catalysts:

1. Adsorption with catalytic regeneration.
2. Oxidation processes using ozone, hydrogen peroxide or gaseous oxygen.

The first area has not been investigated in detail, but shows the great advantage of being formed by a first unit of known technology (adsorption by solid pellets) that can operate in a large range of conditions and efficiently at room temperature. The second stage of regeneration is made by oxidative catalytic treatment. The presence of a catalyst in this second stage (usually a transition metal oxide) makes it possible to (i) operate in milder conditions, (ii) preserve the integrity of the solid, (iii) accelerate the regeneration procedure and (iv) increase the effectiveness of combustion to CO_2.

There are two possible options:

- Use of solid adsorbents thermally stable during regeneration in oxidizing conditions (pure or mixed oxides, zeolites, clays, etc.) that contain elements such as oxides of transition metals (Cu, Mn, Fe, etc.) which catalyze the oxidation of adsorbed substances.
- Use of granular active carbon (GAC) doped with transition metal oxides which make possible the combustion of the adsorbed substances at temperatures below those when the combustion of the active carbon starts (above 300°C) [4,16,17].

The second option is the more interesting, because the properties of the active carbon in the removal of organics from water are well established and active carbon has a high sorption capacity together with a low specificity to single classes of chemicals. A mixed oxide (Fe_2O_3–CuO–Cr_2O_3, for example [4]) is added in an amount of about 5–10% wt. to the active carbon by wet impregnation in a way as to prevent major modifications in the adsorption capacity of the active carbon, guarantee good dispersion of the catalytic component, and have high activity to catalyze the oxidation of adsorbed substances during regeneration. In this way it is possible to have regeneration of the exhausted active carbon in very mild conditions (around 250°C) giving complete combustion of the adsorbed organics instead of pyrolizing them as in the usual regeneration procedure for active carbon. The common procedure for regeneration of active carbon, in fact, is by pyrolysis at temperatures of about 800–850°C with a second stage of hydrothermal treatment to regenerate the pore structure lost during the pyrolysis step. This procedure is a significant part of the cost of the process of water purification using active carbon. However, the difference in the temperature of combustion between the active carbon and the adsorbed substances is still too limited to guarantee the technical feasibility in real operations where the presence of thermal waves and hot spots may lead to the start of runaway phenomena and thus significant safety problems. Furthermore, the technical feasibility has been demonstrated only on lab scale apparatus and for a limited range of molecules. This possibility is thus highly interesting, but needs to be further developed especially in terms of (i) wider temperature differences between the combustion of adsorbed species and of the active carbon, (ii) optimization of the catalyst to improve its performance and avoid possible leaching, (iii) risks of operation and (iv) long term operations.

The other option of using a solid thermally stable under oxidizing conditions (pure or mixed oxides, zeolites, clays, etc.) is technically more feasible. Catalytic components to improve regeneration of the solid are usually transition metal oxides (Cu, Co, etc.), the specific nature and amount of which depend on the modality of regeneration (either wet oxidation at temperatures of around 200–250°C or dry oxidation at temperatures in the 400–500°C range). In the latter case, partial desorption of the adsorbed substances may also occur and thus a second catalytic fixed bed may be necessary to complete combustion. Both methods of regeneration lead to complete regeneration of most solid adsorbents, if a catalytic element is present. Otherwise, regeneration may be incomplete. The main limitations of this option are the (i) low adsorption capacity of most of oxides, zeolites and clays, and (ii) specificity towards some classes of chemicals only, even in the case of modified solids. For example, the adsorption capacity and kinetics of adsorption of alumina towards a complexing agent such as Na-gluconate can be improved to reach levels comparable or even better than those of active carbons when alumina is doped with Ca ions, but with the drawback of reducing to very low values the adsorption capacity towards a corrosion inhibitor such as triethanolamine. Instead, on active carbons good adsorption capacities simultaneously to both these two classes of chemicals are possible. This example makes clear that the use of solid oxide-type adsorbents is not appropriate when a large range of chemicals with different characteristics must be removed by adsorption such as in the case of recycled rinse water.

The second class of processes where the use of solid catalysts leads to improved efficiency, less severe reaction conditions and lower formation of by-products is that of advanced oxidation treatments. The most studied case is that of catalytic wet air oxidation (CWAO) [4,16,18–21], but recently ozonation using solid catalysts has also received increasing attention [13–15,22–25]. Less studied is the case of wet oxidation with H_2O_2 in the presence of solid catalysts, although some interesting data were published recently using zeolites and clays containing Fe and Cu ions [26,27].

