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Catalysis Today 53 (1999) 93–106

CATALYSIS TODAY

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Wastewater treatment: wet air oxidation as a precursor to biological treatment

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Abstract

The use of wet air oxidation as a pretreatment step in the context of an integrated chemical/biological process was investigated for model organic-containing wastewaters. It was found that the selection of suitable wastewaters and pretreatment conditions (i.e. temperature, residence time, use of catalysts) was significant for the effective application of an integrated process. For the systems under consideration, an integrated process was found to be advantageous for treating a polymer-containing wastewater, while mild wet air oxidation alone may suffice to treat a polyphenol-containing wastewater. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Biological oxidation; Heterogeneous catalysts; Integrated treatment; Polyethylene glycols; Polyphenols; Wastewaters; Wet air oxidation

1. Introduction

Many industrial, domestic and natural activities collectively result in the production of vast quantities of hazardous wastes, of which wastewaters comprise about 90%. It was estimated [1] that, in 1989, the US chemical industries alone generated nearly one billion metric tons of hazardous wastewaters which accounted for more than 99% of their annual waste production (including solid wastes and wastewaters). Given these large quantities of wastewater production, it is unsurprising that increasing environmental concerns have focused research on the development of efficient wastewater treatment technologies. The treatment and safe disposal of hazardous organic waste material in an environmentally acceptable manner and at a reasonable cost is a topic of great universal importance. There is little doubt that biological processes will continue to be employed as a baseline treatment process for most organic wastewaters, since they seem to fulfil the above two requirements. However, biological processes do not always give satisfactory results, especially applied to the treatment of industrial wastewaters, because many organic substances produced by the chemical and related industries are inhibitory, toxic or resistant to biological treatment. This is often due to the molecular structure of the substances, which may preclude biological attack due to the size or the shape of the molecule and its associated functional groups. Therefore, alternative technologies such as physico-

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0920-5861/99/$ – see front matter
PII: S0920-5861(99)00105-4

chemical and thermal oxidation processes may be the only viable options for decontaminating a biologically recalcitrant wastewater. However, a chemical oxidation method aiming at complete mineralisation might become extremely cost-intensive since the highly oxidised end-products which are formed during chemical oxidation tend to be refractory to further total oxidation by chemical means. Investment costs for biological processes may range from 5 to 20 times less than those of chemical processes such as ozonation or hydrogen peroxide oxidation, while treatment costs may range from 3 to 10 times less [2]. A comparison of wastewater treatment costs using wet air oxidation, incineration or sewer discharge treatment has been recently reported by Wigston [3]. To achieve 80% COD removal for a wastewater initially containing $50\,g\,l^{-1}$ of COD, treatment costs would be as much as 100–120, 40–50 and $10.5\,£\,t^{-1}$ for incineration, wet air oxidation and sewer discharge respectively.

A potentially attractive alternative to complete oxidation through chemical means would be the use of a chemical oxidation pretreatment step to convert initially biorecalcitrant organics to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biogas, biomass and water. A great deal of research into such integrated processes has been undertaken over the last 10–15 years. In several studies, aqueous solutions of various model organic compounds or actual wastewaters have been subjected to some form of chemical oxidation followed by biological oxidation and a review on this field has been recently published by Scott and Ollis [4]. A variety of chemical and biological processes have been employed in these studies. The chemical pretreatments include, among others, ozonation, UV irradiation, photocatalytic oxidation, hydrogen peroxide, electrochemical oxidation and wet air oxidation, while biological oxidation includes both aerobic and anaerobic, pure and mixed, acclimatised and non-acclimatised cultures. Measures of biodegradability range from simple lumped parameters such as total organic carbon (TOC) (or DOC: dissolved organic carbon), chemical oxygen demand (COD) and biological oxygen demand (BOD) to specific toxicity and biodegradability tests and rates of substrate removal.

Wet air oxidation or wet oxidation (WAO) refers to the aqueous phase oxidation of organics and oxidisable inorganic components at elevated temperatures and pressures using a gaseous source of oxygen (either pure oxygen or air) [5]. Elevated temperatures are required to increase the oxidation rate and enhance the solubility of oxygen in the aqueous solution, while elevated pressures are required to keep water in the liquid state. Water provides an excellent heat transfer medium which enables the process to be thermally self-sustained with relatively low organic feed concentrations. As the concentration of oxidisable organic material increases to roughly 4% [6], the process becomes thermally autogenous and further increases in concentration can lead to potential for energy recovery. From this point of view, WAO is ideally suited to wastewaters which are too dilute to incinerate and too toxic or concentrated for biological treatment [7]. According to Debellefontaine et al. [8], WAO would be suitable for wastewaters with COD loads from 10 to $100\,g\,l^{-1}$, while incineration would be suitable for effluents having a COD greater than about $100\,g\,l^{-1}$ and biological treatment would successfully treat non-toxic effluents with a COD of less than about $10\,g\,l^{-1}$.

An advantageous feature of the WAO process is that it creates minimal air pollution problems since contaminants tend to stay in the aqueous phase [9]. The small amount of gas that is discharged consists mainly of spent air or oxygen and carbon dioxide. Since the degree of oxidation is primarily a function of temperature, oxygen partial pressure and residence time, actual operating conditions depend on the treatment objectives. Typical conditions for total destruction of organics would start from 200°C temperature and 4 MPa pressure, while milder conditions would be necessary or the partial oxidation of organics. The main application of WAO is still the conditioning and/or destruction of waste activated sludge with more than 50% of the total number of WAO plants built being used for this purpose [10]. However, over the last several years, increased interest has been shown in the potential capability of WAO for treating wastewaters containing organic compounds which are not readily biodegradable, or which may be deleterious to biological treatment processes. WAO is usually an expensive process to install and operate because of the severe conditions required. High capital and operating costs are associated with the elevated pressures and temperatures employed, long residence times and use of construction

materials which should be resistant to the high corrosion rates occurring under severe operating conditions.

