



# PROCESSES FOR THE REMOVAL OF RECALCITRANT ORGANICS FROM INDUSTRIAL WASTEWATERS

H. Gulyas

*Technical University of Hamburg-Harburg, Arbeitsbereich  
 Gewässerreinigungstechnik, Eissendorfer Str. 42, D-21073 Hamburg, Germany*

## ABSTRACT

Processes that are suitable for the elimination of recalcitrant organics from industrial wastewaters are reviewed. Most advantageous are separation processes which enable not only reuse of the water phase but also the recycling of the wastewater constituents. Besides separation processes many degradative wastewater techniques are available. However, for the removal of recalcitrant organics biological processes (which are economically beneficial) cannot be chosen, but a variety of nonbiological degradative processes exist which can be divided into oxidative and reductive technologies. The latter are in the research and development state. The chemical oxidative treatment technologies comprise wastewater incineration and wet air oxidation for wastewaters with high organic concentrations, the so-called advanced oxidation processes (AOPs) as e.g. ozone/hydrogen peroxide which generate the nonselective but very powerful oxidant OH radical, and processes with other oxidants as e.g. Fe(VI) compounds or peroxodisulfate. Also electrochemical oxidation of organic wastewater constituents is possible. All degradative processes that do not lead to total mineralization of organic wastewater constituents may form transformation products which sometimes are more toxic than the original organic compounds.

© 1997 IAWQ. Published by Elsevier Science Ltd

## KEYWORDS

Chemical oxidation processes; industrial wastewater; organic wastewater constituents; recalcitrance; wastewater treatment

## INTRODUCTION

Organic constituents of industrial wastewaters which are not biodegradable may enter drinking water by the path sewer/river/river bank filtrate. They also can be incorporated by humans by consumption of aquatic animals. Because of the possibility of adverse effects of organics originating from industrial wastewaters towards human health (which are often unknown) refractory organics also have to be carefully removed.

Wastewater treatment processes for the removal of organics can be divided into four groups: separation processes (concentration of the organics without chemical alteration), degradative processes (oxidative processes intended to mineralize organics to form CO<sub>2</sub>), and processes that chemically modify wastewater constituents but do not lead to mineralization (reductive processes e.g. for dehalogenation). A fourth group is the preparation of wastewaters by the addition of certain chemicals for subsequent treatment by separation or degradation processes: breaking of emulsions, flocculation, precipitation, or pH adjustment.

Different wastewater treatment processes refer to different selectivities concerning the removal of organics, e.g. particle-bound or dissolved, volatile or nonvolatile, hydrophobic or hydrophilic organics. Some

processes are more suitable to eliminate highly concentrated organics (e.g. wastewater incineration or wet air oxidation), whereas others work more economically (and ecologically) if the concentrations of the organics are low (e.g. ozonation). Some of the processes are not very widespread, and some are still in the state of research and development (e.g. freeze concentration and electrochemical reduction).

In fig. 1 strategies for the choice of appropriate treatment processes for the removal of organics from industrial wastewaters are outlined. Reuse of water as well as recycling of wastewater constituents to production processes should be of highest priority when wastewater treatment processes are selected. These aims of pollution prevention technologies can be met by the application of suitable separation processes. Of course, pollution prevention technologies are ecologically beneficial, but the economic benefits are often underestimated. A very important advantage of the application of separation processes with recycling of organic wastewater constituents is the lack of production of the greenhouse gas CO<sub>2</sub> which is immanent in total mineralization of organic compounds.