Although the use of catalysts to improve operations in these advanced oxidation processes (AOP) has been evaluated, it may be noted that the topic has been studied systematically and especially laking is a more thorough investigation with the aim to design ad-hoc catalysts for these operations. Usually catalysts not specifically designed for the purpose and application have been studied with the aim of checking their potential application. However, diffusion problems in the liquid phase are very different from those in the gas phase, for example, and other problems such as wetting characteristics, etc. are critical. Thus, the simple screening of catalysts in large part developed for other kinds of applications and often for gas phase reactions may lead to not fully correct conclusions and can result in a loss of information or potentialities. Better use of the wide background knowledge in catalyst design is thus necessary to prepare specific catalysts for AOP applications.

Some general drawbacks of using catalysts, however, should be mentioned. Key problems in all these catalytic AOP applications, in fact, are (i) leaching of the catalytic active elements, (ii) necessity for further improvements in activity to work in even milder conditions, (iii) optimization of the pore structure of solid catalysts, while maintaining good mechanical properties, and (iv) design of better reactors which optimize the performance of the catalyst.

The case of catalytic wet oxidation with hydrogen peroxide can be discussed as an example of the advantages and problems in using catalysts for AOP processes. Hydrogen peroxide is a clean and relatively safe oxidant for operations in mild conditions, but it must be activated to generate hydroxyl radicals (the active agent) by homolytic scission. H_2O_2 is relatively inert at room temperature and needs to be activated by UV irradiation. However, the quantum efficiency of the process is rather low and thus the cost of the process is high. The alternative possibility, besides to $H_2O_2 + O_3$ combination (peroxone process), is to catalyze the generation of hydroxyl radicals from hydrogen peroxide via a Fenton-type mechanism using Fe^{2+} ions, for example [28,29]. The limited range of pH for operation and the necessity of a post-treatment to remove the iron ions are the major drawbacks of this technology, although it is commercially employed.

These drawbacks can be overcome in principle using solid catalysts, i.e. the same transition metal ions active in the Fenton-type mechanism, but anchored to a rigid matrix which prevents their leaching and precipitation. The logical extension of this concept is to use zeolites or clays as solid matrices to anchor transition metals such as iron and copper [26,27], because these solids (i) have a regular pore structure, and (ii) allow a high dispersion of the transition metal by anchoring it at exchangeable (Brønsted) sites. Furthermore, inside the zeolite cavities local enhancement of the concentration of the reactants is possible (this property depends on the hydrophobic/hydrophilic properties of the zeolite determined by its Si/Al ratio) as well as local changes in the pH and in the ionic strength.

These materials in principle do not act only as a simple physical support for the active transition metal ion, but rather determine the reactivity. However, the difficulty is that it is necessary to have good interaction between the transition metal ion and the solid matrix in order to prevent leaching of the transition metal, but at the same time this type of interaction alters the reactivity of the transition metal. In addition, it is known [30] that during the preparation of transition metal containing zeolites, for example by ion exchange, not only isolated species at exchangeable sites may form, but also partial precipitation of nano(hydr)oxide particles as well as the insertion of the transition metal at zeolite defects occurs, besides the possible precipitation of the transition metal (hydr)oxide at the external surface of the zeolite crystals. Thus, the specific characteristics of the transition metal containing zeolite may depend considerably on the modality of preparation, but specific data on the relationship between preparation, type of transition metal species in the zeolite, rate of leaching and reactivity are missing. Furthermore, the structure of the zeolite is also an important factor determining these characteristics. In addition the extension to other zeo-type materials (MeAPO systems, for example) or mesoporous materials (MCM-41, for example) further broadens the area of investigation. Consequently, conclusions on the suitability of transition metal containing micro- or mesoporous materials for catalytic wet oxidation with hydrogen peroxide cannot be derived based on the preliminary data in the literature [26,27], but the possibility to have stable materials with negligible leaching of the transition metal with a good catalytic behavior in a wide pH range appears to be realistic.

The major drawbacks which can be noted are the (i) reduced reactivity of the transition metal ions when anchored to the rigid microporous matrix, (ii) role of the microporous material in catalyzing the decomposition of hydrogen peroxide to water and oxygen, and (iii) limited accessibility of large molecules towards the inner cavities of microporous materials. The latter problem is not very critical, because the hydroxyl radicals generated at the inner surface of the microporous material can diffuse to the external surface to break the large molecule into smaller fragments which can then diffuse inside the microporous material. The small number of sites at the external surface of the microporous material crystals may be sufficient to break the large molecule into smaller fragments. However, this observation evidences that the dimension of the crystals of the microporous material can be a critical factor to optimize the catalytic behavior. In addition, a wide range of mesoporous or clay-type materials is available and thus the problem of the limited accessibility of large molecules can be overcome in principle by proper design of the catalytic material.