In this light, costs can be significantly reduced by the use of suitable catalysts capable of promoting the wet oxidation under milder operating conditions and shorter residence times. Another potential advantage of catalytic oxidation over the uncatalysed oxidation is that, in the context of an integrated chemical/biological treatment process, the use of a suitable catalyst might alter the selectivity of the uncatalysed oxidation towards the most readily biodegradable intermediates. The catalytic oxidation of organic compounds and organic-containing wastewaters over various homogeneous and heterogeneous catalysts has, therefore, received a lot of attention. Homogeneous catalysts (particularly copper salts) are in general more effective than heterogeneous oxidation catalysts [11–13] and several catalytic WAO treatment units based upon homogeneous catalytic systems (Cu, Fe, Cu–Mn–Fe, Fe/H_2O_2) are known to exist [14]. However homogeneous catalysts suffer from the drawback that their use necessitates a separation step such as precipitation to remove or recover the catalyst ions from the final effluent. In view of this, heterogeneous catalyst systems seem to be more promising for wastewater treatment processes. The development of active, stable and low-cost heterogeneous catalysts has received a great attention. The efficiency of several noble metals (including Pt, Pd, Ru, Rh and many more) and transition metal oxides (including Cu, Fe, Co, Mn, Ni, Sn and many more oxides in various combinations) for the WAO of various classes of organics has been demonstrated in many studies and a recent review on the heterogeneous catalytic WAO of organic pollutants has been presented by Levec and Pintar [15].

The aim of the work described in this paper is to develop a step by step rational methodology for treating organic-containing wastewaters. Such an approach would comprise three steps: (a) the selection of suitable model organic pollutants that are expected to exhibit different degrees of resistance towards chemical and biological oxidation, (b) the application of a chemical oxidation pretreatment process such as WAO with studies focusing on the use of various operating conditions, determination of key intermediates, elucidation of reaction kinetics and mechanisms, impact of pretreatment on biodegradability and (c) the design and operation of an effective integrated treatment process based on useful information obtained in the previous steps. Three case studies are presented to demonstrate the various steps used in this approach.

2. Experimental and analytical

2.1. WAO reactor

Aqueous solutions of model organic compounds were oxidised into a 300 ml stainless steel high pressure autoclave (Baskerville, UK) capable of performing batch or continuous experiments at pressures up to 10 MPa and temperatures up to 300°C. In a typical semibatch run, the aqueous solution of the organic compound was loaded to the autoclave which was then pressurised with nitrogen to the desired pressure. The solution was sparged with nitrogen to remove any traces of oxygen present in the autoclave, and then heated up with a 2 kW electric heater to the set temperature (under nitrogen) while stirring with a gas-inducing type impeller. Whenever a catalyst was used, it was introduced to the solution either in suspension (slurry) or in pellets; in the latter case a rotating basket attached to the impeller was used. As soon as the set temperature was achieved oxygen was continuously fed into the reactor at a flowrate of 1 l min^{-1} to start the reaction. Experiments were carried out at temperatures from 100 to 240°C and an oxygen partial pressure of 3 MPa. Liquid samples of approximately 3 ml were periodically drawn from the reactor through a gas sparge tube located at the bottom of the reactor during a brief shut-off of the gas feed. The liquid samples were then analysed with respect to their TOC and COD contents and the reaction intermediates which had formed during the oxidation.

2.2. Integrated WAO/biological oxidation

For integrated WAO and biological treatment experiments, continuous WAO of aqueous solutions of the organic compound was performed at 150°C and at a residence time of 30 min, with an oxygen partial pressure of 3 MPa. The feedstock was continuously fed from a 5 l feed tank to the reaction vessel through a high pressure diaphragm pump at a flowrate of 9.33 10^{-3} l min^{-1}, while oxygen was continuously sparged

at a flowrate of $1\,l\,min^{-1}$. The reactor contents were stirred through a gas-inducing type impeller at a stirring speed of 1100 rpm, while a 2 kW electric heater was used to heat the reaction vessel to the desired temperature. An adjustable liquid level conductivity probe was used to control the liquid volume in the reaction vessel (this was kept at 0.281) by opening an air actuated liquid outlet valve, and the discharged liquid was cooled down to ambient temperature, collected in a storage tank and subsequently fed to the bioreactor.

Continuous aerobic biological oxidation experiments using both original (unoxidised) solutions of the model organic compound and the wet oxidised solutions were performed simultaneously using two identical fermentation systems (New Brunswick Scientific, UK) at biological residence times varying between 12 and 96 h. The temperature in the bioreactors was held at 35°C, the pH at 7 ± 0.15 units (using 1 M solutions of H_2SO_4 or KOH), the liquid holdup at 1.8 ± 0.05 l, while laboratory air was continuously fed at a flowrate of $0.9\,l\,min^{-1}$ and the stirring speed was set to 210 rpm. A Watson Marlow multichannel pump (Model 205S, Watson Marlow, UK) was used to continuously feed and discharge the vessels, while organic feedstock and nutrient medium were fed to the bioreactors separately at equal flowrates. The experimental setup, procedures and the inoculum used in this study are described in detail elsewhere [16].

2.3. HPLC analysis

Reaction intermediates formed during the oxidation of the organic compound were identified and their concentration profiles were followed by high performance liquid chromatography (HPLC) with an ATI Unicam HPLC system. Different analytical methods were developed to analyse the various intermediates formed during the oxidation of various model organics. These methods are described in detail elsewhere [17].

2.4. Total organic carbon (TOC)

The degree of total oxidation to carbon dioxide that had occurred during WAO and biological oxidation runs was assessed by measuring the liquid phase total organic carbon content. TOC was measured with a Shimadzu 5050 TOC Analyser whose operation was based on combustion/non-dispersive infrared (NDIR) gas analysis. Total carbon (TC) was measured first followed by inorganic carbon (IC). The TOC was determined by subtracting IC from TC. The uncertainty in this assay, quoted as the relative standard deviation of three separate measurements, was never larger than 2% for the range of TOC concentrations measured.

2.5. Chemical oxygen demand (COD)

COD was determined by the dichromate method. The appropriate amount of sample was introduced into commercially available digestion solution (Hach Europe, Belgium) containing sulfuric acid, mercuric sulfate and chromic acid. The mixture was then incubated for 120 min at 150°C in a COD reactor (Model 45600-Hach Company, USA) and the COD concentration was measured colorimetrically using a DR/700 colorimeter (Camlab, UK). The average value of six separate readings was taken, and the deviation of them never exceeded 3% for the range of COD concentrations measured.

2.6. Atomic absorption spectroscopy

Leaching of heterogeneous catalysts in the reaction mixture was assessed by measuring the concentration of dissolved metal components with atomic absorption (Atomic Absorption Analyser-Model AA1106B, Perkin Elmer, UK). $1\,g\,l^{-1}$ atomic absorption standard solutions of the metals under consideration were provided (Aldrich, UK) and diluted to various concentrations with deionised water.