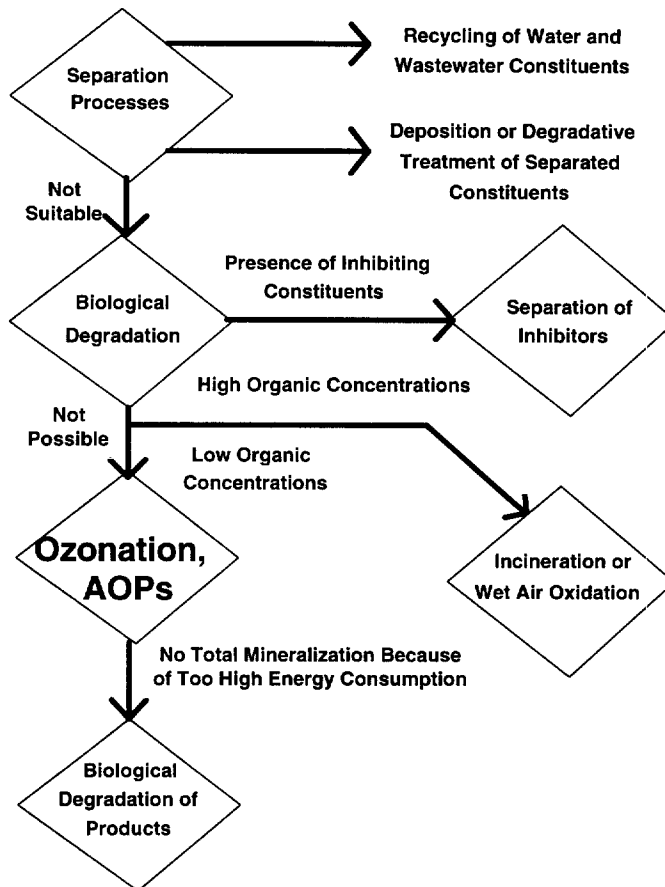


Fig. 1. Decision Strategies for the Choice of Industrial Wastewater Treatment Processes

If recycling of water and/or wastewater constituents is not suitable for any reason, biological processes are preferred to remove organics from wastewater because of low costs compared to other processes. However, degradable organic wastewater constituents normally lead to high production of biological sludges which have to be treated or deposited. If the main part of the organics cannot be degraded by microorganisms,

biological processes are not suitable, of course. On the other hand, if only a small part of the organics is not biodegradable, these substances may be efficiently sorbed to the microorganisms (if their polarity is not too high) and eliminated from wastewater by excess sludge removal.

In the case of generally biodegradable organics which cannot be mineralized because of the presence of inhibiting wastewater constituents (e.g. heavy metals) the inhibitors can be removed prior to biological treatment (e.g. by heavy metal precipitation).

For the removal of refractory organics non-biological degradation processes must be applied if separation processes are unsuitable or not desired (e.g. because of high costs for deposition of separated organics and other wastewater constituents). Wastewaters with high concentrations of recalcitrant organics can be incinerated or purified by wet air oxidation. Both use oxygen as oxidant at elevated temperatures.

Advanced oxidation processes (AOPs, see table 1) and ozonation are economically (and ecologically) unsuitable for wastewaters containing high concentrations of organic constituents, because the consumption of oxidants for total mineralization (e.g. ozone the production of which requires high amounts of energy) is increased with increasing contents of organics. Therefore, AOPs can be used to transform recalcitrant organic wastewater constituents to biodegradable compounds rather than to mineralize them. Then the oxidant consumption is markedly decreased, but a biological stage following the AOP stage is required. However, oxidant doses for optimum biodegradation of the transformed products have to be determined carefully, because too high oxidant doses may even decrease biodegradability (Jones *et al.* 1985).

## SEPARATION PROCESSES

Separation processes suitable for wastewater treatment comprise solid/liquid separation processes (sedimentation, hydrocyclone, centrifugation, flotation, filtration, microfiltration, ultrafiltration), coalescence separation, reverse osmosis, adsorption, extraction and pertraction, stripping, pervaporation, distillation, wastewater evaporation, ion exchange, and freeze concentration.

The separation processes do not distinguish between recalcitrant and biodegradable organic compounds, but different separation processes exhibit different removal selectivities for organics. Reverse osmosis and freeze concentration are rather unselective. Wastewater evaporation separates only non-volatiles while stripping (selective for compounds with high Henry constants), pervaporation and distillation (selective for compounds with low boiling points) are suitable for the removal of volatiles. Extraction and pertraction are selective for compounds with high extractant/water partition coefficients. Activated carbon adsorption is generally limited to the removal of nonpolar substances depending on ash content of the activated carbon (Diamadopoulos *et al.* 1992), while ion exchangers can be used for the separation of organics which dissociate into ions (depending on pH).