The problems of the lower reactivity in organic substrate conversion and higher rate of hydrogen peroxide decomposition with respect to homogeneous catalysts is critical, but can also in principle be solved. Reported in Fig. 6 is an example of comparison of the reactivity in propionic acid conversion by H_2O_2 of Fe^{3+} ions in solution and of Fe^{3+} ions anchored by ion-exchange to a ZSM5 zeolite with an SiO_2/Al_2O_3 ratio of 27. Tests were made in order to have the same amount of iron in both cases. The data in Fig. 6 show that at 70°C the iron/zeolite is more active in propionic acid formation than Fe^{3+} ions in solution, although it gives rise to a higher formation of acetic and formic acid by-products being the iron-zeolite activity very low in acetic acid conversion, whereas the Fe^{3+} ions in solution have also a low, but not negligible activity in acetic acid conversion. Thus, the iron-zeolite shows a higher rate in the breakage of the propionic acid molecule by oxidative attack to form acetic and formic acid, but a lower activity in oxidizing these fragments to CO_2.

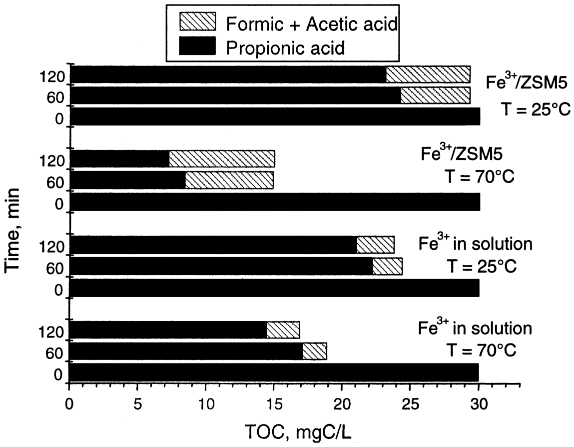

Fig. 6. Comparison of the reactivity in propionic acid conversion of iron ions in solution and anchored to a ZSM5 zeolite as a function of time and temperature during catalytic wet oxidation with hydrogen peroxide. Amount of Fe^{3+} ions = 286 ppm in both cases, pH = 4, initial TOC = 30 mg C l^{-1}, H_2O_2/Substrate = 1.5 of the stoichiometric value.

However, it is possible to improve the activity in the oxidation of acetic acid (one of the most ‘recalcitrant’ molecules) by further modification of the iron-zeolite, i.e. introducing other cocatalytic functions.

At room temperature, however, the iron-zeolite is significantly less active than Fe^{3+} ions in solution. Solid catalysts thus require temperatures higher than room temperature to be effective, although when the initial TOC is high enough to allow autothermic operations (Fig. 3) this aspect may not be critical, and a stable activity of the catalysts is possible. Tests on both the amount of residual iron in the solution after hot filtration and on the activity of the residual solution after hot filtration of the solid catalyst confirm that iron does not leach from the catalyst, although it was observed that this property depends on the modality of catalyst preparation. A slow deactivation of catalyst is present, however, due to the accumulation of residual organics in the zeolite which can be eliminated by periodic calcination of the catalysts.

In conclusion, the use of catalytic technologies for the treatment of recycled rinse water offers several opportunities for the development of innovative and possibly more economic solutions, but an intense research effort is necessary to verify the concept and develop ad-hoc optimized catalysts. In particular, a more strict relationship between knowledge in the field of preparation and characterization of the solid catalysts and knowledge in the field of oxidation technologies for treating polluted water is necessary.

5. Conclusions

The recycle of rinse water is not only a necessity to decrease the negative environmental impact of production on natural resources and improve water management, but also can be an economic opportunity. In this contribution, the case of rinse water from the electronics industry has been used as a guideline for the discussion which may be relevant, however, not only for this type of industry. Some of the general aspects of the techniques to treat rinse water for its recycle were discussed in order to evidence options and opportunities for developing better solutions, although due to the great variety of possible cases, the specific solution must be analyzed case by case. The necessity for more innovative technologies based on the use of catalysts was emphasized. Catalytic technologies for oxidation or for regeneration of exhausted adsorbants offer several opportunities to improve process economics and performances, but more systematic research is needed.

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