2.7. Biochemical methane potential (BMP)

Assessments of anaerobic biodegradability of aqueous solutions of organic compounds were performed using the BMP bioassay. Anaerobic serum bottles containing solutions under consideration, defined media and non-acclimatised anaerobic seed were incubated at 35°C and total gas evolution (i.e. CH_4 and CO_2) was monitored volumetrically using the syringe method. The procedures for sample preparation and gas evolution measurement are described in detail

elsewhere [18]. Blank samples (i.e. containing defined media and seed but without organic substrate) were also prepared and used as control samples. Samples of approximately 3 ml were also periodically drawn from the serum bottle, filtered and centrifuged to remove any solids present and then analysed with respect to dissolved total organic carbon concentration. All the samples were prepared in triplicate and the mean values of three measurements are quoted as results.

2.8. Biological oxygen demand (BOD_5-5 day)

Aerobic biodegradability was assessed by measuring the oxygen uptake by a given sample over a period of 5 days at 20°C, in the dark. Standard BOD_5 tests were carried out by WSP Laboratory (WSP Group plc, Nottingham, UK) using sludge from a local treatment plant. The analytical procedures followed to perform this assay were those described in the Methods for the Examination of Water and Associated Materials (1983).

2.9. Catalysts

Four metal oxide catalysts and five noble metal catalysts have been used in this study. (a) Metal oxides: (i) an iron oxide as FeO(OH) supplied by Aldrich, UK, (ii) a typical CuO·ZnO supported on Al_2O_3, as used for methanol synthesis, provided by ICI Katalco, UK in 5.6 mm pellets, (iii) a CuO·CoO·ZnO supported on Al_2O_3 (Cu/Zn:1.1/1, Cu/Co:6.2/1 molar ratio) supplied by Süd-Chemie AG, Germany, (iv) a Co/Bi composite oxide (Co/Bi:5/1 molar ratio) prepared by coprecipitation of the corresponding nitrate salts. (b) Noble metals: platinum (Pt), palladium (Pd), rhodium (Rh) and rhenium (Re) supplied by Aldrich, UK and ruthenium (Ru) supplied by Acros Chimica N.V., Belgium. In all these latter cases, the noble metal concentration was 0.5% w/w supported on alumina, and the catalysts were in the form of 3.2 mm pellets. The catalysts were crushed and sieved to produce particle sizes between 38 and 106 mm (used in slurry experiments), and were characterised with respect to their BET surface area by nitrogen adsorption.

3. Results and discussion

3.1. Case study A: pretreatment of a polyphenol-containing wastewater

p-Coumaric acid ($C_9H_8O_3$) was chosen as a representative model compound of the biologically recalcitrant polyphenolic fraction present in olive oil processing and wine distilleries wastewaters [19–20]. It belongs to a range of phenolic components comprising gallic, caffeic, gentisic and vanillic acids which are known to inhibit biological treatment of wastewaters from agricultural origin. In a recent study [21], the pretreatment of real olive oil wastewaters by WAO was studied and it was found that the poor biodegradability of the original wastewater (mainly due to the presence of polyphenols and tannins) was significantly improved after WAO pretreatment since the removal of the original inhibitors resulted in a more readily biodegradable mixture.

Aqueous solutions of *p*-coumaric acid of initial concentration of $0.75\,g\,l^{-1}$ (pH = 3.5) were subjected to semibatch WAO at temperatures from 100 to 155°C and an oxygen partial pressure of 3 MPa. To test if the oxidation of *p*-coumaric acid was limited by the amount of oxygen dissolved at 3 MPa oxygen partial pressure, experiments have been performed at 130°C and various oxygen partial pressures. These experiments showed that the reaction was not mass-transfer limited for oxygen pressures above 1.8 MPa since no change in either *p*-coumaric acid removal rate or TOC reduction rate was observed.

Fig. 1 shows the concentration-time profile for TOC and *p*-coumaric acid at 150°C and 130°C, where rapid conversion of *p*-coumaric acid to intermediate compounds occurs during the first minutes of oxidation, accompanied by a relatively small change in TOC. It can be seen that after 30 min at 150°C or 120 min at 130°C, about 80% of the *p*-coumaric acid has been oxidised, while only about 10% of the TOC has been removed.

Since conversion of *p*-coumaric acid alone might be the goal of the chemical oxidation stage of an integrated process it was, therefore, attempted to investigate the kinetics of the uncatalysed *p*-coumaric acid conversion in isolation:

$$p\text{-Coumaric acid} + bO_2 \rightarrow \text{Products}$$

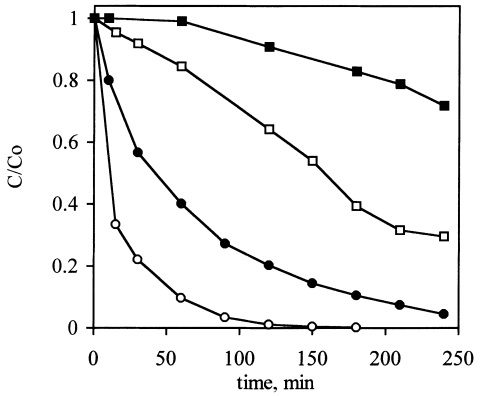

Fig. 1. Concentration profile of *p*-coumaric acid and TOC during the uncatalysed oxidation at various temperatures. -■- TOC at 130°C, -□- TOC at 150°C, -●- *p*-coumaric acid at 130°, -○- *p*-coumaric acid at 150°C.

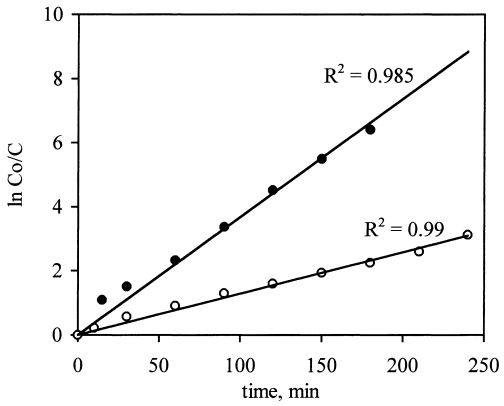

Fig. 2. First order kinetics with respect to *p*-coumaric acid concentration during the uncatalysed reaction. Plot of Eq. (1) -●- 150°C, -○- 130°C.

Since oxygen is in excess and assuming that the rate has a first order dependence on *p*-coumaric acid:

$$\ln\frac{Co}{C} = k_{app}t \quad (1)$$

where *C*o is the initial *p*-coumaric acid concentration, k_{app} is an apparent rate constant and *C* is the *p*-coumaric acid concentration at time *t*.