## RECALCITRANCE OF ORGANICS

The causes of recalcitrance, i.e. the "ability of a substance to remain in a particular environment in an unchanged form", were reviewed by Fewson (1988). Besides wrong conditions of biological wastewater treatment processes (unsuitable pH, temperature etc.) two important reasons for the recalcitrance of organic wastewater constituents exist: a) There are no enzymes available in the biocenosis used for biological wastewater treatment which are suitable for the degradation of the concerning organics. b) The organics can generally be degraded, but the wastewater contains (organic or inorganic) substances that severely inhibit the biocenosis or are toxic towards microorganisms.

In the first case biological treatment is possible for removing the biodegradable portion of organics, but the recalcitrant organics occur in the effluent of the biological wastewater treatment facility as a residual COD. Depending on their quantity and their ecotoxicological behaviour the recalcitrant organics sometimes have

to be removed by additional treatment. In the second case biological treatment is impossible (except dilution of the influent by recirculating the treated effluent or separation of inhibitory or toxic substances before biological treatment). It has to be kept in mind that effluents of biological stages always contain residual concentrations of refractory organics, as high molecular weight compounds - often referred to as humic substances - are formed by microorganisms even from readily biodegradable organic compounds (Hejzlar and Chudoba 1986). These compounds often are inhibitory towards biological processes (Chudoba 1985).

## CHEMICAL OXIDATION PROCESSES

Aerobic biological oxidation belongs to the group of oxidative degradative wastewater treatment processes which also comprise the non-biological processes wastewater incineration, wet air oxidation (using air as oxidant at high pressures of 10 to 220 bar and temperatures between 150°C and the critical temperature of water, 374.2°C), a couple of processes generating OH radicals at normal temperatures (table 1), anodic oxidation, oxidation with peroxodisulfate, and treatment with metal compounds in high oxidation states ( $\text{KMnO}_4$ ,  $\text{K}_2\text{FeO}_4$ ).

Wastewater incineration and wet air oxidation are suitable for wastewaters with high concentrations of organic wastewater constituents. The incineration of wastewaters with a COD below 50 to 100 g/l is not economic, while COD of wastewaters suitable for wet air oxidation should not be below 20 g/l and not exceed 150 g/l.

Organics dissolved in industrial wastewaters can also be oxidized by anodic oxidation. In this process electrons are abstracted from the organic molecules at the anode. During this oxidation radicals and ions of the organics may be formed which react with water resulting in compounds with increased oxidation states of the carbon atoms until finally  $\text{CO}_2$  is formed. Johnson *et al.* (1972) have discussed the mechanisms of anodic oxidation of EDTA. For anodic oxidation of organics the oxygen formation at the anode has to be minimized because it represents an unwanted leakage current reducing the overall current efficiency and the available oxidation potential (Kötz *et al.* 1991). High oxygen evolution overvoltages can be realized by the use of special anode materials as e.g.  $\text{SnO}_2$  (Kötz *et al.* 1991). Another problem during anodic oxidation is the low ionic conductivity of many wastewaters which normally disables the application of anodic oxidation unless salts in concentrations of 10 to some ten g/l are added. However, Murphy *et al.* (1992) developed an electrochemical reactor using proton exchange membranes as electrolytes in place of a liquid electrolyte medium.

Matschiner *et al.* (1994) describe the chemical oxidation of industrial wastewaters with peroxodisulfate. They mention TOC removal efficiencies for organics between 20 % (pyridine) and 100 % (o-cresol). Oxidation by peroxodisulfate can be accelerated by the application of microwaves or by the presence of heavy metals or carbon. During the oxidation of the organic wastewater constituents the peroxodisulfate itself is reduced to sulfate which can be electrochemically regenerated to peroxodisulfate. Matschiner *et al.* (1994) point out that peroxodisulfate is more stable than ozone or hydrogen peroxide which leads to lower oxidant losses during the process. This enhanced stability also enables oxidation of organics at higher temperatures.

Other chemical oxidants are compounds of metals in high oxidation states as e.g. potassium permanganate (Vella *et al.* 1990) or potassium ferrate  $\text{K}_2\text{FeO}_4$  (Farooq and Bari 1986) which contains Fe(VI). Bartzatt and Nagel (1991) showed removal of carcinogenic nitrosamines by potassium ferrate.