Fig. 2 shows the plot of Eq. (1) for the uncatalysed WAO of *p*-coumaric acid and the reaction does indeed appear to be first order with respect to *p*-coumaric acid concentration. This result agrees with the order of oxidation reactions for phenol and phenol-substituted

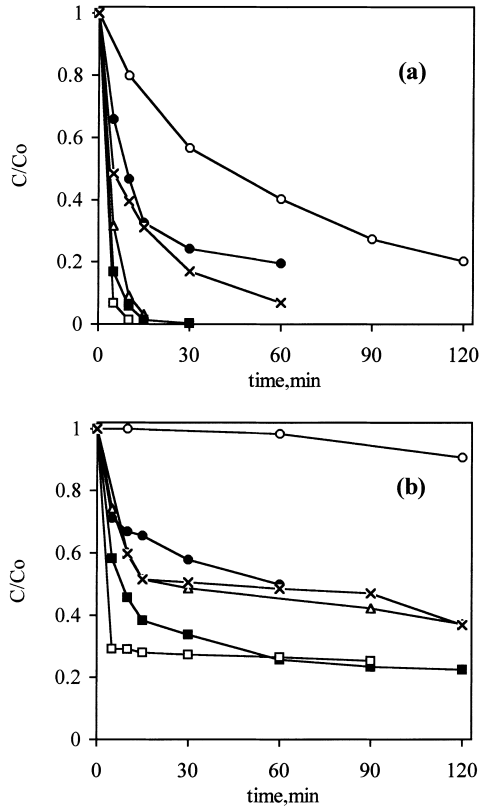

Fig. 3. Concentration profile of *p*-coumaric acid and TOC during oxidation at 130°C with various catalysts in slurry. (a): *p*-Coumaric acid, (b): TOC. -○- Uncatalysed, -●- FeO(OH), -×- Pt/Al, -△- CuO·CoO·ZnO/Al, -■- CuO·ZnO/Al, -□- Co/Bi.

compounds studied elsewhere [22–23]. The apparent rate constants are 3.7×10^{-2} and 1.3×10^{-2} min^{-1} at 150 and 130°C respectively.

Fig. 3 shows the concentration-time profile for *p*-coumaric acid and TOC at 130°C and the five catalysts in slurry, as well as for the corresponding uncatalysed reaction. Comparison of relative catalytic activity between the various catalysts used in slurry experiments was based on a common (BET surface area)/(liquid volume) ratio which ratio was about 4×10^5 m^2 m^{-3}. Co/Bi composite oxide seems to be the most effective for the oxidation of *p*-coumaric acid with almost total destruction achieved after 10 min of oxidation. CuO·CoO·ZnO/Al and CuO·ZnO/Al catalysts are of comparable activity to the Co/Bi oxide while Pt/Al and FeO(OH) give significantly lower oxidation rates. In all cases, however, the rate of

p-coumaric acid removal is significantly higher than that of the uncatalysed reaction. It can be also seen that catalysts are capable of significantly increasing the rate of the uncatalysed total oxidation (i.e. TOC removal). However, at the conditions under consideration, the rates of TOC removal are generally lower than those of *p*-coumaric acid removal presumably due to the presence of intermediates which are more difficult to oxidise than *p*-coumaric acid. Although Co/Bi seems to be the most effective catalyst with respect to *p*-coumaric acid oxidation, the possible leaching of cobalt, a toxic metal, into the treated effluents is undesirable, especially if a further biological treatment step is being considered, since dissolved cobalt could inhibit the microorganisms. From this point of view, more detailed studies have focused on the CuO·ZnO/Al which seems to be the most effective non-cobalt containing catalyst.

By means of HPLC, various compounds were detected during the course of *p*-coumaric acid oxidation (both uncatalysed and catalytic) which can be classified into two groups: (a) aromatic compounds, namely *p*-hydroxybenzaldehyde, *p*-hydroxybenzoic acid, *p*-(1-hydroxyethyl) phenol, *p*-hydroxybenzyl alcohol, hydroquinone and phenol and (b) ring cleavage products, namely oxaloacetic acid, oxalic acid and formic acid. The presence of such compounds in the reaction mixture implies that the conversion of *p*-coumaric acid proceeds through a series of oxidation, decarboxylation and ring-scission reactions.

In further investigations, experiments were performed with a CuO·ZnO/Al catalyst in form of 5.6 mm pellets (introduced in a rotating catalyst basket) and the results are compared to those of the corresponding slurry experiments where the same catalyst is used in form of 38–106 mm suspending particles. Fig. 4 shows the *p*-coumaric acid and TOC concentration profiles at 130°C with CuO·ZnO/Al in form of pellets as well as in form of 38–106 μm particles. It can be seen that the use of catalyst pellets results in *p*-coumaric acid and TOC removal rates which are lower than those obtained during slurry experiments; nevertheless almost complete removal of *p*-coumaric acid was recorded after 60 min of oxidation with CuO·ZnO/Al pellets. These decreased rates observed during the catalyst basket experiments may be due to the intraparticle mass limitations within the catalyst pellets, as well as external transfer limitations introduced by the use of the catalyst basket.

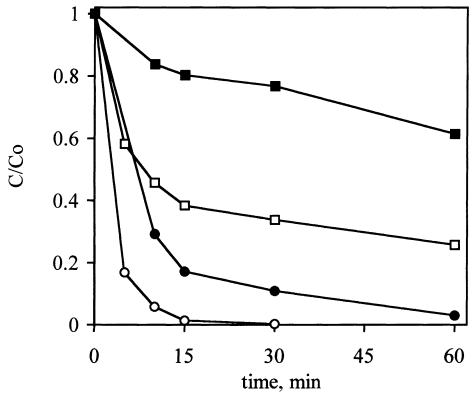

Fig. 4. Concentration profile of *p*-coumaric acid and TOC during slurry and catalyst basket experiments with CuO·ZnO/Al at 130 °C. -■- TOC-basket , -□- TOC-slurry, -●- *p*-coumaric acid-basket, -○- *p*-coumaric acid-slurry.

In further experiments, the stability of the CuO·ZnO/Al catalyst was studied with respect to metal leaching. Catalyst leaching is important for three reasons: (a) an additional treatment step, such as membrane separation or precipitation may be necessary to remove any leached catalyst from the treated effluent especially if a further biological treatment process is to be used, (b) continuous leaching would lead progressively to the deactivation of the heterogeneous catalyst and (c) since homogeneous catalysts, i.e. Cu^{2+}, are known to be effective catalysts for liquid-phase oxidation, dissolved metal ions must be responsible for homogeneously catalysed reactions and a homogeneous-heterogeneous reaction system should be considered rather than a purely heterogeneous reaction.

Samples were withdrawn after 60 min of oxidation at various temperatures (from 100 to 130°C) and catalyst concentrations (from 0.088 to 4.4 g l^{-1}) in slurry, and the concentration of dissolved Cu, Zn and Al metals were measured using atomic absorption. To study the impact of pH on the leaching of the catalyst, experiments were also performed under neutral and alkaline conditions by adjusting the initial pH of *p*-coumaric acid solution to 7 and 12 with NaOH. It was found that neither copper nor zinc leach significantly under alkaline conditions (i.e. pH > 9) while rather high concentrations of dissolved aluminum have been detected

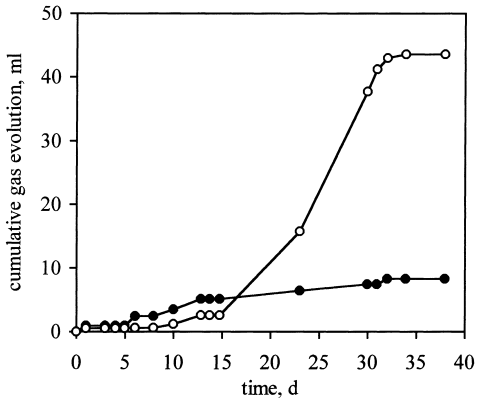

Fig. 5. Cumulative gas evolution during the BMP test. -○- *p*-coumaric acid, -●- control.

under these conditions. Conversely, dissolved copper and zinc have been detected at acidic or even neutral pH values while aluminum remains undissolved. Temperature seems to enhance the extent of metal leaching since when the catalyst was simply introduced in the *p*-coumaric acid solution at pH 3.5, 7 and 12 and ambient temperature, no leaching occurred.

The anaerobic biodegradability of *p*-coumaric acid was assessed using the BMP test. 50 ml of a *p*-coumaric acid solution (initial concentration of $0.74\,g\,l^{-1}$) were mixed with 50 ml of inoculum and total gas evolution was measured volumetrically using the syringe method. Blank samples (i.e. containing defined media and seed but not organic substrate) were also prepared and used as control samples, while all samples were run in triplicate and the mean values of three measurements are quoted as results. Fig. 5 shows the cumulative gas evolution for *p*-coumaric acid and control solutions during the BMP test. It can be seen that biodegradation of *p*-coumaric acid occurs after a 2-week lag-phase during which no gas evolution was observed. After this lag-phase, gas has been produced for the next 20 days and a cumulative gas volume of about 45 ml was measured after a total time of 34 days (including the lag-phase period). At the end of the test (Day 38), liquid samples were taken, filtered with a 0.45 μm disposable filter and analysed with respect to their dissolved TOC content. It was found that 96% TOC removal had occurred for *p*-coumaric acid solution which implies that degradation of *p*-coumaric acid was nearly complete.

Table 1
WAO pretreatment of *p*-coumaric acid

Run no	Temperature (°C)	Time (min)	TOC_{final} (ppm)	COD_{final} (ppm)
1[a]	–	–	494	1330
2	133	60	449.8	1214
3	153	30	436.9	1168
4	155	90	252.6	531.5

[a] Original *p*-coumaric acid solution.

In further experiments, *p*-coumaric solutions were subjected to uncatalysed WAO and the anaerobic biodegradability of the oxidised solutions were assessed using the BMP test. The WAO conditions as well as the final TOC and COD values of the solutions are given in Table 1. Oxidation runs were performed at temperatures from 133 to 155°C and reaction times from 30 to 90 min and the oxidised samples were analysed with respect to their TOC and COD content. Oxidation at 133°C for 60 min and at 153°C for 30 min (runs 2 and 3 respectively) resulted in almost similar TOC and COD reductions, while significant TOC and COD reductions (of about 50 and 60% respectively) were only noted after longer reaction times (run 4).

All the oxidised solutions as well as the original were then neutralised with a measured volume of 1 M NaOH solution to bring the pH to 7.3. 70 ml of each solution were then mixed with 50 ml of inoculum and placed into serum bottles, while all the samples were run in triplicate and mean values are quoted as results. At Days 10 and 38 of anaerobic digestion, liquid samples of approximately 3 ml were withdrawn using a needle which was inserted into the serum bottles. The samples were then filtered with a 0.45 μm disposable filter and analysed with respect to their dissolved TOC content to assess the degree of TOC removal that had occurred during anaerobic digestion. Gas evolution, although not measured daily, was periodically monitored. Fig. 6 shows the mean TOC content for all the samples after 10 and 38 days of digestion. It can be seen that after 10 days of digestion TOC remained nearly unchanged for the original *p*-coumaric acid solution and this was due to the 2-week lag-phase observed in earlier experiments. Very little TOC reduction was observed for runs 2 and 3, while a more pronounced TOC reduction was observed for run 4. However, after 38 days of digestion nearly complete TOC

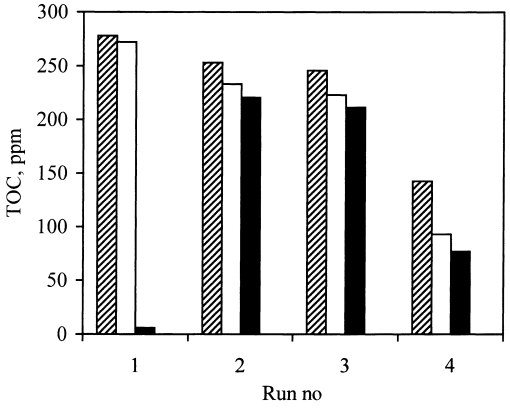

Fig. 6. TOC values during the anaerobic digestion of wet oxidised *p*-coumaric acid solutions. Grid: After inoculation, White: Day 10, Black: Day 38. (Run nos as described in Table 1).