In table 1 chemical oxidation processes generating OH radicals at normal temperatures (AOPs) are listed. Ozone is an oxidant which is often used for drinking-water treatment. But also in wastewater treatment it can be successfully applied. All processes employing ozone need reactors with efficient mass transfer, because the ozone has to be dissolved in water before it can react with wastewater constituents. Packed columns are of great promise because they have high specific gas/liquid interfaces (about 1200  $\text{m}^{-1}$ ). These

specific interfaces are also reached by spray reactors which require high volumes because of the low liquid hold-up, however.

Table 1. Chemical Wastewater Oxidation Processes Generating OH Radicals at Normal Temperatures

Process	Radicals Generated	Reference
Ozonation	$\cdot\text{OH}$ , $\cdot\text{O}_2^-$ , $\text{HO}_2\cdot$ , $\cdot\text{O}_3^-$ , $\text{HO}_3\cdot$	Staehelin <i>et al.</i> 1984
Ozone/Hydrogen Peroxide	$\cdot\text{OH}$ , $\cdot\text{O}_2^-$ , $\text{HO}_2\cdot$ , $\cdot\text{O}_3^-$ , $\text{HO}_3\cdot$	Staehelin and Hoigné 1982, Staehelin <i>et al.</i> 1984
Ozone/UV	$\cdot\text{OH}$	Lee 1981
Hydrogen Peroxide/UV	$\cdot\text{OH}$ , $\text{HO}_2\cdot$	Köppke and von Hagen 1991
Photocatalytical Oxidation	$\cdot\text{OH}$ , $\cdot\text{O}_2^-$	Bahnemann <i>et al.</i> 1991
Photoassisted Fenton Reaction	$\cdot\text{OH}$	Pignatello and Sun 1995
Fenton's Reagent	$\cdot\text{OH}$	Lin and Peng 1995
Irradiation with Accelerated Electrons	$\cdot\text{OH}$ , $\text{H}\cdot$ , $\cdot\text{O}_2^-$ , $\text{HO}_2\cdot$	Kurucz <i>et al.</i> 1991
Gamma-Irradiation	$\cdot\text{OH}$ , $\text{H}\cdot$ , $\cdot\text{O}_2^-$ , $\text{HO}_2\cdot$	Getoff 1986
Ultrasound	$\cdot\text{OH}$ , $\text{H}\cdot$ , $\text{HO}_2\cdot$	Petrier <i>et al.</i> 1992
Ultrasound/Hydrogen Peroxide	$\cdot\text{OH}$	Lin <i>et al.</i> 1996

The dissolved ozone attacks organics with C-C double bonds following the Criegee mechanism (Bablon *et al.* 1991). The products of this reaction are compounds containing carbonyl groups (e.g. aldehydes and ketones) and hydrogen peroxide. On the other hand, in aqueous ozone solutions also a couple of radicals are formed (table 1), among them OH radicals which are very strong and unselective oxidants. OH radical formation is increased with rising pH, because the initial reaction is as follows:



The anion of hydrogen peroxide formed during ozone attack of C-C double bonds (e.g. of humic acids, Beschkov *et al.* 1996, or of lignin derivatives, Gulyas *et al.* 1995) reacts itself with dissolved ozone resulting in more effective OH radical formation than the reaction of ozone with the hydroxide anion, because reaction (2) is about 40 000 times faster than reaction (1):



This effect is utilized in the combination treatment ozone/hydrogen peroxide. Paillard *et al.* (1988) have shown that 1,1,2-trichloroethane is only slowly removed from aqueous solutions by ozonation alone, but significantly faster by the combination ozone/hydrogen peroxide. Normal ozonation reactors can be used for this process which are equipped with hydrogen peroxide addition. The brutto reaction (3) shows that the optimum stoichiometric ratio is 0.5 mol  $\text{H}_2\text{O}_2$ /mol  $\text{O}_3$  which was demonstrated in experiments of Aieta *et al.* (1988) who have treated groundwater contaminated with trichloroethene with ozone/hydrogen peroxide.



In the combination ozone/UV hydrogen peroxide is formed by the reaction of excited oxygen atoms which are generated by photolysis of dissolved ozone. Hydrogen peroxide itself is photolyzed yielding 2 OH radicals:



Esplugas *et al.* (1994) showed TOC removal from aqueous 4-chlorophenol solutions being more efficient in the combination ozone/UV than with ozone alone. UV irradiation alone only had a marginal effect on TOC elimination.