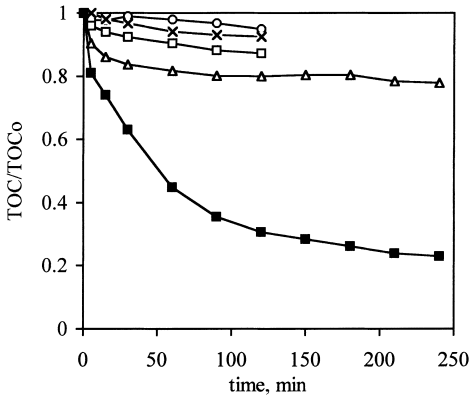

Fig. 7. TOC profile during the oxidation of PEG 10,000 at various temperatures. -○- 110°C, -×- 130°C, -□- 150°C, -△- 190°C, -■- 240°C.

removal was observed for the original *p*-coumaric acid solution, while significant amounts of organic carbon still remained in any of the samples corresponding to runs 2 to 4. These results suggest that, for the conditions under consideration, WAO results in solutions which are, in general, less readily degradable (anaerobically) than the original *p*-coumaric acid solution. Although some of the intermediates formed during WAO may be anaerobically degradable at shorter digestion times than *p*-coumaric acid, the latter is more readily degradable at longer digestion times than the oxidised solutions. (To add to the findings obtained from TOC measurements, it was also observed that the oxidised solutions retained some of their colour after 38 days of digestion.) It is also notable that samples from runs 2 and 3 exhibited a similar behaviour during the BMP test and this is not surprising since runs 2 and 3 resulted in oxidised solutions which, in terms of TOC and COD removal (see also Table 1), were comparable to each other. However, more detailed studies should be needed to investigate the influence of the intermediates on the anaerobic biodegradability of the wet oxidised solutions and identify those that may be responsible for introducing toxic and/or inhibitory effects. Since many of those intermediates formed during WAO of *p*-coumaric acid have been successfully determined, further anaerobic tests should be performed with solutions containing either each known individual intermediate or synthetic mixtures of these intermediates that simulate the wet oxidised effluents. Provided that such tests would reveal the identity of those intermediate compounds which are not readily degradable, suitable WAO conditions should be selected to remove them prior any further biological treatment. However, the possibility that some unknown intermediates formed during wet oxidation may be also toxic and/or inhibitory cannot be disregarded.

3.2. Case study B: pretreatment of a polymer-containing wastewater

Polyethylene glycols (PEG: $OH(CH_2CH_2O)_nH$) are an important group of nonionic synthetic water-soluble polymers commonly used in the production of surfactants, lubricants, pharmaceuticals, antifreezes etc. Several studies have been performed on the biodegradability of various molecular weight (MW) PEGs [24–26] and showed that although even high MW PEGs may be to some extent amenable to biodegradation, the rate of biodegradation substantially decreases with increasing MW, making thus high MW polymers practically non-biodegradable. Therefore, PEG of MW 10,000 has been chosen as a model polymer to be studied.

Aqueous solutions of PEG 10,000 of initial concentration of $1\,g\,l^{-1}$ (pH = 6.8) were subjected to semi-batch WAO at temperatures from 110 to 240°C and an oxygen partial pressure of 3 MPa. Fig. 7 shows the concentration-time profile for TOC during the oxidation of PEG 10,000 at five temperatures. It can be seen that for temperatures from 110 to 190°C, the rate of TOC removal is slow throughout the reaction, with

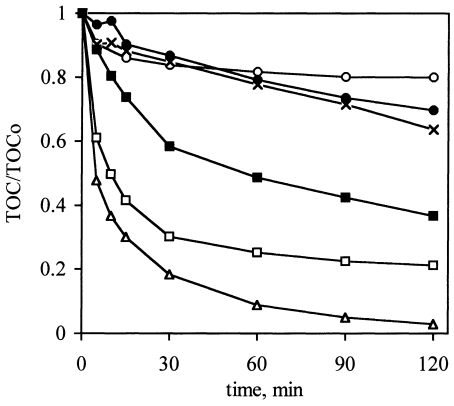

Fig. 8. TOC profile during the oxidation of PEG 10,000 at 190°C and various catalysts in slurry. -○- Uncatalysed, -●- CuO·CoO·ZnO/Al, -×- CuO·ZnO/Al, -■- FeO(OH), -□- Pd/Al, -△- Pt/Al.

only about 20% of the organic content totally oxidised to carbon dioxide after 240 min at 190°C, while almost no total oxidation is observed after 120 min at 110°C; these results imply the presence in the reaction mixture of compounds which are resistant to total oxidation. Conversely, at 240°C the rate of TOC removal increases significantly and almost 80% TOC reduction is achieved after 240 min. However, chromatographic analysis showed that PEG can be fragmented to lower MW compounds even under mild operating conditions. For instance after 5 min at 150°C the original PEG 10,000 was nearly completely converted to lower MW compounds, while only polymeric fractions not larger than about 300 were present in the reaction mixture after 5 min at 190 or 240°C. After 30 min of oxidation no PEG 10,000 was detected at any temperature above 110°C, while only at 110°C some of the original PEG 10,000 still remained in the reaction mixture. These results show the ease with which the original PEG 10,000 can be broken down to its oligomeric fractions and possibly other non-polymeric compounds due to free radical chain mechanisms that are thought to govern thermal oxidation reactions. Chromatographic analysis also showed that formic acid and ethylene glycol were the dominant (in terms of concentration) intermediates detected, while other intermediates (mainly short organic acids) were found in lower concentrations.

Fig. 8 shows the rate of TOC removal during the oxidation of PEG at 190°C with five different catalysts in slurry. Comparison of their relative catalytic activity was based on a common (BET surface area)/(liquid volume) ratio which ratio was about $2 \times 10^5\ m^2\ m^{-3}$. 80 and 97% TOC removals were achieved after 30 and 120 min of oxidation respectively using the Pt/Al catalyst, while less than 20% TOC removal was observed during the uncatalysed run after 120 min. The Pd/Al catalyst resulted in almost 80% TOC removal after 120 min of oxidation. The metal oxide catalysts give rates of TOC removal which are significantly lower than those of the noble metal catalysts. FeO(OH) is of moderate activity, while CuO·ZnO/Al and CuO·CoO·ZnO/Al give rates of TOC removal which are comparable to that of the uncatalysed reaction.

The introduction of a heterogeneous catalyst in the reaction mixture introduces a catalytic cycle through the following reduction-oxidation homolytic reactions of the hydroperoxides (ROOH) that are formed during free radical chain mechanisms [27]:

$$\mathrm{ROOH} + \mathrm{Me}^{(n-1)+} \rightarrow \mathrm{RO}^{\bullet} + \mathrm{Me}^{n+} + \mathrm{OH}^{-} \quad \text{reduction} \tag{2}$$

$$\mathrm{ROOH} + \mathrm{Me}^{n+} \rightarrow \mathrm{ROO}^{\bullet} + \mathrm{Me}^{(n-1)+} + \mathrm{H}^{+} \quad \text{oxidation} \tag{3}$$