Another combination with UV irradiation is the system hydrogen peroxide/UV. The added hydrogen peroxide is photolyzed and gives two OH radicals:



In all photochemical reactions it is important that the photons  $h\nu$  are absorbed by the chemical reaction partners (ozone or hydrogen peroxide). It is known that the absorbance of hydrogen peroxide at higher wavelengths as the absorption maximum (213 nm) is enhanced with increasing pH. Therefore, also the photolysis of hydrogen peroxide (reaction 5) is depending on pH (Rudolph 1994). Increased UV irradiation intensity will enhance the production of OH radicals. However, if the UV intensity is too high, so many OH radicals are formed which are consumed in side reactions (recombination to hydrogen peroxide) without oxidizing organic wastewater constituents. This has to be considered in reactor design. For high UV intensities the brutto reaction is as follows:



Photocatalytical oxidation means the irradiation of suspensions of semiconductor material (e.g.  $\text{TiO}_2$ ) with light the energy  $h\nu$  of which exceeds the band gap energy of the semiconductor (Bahemann *et al.* 1991). Then electrons of the valence band are excited to an energetic state in the conduction band. This forms a pair of an excessive electron in the conduction band  $e_{\text{CB}}^-$  and a positively charged electron hole in the valence band  $h_{\text{VB}}^+$ . The electron as well as the hole can migrate to the surface of the semiconductor where they act as reductive ( $e_{\text{CB}}^-$ ) and as oxidative ( $h_{\text{VB}}^+$ ) agents. At the surface of the photocatalyst water molecules are oxidized to OH radicals by holes:



Dissolved oxygen is reduced by  $e_{\text{CB}}^-$  to superoxide anion radicals:



The superoxide anion radicals themselves form hydrogen peroxide and molecular oxygen, and the hydrogen peroxide is converted to OH radicals by  $e_{\text{CB}}^-$ . However, hydrogen peroxide is only found in traces when  $\text{TiO}_2$  is used as photocatalyst. Moreover, organic solutes of the wastewater can be directly oxidized by  $h_{\text{VB}}^+$  or reduced by  $e_{\text{CB}}^-$ , resp. It has been demonstrated that also solar light can be efficiently utilized for industrial wastewater treatment by photocatalytical oxidation (Bahemann *et al.* 1991).

There are further AOPs: Fenton's reagent (hydrogen peroxide/ $\text{Fe}^{2+}$ ), the photo-assisted Fenton reaction, and irradiation with accelerated electron beams or with  $\gamma$ -quants (table 1). Also treatment with ultrasound or with the combination ultrasound/hydrogen peroxide can be looked at as AOPs.

AOPs are appropriate to eliminate non-biodegradable organics occurring in effluents of biological stages. The recalcitrant organics in biological effluents are either compounds that have passed the biological stage unaltered or compounds that have been formed in the biological stage (e.g. macromolecular compounds sometimes referred to as "humic material" or "dissolved organic matter").

It has to be noted that byproducts are formed during all degradative treatment processes if mineralization is incomplete. Especially ozonation has been examined for byproduct formation and generation of mutagenicity was detected during ozonation of humic substances (Matsuda *et al.* 1992). But also other AOPs form byproducts, e.g. AOX in the processes ozonation, ozone/UV, hydrogen peroxide/UV, ozone/hydrogen peroxide, and hydrogen peroxide/ $\text{Fe}^{2+}$  if  $\text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{I}^-$  are present in the wastewater

(Rudolph 1994). Chan and Larson (1991) demonstrated the generation of mutagens by the ozonation of anilines. Therefore, degradative processes that do not lead to total mineralization have to be carefully investigated concerning the production of toxic products.