The catalyst enhances both propagation through the formation of alkyl peroxy radicals (reaction 3) and decomposition of the hydroperoxides (reaction 2). The effectiveness of the catalyst to promote the oxidation according to reactions (2) and (3) is closely linked to the redox potential of the $Me^{n+}/Me^{(n-1)+}$ couple. Since hydroperoxides are strong oxidants but weak reducing agents, reaction (2) is usually faster than reaction (3) and this is also the case when the metal catalyst is a strong reducing agent. This can apply in the case of FeO(OH) where Fe^{+2} can reduce hydroperoxides resulting in formation of $Fe^{+3}$with regeneration of Fe^{+2} proceeding through reaction (3). Conversely, the fact that the CuO·ZnO/Al and CuO·CoO·ZnO/Al catalysts (where CuO is the main component) exhibited a rather poor catalytic activity can be explained by the fact that Cu is already in its highest oxidation state (+2) and reaction (2) is not favoured while regeneration of Cu^{+1} through reaction (3) is rather unlikely to occur since the redox potential of Cu^{+2}/Cu^{+1} in

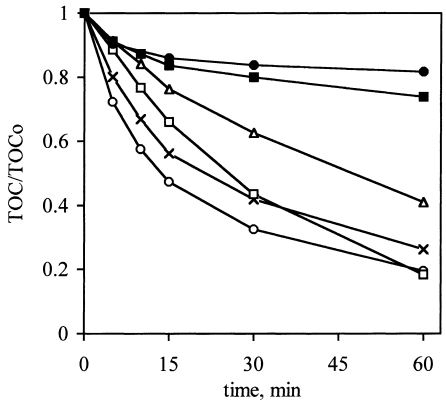

Fig. 9. TOC profile during the oxidation of PEG 10,000 at 190°C with various noble metal catalysts in pellets. -●- Uncatalysed, -■- Re/Al, -△- Rh/Al, -□- Ru/Al, -×- Pt/Al, -○- Pd/Al.

aqueous solution is only 0.15 V – this value is much lower than the redox potential of Fe^{+3}/Fe^{+2} which is 0.77 V [27]. (Although Co^{+3}/Co^{+2} redox potential in aqueous solution is 1.82 V [27], which indicates that CuO·CoO·ZnO/Al should be an effective catalyst, there are relatively few available cobalt sites since the cobalt loading is a factor of 6.2 lower than copper loading.)

In the case of noble metal catalysts, an additional catalytic effect can be introduced due to the ability of these catalysts to perform oxidative addition reactions and insertion reactions and consequently activate the substrate by coordination. This requires the noble metal to be initially in a low oxidation and coordination state to coordinate with the substrate. For noble metals used in this study, the easy transition of Me^0 to higher coordination and oxidation numbers (e.g. from Me^0 to Me^{II} to Me^{IV}) allows the formation of Me-complexes which further promote the oxidation reactions. The superiority of the noble metal catalysts over the metal oxide catalysts used in this study, may be explained by the fact that the transition metal oxides are more stable than the oxides of the noble metals and it is generally accepted that, in this respect, noble metals can be regarded as more effective total oxidation catalysts [28]. Vinke et al. [29] also reported that noble metal catalysts are very effective catalysts for the oxidation of nonionic compounds.

Fig. 9 shows the rate of TOC removal for the oxidation of PEG at 190°C and five noble metal catalysts in the form of pellets. Comparison of their catalytic activity was based on a common (mass of active phase)/(liquid volume) ratio equal to 18.5 g m^{-3}. It can be seen that Pd/Al, Pt/Al and Ru/Al are effective at removing TOC, Rh/Al exhibits a moderate activity while Re/Al is the least active resulting in rates of TOC removal which are not significantly higher than that of the uncatalysed reaction. The fact that Re/Al was supplied and used in an unreduced form may explain its rather low catalytic activity shown in Fig. 9 since rhenium oxides originally present in the catalyst may not favour either the redox activity or the coordination ability of this catalyst.

Improvements in aerobic biodegradability of PEG 10,000 after uncatalysed WAO have been assessed by measuring the BOD_5/COD ratio and comparing the values for the treated samples to those of the original solutions. Table 2 shows the individual BOD_5 and COD values, the BOD_5/COD ratio and the percentage TOC removal for the PEG 10,000 after oxidation at five temperatures and two reaction times. It can be seen that the BOD_5/COD ratio of the original PEG 10,000 solution increases after the oxidation over almost the whole range of experimental conditions shown in Table 2. This increase seems to be due both to a BOD increase and a COD reduction. This is most pronounced at 240°C where the BOD_5 value increases by as much as 100 times and the COD value decreases by as much as 4 times after 120 min of oxidation, while 69.5% TOC removal is achieved by the same time. Even after 30 min of oxidation at 130°C (where little TOC removal (3.4%) is observed) the BOD_5/COD ratio still increases by as much as three times relative to that of the original solution. However, in most cases the individual BOD_5 values increase only by about 2–3 times the value of the original solution. It is also important to notice that the BOD_5/COD ratios after 30 min of oxidation are higher than those at 120 min for all the experiments from 190 to 130°C. Although COD decreased with the reaction time from 30 min to 120 min, BOD was also found to decrease by such an extent so as to result in lower BOD_5/COD ratios. This might be so because as the oxidation proceeds, highly oxidised compounds, such as the short-chain acids, are formed and they either possess less metabolic value or act as inhibitors for the microorganisms used in the BOD test [4]. Suzuki et al. [30] found that the ozonation and subsequent fragmentation of PEG 8000 was accompanied by the formation of formaldehyde, the presence

Table 2
BOD_5, COD, BOD_5/COD ratio and TOC removal during the oxidation of PEG 10,000 at various temperatures and reaction times

	240°C	190°C	150°C	130°C	110°C
$BOD_{5-0\,min}$	1.4	1.4	1.4	1.4	1.4
$COD_{0\,min}$	1856	1856	1856	1856	1856
$100 \times BOD_5/COD_{0\,min}$	0.075	0.075	0.075	0.075	0.075
$BOD_{5-30\,min}$	3.0	3.0	8.0	3.5	1.2
$COD_{30\,min}$	696	1035	1182	1439	1785
$100 \times BOD_5/COD_{30\,min}$	0.43	0.29	0.68	0.24	0.067
$\%(1 - TOC/TOC_o)_{30\,min}$	42.0	16.2	11.5	3.4	2.3
$BOD_{5-120\,min}$	127	1.4	3.0	2.5	1.4
$COD_{120\,min}$	427	981	1074	1244	1453
$100 \times BOD_5/COD_{120\,min}$	29.7	0.14	0.28	0.20	0.10
$\%(1 - TOC/TOC_o)_{120\,min}$	69.5	19.0	15.7	11.0	6.2

of which inhibited the biodegradation of the mixture. The drawbacks of using BOD for assessing the aerobic biodegradability of organics have been recognised since the early fifties [31–33]. The limitations of the BOD test arise mainly from the fact that the microorganisms may not be adapted to utilise the organics present, while the rate of biodegradation also appears to vary with concentration.