## REDUCTION PROCESSES

Also reductive processes may be applied for wastewater treatment: electrochemical reduction and reduction with metallic sodium after extraction with mineral oil. There is some experience with laboratory scale experiments to eliminate AOX (more precisely: EOX) from landfill leachates by extraction with mineral oil. The extracted organic halides are then dehalogenated by pressing metallic sodium into the oil phase at elevated temperatures (Thomanetz *et al.* 1990). Excessive sodium has to be removed by addition of water to the oil phase. This technology contains some risks because of the handling of metallic sodium, however. Electrochemical reduction of organic wastewater constituents is in the state of research and development and presently it is only possible to reduce organics in alcohol/water mixtures because of overvoltage problems. But experts are confident that in the future also organics in aqueous solutions can be electrochemically reduced (Francke, personal communication). As reductive processes are not able to convert organics to CO<sub>2</sub>, electrochemical reduction does not lead to total mineralization, but it may achieve total dehalogenation of AOX (Voss *et al.* 1991) and thus contribute to detoxification of wastewaters.

## REFERENCES

- Aieta, E.M., Reagan, K.M., Lang, J.S., McReynolds, L., Kang, J.-W., and Glaze, W. (1988) Advanced oxidation processes for treating groundwater contaminated with TCE and PCE: Pilot-scale evaluations. *Journal AWWA* **80**, 64-70.
- Bablon, G., *et al.* (1991) Practical application of ozone: Principles and case studies. In: *Ozone in Water Treatment. Application and Engineering*. B. Langlais, D.A. Reckhow, D.R. Brink, eds. Lewis Publishers, Chelsea. Pp 133-316.
- Bahnmann, D., Bockelmann, D., and Goslich, R. (1991) Mechanistic studies of water detoxification in illuminated TiO<sub>2</sub> suspensions. *Solar Energy Materials* **24**, 564-583.
- Bartzatt, R., and Nagel, D. (1991) Removal of nitrosamines from waste water by potassium ferrate oxidation. *Arch. Environ. Health* **46**, 313-315.
- Beschkov, V., Bardarska, G., Gulyas, H., and Sekoulov, I. (1996) Degradation of triethylene glycol dimethyl ether by ozonation combined with UV irradiation or hydrogen peroxide addition. *Wat. Sci. Tech.*, in press.
- Chan, W.F., and Larson, R.A. (1991) Formation of mutagens from the aqueous reactions of ozone and anilines. *Wat. Res.* **25**, 1529-1538.
- Chudoba, J. (1985) Inhibitory effect of refractory organic compounds produced by activated sludge microorganisms on microbial activity and flocculation. *Wat. Res.* **19**, 197-200.
- Diamadopoulos, E., Samaras, P., and Sakellaropoulos, G.P. (1992) The effect of activated carbon properties on the adsorption of toxic substances. *Wat. Sci. Tech.* **25**(1), 153-160.
- Esplugas, S., Yue, P.L., and Pervez, M.I. (1994) Degradation of 4-chlorophenol by photolytic oxidation. *Wat. Res.* **28**, 1323-1328.
- Farooq, S., and Bari, A. (1986) Tertiary treatment with ferrate and ozone. *J. Environ. Eng.* **112**, 301-310.
- Fewson, C.A. (1988) Biodegradation of xenobiotic and other persistent compounds: the causes of recalcitrance. *Trends Biotech.* **6**, 148-153.
- Getoff, N. (1986) Radiation induced decomposition of some chlorinated methanes in water. *Wat. Res.* **20**, 1261-1264.
- Gulyas, H., von Bismarck, R., and Hemmerling, L. (1995) Treatment of industrial wastewaters with ozone/hydrogen peroxide. *Wat. Sci. Tech.* **32**(7), 127-134.
- Hejzlar, J., and Chudoba, J. (1986) Microbial polymers in the aquatic environment - I. Production by activated sludge microorganisms under different conditions. *Wat. Res.* **20**, 1209-1216.

- Johnson, J.W., Jiang, H.W., Hanna, S.B., and James, W.J. (1972) Anodic oxidation of ethylenediaminetetraacetic acid on Pt in acid sulfate solutions. *J. Electrochem. Soc.* **119**, 574-581.
- Jones, B.M., Sakaji, R.H., and Daughton, C.G. (1985) Effects of ozonation and ultraviolet irradiation on biodegradability of oil shale wastewater organic solutes. *Wat. Res.* **19**, 1421-1428.
- Köppke, K.-E., and von Hagel, G. (1991) Überlegungen zur oxidativen Abwasserbehandlung mit Wasserstoffperoxid. *GWF Wasser Abwasser* **132**, 313-317.
- Kötz, R., Stucki, S., and Carcer, B. (1991) Electrochemical waste water treatment using high overvoltage anodes. Part I: Physical and electrochemical properties of SnO<sub>2</sub> anodes. *J. Appl. Electrochem.* **21**, 14-20.
- Kurucz, C.N., Waite, T.D., Cooper, W.J., and Nickelsen, M.J. (1991) High energy electron beam irradiation of water, wastewater and sludge. In: *Advances in Nuclear Science and Technology*. Vol. 22. J.L. Lewins and M. Becker, eds. Plenum Press, New York. Pp. 1-41.
- Lee, M.K. (1981) Study of UV-ozone reactions with organic compounds in water. In: *Chemistry in Water Reuse*, Vol. 2. W.J. Cooper, ed. Butterworths, Ann Arbor. Pp 445-464.
- Lin, J.-G., Chang, C.-N., Wu, J.-R., and Ma, Y.-S. (1996) Enhancement of decomposition of 2-chlorophenol with ultrasound/H<sub>2</sub>O<sub>2</sub> process. *Wat. Sci. Tech.* **34**(9), 41-48.
- Lin, S.H., and Peng, C.F. (1995) A continuous Fenton's process for treatment of textile wastewater. *Environ. Tech.* **16**, 693-699.
- Matschiner, H., Liebau, A., and Thiele, W. (1994) Oxidativer Abbau von Wasserschadstoffen mit Peroxodisulfaten. *Gewässerschutz Wasser Abwasser* **143**, 335-350.
- Matsuda, H., Ose, Y., Sato, T., Nagase, H., Kito, H., and Sumida, K. (1992) Mutagenicity from ozonation of humic substances. *Sci. Tot. Environ.* **117/118**, 521-529.
- Murphy, O.J., Hitchens, G.D., Kaba, L., and Verostko, C.E. (1992) Direct electrochemical oxidation of organics for wastewater treatment. *Wat. Res.* **26**, 443-451.
- Paillard, H., Brunet, R., and Doré, M. (1988) Conditions optimales d'application du système oxidant ozone-peroxide d'hydrogène. *Wat. Res.* **22**, 91-103.
- Petrier, C., Micolle, M., Merlin, G., Luche, J.-L., and Reverdy, G. (1992) Characteristics of pentachlorophenate degradation in aqueous solution by means of ultrasound. *Environ. Sci. Technol.* **26**, 1639-1642.
- Pignatello, J.J., and Sun, Y. (1995) Complete oxidation of metolachlor and methyl parathion in water by the photoassisted Fenton reaction. *Wat. Res.* **29**, 1837-1844.
- Rudolph, J. (1994) AOX-Elimination und AOX-Produktion bei der Oxidation mit H<sub>2</sub>O<sub>2</sub>/UV. *Korr. Abw.* **41**, 1794-1801.
- Staelin, J., Buehler, R.E., and Hoigné, J. (1984) Ozone decomposition in water studied by pulse radiolysis. 2. Hydroxyl and hydrogen tetroxide (HO<sub>4</sub>) as chain intermediates. *J. Phys. Chem.* **88**, 5999-6004.
- Staelin, J., and Hoigné, J. (1982) Decomposition of ozone in water: Rate of initiation by hydroxide ions and hydrogen peroxide. *Environ. Sci. Tech.* **16**, 676-681.
- Thomanetz, E., Jung, D., and Roeder, W. (1990) Physikalisch-chemische Eliminationsverfahren für Chlororganika aus hochkontaminierten Wässern und Entsorgung der hierbei anfallenden Reststoffe. In: *Seminar Altlasten am 1./2. März 1990*. Forschungs- und Entwicklungsinstitut für Industrie- und Siedlungswasserwirtschaft e.V., Stuttgart. P. 19.
- Vella, P.A., Deshinsky, G., Boll, J.E., Munder, J., and Joyce, W.M. (1990) Treatment of low level phenols (µg/L) with potassium permanganate. *Res. J. WPCF* **62**, 907-914.
- Voss, J., Altrogge, M., Wilkes, H., and Francke, W. (1991) Electroreduction of organic compounds XVIII. Electrochemical dehalogenation of chlorinated dibenzofurans and dibenzo-p-dioxins in methanol. *Z. Naturforsch.* **46b**, 400-402.