3.3. Case study C: integrated treatment of a PEG 10,000-containing wastewater

Continuous uncatalysed WAO of PEG 10,000 was performed at a temperature of 150°C and a residence time of 30 min; under these WAO conditions only about 7% TOC removal occurred. These conditions were chosen since from previous semibatch experiments it is known that a temperature of 150°C and a reasonable residence time of 30 min results in significant polymer fragmentation. Although the reactor was operated in continuous mode, which would alter the distribution of intermediates relative to the semibatch case, similar conditions were employed as an approximation. Both the wet oxidised and the unoxidised solutions of PEG 10,000 were then inoculated and subjected to batch aerobic oxidation for about 310 h to allow the culture to adapt to the organic feedstock. At the end of this acclimation experiment 70 and 45% TOC removal occurred for the oxidised and unoxidised solutions respectively.

After this acclimation period, both the wet oxidised and the unoxidised solutions were subjected to continuous aerobic oxidation at biological residence times (τ_b) from 12 to 96 h and the results are summarised in Table 3. (TOC values are averaged during steady state biological oxidation at any given τ_b and mean values are quoted as results). The results clearly show that WAO of PEG 10,000 at mild operating conditions (30 min at 150°C) can drastically improve the aerobic biotreatability of the original solution. At residence times (τ_b) as low as 12 h, an 80% TOC removal could be achieved during the aerobic oxidation of the wet oxidised solution, while the original solution could not be practically biodegraded under these conditions. Even at residence times as high as 96 h, the biodegradation rate of the oxidised solution was clearly higher than that of the original solution.

Therefore, a two-step process comprising a short WAO step followed by aerobic treatment may reduce the reactor space time required to treat PEG 10,000 by at least an order of magnitude. For instance, an overall 80% TOC removal could be achieved whenever WAO was coupled with a 12 h residence time subsequent biological treatment, while only about 60–70% TOC removal could be achieved after a 96 h residence time direct biological treatment.

4. Conclusions

Integration of chemical and biological processes can provide economically viable and environmentally friendly wastewater treatment options for purifying wastewaters that are not readily biodegradable. An efficient integrated chemical/biological process would consist of a brief chemical pretreatment step to

Table 3
Mean TOC removal during integrated WAO/biological treatment of PEG 10,000. TOCo (as fed in the WAO reactor) = 550 ± 7 ppm. WAO conditions: 30 min at 150°C

Biological residence time, τ_b (h)	TOC after WAO (ppm)	TOC after biological oxidation (ppm)	Overall TOC removal for integrated treatment (%)
0	514.5	–	6.8
12	512	109 ± 5	80.3 ± 0.8
12	–	526 ± 8	4.8 ± 1.4
48	511.6	48 ± 7	91.2 ± 1.3
48	–	353 ± 70	35.3 ± 12.9
96	518.7	36 ± 5	93.5 ± 0.8
96	–	179 ± 28	67.9 ± 5

convert initially bioresistant compounds to more readily biodegradable intermediates, followed by a subsequent biological process. Studies on the properties of the pretreated effluent are important since these properties may play a key role in the efficiency of an integrated process, provide insight into the exploitable synergisms obtained by process integration and allow a rational approach to be followed in process design. In this context, the WAO of two model organic compounds, namely *p*-coumaric acid and polyethylene glycol that are typically found in wastewaters of agricultural origin and from polymer manufacturing respectively was investigated. The successful operation of a continuous integrated WAO/aerobic process to treat polyethylene glycol was also demonstrated in this study.

p-Coumaric acid can be easily oxidised even under mild operating conditions to various aromatic and aliphatic intermediates through a series of oxidation, decarboxylation and ring-scission reactions. WAO reactions are generally thought to be governed by free radical mechanisms. Such mechanisms were found capable of rapidly fragmenting polyethylene glycol to lower molecular weight compounds such as oligomers and short-chain acids within very short reaction times and at relatively low temperatures. These compounds were found to be refractory to further total oxidation even under severe operating conditions.

Catalysis may also play an important role in WAO processes promoting reactions under milder operating conditions and shorter residence times. Several heterogeneous catalysts, including metal oxides and noble metals, were used in this study and it was found that they were generally capable of increasing the rates of the corresponding uncatalysed total oxidation. However, in the context of an integrated process where the role of wet oxidation pretreatment would be the conversion of original compounds to intermediates rather than complete mineralisation, the use of heterogeneous catalysts (although offering improved total oxidation rates) may be detrimental to the efficacy of the subsequent biological step. Taking also into account potential drawbacks associated with the use of heterogeneous catalysts, such as catalyst stability and deactivation, toxicity of leached metals, need of additional process steps to recycle or remove the catalysts, their use should be critically examined.

An integrated process comprising a short WAO step under mild operating conditions followed by continuous aerobic oxidation was setup and operated to treat PEG of 10,000 MW. Although PEG 10,000 was found to be biodegradable at the conditions under consideration, WAO pretreatment resulted in effluents whose biodegradation rates were significantly higher than that of the original polymer. Lower molecular weight compounds, such as oligomers and short-chain acids that accompany the rapid fragmentation of the original polymer and are highly resistant to further total oxidation, seem to be more readily biodegradable than the original polymer. Therefore, the fragmentation of high molecular weight polymers to lower molecular weight compounds would be an important consideration in deciding when biological oxidation should commence within the context of an integrated process. The beneficial effects arising from the integrated process can be summarised by the fact that the overall reactor space time required during integrated treatment is almost an order of magnitude less than that for a direct biological treatment of PEG 10,000, thus making the integrated process an attractive option to treat waste-

waters containing such polymers. Although an integrated process was not established in the case of *p*-coumaric acid, an attempt was made to assess the effect of WAO on anaerobic biodegradability of the oxidised solution by means of simple anaerobic tests. Anaerobic biodegradability tests using non-acclimatised microorganisms showed that *p*-coumaric acid was more readily degradable than its wet oxidised solutions under the conditions employed in this study. Although this result may suggest that an integrated process may not be a useful option for treating *p*-coumaric acid-containing wastewaters, more evidence is required to support this argument. Further investigations would probably involve the use of acclimatised cultures, aerobic conditions and different WAO conditions.

Acknowledgements

The authors wish to thank the Commission of the European Communities for the financial support of this work under grant n° EV5V-CT93-0249.

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